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**The influence of molybdenum and vanadium on the
activity and selectivity of a cobalt Fischer-Tropsch
catalyst**

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molybdenum or vanadium than that used in this study may be beneficial for activity of the catalyst.

The incorporation of molybdenum oxide and vanadium oxide in the formulation of a cobalt-based Fischer-Tropsch catalyst introduced strong acidic sites as determined by DFT and NH_3 -TPD in combination with the isopropanol test reaction. The increased acidity resulted in decreased chain growth probabilities and increased the methane selectivities of the catalysts tested at 20bar_a and 220°C. The influence of the increased acidity on the Fischer-Tropsch selectivity at 1bar_a and 240°C was negligible and the chain growth probabilities of the cobalt catalysts containing vanadium or molybdenum were similar to the cobalt catalyst containing no vanadium or molybdenum.

Synopsis

The Fischer-Tropsch synthesis is the catalytic conversion of synthesis gas, a mixture of hydrogen and carbon monoxide, yielding long chain hydrocarbons. Desired products in the Fischer-Tropsch synthesis can be low and intermediate molecular weight olefins, liquid hydrocarbons (C_{5+}) and/or linear C_{20+} hydrocarbons. Olefins are used as an intermediate in the petrochemical industry, whereas liquid hydrocarbons (C_{5+}) can be used as fuel. Methane is an undesired product of the Fischer-Tropsch synthesis and its formation should be minimized.

Fischer-Tropsch catalysts typically contain metals such as iron, cobalt and ruthenium. In this study a supported cobalt catalyst was used, in which cobalt was put on the support by colloidal impregnation. Some literature on CO hydrogenation indicates that molybdenum oxide and vanadium oxide used as a promoter may be beneficial for the activity and selectivity of a cobalt based catalyst. To eliminate the structural influence on the selectivity by using commercial MoO_3 and V_2O_5 supports, an alumina support was modified with molybdenum and vanadium in attempt to create molybdenum and vanadium oxide layer covering the alumina surface.

Modifying an alumina support with the aim to cover it with molybdenum or vanadium or using molybdenum or vanadium as support may lead to dissolution during catalyst preparation and deposition of these oxides on the cobalt surface.

Thus, the incorporation of vanadium or molybdenum as a support modifier in the cobalt Fischer-Tropsch catalysts leads to a decrease of the available metal surface area for the Fischer-Tropsch synthesis, and hence a reduced activity might be expected. The observed reduction was however less than expected. Estimated kinetic parameters in the rate expression proposed by Yates and Satterfield [1991] taking into consideration the reduced metal surface area showed that the addition of molybdenum or vanadium increased the activity of the individual cobalt sites. This may indicate that lower levels of

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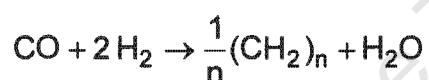
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1 Introduction

1.1 Background

The Fischer-Tropsch synthesis is the catalytic conversion of synthesis gas, a mixture of hydrogen and carbon monoxide, yielding long chain hydrocarbons. Fischer-Tropsch catalysts typically contain metals such as iron, cobalt and ruthenium. The Fischer-Tropsch reaction over a cobalt catalyst, where the formation of long hydrocarbons is accompanied by the formation of water, can be written as follows:



The interest in Fischer-Tropsch synthesis is on the increase as the reserves of crude oil are depleted and/or the price of crude rises [Dry, 2002]. Some large oil fields are associated with high levels of natural gas. Flaring of this associated gas has a negative environmental impact. Therefore the construction of Fischer-Tropsch plants are considered to utilise the associated natural gas [Dry, 2002].

Oryx, a joint venture between Qatar Petroleum and Sasol of South Africa, is constructing a gas-to-liquids (GTL) Fischer-Tropsch plant in Qatar to produce 34,000 barrels/day of liquids from methane-rich natural gas from the Qatar North gas field [N.N.1, 2006] to obtain a Fischer-Tropsch derived diesel, which is more environmentally friendly relative to crude oil derived diesel due to its lower emissions [Knottenbelt, 2002].

Synthesis gas can be obtained by converting natural gas or coal by steam reforming, partial oxidation or gasification [Iglesia *et al.*, 1993]. Synthesis gas manufacturing is typically responsible for 60-70% of the capital investments of a Fischer-Tropsch plant and the associated operating cost [Rostrup-Nielsen,

2002; Dry, 2004]. Subsequent synthesis gas conversion steps such as Fischer-Tropsch and related processes must therefore manufacture the desired products with high selectivity in order to minimise extensive recycle of undesired products to the initial gas generation step [Iglesia *et al.*, 1993].

Desired products in the Fischer-Tropsch synthesis can be low and intermediate molecular weight olefins, liquid hydrocarbons (C_{5+}) and/or linear C_{20+} hydrocarbons. Olefins are used as valuable intermediates in the petrochemical industry, whereas liquid hydrocarbons (C_{5+}) can be used as automotive fuel. Methane is an undesired product of the Fischer-Tropsch synthesis and its formation should be minimized.

The products obtained in the Fischer-Tropsch synthesis are very different from what would be expected from thermodynamic equilibrium [Dry, 2004]. Under typical Fischer-Tropsch conditions methane is expected to be the dominant product with a selectivity larger than 99 wt.-%. In reality, the methane selectivity can be limited to industrially acceptable values of 5-15 wt.-%. The product spectrum typically contains linear hydrocarbons, n-paraffins and n-olefins, branched hydrocarbons (mainly mono-methyl branched), and oxygenates, such as alcohols, aldehydes and ketones. A thermodynamically controlled product spectrum would be dominated by the presence of paraffins. However, the Fischer-Tropsch product distribution contains relatively large amounts of olefins. Thus, the formation of various products in the Fischer-Tropsch synthesis, and thereby the product selectivity, appears to be controlled by mechanistic and kinetic factors. The factors affecting the product selectivity, such as catalyst formulation and kinetic parameters, are thus a primary focus in improving the Fischer-Tropsch synthesis.

1.2 Metals with significant Fischer-Tropsch activity

Vannice [1977] tested the activity of group VIII metals in CO-hydrogenation. Only the metals iron, nickel, cobalt and ruthenium have the required activity in the Fischer-Tropsch synthesis for commercial application [Dry, 2002; Dry, 2004]. With nickel as a catalyst the selectivity for methane is too high for commercial applications. Ruthenium is relatively scarce and thus very

expensive, which makes it unsuitable for application in large industrial processes. Therefore, only iron and cobalt are viable catalyst for commercial application [Dry, 2002].

Cobalt is one of the most active metals in CO-hydrogenation [Vannice, 1977; Van Berge and Everson, 1997], which needs to be applied at relatively low temperatures (less than 240°C), since methane selectivity drastically increases at higher temperatures [Dry, 2002]. The product distribution of the Fischer-Tropsch synthesis over cobalt-based catalysts contains more paraffins than the product distribution obtained over iron-based catalysts, since cobalt is a stronger hydrogenating catalyst than iron [Dry, 2002]. Cobalt-based catalysts are mainly used for the conversion of synthesis gas with a high selectivity to waxes, which are subsequently hydro-cracked to obtain diesel.

Fischer-Tropsch synthesis over cobalt-based catalysts produces mainly water as a co-product in the hydrocarbon synthesis whereas in iron-based Fischer-Tropsch synthesis, water and carbon dioxide are produced as co-products [Xu *et al.*, 1998]. Under typical Fischer-Tropsch conditions cobalt catalysts do not show any significant water gas shift activity [Van Berge and Everson, 1997], although a significant amount of CO₂ can be produced on highly dispersed poorly reduced cobalt catalyst [Reuel and Bartholomew, 1984]. The co-formation of the greenhouse gas CO₂ in the Fischer-Tropsch synthesis is undesired. The CO₂-footprint of Fischer-Tropsch derived fuels is larger than that of crude oil derived fuel [Dry, 1999], but can be minimised by minimising the production of CO₂ in the Fischer-Tropsch process.

1.3 Reaction pathways in the Fischer-Tropsch synthesis

Product formation in the Fischer-Tropsch synthesis is kinetically controlled in a polymerisation type of reaction. The reaction pathway for the formation of the various product compounds is therefore of great interest. Various mechanistic reaction pathways have been proposed in literature [Claeys and Van Steen, 2004].

Introduction

In the 'alkyl' mechanism chain initiation is envisaged to take place via dissociative CO chemisorption, by which surface carbon and surface oxygen species are generated. Surface oxygen is removed from the surface by reaction with adsorbed hydrogen yielding water. According to this reaction scheme, surface carbon species is converted into a surface CH_2 -species, which can either react with surface hydrogen yielding a surface CH_3 -species or act as the monomer in the Fischer-Tropsch polymerization reaction. The surface CH_3 -species is regarded as the chain initiator in this polymerisation reaction, which can either desorb by reacting with surface hydrogen yielding methane or grow by reaction with a monomeric species. Product formation is envisaged to take place by β -hydrogen abstraction yielding 1-olefins or by hydrogen addition yielding n-paraffins as primary products.

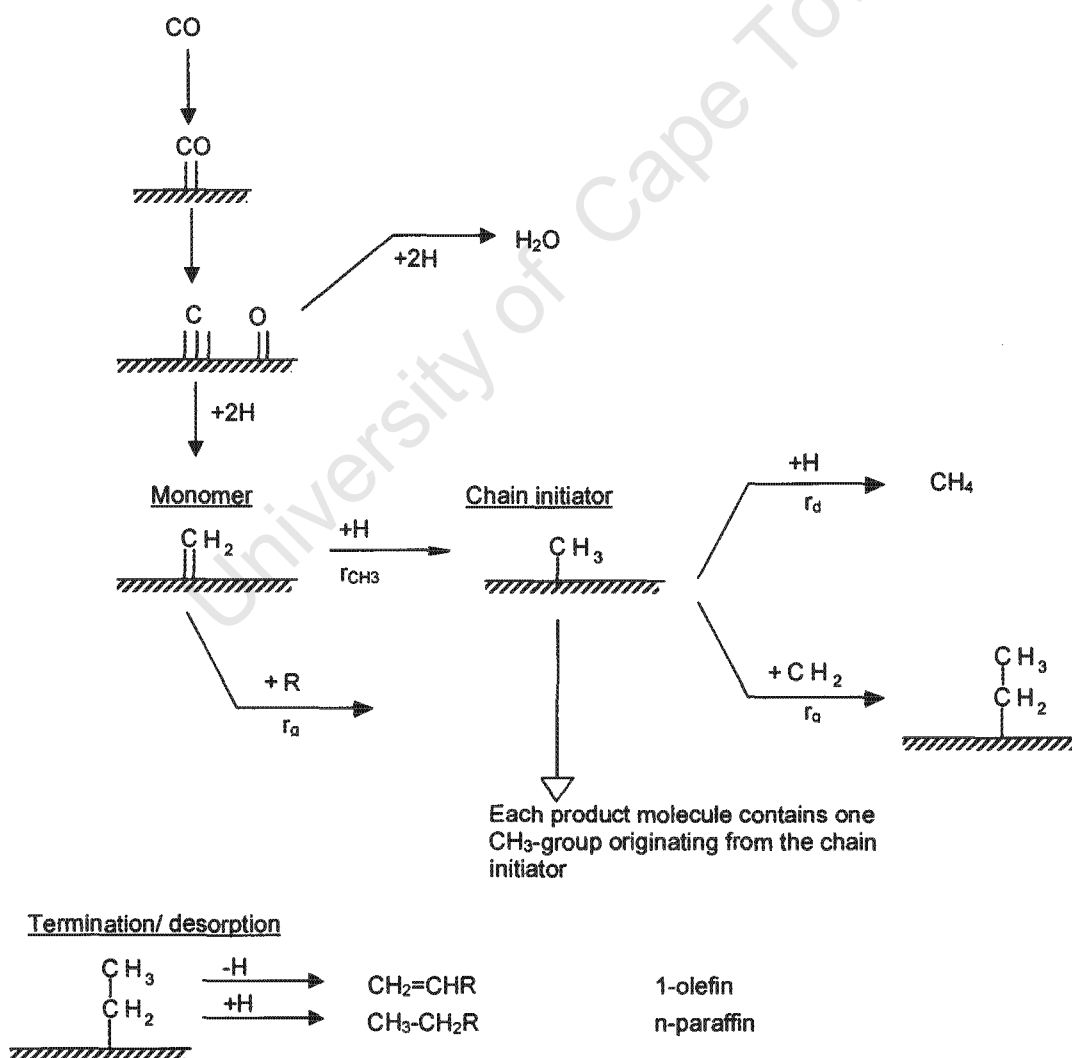


Figure 1.1: Possible reaction pathways in the Fischer-Tropsch synthesis according to the 'alkyl' mechanism [Claeys and Van Steen, 2004]

The product distribution in the Fischer-Tropsch synthesis can be modelled as a polymerization reaction utilizing a C_1 monomer [Herington, 1946], e.g. a CH_2 surface species. Figure 1.2 depicts the idealized Fischer-Tropsch surface polymerization, in which only the formation of a single product is considered. The co-adsorption of carbon monoxide and hydrogen on the surface may lead to the formation of the monomeric species and a chain starter, a C_1 surface species, Sp_1 . The C_1 surface species, Sp_1 , can either desorb to form a C_1 product molecule (Pr_1 , which may be methane) or grow via insertion of a C_1 monomer to form a C_2 surface species, Sp_2 . The C_2 surface species, Sp_2 , can either desorb to form a C_2 product molecule, Pr_2 , or grow further. This process can be repeated indefinitely yielding surface species Sp_N and product molecules Pr_N with N carbon atoms.

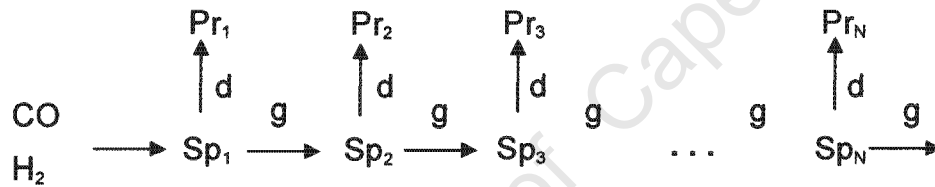


Figure 1.2: Ideal chain growth assuming formation of type of products (Pr_N) only. (Sp_N : surface species; Pr_N : product molecule; N : carbon number; d : desorption; g : growth) [Claeys and Van Steen, 2004]

The product distribution can be easily modelled using this simple reaction scheme without any further assumption regarding the actual reaction pathway and its kinetics. The rate of formation of a product compound with N carbon atoms, Pr_N , equals the rate of desorption of the surface species Sp_N :

$$r_{PrN} = r_{dN} = \frac{r_{dN}}{r_{dN} + r_{gN}} \cdot (r_{dN} + r_{gN}) \dots\dots\dots (1.1)$$

At steady-state the rate of formation of the surface species Sp_N equals its consumption:

$$r_{gN-1} = r_{dN} + r_{gN} \dots\dots\dots (1.2)$$

$$r_{PrN} = r_{dN} = \frac{r_{dN}}{r_{dN} + r_{gN}} \cdot r_{gN-1} \dots\dots\dots (1.3)$$

Each surface species has two possible pathways for further reaction, i.e. growth or desorption. The probability for desorption of a surface species with N carbon atoms, Sp_N , can now be defined as the rate of desorption relative to the rate for further reaction:

$$p_{dN} = \frac{r_{dN}}{r_{dN} + r_{gN}} \dots\dots\dots (1.4)$$

Similarly, the probability for chain growth can be defined:

$$p_{gN} = \frac{r_{gN}}{r_{dN} + r_{gN}} = 1 - p_{dN} \dots\dots\dots (1.5)$$

Thus, the rate of formation of a product molecule with N carbon atoms, Pr_N , can be modelled as:

$$r_{PrN} = r_{dN} = p_{dN} \cdot r_{gN-1} = p_{dN} \cdot p_{gN-1} \cdot r_{gN-2} = \dots = p_{dN} \cdot p_{gN-1} \cdot \dots \cdot p_{g2} \cdot p_{g1} \cdot r_{Sp1} \dots\dots\dots (1.6)$$

Since all product compounds originate from the surface species Sp_1 , the molar content of the product compound, Pr_N , in the total product is given by:

$$n_{PrN} = \frac{r_{PrN}}{r_{Sp1}} = p_{g1} \cdot p_{g2} \cdot \dots \cdot p_{gN-1} \cdot p_{dN} \dots\dots\dots (1.7)$$

The molar product distribution is thus given by the Anderson-Schulz-Flory distribution, if the chain growth probability is independent of carbon number:

$$n_{PrN} = p_g^{n-1} \cdot p_d \dots\dots\dots (1.8)$$

The experimentally obtained product distribution shows some noticeable deviations from the ideal Anderson-Schulz-Flory distribution, such as a higher than expected molar methane selectivity, a lower than expected selectivity for C_2 -products and an increase in the chain growth probability with increasing carbon number. The latter two aspects can be ascribed to the re-adsorption of reactive product compounds and their incorporation in the chain growth process [Claeys and Van Steen, 2004]. The re-incorporation of reactive product compounds leads to an increase in the chain growth probability with increasing carbon number (either through diffusional or adsorption effect). Furthermore, the incorporation of reactive product compounds into the chain

growth process leads to a decrease in the methane selectivity in C-% leaving the molar methane selectivity unaltered – see Appendix A for formal derivation).

Re-adsorption of reactive product compounds on a typical Fischer-Tropsch site is only one of the consecutive reactions which primary products formed in the Fischer-Tropsch synthesis may undergo. Secondary reactions may also involve an atypical Fischer-Tropsch site (e.g. acid site when a zeolite is used as support). The concept of primary and secondary reactions on various sites is illustrated in Figure 1.3.

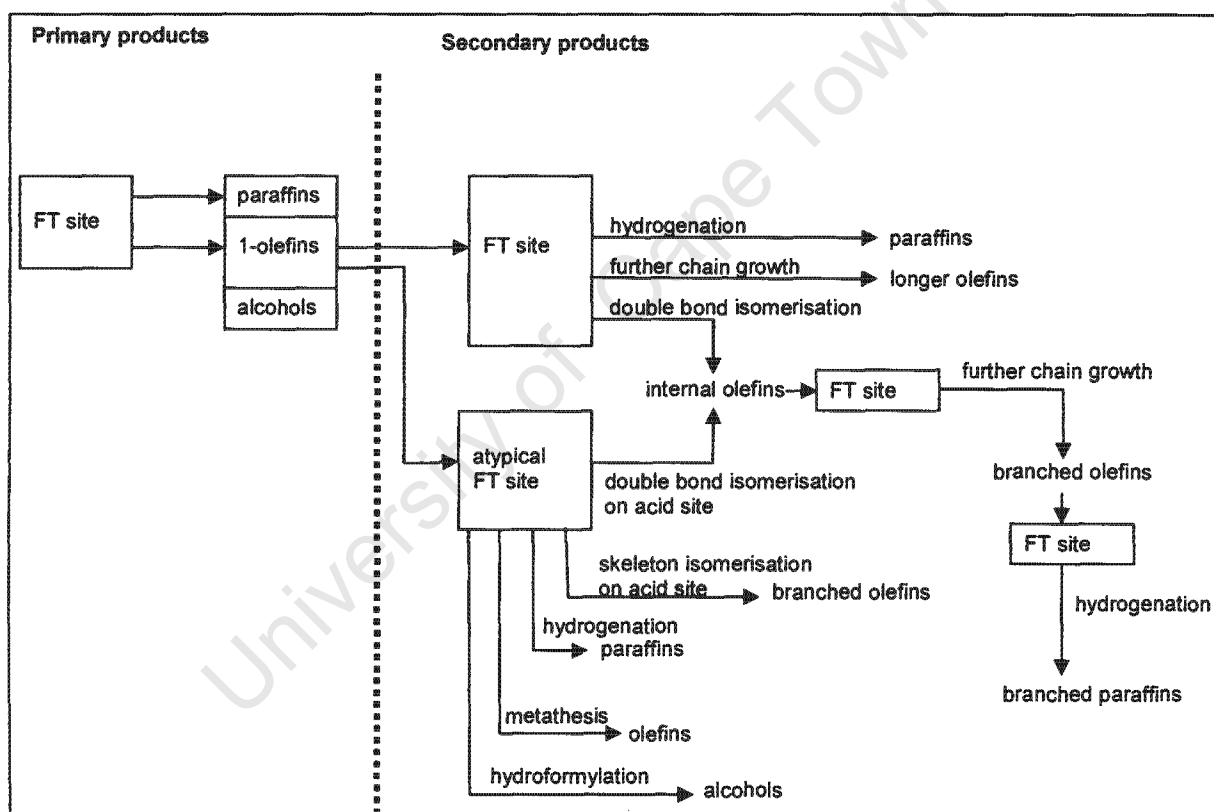


Figure 1.3: Primary and secondary pathways for product formation during Fischer-Tropsch synthesis on typical and atypical Fischer-Tropsch sites

1.4 Changing the selectivity in the Fischer-Tropsch synthesis

Selectivity in cobalt-based Fischer-Tropsch synthesis is aimed at the production of long chain hydrocarbons. The selectivity can be directed by varying the operating conditions, structural characteristics of the catalyst and

chemical composition of the catalyst. The influence of the operating conditions on the selectivity reflects the intrinsic kinetic response of the catalytic system to the change in the reactor conditions. The structural characteristics of the catalysts play an important role, when mass and heat transfer limitations affect the performance of the catalysts [Iglesia *et al.*, 1995]. The chemical composition of the catalysts may affect the selectivity of a catalyst by promotion of the active site or introduction of new functionalities in the catalyst. The parameters affecting selectivity cannot always be seen in isolation. A variation on the chemical composition of the catalyst may lead to a change in the structural characteristics of the catalyst and/or to a change in the catalyst activity, which will lead to a change in the process conditions at the active site.

1.4.1 Operating parameters

Partial pressures

The partial pressure of the kinetically relevant compounds prevalent near the active site will affect the activity and the selectivity in the Fischer-Tropsch synthesis. This includes the reactants, carbon monoxide and hydrogen, but also the main product compounds, water and carbon dioxide, and reactive organic product compounds, such as olefins and alcohols. The relative importance of the partial pressure of these compounds is related to the adsorption strength of these compounds on the catalytic site. CO chemisorption is generally much stronger than H_2 chemisorption [Snel *et al.*, 1987; Toyoshima and Somorjai, 1979]. Furthermore water was found to lower the heat of adsorption of hydrogen on nickel, platinum, rhodium and iridium [Zakumbaeva, 1979].

Dry [2004] argued that a higher partial pressure of carbon monoxide will result in a higher catalyst surface coverage with adsorbed monomers, whatever the chemical make-up of these monomers is. A higher coverage by the monomers will result in a higher chain growth probability. The catalytic activity is expected to pass through a maximum with an increase in the partial pressure

of carbon monoxide [Huff and Satterfield, 1984; Yates and Satterfield, 1991; van Steen and Schulz, 1999].

The probability of chain termination by hydrogenation will increase with an increase in the hydrogen partial pressure. Overall it could be argued that the higher the H_2/CO ratio, the higher the probability of chain termination and thus the higher the selectivity of methane and the lower molecular mass hydrocarbons [Dry, 2004] as observed by Vannice [1975] and Yates and Satterfield [1992].

The product compound water competes with carbon monoxide and hydrogen for vacant sites on the catalyst surface. However, water may dissociate on metal surfaces yielding surface hydrogen and surface hydroxyl groups as observed on nickel, rhodium and iridium [Zakumbaeva, 1979]. Water may decrease the carbon surface coverage [Claeys and Van Steen, 2002], thus increasing the water partial pressure may lead to an increase in the catalytic activity due to an increase in the number of vacant sites [Kim, 1989; Claeys and Van Steen, 2002]. Furthermore, with an increase in the water partial pressure the methane selectivity (in C-%) decreased and the C_{5+} -selectivity increased for a cobalt-based [Kim, 1989; Krishnamoorth *et al.*, 2002] and a ruthenium-based [Claeys and Van Steen, 2002] catalyst. Furthermore, the selectivity for olefins and especially for 1-olefins increases with increasing water partial pressure [Kim, 1989; Claeys and Van Steen, 2002; Krishnamoorthy *et al.*, 2002]. Iglesia [1993] stated that secondary hydrogenation of primarily formed 1-olefins is strongly inhibited by water.

The influence of the partial pressure of the reactive product compounds on the selectivity of the Fischer-Tropsch synthesis is typically investigated by co-feeding olefins to the Fischer-Tropsch reactor. Olefin double bond isomerisation is typically observed [Schulz and Claeys, 1999]. The selectivity for isomerisation for the added olefin increases with increasing partial pressure of carbon monoxide [Schulz *et al.*, 1993; Schulz and Claeys, 1999]. CO inhibits olefin hydrogenation reactions [Iglesia *et al.*, 1993; Schulz and Claeys, 1999]. It was found that the addition of an olefin to the feed had

almost no influence on the methane selectivity (in C-%) [Schulz and Claeys, 1999]. It was therefore concluded that hydrogenolysis of olefins leading to methane is negligible. Large additions of ethene even led to a decrease in the methane selectivity [Kim and Hill, 1985; Iglesia and Madon, 1987; Schulz and Claeys, 1999] and an increase in the C₅₊ selectivity. Re-adsorption of reactive product compounds and incorporation in the chain growth process may lead to a decrease in the methane selectivity (in C-%) and an increase in the C₅₊-selectivity (see Appendix A).

Krishnamoorthy *et al.* [2002] stated that the observed shift in the product selectivity is similar whether the water partial pressure was increased by addition of water to the feed or by increase in the residence time and thus CO-conversion. However, an increase in the CO-conversion by increasing the residence time will not only lead to an increase in the water partial pressure, but simultaneously decrease the partial pressures of carbon monoxide and hydrogen. Furthermore, the extent of secondary reactions will increase due to an increase in the residence time. Therefore, the shift in the selectivity upon changing the CO-conversion cannot simply be ascribed to an increase in the water partial pressure as suggested by Krishnamoorthy *et al.* [2002].

Drastic changes in selectivity can be affected by increasing the reactor pressure for a cobalt catalyst [Van Berge and Everson, 1997]. An increase in the pressure resulted in an increase of the chain growth probability. An increase in pressure will increase the partial pressures of both the reactants and products. An increase in the olefin and water partial pressures may therefore lead to a decrease in the methane selectivity and an increase in the chain growth probability.

Temperature

For all Fischer-Tropsch catalysts an increase in operating temperature results in a shift in selectivity towards lower carbon number products and to more hydrogenated products [Dry, 2002; Dry, 2004]. An increase in the reactor temperature from 170 to 210°C for a cobalt catalyst decreased the olefin content due to secondary hydrogenation [Schulz and Claeys, 1999]. The

degree of branching increases and the amount of secondary products formed such as ketones and aromatics also increases as the temperature increases when an iron based catalyst is used [Dry, 2002; Dry, 2004]. With a cobalt based catalyst the relative rate of formation of iso-C₅ seems to pass through a minimum [Claeys and Van Steen, 2004].

1.4.2 Structural characteristics of the catalyst

The selectivity in the Fischer-Tropsch synthesis is heavily affected by the reaction conditions prevalent near the active site, at which the reaction takes place. Thus, the selectivity of the reaction is expected to be strongly altered, if the reaction takes place under mass transfer limiting conditions [Iglesia *et al.*, 1993]. The concentration of the reagents will be higher at the pore mouth of the catalyst particle and lower towards the middle of the catalyst particle, when transport limitations are present. For isothermal reactions, such as the Fischer-Tropsch synthesis over catalysts with liquid filled pores, the rate of reaction will decrease if mass transfer limitations are present.

The Fischer-Tropsch synthesis has two reactants, viz. carbon monoxide and hydrogen. Diffusion limited CO arrival at an active site which is deep inside the pores, will lead to high H₂/CO ratios at catalytic sites since diffusion of hydrogen is faster than CO for all diffusion regimes. The high hydrogen to carbon monoxide ratio at the catalytically active site in the catalyst particle will lead to the primary formation of shorter hydrocarbons and thus a decrease in the C₅₊ selectivity.

Diffusion limited removal of reactive products such as olefins increases their secondary conversion by olefin re-adsorption which may lead to chain initiation, reactions that increase product molecular weight, or hydrogenation which lead to lighter products [Iglesia *et al.*, 1993].

Diffusion limitations are introduced through characteristics of the reactant and catalyst characteristics. Iglesia *et al.* [1995] described how the Thiele modules, ϕ , can be split up into two components, the diffusivity reactive

parameter, ψ_n , which depends on the properties of the reactant, and structural parameter, χ which depends on the properties of the catalyst.

$$\phi^2 = \left(\frac{2 \cdot H_{CO} \cdot R_{CO}^*}{C_T \cdot P_T \cdot D_{CO}} \right) \cdot \left(\frac{R_0^2 \cdot \varepsilon \cdot \theta_{Co}}{r_p} \right) = \Psi_{CO} \cdot \chi \dots\dots\dots (1.9)$$

with H_{CO}	Henry's constant for CO	[Pa]
R_{CO}^*	rate of CO consumption	[mol s ⁻¹ g _{cat} ⁻¹]
P_T	total pressure	[Pa]
C_T	molar concentration of liquid phase	[mol m ⁻³]
D_{CO}	effective diffusivity of CO within catalyst	[m ² s ⁻¹]
R_0	catalyst pellet radius	[m]
ε	pellet porosity	[-]
θ_{Co}	cobalt site density	[g atom surface Co m ⁻²]
r_p	mean pore radius	[m]
ψ_{CO}	diffusivity reactive parameter for CO	[m]
χ	structural parameter	[m ⁻¹]

The influence of the structural parameter χ on the product selectivity in the Fischer-Tropsch synthesis was investigated and explained by Iglesia [1995; 1997a; 1997b] (see Figure 1.4). At small χ values the selectivity to C₅₊ products is low with corresponding high methane selectivity. With increasing value for the structural parameter, the C₅₊-selectivity increases. This can be attributed to increased diffusion restrictions, which decrease chain termination probabilities due to increased intrapellet olefin concentration and longer intrapellet residence times. This increases the probability of olefin re-adsorption resulting in an increase in the C₅₊ selectivity.

At higher values for the structural parameter, χ , the selectivity to C₅₊ products is reduced and correspondingly methane selectivity increases. This can be explained by CO transport limitations, leading to high effective H₂/CO ratios at catalytic sites, which increase the chain termination probability and the extent of secondary hydrogenation of 1-olefins leading to a lighter and more paraffinic product.

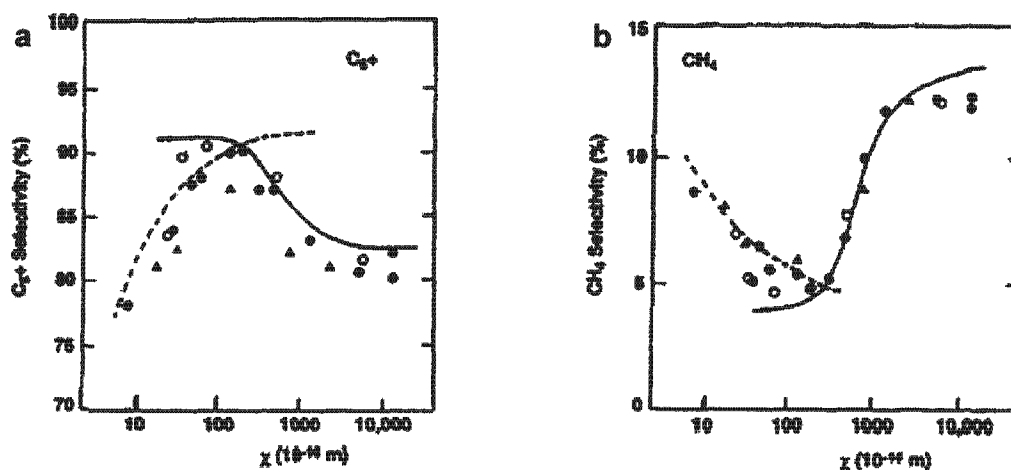


Figure 1.4: Effect of structural parameter, χ on the selectivity in the Fischer-Tropsch synthesis. Curves obtained by simulation. Data points: $\circ$ dispersion/support effects; $\blacktriangle$ pellet size variations; $\bullet$ eggshell thickness variations (a) C_{5+} selectivity; (b) CH_4 selectivity. (473K, 2000kPa, $H_2/CO=2$: $X_{CO}=55-65\%$ [Iglesia, 1997a; 1997b].

At intermediate χ values a maximum C_{5+} selectivity and a minimum CH_4 selectivity were obtained. At intermediate χ values, the olefin removal is limited, enhancing their reaction while still permitting rapid access of reactants to the reaction sites. An ideal catalyst is therefore one with intermediate χ values, which is optimised around dispersion effects and transport limitations for C_{5+} selectivity.

One of the characteristics of the catalyst contained in the structural parameter, is the pore radius of the catalyst. Espinosa *et al.* [1998] stated that the pore size for a cobalt catalyst should be at least 12nm for optimum wax selectivity. Saib *et al.* [2002] investigated the C_{5+} and methane selectivity over a series of Co/SiO₂ catalysts. They found the C_{5+} and methane selectivity passed through a maximum and minimum respectively at a pore size of 10nm for cobalt catalyst supported on silica.

1.4.3 Chemical composition of cobalt catalyst for the Fischer-Tropsch synthesis

Due to the relative high cost of cobalt, it is important to minimise the cobalt content, which and at the same time having a high cobalt metal surface area. This can be achieved by supporting the cobalt on stable oxides having the required surface areas and pore size distributions [Dry, 2004]. The most popular supports for Fischer-Tropsch synthesis are silica, alumina, titania, magnesia and zirconia. The choice of a support is dictated by several considerations including basicity, dispersion effect, electronic modifications and strong-metal support interaction [Adesina, 1996]. The modification of a support may have a similar effect as using a different type of support.

Acidic characteristics of the support may influence the selectivity. For example, it was found that an alumina support with a lower acidity favoured C_{5+} selectivity [Zhang *et al.*, 2003]. Acidic supports like zeolites also affect the selectivity of a cobalt-based Fischer-Tropsch catalyst by secondary reactions like oligomerisation, isomerisation, cracking and hydrogen transfer, resulting in a lighter, more branched product distribution [Bessell *et al.*, 1993]. The methane selectivity decreased and the C_{5+} selectivity increased as the acidity of the zeolite supported cobalt Fischer-Tropsch catalysts decreased as tested by increasing the Si/Al ratio of the zeolite [Ravishankar *et al.*, 2005].

Noble metal promoters such as Pt and Re can be added to cobalt-based Fischer-Tropsch catalysts to increase the cobalt metal surface area by increasing the degree of reduction of the cobalt [Vada *et al.*, 1995]. When small amounts of these promoters were added, the CO conversion increased without changing the selectivity [Schanke *et al.*, 1995; Vada *et al.*, 1995].

Other types of promoters may also be added to increase the C_{5+} -selectivity and decrease the methane selectivity of a cobalt-based Fischer-Tropsch catalyst. For example, Gd promotion of a cobalt catalyst decreased the CH_4 selectivity [Huber *et al.*, 2001]. Feller *et al.* [2000] has reported an increase in the C_{5+} -selectivity and a concomitant decrease in the methane selectivity for

the addition of an optimum amount of Zr to a cobalt-based Fischer-Tropsch catalyst.

Some literature on CO hydrogenation indicates that molybdenum oxide and vanadium oxide used as promoters may be beneficial for the activity and selectivity of a cobalt based catalyst. Molybdenum oxide used as a promoter increased the activity (CO conversion) for Rh [Trunschke *et al.*, 1989; Shen *et al.*, 1994], Pt [Choi and Lee, 1997] and Ru [Takahashi *et al.*, 1986] catalysts. A decrease in activity was also found when molybdenum oxide was used as promoter for Rh [Te *et al.*, 1994] and Co [Chen and Adesina, 1994] catalysts. The effect of the molybdenum oxide as promoter on the catalysts may depend on the molybdenum oxide loading since it was found that the activity in CO hydrogenation as a function of the molybdenum oxide loading went through a maximum for a nickel catalyst [Aksoylu and Önsan, 1998].

Jackson *et al.* [1986] used molybdenum oxide as a support for nickel, rhodium and iron catalysts instead of silica. The activity in CO hydrogenation of nickel and rhodium catalysts increased when these were supported on molybdenum oxide instead of silica. However, this was not the case when iron was supported on molybdenum oxide instead of on silica. The methane selectivity decreased when molybdenum oxide was used as support for rhodium. No change in the methane selectivity was observed when iron was supported on molybdenum oxide.

Molybdenum oxide as promoter, increased the chain growth probability in the Fischer-Tropsch synthesis over cobalt [Chen and Adesina, 1994] and ruthenium [Takahashi *et al.*, 1986] based catalysts. Nickel catalyst with different molybdenum oxide and nickel loadings indicated that molybdenum only had in some catalysts a beneficial effect on the selectivity by decreasing the methane selectivity [Aksoylu and Önsan, 1998].

The addition of vanadium oxide as a promoter to a cobalt-based catalyst [Guerrero-Ruiz *et al.*, 1994] and a ruthenium-based catalyst [Takahashi *et al.*, 1986; Guerrero-Ruiz *et al.*, 1994] increased its activity in the Fischer-Tropsch

synthesis. Vanadium oxide partially covering a rhodium film indicated that the activity went through a maximum as the vanadium oxide concentration on the surface is increased [Boffa *et al.*, 1993; Reichl and Hayek, 2002].

Vanadium oxide as promoter increased the chain growth probability in the Fischer-Tropsch synthesis over cobalt [Guerrero-Ruiz *et al.*, 1994; Zwane, 2004] and ruthenium [Takahashi *et al.*, 1986; Guerrero-Ruiz *et al.*, 1994] based catalysts. A decrease in the methane selectivity was also observed with increasing vanadium loading on a rhodium film [Reichl and Hayek, 2002].

Molybdenum oxide and vanadium oxide as part of the chemical composition of the catalyst may assist in the dissociation of CO when the carbon monoxide is bonded with its carbon atom to a metal atom and with its oxygen atom to a partially reduced promoter ion (see Figure 1.5) [Sachtler *et al.*, 1985]. The activity may increase, if the formation of surface carbon by CO dissociation is the rate determining step. The C_{5+} selectivity may increase with a corresponding decrease in the CH_4 selectivity, if the carbon surface coverage increases leading to an increase in the monomer and chain initiator surface coverage and a decrease in the hydrogen surface coverage.

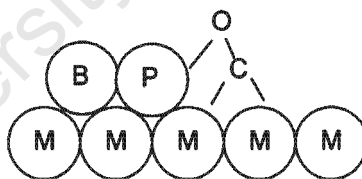


Figure 1.5: CO adsorbed with carbon bonded to the surface metal, M, and the oxygen to the promoter, P (B is an anion which compensates the charge of P) [Sachtler *et al.*, 1985]

1.5 Scope of the study

The addition of molybdenum oxide or vanadium oxide to the formulation of catalysts for the Fischer-Tropsch synthesis has been reported to be beneficial in some cases [Chen and Adesina, 1994; Guerrero-Ruiz *et al.*, 1994; Takahashi *et al.*, 1986]. The origin of the reported improved performance of

these catalysts is not clear, but might be ascribed to a promoter effect [Sachtler *et al.*, 1985]. In this study the effect of the addition of molybdenum oxide and vanadium oxide to the formulation of a cobalt-based Fischer-Tropsch catalyst is investigated in depth.

The incorporation of molybdenum oxide and vanadium oxide in the formulation of a cobalt-based Fischer-Tropsch catalyst may introduce additional acidic sites. It is well-known that supported molybdenum oxide catalysts [Pantoja *et al.*, 1993; Rodrigues-Ramos *et al.*, 1995; Keller *et al.*, 2000; Benadda *et al.*, 2003] and supported vanadium oxide catalysts [Khadar, 1995; Ferreira and Volpe, 2002; Chary *et al.*, 2003] have acidic properties.

The presence of acid sites in supported cobalt-based Fischer-Tropsch catalysts may negatively influence the selectivity for the formation of the desired products, i.e. the formation of C₅₊-hydrocarbons [Bessell *et al.*, 1993; Zhang *et al.*, 2003]. Cobalt as a Fischer-Tropsch catalyst is used in its reduced form [Iglesia *et al.*, 1993]. The effect of the reduction on the acidic properties of supported molybdenum oxide and vanadium oxide is presently unclear.

The role of acidity in cobalt-based Fischer-Tropsch catalysts on molybdenum oxide and vanadium oxide modified supports has not been fully explored. The acidity of molybdenum oxide and vanadium oxide on alumina is investigated using DFT-cluster calculations. The formal oxidation state and the coordination of the transition metal in the cluster are varied to obtain insight in the effect of reduction on the change in the acidity.

Molybdenum oxide and vanadium oxide can be introduced in the catalyst chemical formulation in three ways:

- (a) as a support
- (b) as a support modifier
- (c) promoter

The surface area of commercially available vanadium oxide and molybdenum oxide is very low. For example, the molybdenum oxide support used by

Introduction

Jackson *et al.* [1996] had a very low surface area of $0.3\text{m}^2/\text{g}$ in comparison with SiO_2 which had a surface area of $280\text{m}^2/\text{g}$. The difference in the structure of the two supports used in that study will have led to different structural parameters, which also affects the selectivity. A selectivity change using commercially available vanadium oxide or molybdenum oxide may thus be due to a chemical influence and/or a structural influence. To eliminate the structural influence on the selectivity by using commercial MoO_3 and V_2O_5 supports, typical supports like alumina or silica can be modified with molybdenum and vanadium in order to create molybdenum and vanadium oxide layer covering the alumina or silica surface. This may yield a support with the structural parameters of the alumina support with similar chemical properties of molybdenum and vanadium oxides. Cobalt will be brought onto these supports and the resulting catalysts will be characterized, amongst others for their acidic properties, and for the activity and selectivity in the Fischer-Tropsch synthesis.

2 **Acidity of molybdenum and vanadium clusters – DFT study**

2.1 **Introduction**

Acid sites have been reported to be present on supported molybdenum [Pantoja *et al.*, 1993; Rodríguez-Ramos *et al.*, 1995; Keller *et al.*, 2000; Benadda *et al.*, 2003], and vanadium [Khadar, 1995; Ferreira and Volpe, 2002; Chary *et al.*, 2003]. The Brønsted acidity seems to increase with an increase in the molybdenum loading [Pantoja *et al.*, 1993; Rodríguez-Ramos *et al.*, 1995] and vanadium loading [Khadar, 1995] and might thus be ascribed to the presence of either molybdenum or vanadium on the surface.

Reduction of the supported molybdenum or vanadium will alter the acidic properties of the material [Ishida, 1971; Segawa and Hall, 1982; Suarez *et al.*, 1985; Benadda *et al.*, 2003]. Suarez *et al.* [1985] observed over a supported molybdenum oxide catalyst that a limited amount of reduction increases the Brønsted acidity. This behaviour can be explained by the calculations of Tokarz-Sobieraj *et al.* [2005] (see Figure 2.1). Hydrogen treatment will first lead to the formation of surface hydroxyl groups during reduction [Massoth 1973, Tokarz-Sobieraj *et al.*, 2005,]. The formation of hydroxyl groups is supported by the observed water release during the re-oxidation step after a reduction step of bulk MoO₃ [Matsuda *et al.*, 2000].

Acidity of Mo- and V-containing clusters

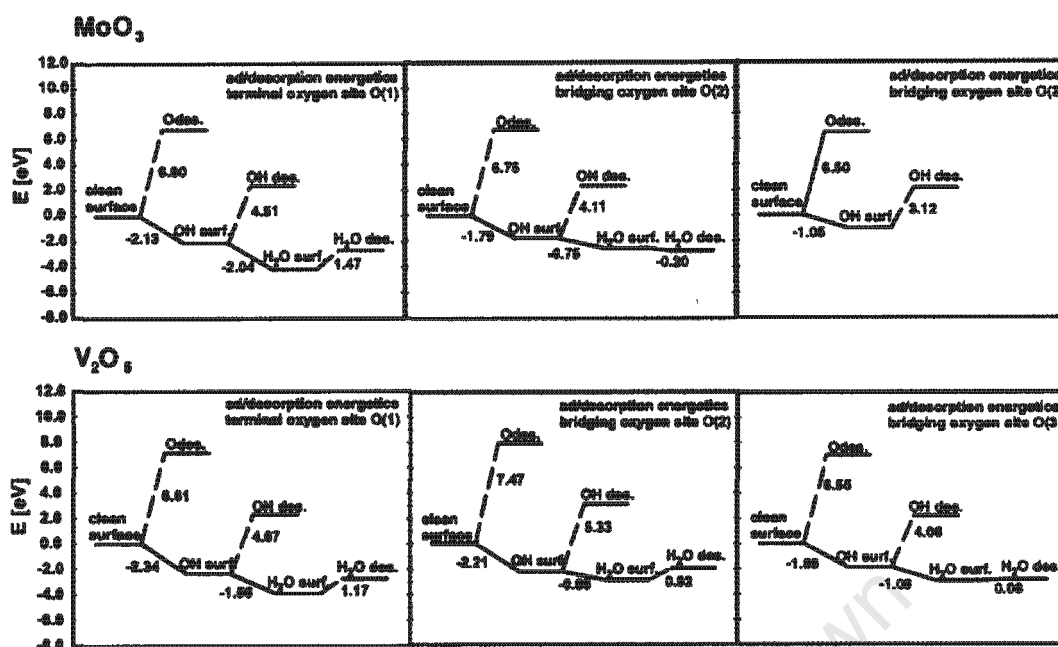


Figure 2.1: Energetic scheme of formation of different type of oxygen vacancy as results of removal O, OH, H₂O in the case of molybdenum oxide and vanadium oxides [Tokarz-Sobieraj *et al.*, 2005]

The generation of surface hydroxyl groups increases the number of the acid sites present in the catalyst. Recombination of the surface hydroxyl groups, yielding water, lead to a decrease in the number of acid sites.

The acidity of a support is not only a function of the number of acid sites present, but also of the strength of the acid sites. Various methods have been proposed in literature to quantify the strength of acid sites, viz. by determination of the:

- deprotonation energy [Van Santen, 1997; Sierka *et al.*, 1998; Yuan *et al.*, 2002; Lo and Trout, 2004]
- heat of adsorption of NH₃ [Brand *et al.*, 1992; Kyrilidis *et al.*, 1995; Yuan *et al.*, 2002; Lo and Trout, 2004].
- OH-bond length and the ionicity of the OH bond [Langenaeker *et al.*, 1994]
- OH-stretching frequencies [Brand *et al.*, 1992; Sierka *et al.*, 1998]
- charge on the proton of the OH group [Yuan *et al.*, 2002]
- Fukui function which gives a measure towards nucleophilic attack [Kyrilidis *et al.*, 1995].

Acidity is a complex measure and should be related to the base of interest. In this study reactions of olefins on acidic sites are of interest, since they may undergo double bond isomerisation and thus alter the product selectivity in the Fischer-Tropsch synthesis [Schulz and Claeys, 1999]. Hence, it is of interest to correlate the strength of the acid sites with the rate of olefin activation, which may lead to double bond isomerisation. The rate of a reaction is dependent on the activation energy, thus information on the structure and stability of the transition state is required.

Kazansky and Senchenya [1989] proposed that the surface intermediates of high temperature catalytic conversions of hydrocarbons on acid sites are not simply ionic as is usually supposed. Instead, the carbenium ionic properties of the hydrocarbon are the characteristics of the transition state (see Figure 2.2). In solids, the solvation by water in liquids, is replaced by the interaction of the adsorbed carbenium ions with the basic surface oxygen of the solids. Therefore, depending on the basicity of the surface oxygen, proton transfer to adsorbed olefins results in the formation of more or less covalent surface alkoxides rather than carbenium ions [Kazansky, 1999]. Boronat *et al.* [2004] showed with molecular modelling calculations that the formation of a covalent alkoxide for isobutylene depends on the position and local geometry of the Brønsted site. In this study the formation of secondary alkoxide species is investigated, since their formation on acidic sites show a lower activation energy [Rozanska *et al.*, 2002, 2003] (see Figure 2.2). They are viewed as precursors in the double bond isomerisation.

In this study the acidity of the support as determined by the deprotonation energy and the heat of NH_3 -adsorption is correlated with the activation energy of the alkoxide formation as proposed by Van Santen [1997].

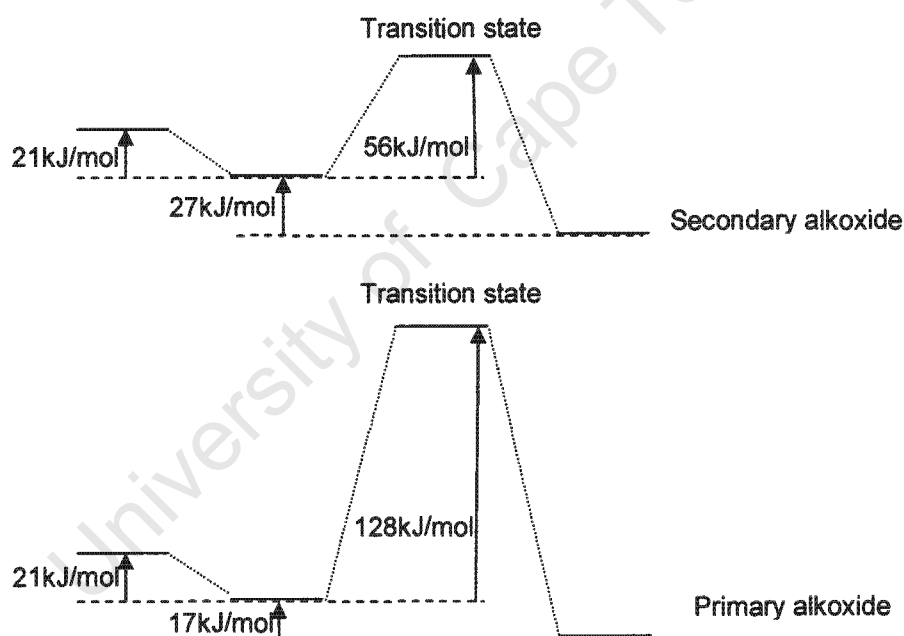
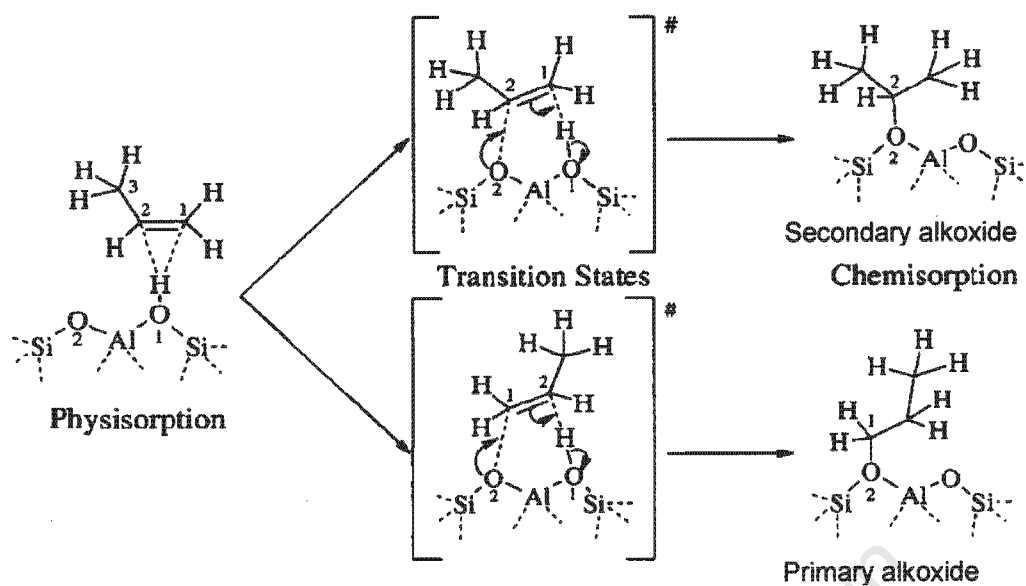


Figure 2.2: Reaction mechanisms involved in the formation of a primary and a secondary alkoxide species on an acidic zeolite from propene [Rozanska *et al.*, 2002]

2.2 Methodology and computational details

2.2.1 Chosen structure of the Al-Mo-O and Al-V-O-clusters

The deprotonation energy, heat of adsorption of ammonia and propene were determined using Al-Mo-O-clusters and Al-V-O-clusters. These clusters may mimic the behaviour of molybdenum oxide or vanadium oxide supported on γ - Al_2O_3 .

The structures of these clusters were based on the structure of a low coordination Al-Mo-O-cluster with Mo in the formal oxidation state of +6 as suggested by Ramani *et al.* [1999] (see Figure 2.3). The formal oxidation state of the molybdenum in the Al-Mo-cluster and the vanadium on the Al-V-clusters were changed by changing the ligands on the molybdenum and vanadium. These small clusters were chosen to have reasonable calculation times with the available hardware. The calculated values for the deprotonation energy, the heat of adsorption of NH_3 and propene will not resemble that on surfaces, but the trends as a function of the formal oxidation state are believed to be valid.

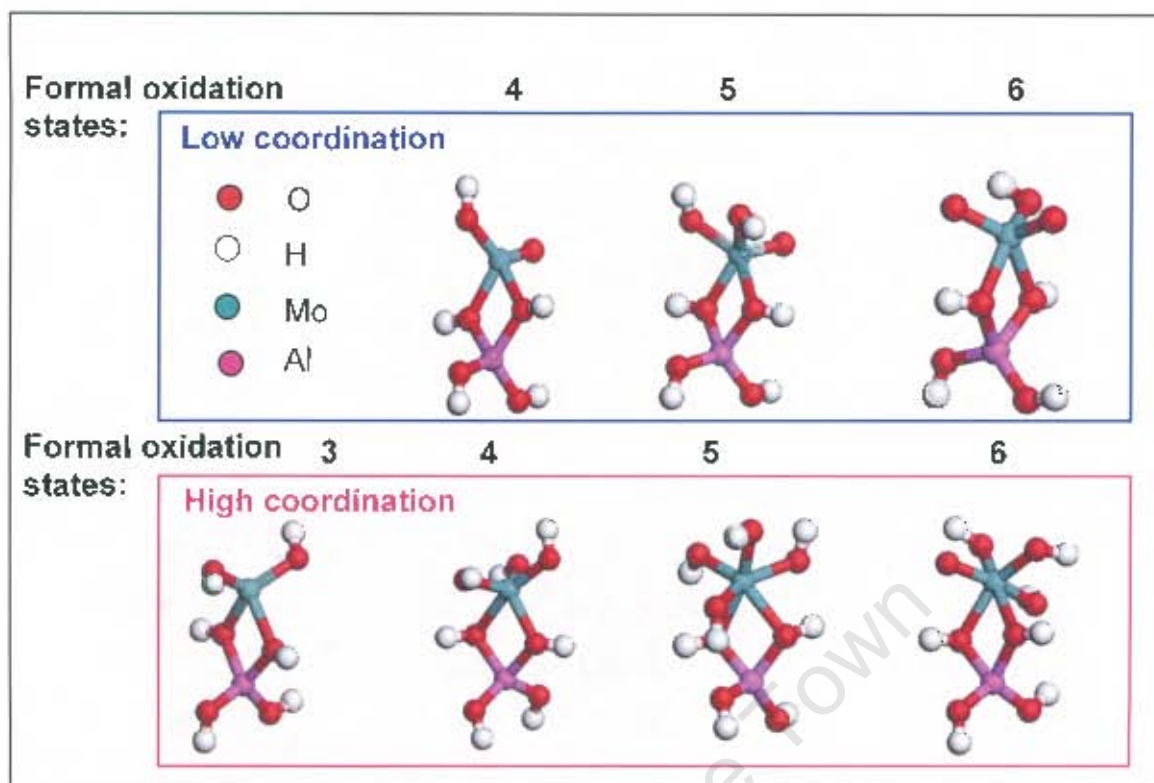


Figure 2.3: Al-Mo-O-clusters with different formal oxidation states for Mo. The structures of the Al-V-O-clusters are similar. The formal oxidation state of +6 was not used for Al-V-O-clusters.

2.2.2 Computational details

The calculations were done using the program Materials Studio (Accelrys Inc.) employing DFT-GGA (general-gradient approximation) implemented within the DMol³ code [Delly, 1990, 2000]. All electrons were included in the calculations. A double numerical base set with d-functions (DND) was employed. Geometry optimization calculations were done with auto-multiplicity, which was shown to give the minimum energy (see Appendix B). All calculations were performed in the gaseous phase using the GGA-BLYP functional and the obtained energies should be accurate within 5-10% (see Appendix B). Stable intermediates were characterized as local minima by ensuring the absence of imaginary frequencies in the vibrational analysis, which also enabled correction of the electronic energies for zero-point vibrations. The energy convergence tolerance was 2.0×10^{-5} Ha, the basis set cut-off radius was 5.5 Å, the maximum force 0.004 Ha/Å, and the maximum

displacement 0.005Å. The minimum electronic energies, E_{elec} , are static energies at 0K in vacuum.

2.2.3 Calculation of deprotonation energy and heat of adsorption

The deprotonation energy of molybdenum and vanadium containing alumina clusters, heat of adsorption of NH_3 on these clusters and the formation of alkoxide species from propene on these clusters were determined using geometry optimized calculations based on the density functional theory (DFT).

The deprotonation energy was determined by removal of a proton of a hydroxyl group solely attached to molybdenum or vanadium. This was done to mimic the acidity of molybdenum or vanadium on an alumina surface. The deprotonation energy is then calculated by:

$$\Delta E_{\text{rxn}}^{\text{DK}} = (E + \text{ZPE})_{\text{anion}} - (E + \text{ZPE})_{\text{neutral}} \quad (2.1)$$

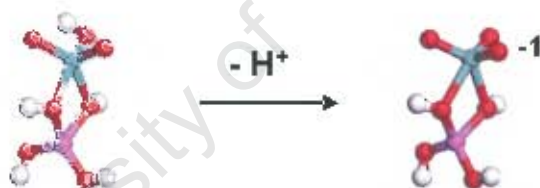


Figure 2.4: Structures of a low coordination Al-Mo-O-cluster and its anion with molybdenum in a formal oxidation state of +6

The heat of adsorption of ammonia was determined by adsorbing ammonia on the hydroxyl group solely attached to either molybdenum or vanadium. The adsorbed structure was further constrained by forbidding the interaction of adsorbed ammonia with the bridging OH-groups in order to maximize the likelihood that the structure resembles the state on a heterogeneous surface.

$$\Delta F_{\text{rxn}}^{\text{DK}} = (F + \text{ZPE})_{\text{cluster with adsorbed NH}_3} - (E + \text{ZPE})_{\text{NH}_3} - (E + \text{ZPE})_{\text{cluster}} \quad (2.2)$$

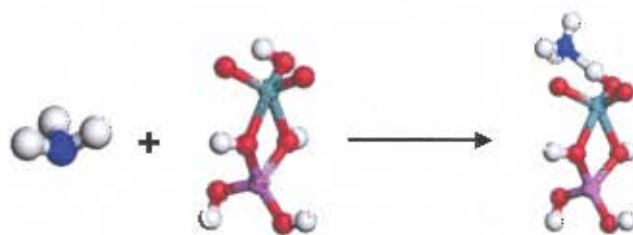


Figure 2.5: Ammonia adsorption on a low coordination Al-Mo-O-cluster with molybdenum in a formal oxidation state of +6

Of primary interest in this study, was the interaction of olefins with these clusters. The adsorption energy of propene was calculated by optimizing the propoxide cluster, in which propene was attached at the secondary carbon atom to an oxygen atom solely attached to the molybdenum or vanadium. Hydrogen transfer will take place in this adsorption step. This is in contrast to ammonia adsorption, in which hydrogen transfer is not required. The structure containing the alkoxide group was again constrained to minimize the interaction with the bridging hydroxyl-groups (similar to the case for ammonia adsorption). This was done to resemble the expected interaction on a heterogeneous surface. The heat of adsorption of propene was calculated by:

$$\Delta E_{\text{rxn}}^{\text{0K}} = (E - \text{ZPE})_{\text{propoxide}} - (E + \text{ZPE})_{\text{propene}} - (E + \text{ZPE})_{\text{cluster}} \dots\dots\dots (2.3)$$

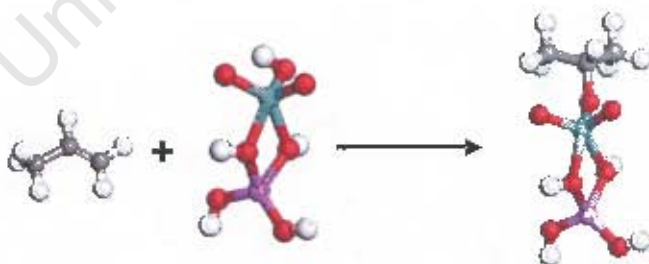


Figure 2.6: Propene adsorption on a low coordination Al-Mo-O-cluster forming a propoxide with molybdenum in a formal oxidation state of +6

2.2.4 Calculation of the activation energy for olefin conversion

The activation energy for the transformation of a secondary propoxide species in physisorbed propene was investigated, since this seems to be the most demanding step in olefin conversion over acids [Rozanska *et al.*, 2002]. An estimated activation energy was determined by

- a proton addition to the primary carbon of the double bond in propene from a hydroxyl group solely attached to molybdenum or vanadium
- b constraining the H (acid)-O bond and incrementally stretching the H(acid)-O bond incrementally (see Figure 2.7)
- c the constrained structures were optimised and the energy was calculated for each incremental stretch of the H(acid)-O bond
- d the energy of the stable alkoxide species was subtracted from the energy of the cluster with the stretched H(acid)-O bond
- e The estimated activation energy is taken as the highest difference obtained

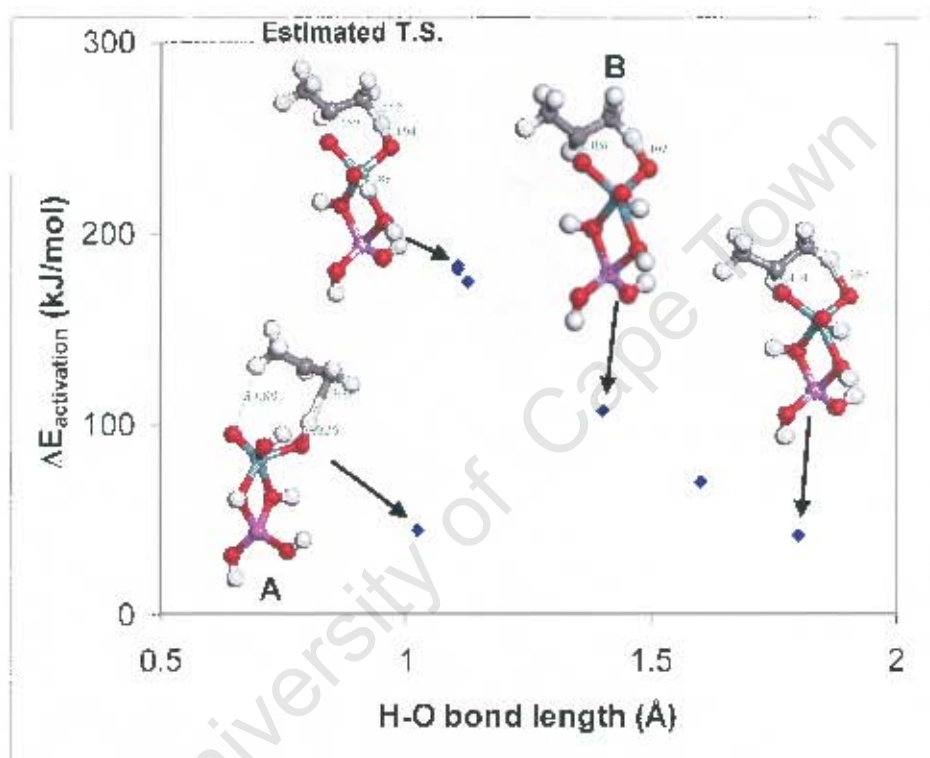
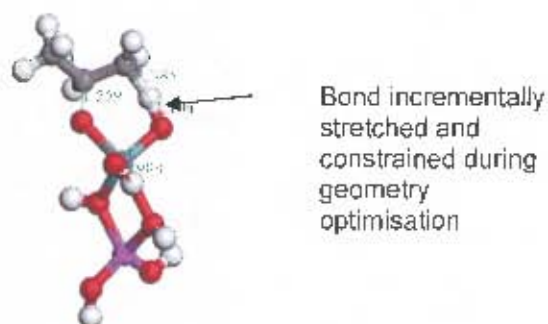


Figure 2.7: An example of energies calculated at different H-O bond lengths (constrained bond during geometry optimisations).

The calculation can also be performed starting from the stable alkoxide species. The C-O bond of the stable alkoxide can be constrained and incrementally stretched. The difference in energy between the cluster with the stretched C-O bond which has the highest energy, and the energy of the stable alkoxide, can also be taken as the estimated activation energy. The activation energy obtained by using both methodologies was very similar (116 vs. 107 kJ/mol).

In a two dimensional potential energy diagram, the transition state has only one imaginary frequency. In a many dimensional potential energy surface, meta-stable species, which might be transition states on multiple reaction pathways, may have multiple imaginary frequencies [N.N. 5, 2003]. However, when the two negative frequencies are obtained for the estimated transition state during the method employed in this study it was an artefact of the method. The species taken as the estimated transition state may be very near the true transition state. In the case of such an estimated transition state species, a true maximum is not present since the energy on the one side of the two dimensional potential energy diagram will be higher leading to an additional imaginary frequency. Further more, the reaction pathway forced by constraining the bond length may not be the lowest energy pathway.

Structures with a short and a longer H(acid)-bond and a shorter H(acid)-bond than the estimated transition state species were used as starting structures to perform a transition state search (e.g. structures A and B in Figure 2.7), since the estimated transition state species had more than one imaginary frequency. The transition state search resulted in clusters with 2 to 4 imaginary frequencies. The imaginary frequency that corresponds to the reaction coordinate was used to search for a maximum in the reaction coordinate. The energy was minimised in the other directions. The transition state optimisation yielded a transition state with only one imaginary frequency that may indicate that true transition states were found.

2.3 Stability of high coordination and low coordination Al-Mo/V-O-clusters

The structures of the clusters were based on a low coordination structure of an Al-Mo-O-cluster with molybdenum in the formal oxidation state +6 as by Ramani *et al.* [1999] (see Figure 2.3). The low coordination cluster can be transformed in a high coordination cluster by reaction with water:

Low coordination cluster + water → high coordination cluster

Table 2.1 shows the relative stability of the high coordination cluster relative to the low coordination cluster at 0K. The low coordination Al-Mo-O-cluster is thermodynamically favoured in comparison to the high coordination Al-Mo-O-cluster. The high coordination state becomes even less favoured with an increase in the formal oxidation state of molybdenum in the cluster. The Gibbs free energy for the transformation of the low coordination Al-Mo-O-cluster into the high coordination Al-Mo-O-clusters increases with an increase in the temperature indicating the high coordination Al-Mo-clusters becomes even less thermodynamically favourable at higher temperatures (see Figure 2.8). The stability of the low coordination Al-Mo-O-cluster with molybdenum in the formal oxidation state of +6 corroborates the finding by Tokarz-Sobieraj *et al.* [2005]. They reported that the recombination of surface hydroxyl groups yielding water on MoO₃ was energetically favourable with a difference in stability between a hydroxylated surface and a dehydroxylated surface starting from a terminal oxygen O(1) site of 54.9kJ/mol, which compares favourably with the value reported here for the Al-Mo-O-cluster with molybdenum in the formal oxidation state of +6 of 52kJ/mol.

Table 2.1: Relative stability of high coordination clusters relative to low coordination clusters at 0K

Formal oxidation state	ΔE^1 (kJ/mol)	
	Al-Mo-O-clusters	Al-V-O-clusters
6+	52	
5+	36	41
4+	4	-30

$$1: \Delta E = E_{\text{high coordination cluster}} - (E_{\text{low coordination cluster}} + E_{\text{H}_2\text{O}})$$

The low coordination cluster for Al-V-O clusters with vanadium in the formal oxidation state of +5 is also favoured over the high coordination state. The obtained energy difference between the high coordination state and the low coordination state (41kJ/mol) corresponds well with the reported difference between the stability of a hydroxylated and a dehydroxylated V₂O₅-surface

starting from a terminal oxygen O(1) site of 37.6 kJ/mol as reported by Tokarz-Sobieraj *et al.* [2005].

The stability of the low coordination Al-V-O-cluster decreases with a decrease in the formal oxidation state of the vanadium in the cluster (in a similar way as observed for the Al-Mo-O-cluster). The high coordination Al-V-O-cluster becomes favoured with vanadium in the formal oxidation state of +4 at -273°C, but is unfavourable at a typical cobalt based Fischer-Tropsch temperatures of 220°C (see Figure 2.8).

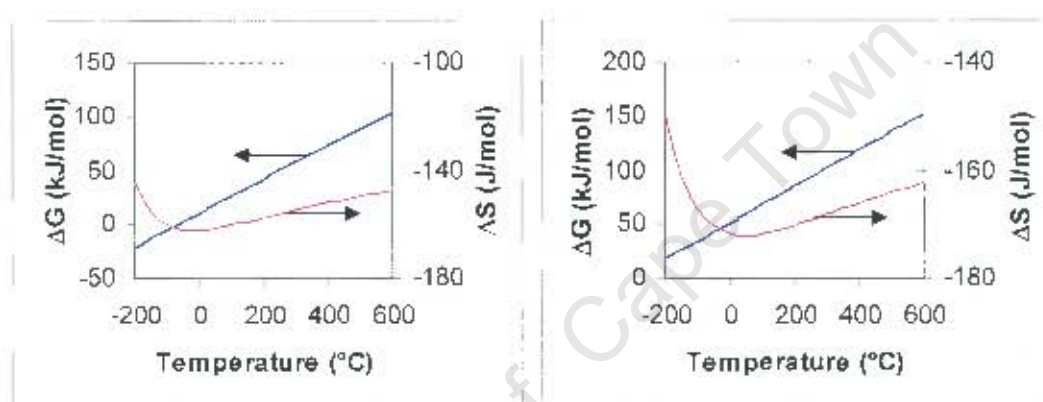


Figure 2.8: An example of the change in the Gibbs free energy and entropy for the formation of a high coordination complex from a low coordination complex and water as a function of temperature (similar graphs were obtained for the other clusters)

left: Al-V-O-cluster with vanadium in the formal oxidation state of +4

right: Al-Mo-O-cluster with molybdenum in the formal oxidation state of +4

The charge on the molybdenum in the Al-Mo-O-cluster changes significantly with a change in the formal oxidation state as determined by the oxygen and hydroxyl ligands around the molybdenum atom. The charge on the vanadium in all Al-V-O-clusters was similar for the different formal oxidation states (see Figure 2.9).

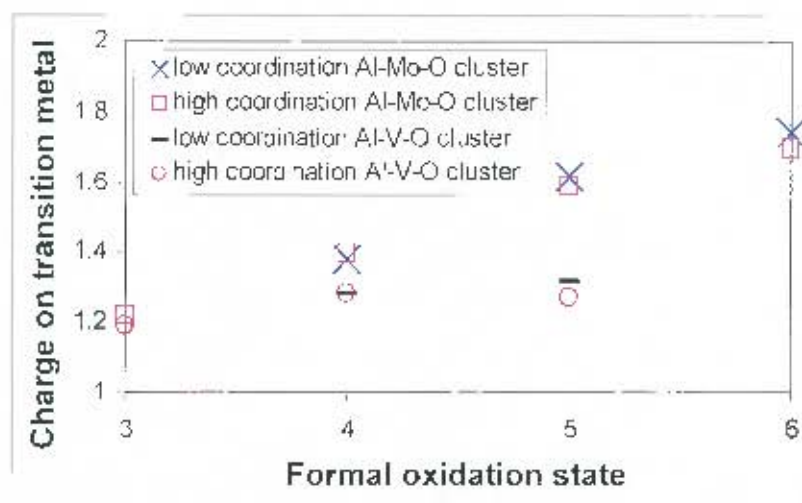


Figure 2.9: Mulliken charges on the transition metal in the clusters as a function of the formal oxidation state

2.4 Characterization of acidity of Al-Mo-O-clusters

2.4.1 Deprotonation energy of Al-Mo-O-clusters

Acidity is classically characterised using either the deprotonation energy or the heat of adsorption of ammonia. Figure 2.11 shows the deprotonation energy as a function of the formal oxidation state of Mo. The deprotonation energy increases with decreasing formal oxidation state indicating a decrease in the strength of the acid site, since it becomes more energy costly to remove a proton. It may therefore be concluded that the strength of the acid sites on the Al-Mo-cluster decreases with a decrease in the formal oxidation state of the molybdenum, which concurs with the findings reported in literature of a decrease in acidity with increasing degree of reduction [Segawa and Hall, 1982; Suarez *et al.*, 1985; Benadda *et al.*, 2003] (after an initial increase due to generation of additional hydroxyl groups [Tokarz-Sobieraj *et al.*, 2005]). The deprotonation energy for the high coordination Al-Mo-O-clusters are lower than that of the low coordination Al-Mo-cluster. This may be explained by the larger number of oxygen atoms that can delocalise the negative charge on the Al-Mo-O-cluster.

The experimental Brønsted acid strength increased considerably with the number of terminal oxygens, e.g. $\text{Si}(\text{OH})_4 \ll \text{PO}(\text{OH})_3 \ll \text{SiO}_2(\text{OH})_2$ [Bernholc

et al., 1987]. They used the terminal oxygen effect (i.e. ease of proton removal due to charge delocalisation) to predict an acidity order of $\text{Ti}(\text{OH})_4 < \text{NbO}(\text{OH})_3 < \text{WO}_2(\text{OH})_2$ for unsupported clusters, which was confirmed experimentally. However the terminal oxygen effect alone cannot explain the trends among the supported transition metal oxide catalysts, since the support may also play a role in electron delocalisation.

Not only the terminal oxygen groups can delocalise the negative charge. Hydroxyl groups can also delocalise negative charge albeit less effective than the terminal oxygen groups (see Figure 2.10). A larger extent of delocalisation of the negative charge, results in a lower deprotonation energy, i.e. higher is the strength of the acid site.

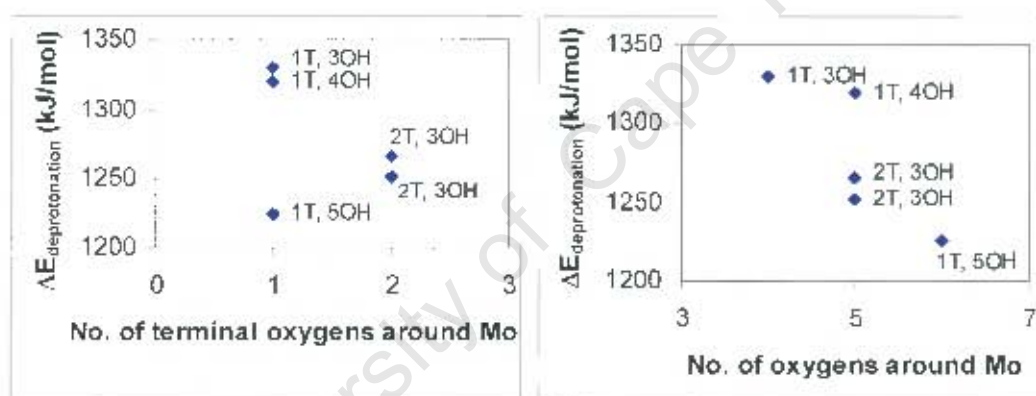


Figure 2.10: Correlation between the deprotonation energy and terminal oxygen groups and hydroxyl groups

left: Correlation between the deprotonation energy and the number of terminal oxygen groups around the molybdenum

right: Correlation between the deprotonation energy and the number of terminal oxygen and hydroxyl groups around the molybdenum

Date labels: T- terminal oxygen group

OH- hydroxyl group

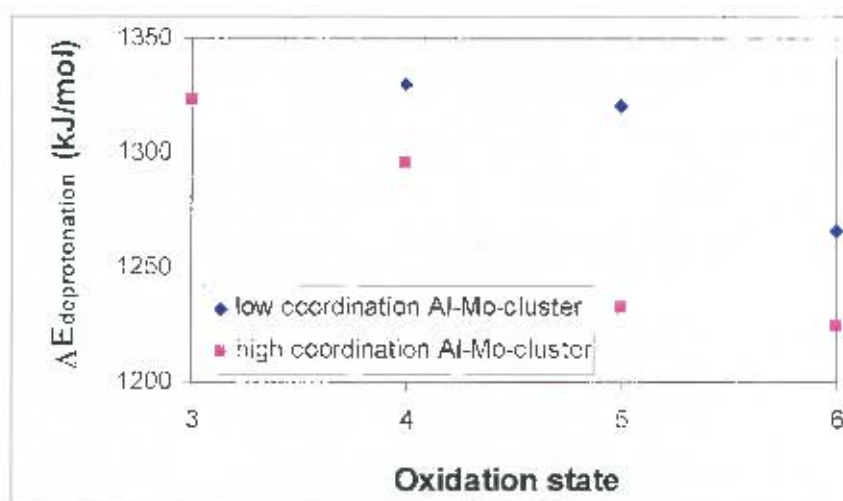


Figure 2.11: Calculated deprotonation energy of Al-Mo-O-clusters as a function of the formal oxidation state of molybdenum in the cluster

Based on deprotonation energy calculations, the Al-Mo-O-clusters are more acidic than Al-Al-O-clusters, for which a deprotonation energy of 1499 kJ/mol was obtained (both aluminium atoms in tetrahedral coordination). The deprotonation energy for the identical Al-Al-O-cluster was determined as 1390 kJ/mol by Handzlik *et al.* [2001]. The deprotonation energies for larger alumina clusters (24 and 9 aluminium atoms) containing octahedral and tetrahedral aluminium atoms were between 1200 and 1470 kJ/mol [Handzlik *et al.*, 2001]. The deprotonation energy of 1327 kJ/mol was reported for a $\text{Al}(\text{OH})_3 \cdot \text{H}_2\text{O}$ cluster [Van Santen, 1997]. The deprotonation energy of chabazite (zeolite) was between 1175 to 1181 kJ/mol [Lo and Trout, 2004], faujasite (zeolite) was between 1290 and 1378 kJ/mol (Si-O-Al cluster) [Sierka *et al.*, 1998], and 1264 kJ/mol for a Si-O-Al-O-Si cluster [Van Santen, 1997]. In this study a deprotonation energy of 1342 kJ/mol was calculated to remove a proton from the hydroxyl group on the Si atom in a Si-Al-O-cluster. A lower deprotonation energy of 1228 kJ/mol was calculated to remove a proton from the hydroxyl group between the Si and Al atoms in a Si-Al-O-cluster.

It may thus be concluded that the acidity follows the order: zeolites (Si-Al-O-clusters) > Mo-Al-O-clusters ~ $\text{Al}(\text{OH})_3 \cdot \text{H}_2\text{O}$ clusters > Al-Al-O-clusters.

Influence of number of molybdenum atoms in a cluster

Heterogeneous surface may contain Mo-O-Mo clusters, especially if high molybdenum loadings are applied. This may affect the acidic properties of the material. Hence, the deprotonation energy of $(\text{Mo-O})_x$ -clusters was determined. The deprotonation energy decreases with an increase in the number of molybdenum atoms in the -6 formal oxidation state in a cluster without aluminium (see Figure 2.12). This can be explained by an improved delocalisation of the remaining negative charge. The calculated deprotonation energy is dependent on the chosen structure and the position of the removed proton.

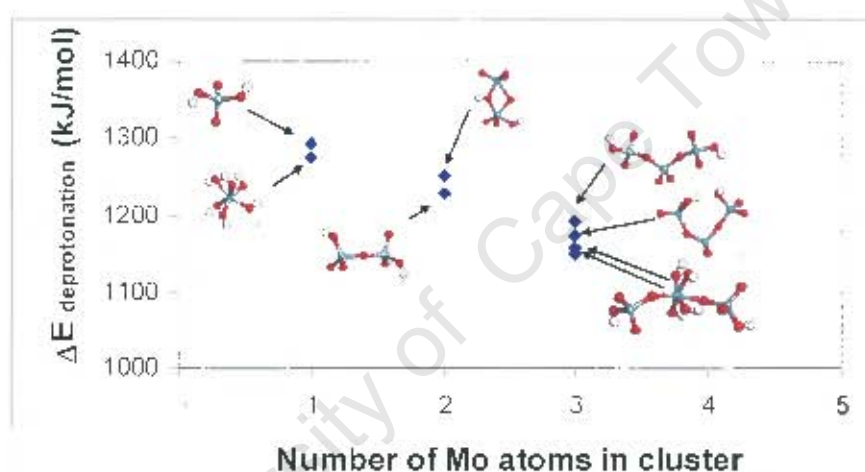


Figure 2.12: Influence of number of molybdenum atoms in cluster on the deprotonation energy

Influence of number of alumina atoms representing the support in an Al-Mo-O-cluster

The number of alumina atoms representing the support was increased to verify whether the trends as a function of the formal oxidation of the transition metal remain the same. The deprotonation energy for the $+6$ formal oxidation state was lower than that for the $+4$ formal oxidation state independent of the number of alumina atoms in the Al-Mo-O-cluster and the configuration of the alumina atoms within the Al-Mo-O-cluster (see Figure 2.13 and Figure 2.14). Therefore small clusters containing only one alumina atom may be used to study the acidity characteristics as a function of the formal oxidation state.

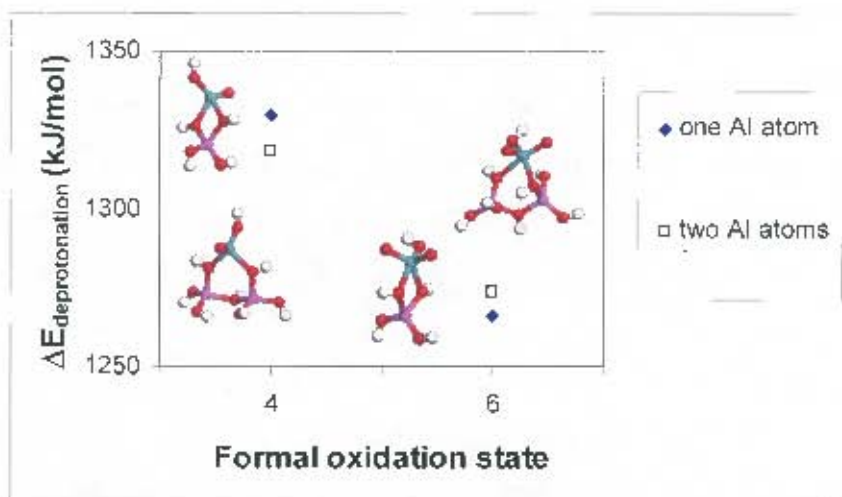


Figure 2.13: Influence of number of aluminium atoms in cluster on the deprotonation energy with alumina support based on clusters proposed by Ramani *et al.* [1999]

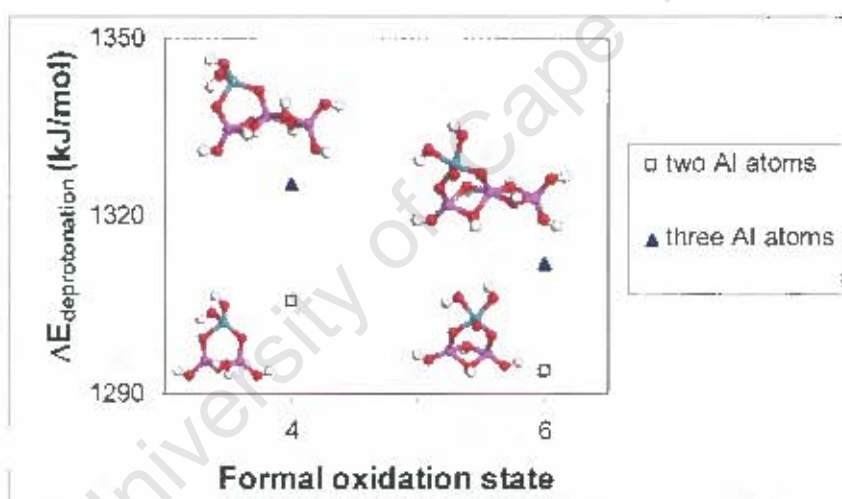


Figure 2.14: Influence of number of aluminium atoms in cluster on the deprotonation energy with alumina support based on clusters proposed by Handzlik [2003].

2.4.2 Heat of adsorption on Al-Mo-O-clusters

Heat of adsorption of ammonia

Acidity can be experimentally determined by e.g. ammonia adsorption/desorption experiments. The heat of adsorption of ammonia can also be determined using DFT-calculation to obtain a relative scale of acidity.

In the determination of the heat of adsorption of ammonia, the configuration of the possible NH_3 -cluster was restricted. In clusters containing a single Mo-atom, the interaction of the adsorbing ammonia was restricted to the interaction with the hydroxyl-groups solely attached to the molybdenum, since it is expected that this type of interaction is most likely to occur on heterogeneous surfaces.

Slight changes in the configuration in both the bare cluster and in the ammonia-cluster species show small changes in energy (see Figure 2.15). These values were obtained as the converged value for the optimised structure implying the presence of local minima in the search of the geometry-optimized structures. Hence, some uncertainty exists in the determination of the heat of adsorption of ammonia. Despite these variations a clear trend in the NH_3 adsorption energy as a function of the molybdenum formal oxidation state can be observed.

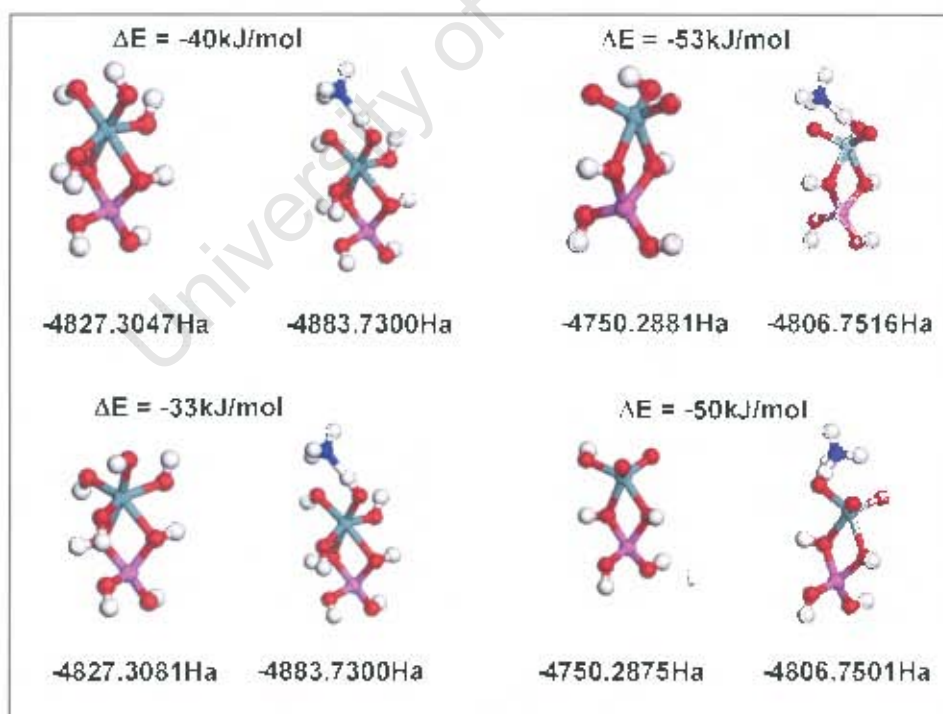
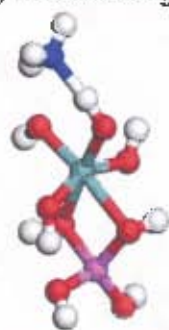


Figure 2.15: Influence of slight configuration changes in the Al-Mo-O-cluster on the energy and the resulting heat of adsorption

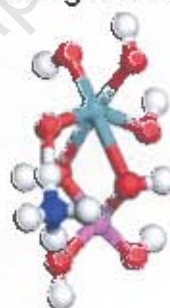
Figure 2.16 demonstrates the difference between the configurations, when the NH_3 interacts with more than one hydroxyl group on a cluster containing a single molybdenum atom. The interaction of the adsorbed ammonia with a second hydroxyl group leads to a dramatic increase in the H-O bond length of the hydroxyl group, on which ammonia is adsorbed (1.606 Å vs. 1.044 Å, when ammonia does not interact with other hydroxyl groups). This is accompanied by a decrease in the H-N bond length of the proton on the hydroxyl group and ammonia. Thus, the interaction with more than one hydroxyl group in the cluster leads to a stronger proton transfer characteristic in the ammonia adsorption step. Furthermore, the calculated heat of adsorption increases dramatically if the interaction with other hydroxyl groups is allowed. Similar observations were made by Teunissen *et al.* [1992] and Kyridis *et al.* [1995] for the interaction of ammonia in silica-alumina structures such as zeolites.

NH_3 interacting with one site



$\Delta E = -33 \text{ kJ/mol}$

NH_3 interacting with a multiple sites



$\Delta E = -60 \text{ kJ/mol}$

Figure 2.16: Influence of the structure on the NH_3 adsorption energies.

The heat of adsorption of NH_3 on Al-Mo-O-clusters containing single Mo-atom with ammonia interacting with a hydroxyl group solely attached to a molybdenum atom decreases with a decrease in the formal oxidation state of molybdenum (see Figure 2.17 and Appendix C for optimised geometries). Furthermore, the heat of adsorption is dependent on the coordination of the molybdenum atom with high coordination sites adsorbing ammonia weaker than low coordinating sites. A decrease in the heat of adsorption of NH_3 indicates a decrease in the strength of the acid site. Thus, the strength of the acid sites on the Al-Mo-O-cluster decreases with a decrease in the formal

oxidation state of the molybdenum. This was also concluded from the calculation of the deprotonation energy, and a strong correlation between the deprotonation energy and the heat of adsorption of ammonia is obtained.

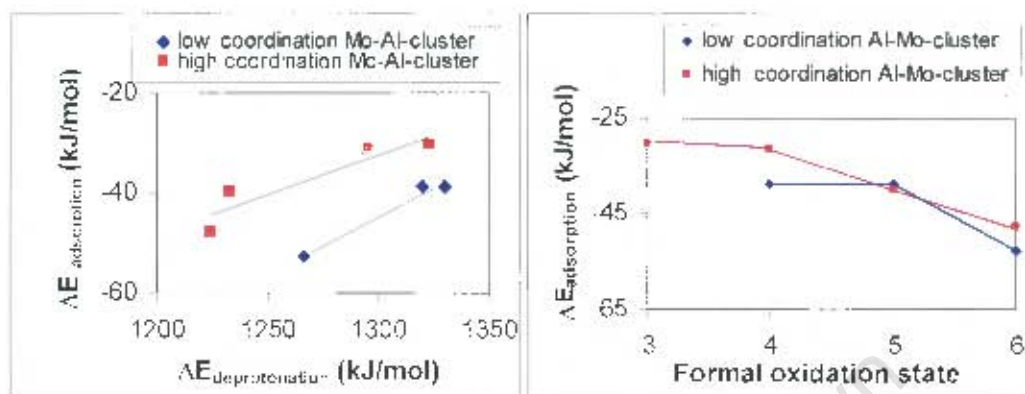


Figure 2.17: Adsorption energy of ammonia on Al-Mo-O-clusters

- left: Correlation between deprotonation energy and the heat of adsorption of ammonia
- right: Heat of adsorption as a function of the formal oxidation state

The description of heterogeneous surfaces with small clusters fails, if heat of adsorption of NH_3 is influenced by the presence of adjacent acid sites, which are accessible to ammonia in heterogeneous surfaces. This might occur if Mo-O-Mo species are present on an alumina, whose surface is coated with molybdenum. The interaction of adsorbed ammonia with a hydroxyl group on an adjacent molybdenum atom in an Al-Mo-O-cluster containing two molybdenum atoms is demonstrated in Figure 2.18. The additional interaction of the adsorbed ammonia with adjacent hydroxyl groups lead to an increase in the heat of adsorption. The additional interaction leads to an increase in the H-O-bond length on the adsorption site and thus a stronger proton transfer. A similar observation has been made by Theunissen *et al.* [1992], who showed that the interaction of ammonia with more than one site leads to the formation of a NH_4^+ cation, which strongly interacts with the anionic cluster. In zeolites, the measured adsorption energy corresponds to the adsorption energy for the interaction of ammonia with more than one site on a zeolite [Kyrilidis *et al.*, 1995, Teunissen *et al.*, 1992].

The importance of the local environment on the heat of adsorption of ammonia has been well described in literature. For example, the calculated adsorption energy of ammonia were obtained between -136 to -149 kJ/mol for chabazite (zeolite) [Lo and Trout, 2004]. The ammonia was situated in a ring configuration. A calculated adsorption energy of ammonia -107 kJ/mol was found for an alumina silica oxide cluster [Yuan *et al.*, 2002]. An ammonia adsorbed in single bonded configuration on a zeolite cluster had an adsorption energy between -60 and -69 kJ/mol [Teunissen *et al.*, 1992]. An ammonia molecule bonded in double or triple coordination had an adsorption energy of between -110 and -112 kJ/mol [Teunissen *et al.*, 1992]. Experimentally the heat of adsorption of ammonia on alumina supported molybdenum was found to be ~100 kJ/mol [Niwa *et al.*, 2003]

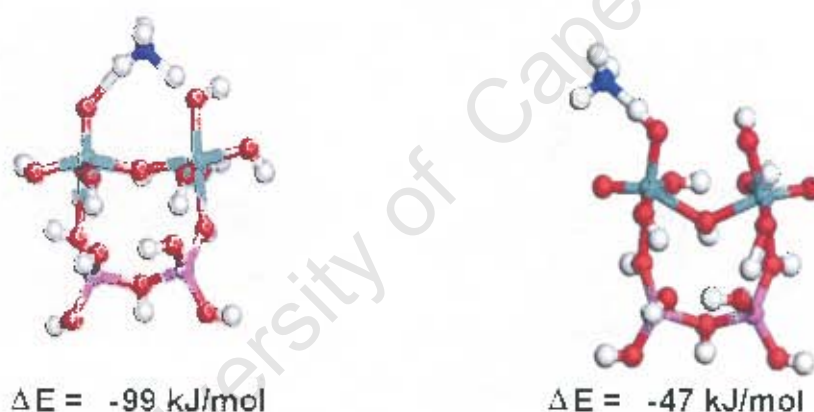


Figure 2.18: Increase in NH_3 adsorption energy when NH_3 interacts with adjacent hydroxyl group in Al-Mo-O-clusters containing two molybdenum atoms

Heat of adsorption of propene

The adsorption of propene on an Al-Mo-O-cluster may yield a prop-2-oxide intermediate on the cluster. The heat of adsorption of propene yielding the prop-2-oxide on the cluster was modelled along the same lines as the heat of adsorption of ammonia, i.e. with restricted configurations to those, which are feasible intermediates in possible adsorption intermediates on heterogeneous surfaces. Figure 2.19 shows the heat of adsorption of propene as a function of

the formal oxidation state of molybdenum in the cluster and its coordination state. The heat of adsorption of propene is not a strong function of the formal oxidation state of molybdenum, when molybdenum is in the low coordination state. For molybdenum in the high coordination state, the strength of adsorption of propene became again weaker going from a formal oxidation state of 3+/4+ to 6+.

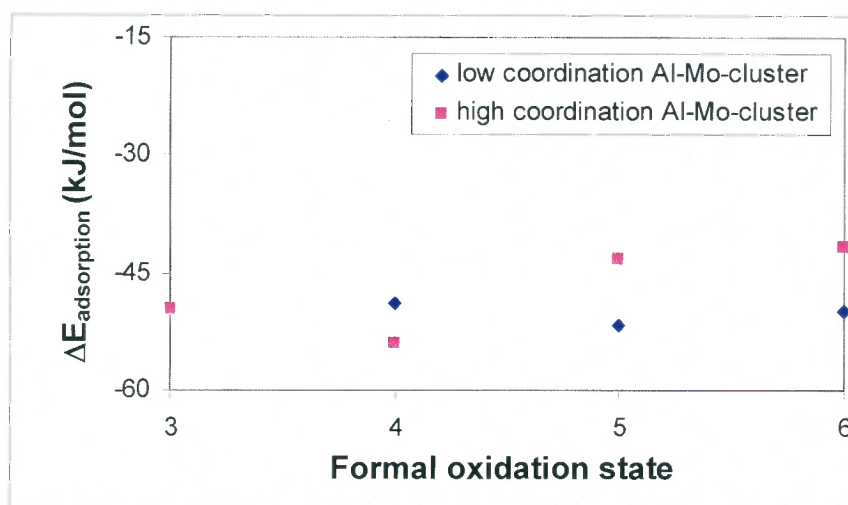


Figure 2.19: Heat of adsorption of propene on Al-Mo-O-clusters yielding a prop-2-oxide as a function of the formal oxidation state of molybdenum

The heat of adsorption of propene does not correlate well with the heat of adsorption of ammonia (see Figure 2.20).

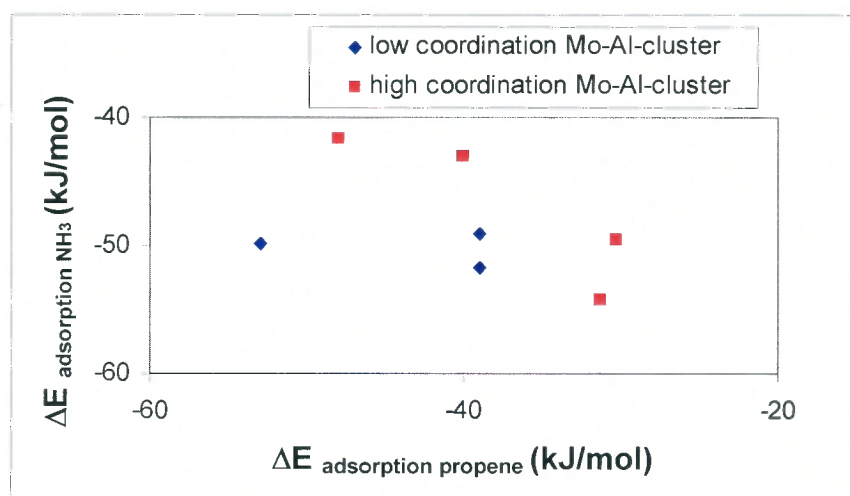


Figure 2.20: The heat of adsorption of NH_3 and as a function of the heat of adsorption of propene yielding a prop-2-oxide on Al-Mo-O-clusters

The bond between the hydrogen and the Mo-Al-O cluster becomes more ionic when the ammonia adsorbs stronger to the Mo-Al-O cluster (see Figure 2.21). Therefore the heat of adsorption of ammonia will correlate with the deprotonation energy which is a measure on how easily the proton can be separated from the Mo-Al-O cluster (see Figure 2.17).

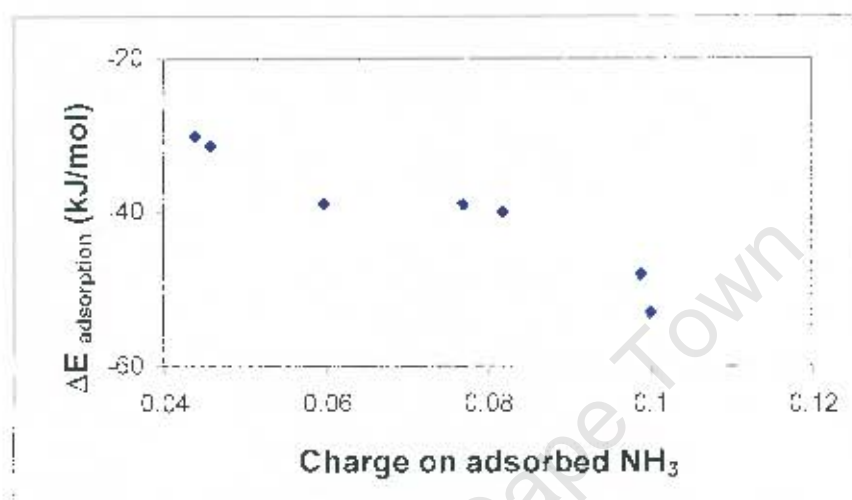


Figure 2.21: The heat of adsorption of NH_3 and as a function of the charge of the adsorbed NH_3 on the Al-Mo-O-clusters

In the case of the propene adsorbing onto the Mo-Al-O cluster as an alkoxide, the proton has already been subtracted from the Mo-Al-O cluster resulting in a protonated propene species. Thus during the calculation of the adsorption of propene, only the stability of the reagents and products which contains covalent like bonds, are used and the energy required during the reaction where the proton will be abstracted from the Mo-Al-O cluster (activation energy) was not taken into account. Thus the adsorption of propene as an alkoxide will not be a function of the deprotonation energy (see Figure 2.22) or the strength of acidity as determined by the adsorption energy of NH_3 (see Figure 2.20)

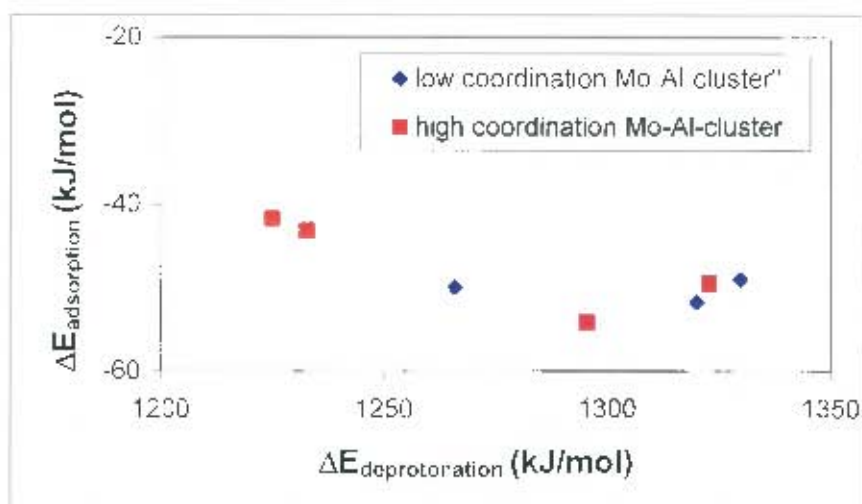


Figure 2.22: The heat of adsorption of propene yielding a prop-2-oxide as a function of the deprotonation energy

2.4.3 Olefin reactions over Al-Mo-O-clusters

The real interest in this study is in the acidic properties of surface modified alumina with e.g. molybdenum oxide responsible for possible occurrence of side reactions, such as double bond isomerisation. The heat of adsorption of propene is not correlated with e.g. the rate of double bond isomerisation on acid sites [Rozanska *et al.*, 2002].

The interaction of an olefin (such as propene) with Al-Mo-O-clusters can lead to the formation of various hydrocarbon species (see Figure 2.23). The interaction of an olefin with a high coordination Al-Mo-O-cluster may lead to the formation of an alcohol and the cluster in the low coordination state. Figure 2.24 shows a reaction path analysis of the interaction of propene with a high coordination clusters yielding iso-propanol. This reaction is feasible for molybdenum in the formal oxidation state of +4, +5 and +6 and vanadium in the formal oxidation state of +4 and +5, but is more favoured when the transition metal is in a higher formal oxidation state. This result is similar to those reported for the transformation of a high coordination Al-Mo-O-cluster into a low Al-Mo-O-cluster under elimination of water (see Table 2.1).

The interaction of an olefin with Al-Mo-O-clusters may lead to an alkoxide species or to an alkyl species. The formation of each of these species may lead upon desorption to double bond isomerisation. The high coordination Al-Mo-O-cluster with molybdenum formal oxidation states of +5, +4 and +3, do not contain basic (open) oxygen atoms and thus the concerted mechanism to form the alkoxide species is not possible. The activation energy with a proposed ionic mechanism, with no electrostatic interaction between the anion and cation, is very high, hence double bond isomerisation is kinetically inhibited over an alkoxide species.

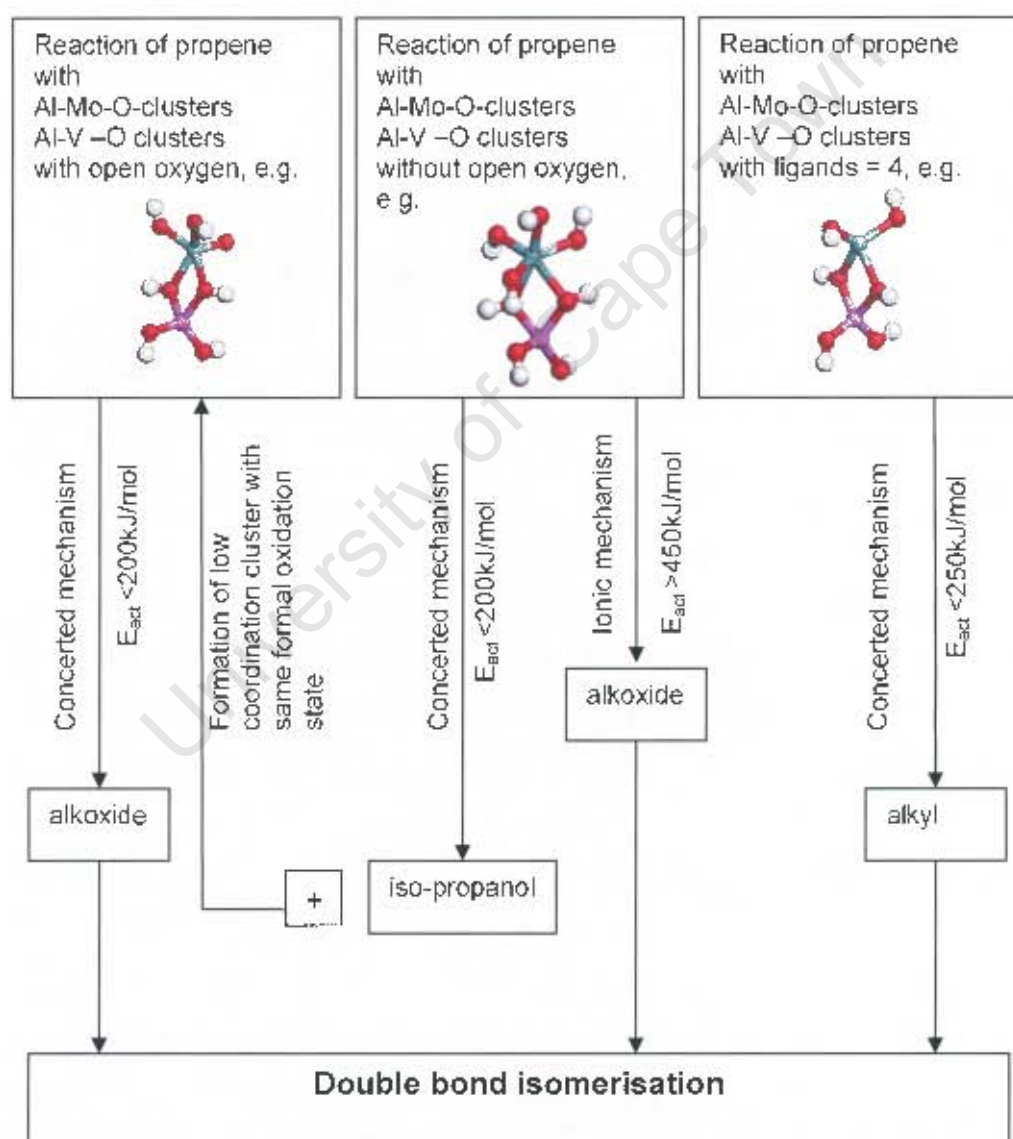


Figure 2.23: Interaction of an olefin (such as propene) with Al-Mo-O-clusters leading to the formation of various hydrocarbon species

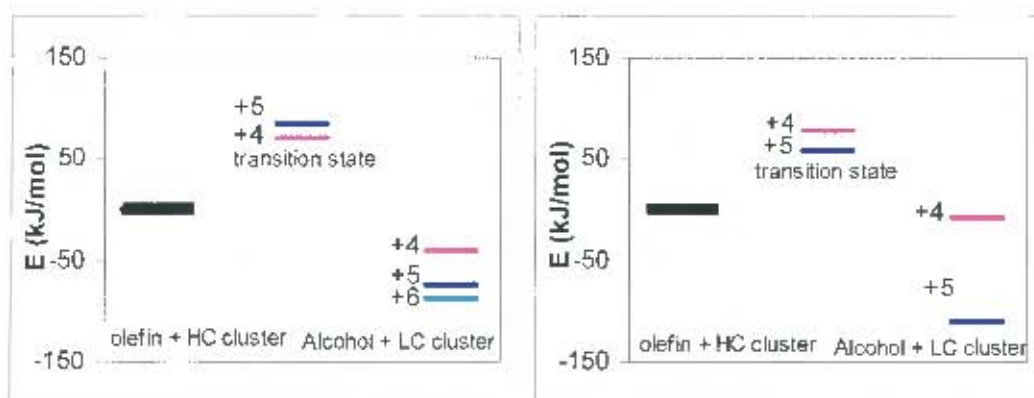


Figure 2.24: Reaction pathway analysis for the interaction of an olefin (propene) with a high coordination clusters yielding an alcohol (iso-propanol) and a low coordination cluster

Left: Interaction of propene with high coordination Al-Mo-O-clusters

Right: Interaction of propene with high coordination Al-V-O-clusters

Activation energy for olefin desorption from alkoxide species on Al-Mo-O-clusters

The interaction of an olefin with a low coordination Al-Mo-O-cluster may lead to the formation of an alkoxide species. A reversal of the reaction pathway may lead to the formation of double bond isomers. The cleavage of the C-O bond of the alkoxide, to obtain the desorbed olefin, requires the most energy [Rozanska *et al.*, 2002]. The rate of this particular reaction step should therefore be a more appropriate measure for comparison of the influence on the formal oxidation state on the rate of double bond isomerisation, rather than the heat of adsorption of an olefin.

The activation energy was determined by incrementally increasing the H(acid)-O-bond, which in the optimised structure lead to a decrease in the C-O bond length (see Figure 2.25). With increasing H-O bond length, the energy passes through a maximum. The position of the maximum is found at different H-O bond lengths for the various formal oxidation states. An alternative way of looking at the change is to view the change in the relative energy as a function

of the change in the C-O bond length relative to the C-O bond length in the stable propoxide Al-Mo-O-cluster. An increase in the C-O bond length of up to 10% leads to an increase in the relative energy. A further increase in the C-O bond length leads to a decrease in the energy.

The maximum energy observed correspond to the estimated activation energy for olefin desorption, which was the lowest for the cluster with molybdenum in the highest formal oxidation state. The maximum energy is not obtained at the same H-O bond length for the various formal oxidation states. The transition state is however achieved upon increasing the C-O bond length with ca. 10%. The Mulliken charge on the protonated olefin carbon fraction (C_3H_7) of the transition states varied between +0.55 and +0.60 indicating significant proton transfer in the transition state structure.

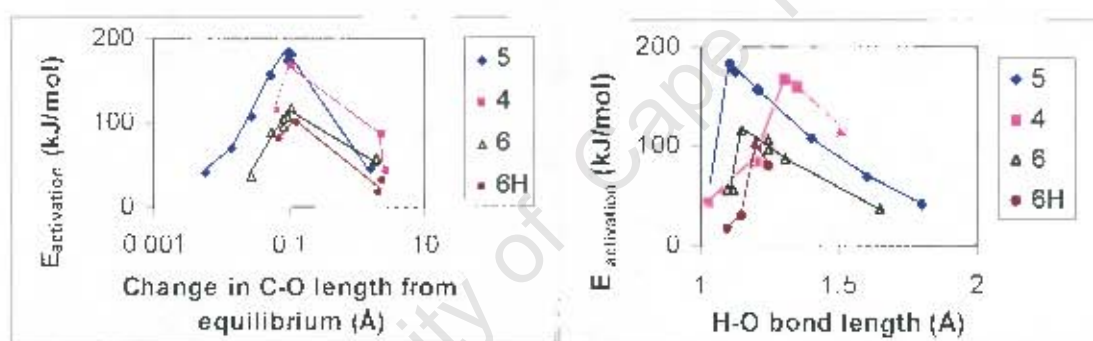


Figure 2.25: Change in the energy of the cluster relative to the energy of the stable propoxide Al-Mo-O-cluster upon stretching the H-O bond length

left: Change in energy as a function of the H-O bond length

right: Change in energy as a function of the change in the C-O bond length from its value in the equilibrium propoxide cluster

legends: 6H high coordination cluster

4,5,6 low coordination clusters

The activation energy may be correlated to the deprotonation energy [Van Santen, 1997]. This correlation is only valid when the reaction pathway is the same for all the Al-Mo-O-clusters and Mo-Mo-O-cluster. The optimised activation energy correlates with the deprotonation energy when reaction

proceeds over the alkoxide (see Figure 2.26). Therefore the rate of double bond isomerisation may thus be correlated to the strength of the acid site.

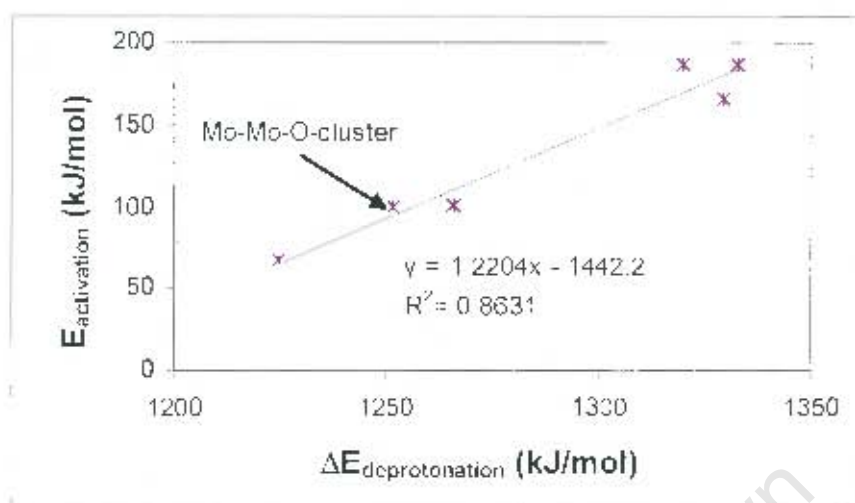


Figure 2.26: Correlation between the deprotonation energy and the activation energy (optimised) for olefin desorption.

Activation energy for olefin desorption from alkyl species on Al-Mo-O-clusters

An alternative reaction pathway for double bond isomerisation was considered, i.e. via the formation of an alkyl species. The reaction cannot proceed, if the molybdenum in the Al-Mo-O-cluster has more than 4 ligands. Hence, only the reaction over a low coordination Al-Mo-O-cluster with molybdenum in the +4 formal oxidation state and over a high coordination Al-Mo-O-cluster with molybdenum in the +3 formal oxidation state was considered.

The Al-Mo-O-cluster with molybdenum in the +4 formal oxidation state containing the alkyl species are more stable than the cluster containing the alkoxide species (see Figure 2.27), i.e. the adsorption of an olefin on these clusters will preferentially lead to the formation of an alkyl species. Similar activation energies were obtained. The obtained activation energy for the desorption pathway of the alkyl species is similar to that of the alkoxide species on the low coordination Al-Mo-O-cluster with molybdenum in the formal oxidation state of +4. The high coordination Al-Mo-O-cluster with molybdenum in the +3 formal oxidation state can thus catalyse double bond

isomerisation, via the formation of an alkyl, in the absence of a basic (open) oxygen. An activation energy of 197 kJ/mol was obtained to cleave the Mo-C bond to obtain the desorbed olefin. Thus, not feasible at Fischer-Tropsch conditions.

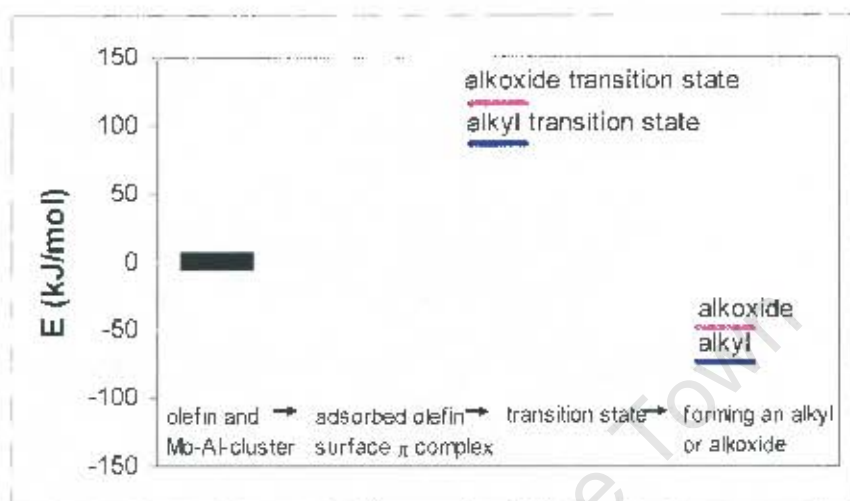


Figure 2.27: Reaction pathway analysis for the adsorption/desorption of an olefin yielding an alkyl or an alkoxide species on the cluster over a low coordination Al-Mo-O-cluster with molybdenum in the +4 formal oxidation state

2.5 Characterization of acidity of Al-V-O-clusters

The acidity of Al-V-O-clusters was characterized with a view to their activity for acid catalysed olefin reactions, such as double bond isomerisation. Similarly to the considerations for the Al-Mo-O-clusters, the acidity of Al-V-O-clusters was characterized by its deprotonation energy, heat of adsorption of ammonia, heat of adsorption of propene, and the activation energy for the transformation of the olefin.

2.5.1 Deprotonation energy of Al-V-O-clusters

The deprotonation energy of Al-V-O-clusters increases with a decrease in the formal oxidation state of vanadium in the cluster (see Figure 2.28). An increase in the deprotonation energy indicates a decrease in the strength of the acid site, since it becomes more energy costly to remove a proton. It may therefore be concluded that the strength of the acid sites on the Al-V-cluster decreased with a decrease in the formal oxidation state of the vanadium.

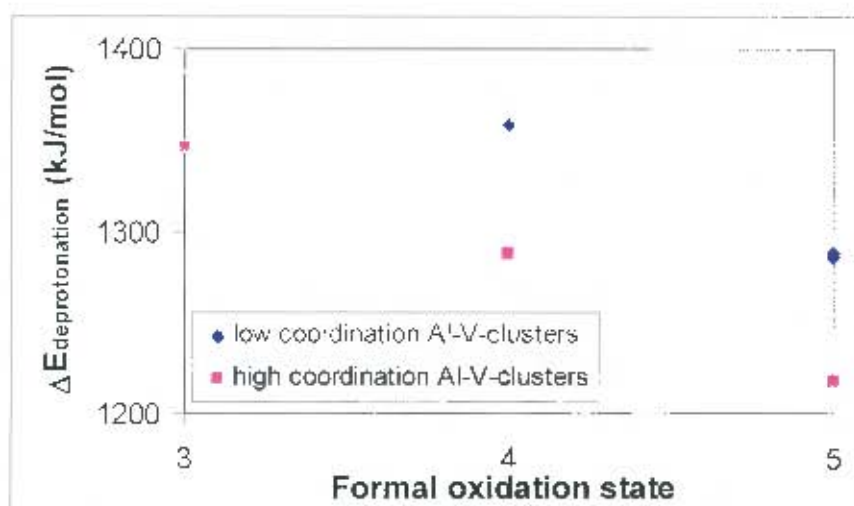


Figure 2.28: Deprotonation energy of Al-V-O-clusters as a function of the formal oxidation state of vanadium in the cluster.

The deprotonation energy for the high coordination Al-V-O-clusters are lower than that of the low coordination Al-V-O-clusters with the vanadium in the same formal oxidation state. This may be explained by the higher number of oxygen atoms that can delocalise the negative charge on the Al-V-O-cluster.

The Al-V-O-clusters discussed above are investigated, since they could represent isolated vanadium atoms on a heterogeneous alumina surface. However, the presence of larger vanadium clusters, especially at high vanadium loading, cannot be excluded. Hence, the acidic characteristics of V-O-clusters with more than one vanadium atom was investigated as well.

The deprotonation energy decreases with an increase in the number of vanadium atoms with vanadium in the formal oxidation state +5 in clusters without aluminium (see Figure 2.29). This may be explained by a better delocalisation of the remaining negative charge over the larger cluster, after the proton removal.

The structure of the original cluster from which the proton is subtracted also influences the deprotonation energy, as illustrated for clusters with 2 vanadium atoms. A higher deprotonation energy was estimated for structures containing bridging oxygen atoms compared to linear structures. This can

again be attributed to the ability of the structure to accommodate the negative charge originating from proton removal.

The position of the proton has a smaller influence on the deprotonation energy as illustrated for the cluster containing three vanadium atoms. This emphasizes the importance of the stabilisation of the negative charge in the cluster upon proton removal in the determination of the deprotonation energy and thus of the acidic properties of the cluster.

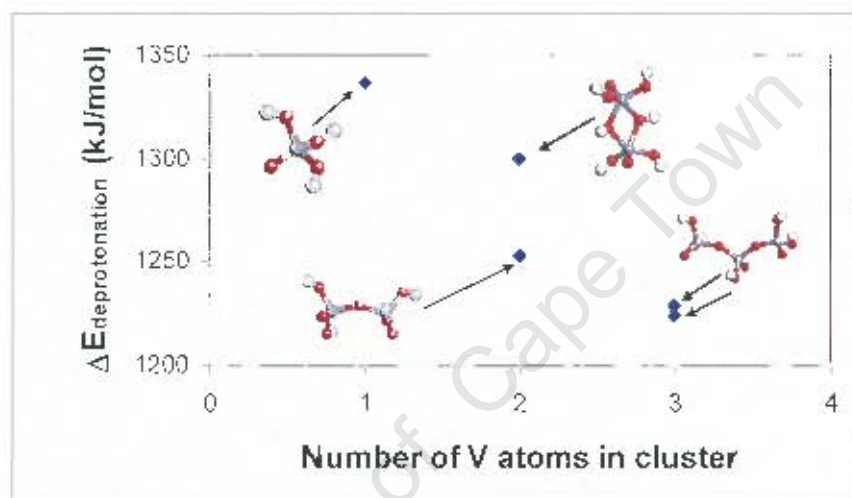


Figure 2.29: Influence of number of vanadium atoms in V-O-clusters with vanadium in the formal oxidation state of +5 on the deprotonation energy

2.5.2 Heat of adsorption on Al-V-O-clusters

Heat of adsorption of ammonia

The acidity of Al-V-O-clusters was also characterized by the heat of adsorption of ammonia. The heat of adsorption of NH_3 decreased with a decrease in the formal oxidation state of vanadium (see Figure 2.30). The deprotonation energy correlates well with the heat of adsorption of NH_3 . Thus, the strength of the acidic site decreases when the formal oxidation state of vanadium oxide decreases. Similarly, it was observed in literature that the heat of adsorption of NH_3 is lower on a bidentate vanadium cluster with a formal oxidation state of +4 in comparison to a bidentate vanadium cluster

with an formal oxidation state of +5 as determined with DFT [Anstrom *et al.*, 2002].

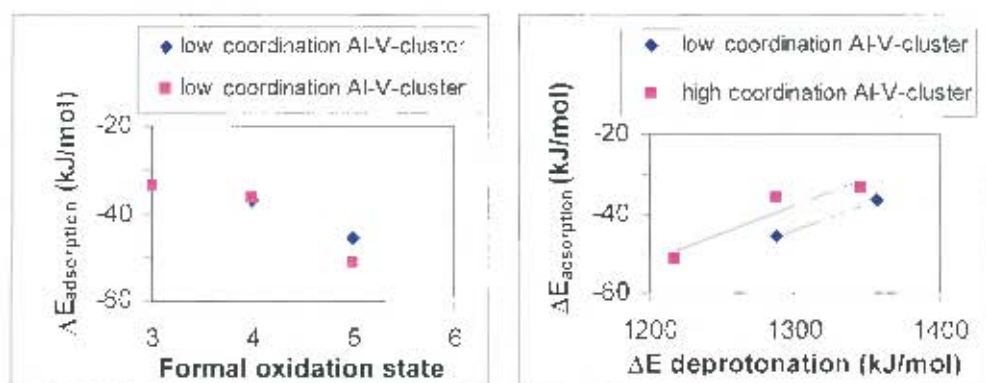


Figure 2.30: Adsorption energy of ammonia on Al-V-O-clusters

- left: Heat of adsorption as a function of the formal oxidation state
- right: Correlation between deprotonation energy and the heat of adsorption of ammonia

The heat of adsorption of ammonia on aluminium supported vanadium decreased from ~200 kJ/mol to ~25 kJ/mol with an increase in the surface coverage of ammonia [Gervasini *et al.*, 2004]. The heat of adsorption of ammonia on titania and zirconia supported vanadium was ~100 kJ/mol [Niwa *et al.*, 2003]. Thus, the calculated heat of adsorption of NH_3 compares with the heat of adsorption of NH_3 at a high surface coverage.

Heat of adsorption of propene

The heat of adsorption of propene yielding a prop-2-oxide species decreases with a decrease in the formal oxidation state of vanadium in the cluster (see Figure 2.31). It should however be noted that the dependency of the heat of adsorption of propene on the formal oxidation state of vanadium in the cluster is less strong than the dependency on the heat of adsorption of ammonia. The heat of adsorption going from a formal oxidation state of +3 to a formal oxidation state of +5 changes from 45 kJ/mol to 55 kJ/mol, whereas the heat of adsorption of ammonia changes from ca. 32 kJ/mol to 55 kJ/mol.

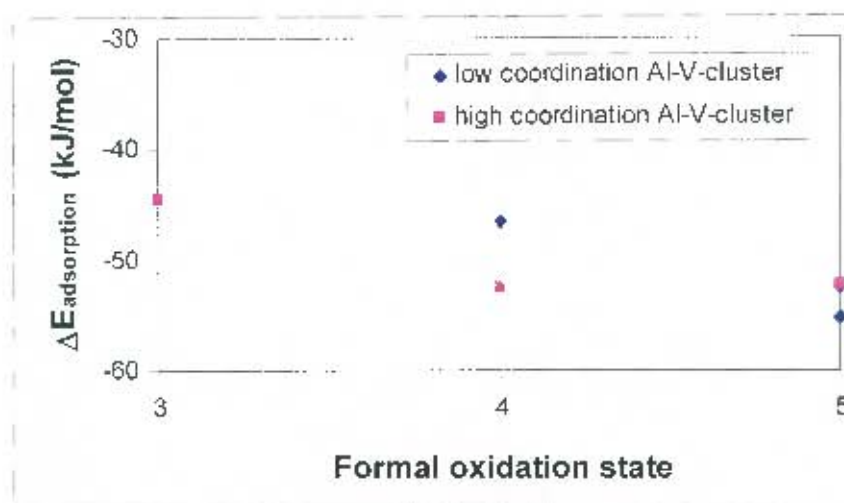


Figure 2.31: Adsorption energy for the adsorption of propene on Al-V-O-clusters yielding a propoxide as a function of the formal oxidation state of vanadium

2.5.3 Olefin reactions over Al-V-O-clusters

The real interest in this study is in the acidic properties of surface modified alumina with e.g. vanadium oxide responsible for possible occurrence of side reactions, such as double bond isomerisation. The rate of double bond isomerisation should be correlated with the activation energy of the transition state rather than with the heat of adsorption of the olefin [Rozanska *et al.*, 2002]. This correlation is however only valid when the reaction pathway is the same for all Al-V-O-clusters.

Activation energy for olefin desorption from an alkoxide species on Al-V-O-clusters

Figure 2.32 shows the activation energy for the olefin desorption from the alkoxide species on low coordination Al-V-O-clusters with vanadium in the formal oxidation state of either +5 or +4. The activation energy correlates well with the deprotonation energy. Therefore the rate of double bond isomerisation over Al-V-O-clusters may be correlated to the strength of the acid site.

In the transition states, the Mulliken charges on the protonated olefin carbon fraction (C_3H_7) of the transition states were 0.526 and 0.574 indicating significant proton transfer in the transition state structure.

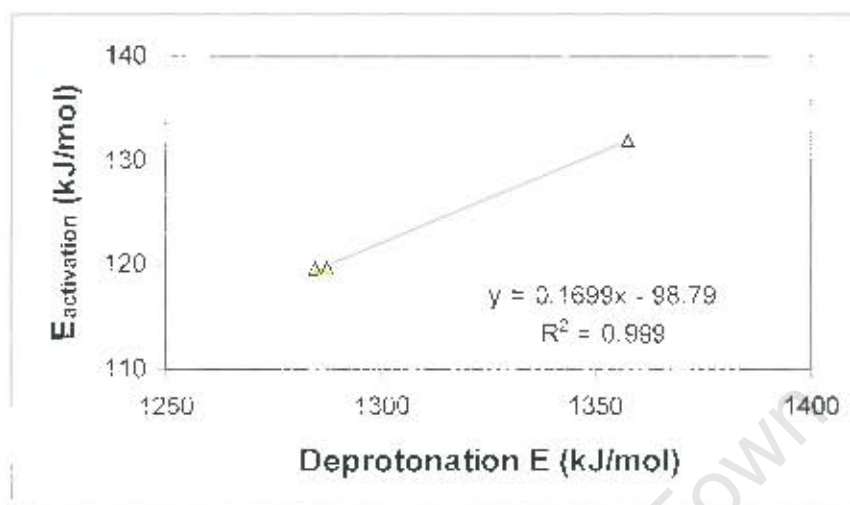


Figure 2.32: Correlating the deprotonation energy with the activation energy for the olefin desorption from propoxide intermediate from low coordination Al-V-O-clusters with vanadium in the formal oxidation state of +4 or +5

Alternative pathway for double bond isomerisation and other reactions between olefins and Al-V-O-clusters

The high coordination Al-V-O-clusters with vanadium in formal oxidation states of +5, +4 or +3, do not contain basic oxygen groups. Hence, double bond isomerisation over these clusters cannot proceed over an alkoxide species.

An alternative reaction pathway can be formulated for high coordination Al-V-O-clusters with vanadium in the formal oxidation state of +3, viz. double bond isomerisation proceeding via an alkyl species. An activation energy of 165 kJ/mol was obtained to cleave the V-C bond to obtain the desorbed olefin. High coordination Al-V-O-clusters with vanadium in the +3 formal oxidation state can thus catalyse double bond isomerisation, via the formation of an alkyl, despite the absence of a basic oxygen in the cluster.

The formation of the alkyl species for the low coordination Al-V-O-cluster with vanadium in the +4 and +5 formal oxidation state was thermodynamically unfavourable. Hence, this reaction pathway is ruled out for double bond isomerisation over these clusters.

2.6 Comparison of Al-Mo-O-clusters with Al-V-O-clusters

The deprotonation energy may be taken as a measure of the strength of the acid sites on Al-Mo-O-clusters and Al-V-O-clusters. In general, a good correlation between the deprotonation energy and the heat of adsorption of ammonia is obtained. The latter is often used as an experimental measure to determine the strength of the acid sites.

The deprotonation energy typically increases with a decrease in the formal oxidation state reflecting a decrease in the strength of the acid sites with a decrease in the formal oxidation state. The deprotonation energy of low coordination clusters is generally higher than the deprotonation energy of high coordination clusters. The deprotonation energy of Al-V-O and Al-Mo-O-clusters is significantly lower than the deprotonation energy of Al-Al-O-clusters (with aluminium in the tetrahedral coordination), which was estimated to be 1499 kJ/mol implying that vanadium and molybdenum modified aluminas can have significantly stronger acid sites than alumina. The deprotonation energy of the low coordination Al-Mo-O-cluster in the formal oxidation state of +6 is lower than the deprotonation energy of the low coordination Al-V-O-cluster in the formal oxidation state of +5. Thus, the obtained order of acidity for unreduced clusters is:

Al-Mo-O-cluster $\approx$ (slightly less) Al-V-O-cluster $\gg$ Al-Al-O-clusters.

The obtained order of acidity concurs with the relative acidity observed by Bernholc *et al.* [1987]. Niwa *et al.* [2003] also reported the strength of acidity of unreduced supported molybdenum oxide higher than unreduced supported vanadium oxide.

Figure 2.33 shows the activation energy for the desorption of an alkoxide or alkyl species on a cluster as an indication of the rate at which acid catalysed

double bond may occur as a function of the formal oxidation state of molybdenum or vanadium in the cluster. The lowest activation energy of 67 kJ/mol was obtained with Al-Mo-O-clusters with molybdenum in the formal oxidation state of +6. This may thus result in the highest rate of double bond isomerisation. The activation energy increases with a decrease in the formal oxidation state of molybdenum or vanadium in the cluster. The activation energies for desorption from the Al-V-O-clusters are lower than those from the Al-Mo-O-clusters when compared at the same formal oxidation state. Thus, the rate of double bond isomerisation is expected to be higher on Al-V-O-clusters than on Al-Mo-O-clusters, if molybdenum and vanadium are in the same formal oxidation state.

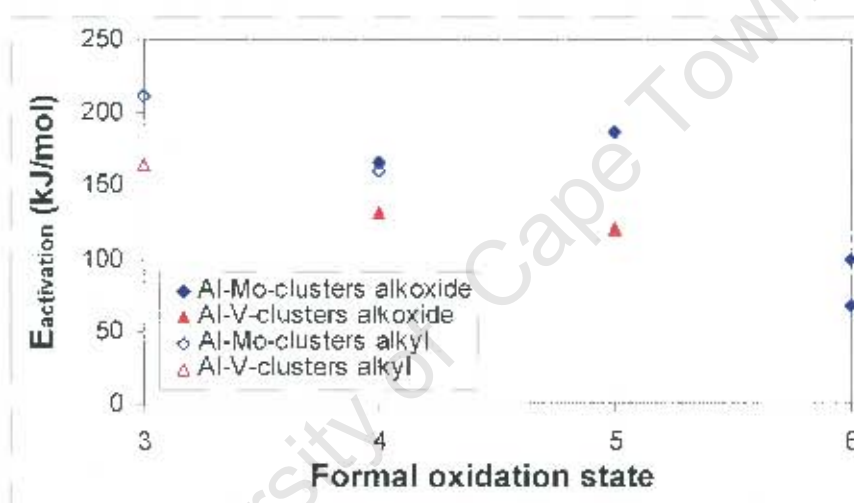


Figure 2.33: Activation energy for desorption of an olefin from an alkoxide or alkyl Al-Mo-O or Al-V-O cluster as a function of the formal oxidation state of vanadium or molybdenum

The activation energy of the olefin desorption correlates well with the C-O bond length of the transition state of the low coordination Al-Mo-O-clusters and Al-V-O-clusters (see Figure 2.34). The high coordination Al-Mo-O-cluster with molybdenum in the formal oxidation state of +6 appears to be an exception with a much longer C-O bond length of 2.28 Å. Additional interaction of the hydrocarbon fraction with the Al-Mo-O-cluster may have led to additional stabilisation, and hence a longer C-O bond.

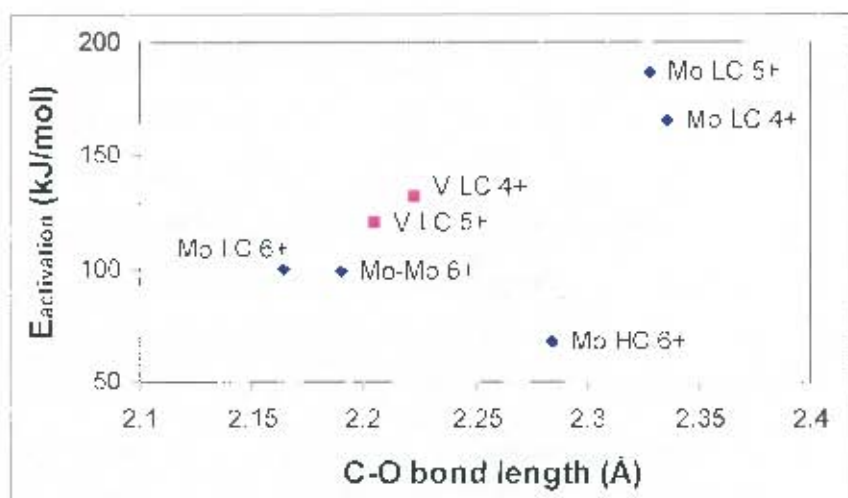


Figure 2.34: Correlating the activation energy for desorption of an olefin from Al-V-O and Al-Mo-O-clusters and the C-O bond length in the transition state

2.7 Concluding remarks

The clusters containing Mo and V have a higher strength of acidity than that of an Al-Al-O-cluster. This may indicate that vanadium and molybdenum modified alumina supports may have significantly stronger acid sites than alumina. This would result in an increase in the extent of double bond isomerisation of the olefins formed in the Fischer-Tropsch reaction.

The strength of the acid sites increases with an increase in the number of molybdenum and vanadium atoms in the clusters. At low loadings the molybdenum oxide and vanadium oxide molecules may exist as highly dispersed monomeric species with (or without) low levels of polymeric species. With an increase in the molybdenum and vanadium loadings the amount of polymeric species will increase [Benitez *et al.*, 2003; Hu *et al.*, 1995; Deo and Wachs, 1991; Weckhuysen and Keller, 2003]. Thus, an increase in the strength of the acid sites may be expected with an increase in the molybdenum and vanadium loading in the catalysts if the oxidation state remains identical. An increase in the double bond isomerisation activity with an increase in the molybdenum and vanadium loading in the catalyst during the Fischer-Tropsch reaction may thus be expected.

3 Experimental

3.1 Catalyst and support preparation

3.1.1 Preparation of modified support materials

An alumina support was modified with molybdenum oxide or vanadium oxide to obtain a support with the structural characteristics of the original support material, but with the chemical characteristics of molybdenum oxide and vanadium oxide.

Vanadium oxide and molybdenum oxide can be added to the support in various ways, viz. impregnation (slurry and incipient wetness), controlled adsorption, precipitation, chemical vapour deposition or thermal spreading. Controlled adsorption should result in a thinly, evenly distributed molybdenum oxide and vanadium oxide layer on the alumina support.

The adsorption of molybdenum or vanadium containing ions can be achieved using an aqueous suspension of the support material, since alumina surfaces are polarised in aqueous suspensions. The polarisation depends on the pH of the aqueous solution. The support surface carries a net positive charge at pH-values lower than the iso-electric point of the surface, and a net negative charge at pH-values larger than the iso-electric point. Anions are adsorbed from the aqueous suspension, if the surface carries a net positive charge.

Experimental

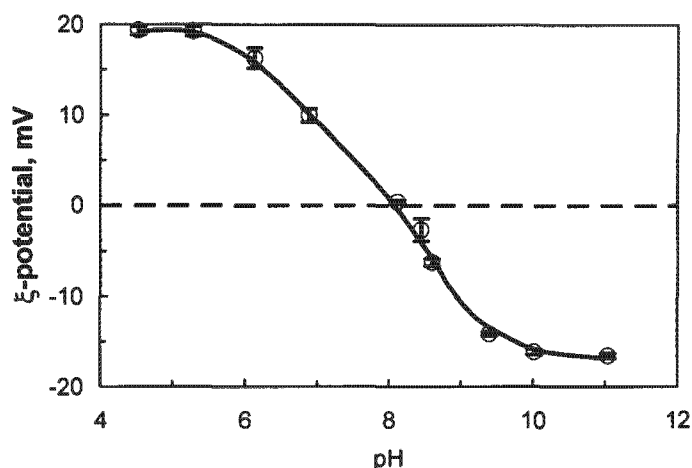


Figure 3.1: ξ -potential measurement of γ - Al_2O_3 (Pluralox SCCa 5-150, Sasol Germany GmbH) as a function of pH (pH was varied by addition of either aqueous NH_3 -solution or HNO_3) [Zwane, 2004].

Figure 3.1 shows the zeta-potential of the support material used in this study γ - Al_2O_3 (Sasol Germany GmbH Batch 9574 5/150 Pluralox SCCa; $S_{\text{BET}}=162\text{m}^2/\text{g}$; $d_{\text{pore}}=11.5\text{nm}$). The iso-electric point of this type of alumina is at a pH-value of ca. 8. A pH-value less than 8 will result in a net positive charge on the surface, and renders the material suitable for adsorption of anions.

The adsorption of molybdenum and vanadium anions was performed at a pH-value of 6. A much lower pH cannot be used, since the alumina can dissolve at a pH differing significantly from the iso-electrical point [Barradas *et al.*, 2002]. The aluminium support was modified with molybdenum by adsorption-deposition of ammonium heptamolybdate and vanadium by adsorption-deposition of ammonium meta-vanadate.

The amount of anions adsorbed during controlled adsorption, and thus the amount of molybdenum and vanadium that can be deposited on a support using this method is limited. The amount that can be adsorbed depends on the concentration of the metal anion and the pH of the solution containing the metal anion [Van Veen *et al.*, 1990; Wang and Hall, 1982].

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Higher loadings with molybdenum or vanadium can be achieved by employing an adsorption-deposition technique, in which first the metal anion is adsorbed and the remaining metal ions in the solution are deposited on the surface by evaporating water. Subsequent calcination of the support material at temperatures substantially above the Tamann-temperature (MoO_3 : 264°C ; V_2O_5 : 209°C) may lead to thermal spreading of the oxide over the $\gamma\text{-Al}_2\text{O}_3$ -support [Knözinger and Taglauer, 1993].

Preparation of alumina support material modified with molybdenum

Alumina support material was modified with between 0 and 21wt.-% molybdenum (see Table 2.1). The appropriate amount of ammonium heptamolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot\text{H}_2\text{O}$; Saarchem; $\text{MoO}_3 > 81.5\%$) was dissolved in 100ml demineralised water material leading to initial Mo(VI)-concentrations between 0.17 and 0.58mol/litre. The appropriate amount of alumina (Sasol Germany GmbH Batch 9574 5/150 Puralox SCCa) was added to the molybdenum containing solution and the pH was adjusted to 6.1 using nitric acid (AR, Orion Chemicals, 55%). At this pH-value, molybdenum is initially present as $\text{Mo}_7\text{O}_{24}^{6-}$ [Baes and Mesmer, 1976]. Only at much lower Mo(VI) concentrations of ca. 0.02mol/litre will molybdenum be present as MoO_4^{2-} . Hence, it might be assumed that adsorption of the heptamolybdate anion takes place during the adsorption step. After the solution was stirred for another 29hrs, the stirring was stopped and the mixture was left to age overnight.

Only a limited amount of molybdenum can be adsorbed on an alumina support. A MoO_3 -coverage of the alumina surface corresponding to ca. 0.3 monolayers was obtained at equilibrium at a pH-value of 6 with a starting concentration of 0.05mol/litre of molybdenum by Wang and Hall [1982]. This indicates that a one-step controlled adsorption process will not lead to molybdenum-modified alumina support materials with high coverage of the alumina surface.

Experimental

Higher molybdenum loadings can be obtained by controlled adsorption followed by deposition. Subsequent to the controlled adsorption step, water was removed in a rotar vapour at 120°C and atmospheric pressure with a rotation speed of 100rpm. The drying lasted 6h. The obtained materials were calcined in a fixed bed reactor. The catalyst was heated at a rate of 3°C/min to 550°C and was kept at 550°C for 12hrs in an air flow of 22ml(STP)/min. The high calcination temperature was chosen to enable thermal spreading of the resulting MoO₃ over γ -Al₂O₃ [Knözinger and Taglauer, 1993].

Table 3.1: Molybdenum oxide modified alumina supports prepared

Support name	Mo loading ¹ (wt-%)	MoO ₃ loading (theoretical monolayer ²)
0 Sup	0.0	0.0
4 Mo Sup	4.0	0.3
12 Mo Sup	11.6	0.9
16 Mo Sup	15.5	1.3
19 Mo Sup	19.3	1.8
21 Mo Sup	21.2	2.0

¹: Molybdenum assumed to be present in the support as MoO₃

²: Calculated using a surface area of γ -Al₂O₃ of 162m²/g and the area covered by a MoO₃-unit of 1.7·10⁻¹⁹m²

Preparation of alumina support material modified with vanadium

Alumina support material was modified with between 0 and 16wt.-% vanadium (see Table 2.2). The appropriate amount of ammonium meta-vanadate (NH₄VO₃; Sigma; 99.8%) was suspended in 100ml demineralised water material leading to initial V(V)-concentrations of ca. 0.04mol/litre, due to the limited solubility of NH₄VO₃ at room temperature (4.4g/litre [Perry et al., 1997]). The appropriate amount of alumina (Sasol Germany GmbH Batch 9574 5/150 Puralox SCCa) was added to the molybdenum containing solution and the pH was adjusted to 6.1 using nitric acid (AR, Orion Chemicals, 55%). At this pH-value, the main vanadium species is V₁₀O₂₈⁶⁻, although substantial amounts of V₄O₁₂⁴⁻, V₃O₉³⁻ and V₁₀O₂₇(OH)⁵⁻ will be present as well [Baes and Mesmer, 1976]. Hence, adsorption of the vanadium poly-anions takes place

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during the adsorption step. After the solution was stirred for another 29hrs, the stirring was stopped and the mixture was left to age overnight.

Only a limited amount of vanadium can be adsorbed on an alumina support. The resulting vanadium coverage of an alumina surface is between 0.2 and 0.4 monolayers depending on the pH of the solution starting with a vanadium concentration of 0.05mol/litre [Wang and Hall, 1982].

The controlled adsorption step was followed by deposition of vanadium through the evaporative removal of water at 120°C and atmospheric pressure in a rotar vapour with a rotation speed of 100rpm. At these temperatures, the remaining ammonium meta-vanadate will dissolve and by removal of the water be deposited on the alumina surface. The drying step lasted 6hrs. The obtained materials were calcined in a fixed bed reactor. The catalyst was heated at a rate of 3°C/min to 550°C and was kept at 550°C for 12hrs in an air flow of 22ml(STP)/min. The high calcination temperature was chosen to enable thermal spreading of the resulting V_2O_5 over $\gamma-Al_2O_3$ [Knözinger and Taglauer, 1993].

Table 3.2: Vanadium oxide modified alumina supports prepared

Support name	V loading ¹ (wt-%)	V_2O_5 loading (theoretical monolayer ²)
0 Sup	0.0	0.0
3 V Sup	2.9	0.3
5 V Sup	5.1	0.5
9 V Sup	8.6	0.9
16 V Sup	16.1	2.0

¹: Vanadium assumed to be present in the support as V_2O_5

²: Calculated using a surface area of $\gamma-Al_2O_3$ of 162m²/g and the area covered by a V_2O_5 -unit of $2.4 \cdot 10^{-19}m^2$

3.1.2 Preparation of cobalt catalysts on the modified support materials

A large variety of methods has been reported to bring cobalt metal on a support. The most commonly used method is the incipient wetness method [Van Steen *et al.*, 1996; Feller *et al.*, 1999; Saib *et al.*, 2002]. The interaction

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between the metal ions in the impregnation solution and the support strongly affects the resulting catalyst.

In this study an alternative catalyst preparation through colloid impregnation [Roy *et al.*, 2001] was used in an attempt to keep the resulting cobalt crystallites similar for all catalysts prepared. Cobalt nitrate was precipitated with ammonium hydroxide in the absence of the molybdenum and vanadium oxide modified supports. The formed cobalt hydroxide colloids were subsequently impregnated on the various supports.

A mass of 50g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 1 litre of demineralised water. A volume of 316ml of the cobalt solution was pipetted in a beaker and stirred rapidly. A volume of 10ml of 4M NH_4OH was added to the cobalt solution while stirring fast yielding a pH of 7.8 ± 0.2 . The mixture was stirred for a further 15 minutes. The formed precipitate was separated from the liquid by centrifuge at 5000rpm for 5 minutes. The remaining liquid had a pink colour indicating that not all cobalt was precipitated out. The efficiency of this precipitation method was typically $64 \pm 3\%$. An excess of cobalt nitrate was used to compensate for the cobalt that did not precipitate out in order to obtain a catalyst containing 10wt.-% Co in its calcined form. The precipitate was mixed with 17.28g $\gamma\text{-Al}_2\text{O}_3$ (Sasol Germany GmbH Batch 9574 5/150 Puralox SCCa) or same amount of molybdenum and vanadium modified alumina support.

The catalyst precursor was dried overnight at 125°C followed by calcination in air (819ml(STP)/minute) at 250°C (heating rate of $6^\circ\text{C}/\text{minute}$) for 6.5hrs. Tables 2.3 and 2.4 give an overview of the prepared catalysts.

Experimental

Table 3.3: Overview of catalysts used in this study

Catalyst	Support	MoO ₃ loading (theoretical monolayer ¹)	Mo loading ² (wt-%)	Co loading ² (wt-%)
0 Cat	0 Sup	0.0	0.0	10.2
4 Mo Cat	4 Mo Sup	0.3	3.4	10.2
12 Mo Cat	12 Mo Sup	0.9	10.0	10.2
16 Mo Cat	16 Mo Sup	1.3	13.5	10.2
19 Mo Cat	19 Mo Sup	1.8	16.8	10.2
21 Mo Cat	21 Mo Sup	2.0	28.4	10.2
Catalyst	Support	V ₂ O ₅ loading (theoretical monolayer ¹)	V loading ² (wt-%)	Co loading ² (wt-%)
0 Cat	0 Sup	0.0	0.0	10.2
3 V Cat	3 V Sup	0.3	2.5	10.2
5 V Cat	5 V Sup	0.5	4.5	10.2
9 V Cat	9 V Sup	0.9	7.5	10.2
16 V Cat	16 V Sup	2.0	14.0	10.2

¹: Calculated using a surface area of γ -Al₂O₃ of 162m²/g and the area covered by a MoO₃-unit of $1.7 \cdot 10^{-19}$ m² or a V₂O₅-unit of $2.4 \cdot 10^{-19}$ m²

²: Metal content in the calcined catalyst assuming molybdenum to be present as MoO₃ vanadium to be present as V₂O₅ and cobalt to be present as Co₃O₄

3.2 Physio-chemical characterisation of support materials and catalysts

3.2.1 Brunner Emmet Teller (BET) – analysis

BET analyses were performed on a Tristar Micrometrics analyser with the calcined catalysts to determine surface area and pore volume. The samples were evacuated in He for at least 8hrs at 250°C before the analyses.

3.2.2 X-ray diffraction (XRD)

XRD characterisation were carried out using a Philips PW 1390 diffractometer with Cu-K α radiation ($\lambda=1.5418\text{\AA}$, 40kV, 20mA) and a step size of $2\theta=0.01^\circ$.

Experimental

3.2.3 Transmission electron microscopy (TEM)

Transmission electron microscope pictures were taken using a LEO 912 OMEGA operating at 120kV. The samples were crushed in 3ml of hexane in 5-ml sample bottles using a glass rod. Two drops of the hexane with the fine particles dispersed were dropped on carbon coated copper grids. The sample loaded copper grids were covered with a thin plastic layer. The grids containing the samples were viewed at different magnifications.

3.2.4 Temperature Programmed Reduction (TPR)

Temperature programmed reduction experiments were performed using Micromeritics Autochem 2910 apparatus. Hydrogen (5.6 vol%) in argon with a total flow of 46ml(STP)/min was used as the reducing gas. A thermal conductivity detector (TCD) was used to determine the change in the hydrogen concentration. The temperature was controlled with a thermocouple inside the quartz tube located just above the sample. The water forming during the reduction was not trapped since this will result in a small change in the flow through the TCD. The change in thermal conductivity of the gas due to the presence of water is small since the thermal conductivity of water in the gas phase at room temperature is comparable to that of argon.

About 0.3g of catalyst sample was loaded in the quartz tube with the catalyst bed sitting on silane treated glass wool. The catalyst was dried in argon (52ml (STP)/min) for 30min at 120°C after which the system was allowed to cool down to ~50°C. Gas supply was then switched from Ar to a 5.6 vol% H₂-Ar (46ml(STP)/min) mixture. The temperature was then ramped at 10°C/min from ~50°C to 1000°C and was kept at this temperature for 1 hour. The TPR was calibrated with AgO.

3.2.5 Determination of degree of reduction by thermogravimetric analysis (TGA)

The degree of reduction of cobalt is important, since the Fischer-Tropsch reaction is catalysed by metallic cobalt [Iglesia *et al.*, 1993]. The degree of

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reduction of the catalysts was determined with Stanton Redcroft STA-780 series thermogravimetric analyser (TGA).

The catalyst (50mg) was reduced at 425°C in pure hydrogen (37ml (STP)/min) for 8 to 10hrs. A heating rate of 1°C/minute was used. During the reduction step the observed mass loss originates from adsorbed water and reduction of cobalt oxide or the support, i.e. molybdenum oxide/vanadium oxide in the modified support material. After reduction the catalyst was cooled to 350°C and flushed for 30minutes with nitrogen. The catalyst was subsequently oxidised with air at 350°C until no mass gain was observed. The oxidation step was done at 350°C to obtain Co₃O₄. At higher oxidation temperature auto-reduction of Co₃O₄ to CoO may occur [Sewell *et al.*, 1996]. Nitrogen was passed over the catalyst again. The mass increase due to oxidation was calculated from the mass during the nitrogen step before the oxidation and after the oxidation step.

3.2.6 X-ray photoelectron spectroscopy (XPS)

XPS analyses were performed on the catalyst to determine the oxidation state of the molybdenum oxide and vanadium oxide. The XPS analyses were performed by the CSIR (Pretoria, South Africa) using Physical Electronics (PHI), Quantum2000 XPS analyser. Al K α radiation (1486eV, 20W, 100 microns beam diameter) was used as the X-ray source. The catalyst was pre-reduced at 425°C for 8hrs in pure H₂ using a heating ramp of 2°C/minute.

The software package used to evaluate the data was Multipak 6.1A. Deconvolution of the spectra was performed using an iteration algorithm until the best fit was obtained with a Gaussian-Lorentzian mix on a Shirley background.

3.2.7 Chemisorption

Static chemisorption of hydrogen

Chemisorption of hydrogen was performed on a Micrometrics ASAP 2000 and 201C. About 1g of catalyst sample was loaded into the glass reactor. The catalysts were pre-reduced at 425°C in pure hydrogen for 8hrs with a ramp rate of 2°C/min. The catalyst was evacuated for at least 2hrs at 425°C. Hydrogen was chemisorbed at 125°C with an equilibrium interval of 30 seconds.

Temperature Programmed Desorption of CO (CO-TPD)

Temperature programmed desorption experiments were performed using Micrometrics Autochem 2910 apparatus. The catalyst (0.5g) was reduced at different temperatures (mostly 425°C) in pure hydrogen (50ml(STP)/min) for 8hrs. A ramp rate of 2°C/minute was used. Subsequently, the catalyst sample was exposed to 20 pulses of CO (0.021cm³ (STP)/pulse) with 60 minutes of flushing with helium in between each pulse. After the CO exposure, the catalyst was heated with a ramp rate of 10°C/minute and desorption of the chemisorbed CO was determined with a TCD. Helium (10ml(STP)/min) was used as flush gas during the desorption for the maximum TCD sensitivity.

3.2.8 Temperature programmed desorption of ammonia (NH₃-TPD)

Temperature programmed desorption of ammonia was used as one of the means to characterise the acidity of the reduced catalyst. The experiments were carried out in a home-built TPD apparatus [Callanan van Steen, 2000]. The gas flows were controlled with calibrated mass flow meters. The gasses were passed through a packed bed of catalyst in a quartz tube. The catalyst (0.25-0.36g) was pre-reduced at 425°C for 8hrs in pure hydrogen (55ml(STP)/min) using a heating ramp of 2°C/min. Subsequently, the catalyst was cooled down to 50°C and NH₃ (1% NH₃ in He, total flow 55ml(STP)/min) was adsorbed at 50°C for 30 minutes. The catalyst was flushed at 50°C for 5hrs with He (55ml(STP)/min). After the flushing step, the catalyst was heated with a heating rate of 10°C/min to desorb NH₃. The effluent was monitored using a TCD. The desorbed NH₃ was trapped in 0.01M H₂SO₄ solution. The

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total amount of ammonia was quantified by back-titration of sulphuric acid in the trap with 0.01M NaOH solution and phenolphthalein as an indicator.

3.3 Characterising of activity for side reactions

The modified supports may catalyse additional reactions, affecting the selectivity of cobalt-based Fischer-Tropsch synthesis due to the introduction of additional sites upon the introduction of transition metal oxides within the catalyst (see Chapter 2). Acid sites are expected to be present in the catalysts with molybdenum and vanadium modified supports, since they have been shown to be present in supported molybdenum oxide catalysts [Pantoja *et al.*, 1993; Rodrigues-Ramos *et al.*, 1995; Keller *et al.*, 2000; Benadda *et al.*, 2003] and supported vanadium oxide catalysts [Khadar, 1995; Ferreira and Volpe, 2002; Chary *et al.*, 2003] (see also chapter 2).

3.3.1 Dehydration of iso-propanol

The dehydration of iso-propanol yielding propene and diisopropylether can be used to characterise the acidic properties of the catalysts [Bej *et al.*, 2003; Benadda *et al.*, 2003; Perez-Cadenas *et al.*, 2003.] Over basic sites, the conversion of iso-propanol may lead to the formation of acetone [Bej *et al.*, 2003]. The presence of acid sites within the catalyst may lead to typically acid catalysed side reactions, such as double bond isomerisation, skeletal isomerisation, alcohol dehydration, etc.

The dehydration of iso-propanol was performed in a fixed bed reactor (also used for the Fischer-Tropsch synthesis – see Chapter 3.4 for a detailed description of the reactor set-up).

The catalyst (ca. 0.5g catalyst) was mixed with silicon carbide ($d_p=400\mu\text{m}$; $m=3.1\text{g}$) to reduce axial and radial temperature gradients. Silicon carbide was shown to be inert in the dehydration of iso-propanol under the reaction conditions studied. The catalyst was reduced at 425°C for 8hrs (heating rate 1°C/min) in pure hydrogen (60ml(STP)/min).

Experimental

The reactor set-up was slightly modified to accommodate a saturator made out of glass containing the iso-propanol (Kimix; purity > 99.7%). Argon was bubbled through iso-propanol at room temperature resulting in a partial pressure of iso-propanol of ca. 0.06bar. The iso-propanol/argon stream bypassed the reactor for at least 30min to avoid contact of the catalyst with oxygen.

The dehydration of iso-propanol was performed at 220°C and atmospheric pressure. The argon flow rate was increased step-wise every 30minutes to obtain results at different space velocities. After the last data point the flow was decreased again to see whether deactivation had occurred. Samples of the effluent stream were taken using the ampoule sampling technique [Schulz and Nehren, 1986].

The organic products were obtained by analysis of ampoule samples on a GC (Varian 3400 Series) equipped with a flame ionisation detector (FID).

3.3.2 Conversion of 1-hexene

Supported molybdenum oxide has been known to be able to catalyse the metathesis reaction [Banks, 1981]. In order to investigate the occurrence of side reactions, such as double bond isomerisation, skeletal isomerisation and metathesis, the conversion of 1-hexene was performed.

The conversion of 1-hexene was performed in a fixed reactor (also used for the Fischer-Tropsch synthesis - see Chapter 3.4 for a detailed description of the reactor set-up). The reactor set-up was slightly modified to accommodate a glass saturator containing the 1-hexene (Merck; purity >96%). Argon was bubbled through 1-hexene at room temperature resulting in a 1-hexene partial pressure of ~0.2bar.

The catalyst (ca. 0.2g) was reduced at 425°C for 8hrs, (heating rate 1°C/min) in pure hydrogen (60ml(STP)/min). Argon was bubbled through 1-hexene at room temperature and bypassing the reactor for at least 30 minutes to remove

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any oxygen before the argon/1-hexene stream was sent over the pre-reduced catalyst.

The conversion of 1-hexene was performed at 220°C and atmospheric pressure. The argon flow rate was increased step-wise every 30 minutes to obtain results at different space velocities. Samples of the effluent were taken using the ampoule technique [Schulz and Nehren, 1986].

3.4 Fischer-Tropsch synthesis

Fixed bed reactor set-up

The reduction of the catalyst and most of the Fischer-Tropsch synthesis reactions were performed in a fixed bed reactor set-up (see Figure 3.2). The reactor set-up consists of a gas delivery section, reactor section and product work-up section.

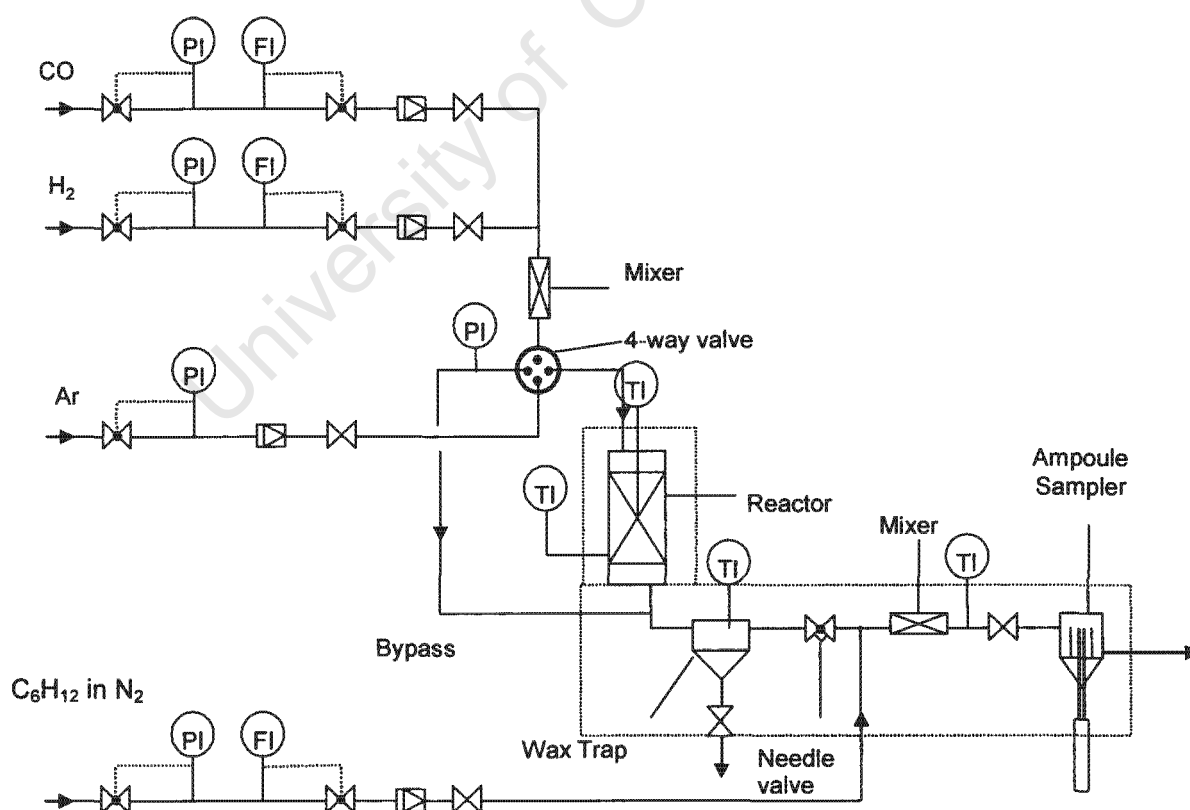


Figure 3.2: Flow diagram of the fixed bed reactor set-up for the Fischer-Tropsch synthesis

Experimental

The gases carbon monoxide (Afrox, purity 3.7) and hydrogen (Air Liquide, purity 5) were controlled individually and mixed. The composition of the feed gas was determined by leading the feed gas mixture over the reactor by-pass. The H_2/CO ratio was analysed online with a gas chromatograph with a thermal conductivity detector to ensure that a H_2/CO ratio of 2 was obtained as expected from the MFC calibrations. At the start of the reaction, the 4-way valve was switched and the feed gas flowed through the reactor. Argon was added under reaction conditions to the product stream to control the reactor pressure. A known amount of cyclohexane in nitrogen was added to and mixed with the product effluent stream as an internal standard for data analysis.

The fixed bed reactor was heated electrically and consisted of a stainless steel reactor with an ID of 10mm with an isothermal zone of 4.5cm. The temperature was measured in the centre of the catalyst bed with a thermocouple. A mixture of catalyst (ca. 0.5g) and silicon carbide ($d_p=400\mu\text{m}$; $m=3.1\text{g}$) was loaded in the centre of the isothermal zone (bed length: ca. 4cm). The catalyst was mixed with silicon carbide to reduce axial and radial temperature gradients. The catalyst was kept in place by plugs of glass wool at the top and bottom of the catalyst bed. Coarse silicon carbide (10 g) was packed on top as a pre-heating zone.

Liquid products were separated from the gas stream in the wax trap operating at 190°C and reaction pressure.

Samples of the product stream were taken after pressure reduction to atmospheric pressure using the ampoule sampling technique. The organic product distribution ($\text{C}_1\text{-C}_{20}$) was determined from this product stream. The inorganic gases and methane content of the product effluent were analysed using an on-line GC equipped with a TCD.

Experimental

The Fischer-Tropsch synthesis was performed over the reduced catalyst. The reduction was performed in-situ at 425°C for 8hrs with a flow of 60ml(STP)/min at atmospheric pressure. A heating rate of 1°C/minute was used. After reduction the system was cooled to 220°C and pressurised with argon. The synthesis gas mixture (23 ml(STP)/min for most of the runs), as mixed by mass flow controllers (MFC) from pure gasses, was introduced through the by-pass.

Under the applied reaction conditions the contribution of internal (see Appendix I) and external mass transfer limitations (see Appendix F.2.3) can be neglected.

Slurry bed reactor

A limited number of experiments were performed in a slurry bed reactor, which is similar in set-up as been used by Van Steen [1993].

The catalyst was reduced ex-situ at 425°C for 8hrs in pure hydrogen (380ml(STP)/min) and atmospheric pressure. A heating rate of 1°C/minute was used. After reduction the catalyst was covered with wax to protect it against oxidation.

The pre-reduced catalyst (10g) was used in the slurry reactor (volume ~500ml). A stirring speed of 30% was used to avoid external mass and heat transfer limitations through the boundary layer (see Appendix G). The temperature was controlled with a thermocouple inside the reactor. The Fischer-Tropsch synthesis was performed at 220°C, 20 bar_a and 200ml (STP)/min synthesis gas with a H₂/CO ratio of 2. A flow of 0.8ml(STP)/min of NH₃ was added to the synthesis gas to investigate the influence of the presence of acid sites in the Fischer-Tropsch catalyst.

A known amount of cyclohexane in nitrogen was added to the reactor effluent by means of a mass flow controller after the wax trap as an internal standard. Online analyses of the permanent gasses were done with a thermal conductivity detector. Simultaneously glass ampoules [Schulz and Nehren,

Experimental

1986] were taken which was used to analyse the hydrocarbon products with a gas chromatograph with a flame ionisation detector.

Gas analyses

The permanent gasses were analysed on a Varian model 3700 gas chromatograph equipped with a thermal conductivity detector (TCD). Argon was used as carrier gas with a head pressure of 2bar. The separation was achieved on a Carbosieve II column, operating isothermally at 170°C. The TCD was calibrated with a calibration gas mixture from MG Fedgas containing H₂ (14.7%), N₂ (15.2%) CO (15.5%) CO₂ (15.1%) and CH₄ (14.7%); the balance being argon

Organic products of the Fischer-Tropsch reaction was characterised by analysis of ampoule samples on a GC (Varian 3400 Series) equipped with a flame ionisation detector (FID). This GC was installed with a cryogenic system a feature which enabled product analysis to be performed over a wide temperature range (-60°C to 280°C) (see Appendix E).

4 Characterization and performance of Co/MoO₃/γ-Al₂O₃

4.1 Characterization of modified support materials

The γ-Al₂O₃ support was modified with molybdenum by controlled adsorption of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·H₂O) followed by deposition of the excess amount of molybdenum. The deposition following the controlled adsorption step was needed to achieve larger molybdenum loadings, since the adsorption capacity of alumina is limited [Wang and Hall, 1982].

Figure 4.1 shows the XRD-patterns of the calcined alumina support, on which various amount of molybdenum has been put. All samples show the diffraction lines for γ-Al₂O₃. The intensity of the characteristic Al₂O₃-diffraction peaks decrease with increasing molybdenum content. However, the observed decrease in the peak intensity (41%) is stronger than expected based on the decreased alumina content (wt-%) in the support (32%) (an even smaller decrease in the intensity is expected when taking the increase in density of the catalyst due to the addition of molybdenum oxide into account).

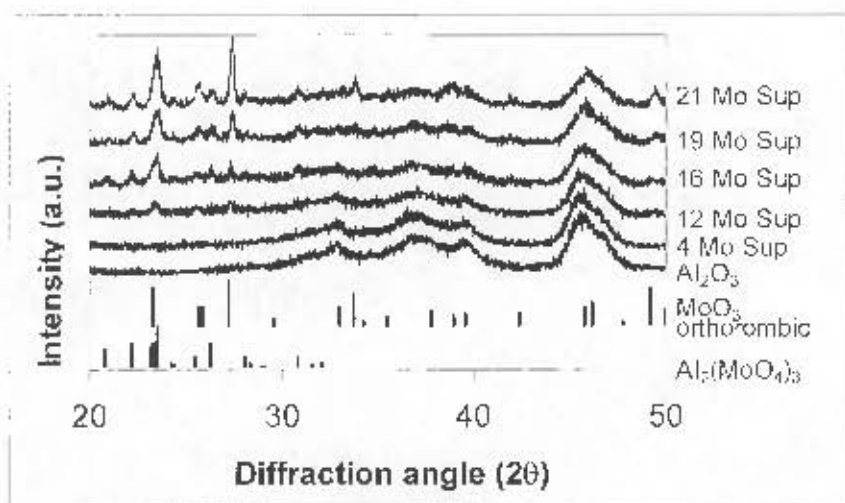


Figure 4.1: XRD spectrum of γ -Al₂O₃-support (Pluralox SCCa 5-150) modified with molybdenum prepared using controlled adsorption-deposition technique and the diffraction lines of Al₂O₃ (unmodified), MoO₃ and Al₂O₃, and Al₂(MoO₄)₃.

Additional diffraction lines are observed with increasing molybdenum content and in particular for catalyst with a molybdenum loading larger than 12wt.-%. This molybdenum loading corresponds theoretically to 0.9 monolayers of MoO₃ on this support. These diffraction lines can be ascribed to crystalline MoO₃ and Al₂(MoO₄)₃. The intensity of the MoO₃ diffraction peaks normalised relative to the alumina increased with an increase in the molybdenum oxide loading in the modified supports (see Figure 4.2). The intensity of the aluminium molybdate diffraction peaks normalised relative to the alumina increased and levelled off with an increase in the molybdenum oxide loading in the catalyst. The reaction between the alumina and the molybdenum may occur during the wet preparation step [Van Veen *et al.*, 1990] or during calcination [Leung *et al.*, 1998]. The rate of alumina dissolution during the preparation step or rate of solid state diffusion may be slow, resulting in a levelling off of the Al₂(MoO₄)₃ formation with an increase in the molybdenum oxide loading. The formation of aluminium molybdate was also observed by Jacobs [2002] for alumina supports with high molybdenum coverage. XRD thus indicates that evenly spread monolayer or multilayer of molybdenum oxide is not formed with the employed synthesis technique.

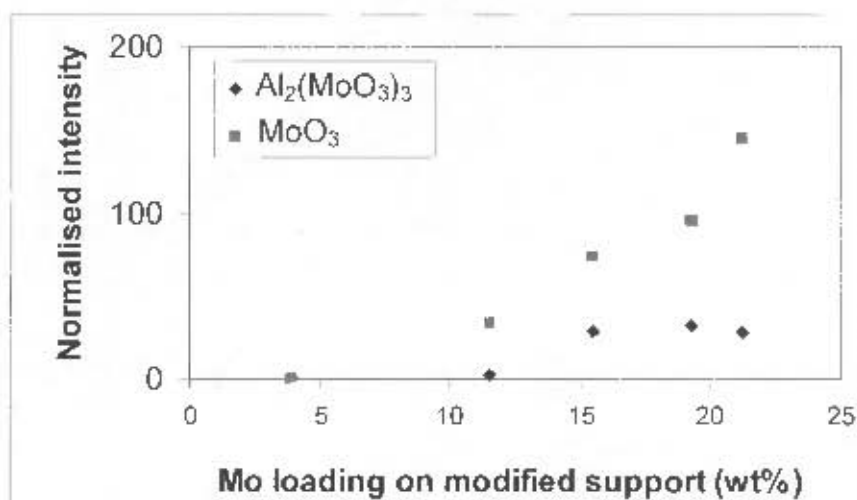


Figure 4.2: Normalised intensities of MoO₃ (28° 2θ) and Al₂(MoO₄)₃ (22° 2θ) relative to Al₂O₃ (46° 2θ) in the XRD spectrum of γ-Al₂O₃-support (Pluralox SCCa 5-150) modified with molybdenum prepared using controlled adsorption-deposition technique.

The morphology of the modified support changed significantly upon the addition of larger amounts of molybdenum (see Figure 4.3). The introduction of a large amount may have transformed the small Al₂O₃-particles into large needle-shaped crystallites. This might be ascribed to the formation of crystalline orthorhombic Al₂(MoO₄)₃. The needle-shape crystallites in the TEM picture may also be due to orthorhombic MoO₃ which is known to form needle-shaped structures [Beato, 2005].

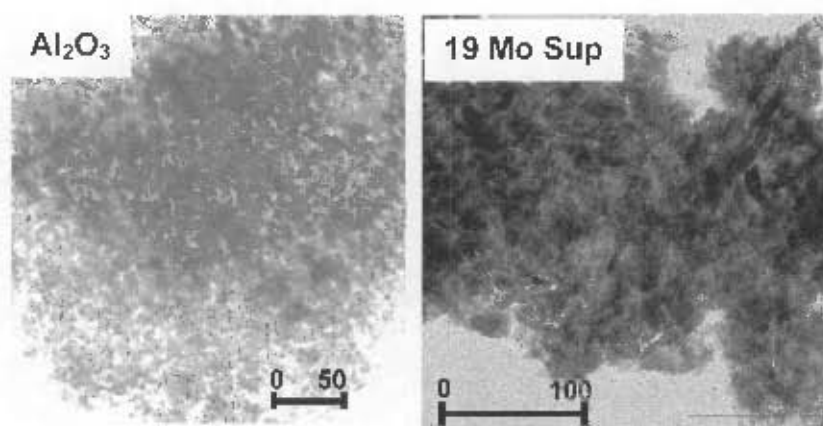


Figure 4.3: Change in support morphology as observed using TEM (scale in nm)

- Left: TEM image of the unmodified support ($\gamma\text{-Al}_2\text{O}_3$, Pluralox SCCa 5-150) [Zwane, 2004]
- Right: $\gamma\text{-Al}_2\text{O}_3$ -support (Pluralox SCCa 5-150) modified with 19wt.-% Mo by the controlled adsorption-deposition technique

4.2 Characterization of cobalt catalysts on the modified support materials

Cobalt was added to the MoO_3 -modified $\gamma\text{-Al}_2\text{O}_3$ support material by colloidal impregnation. Cobalt was precipitated from a cobalt nitrate solution with ammonia as a precipitating agent and the precipitate was put on the support. The aim of this method was to form cobalt hydroxide crystals of which size are independent of the support.

The mixing of cobalt oxide (Co_3O_4) with MoO_3 was investigated separately. Mixtures containing 50 wt% MoO_3 and 50 wt% Co_3O_4 were prepared with and without various solvents. The mixtures were left in the solvents for 20 minutes before drying. The solvents were evaporated on a hot plate and the mixtures were further dried in an oven at 120°C for about 20min. The resulting interaction between cobalt(II,III)oxide and molybdenum oxide was investigated by reduction with a TGA-analysis.

Figure 4.4 shows the reduction of unsupported MoO_3 and Co_3O_4 as monitored using TGA and mixtures of Co_3O_4 and MoO_3 . Cobalt(III,II)oxide and molybdenum oxide were also mixed dry and using n-hexane as a solvent. The reduction profile of the dry mixture and the mixture prepared with n-hexane are similar to reduction profile of the separate oxides. Mixing the oxides using oxygenated solvents, such as DIPE, hexanol or water yielded an increase in the temperature at peak maximum of the reduction peak for Co_3O_4 . The increase in the temperature at peak maximum of the Co_3O_4 reduction peak indicates some interaction between the cobalt and molybdenum. Molybdenum oxide can dissolve in these solvents, e.g. 1.07g per 1kg of water at 18°C [Weast and Astle, 1985]. Furthermore, methanol has been reported as a solvent for controlled adsorption of MoO_3 on MgO [Zdrasil, 2001]. The dissolved MoO_3 can deposit on the surface of the Co_3O_4 , which may retard the rate of reduction of cobalt. A similar effect might be expected in the prepared catalyst, since the catalyst preparation proceeds via an aqueous impregnation of the cobalt precipitate on the molybdenum oxide modified support. Some MoO_3 is present in the supports with a high MoO_3 -loading (see Figure 4.1).

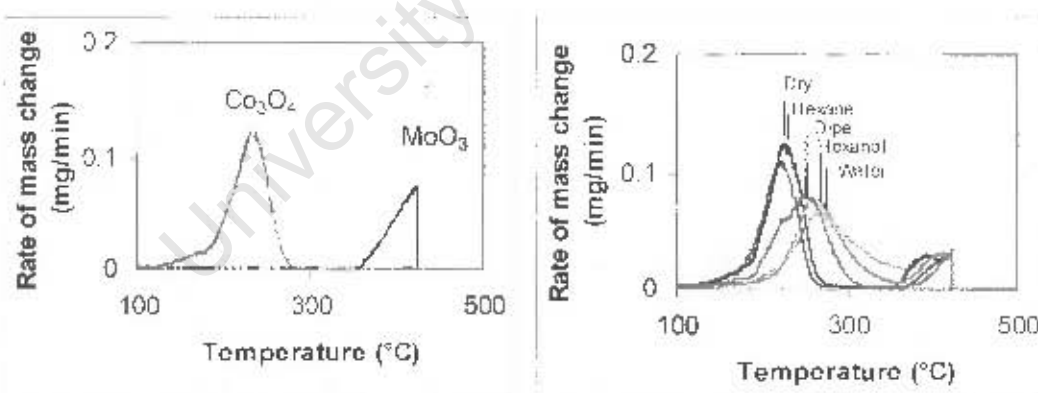


Figure 4.4: Reduction profile of mixtures of MoO_3 (25mg) and Co_3O_4 (25mg) in hydrogen with a heating rate of 1°C/min

Left: Reduction profile of the separate oxides MoO_3 and Co_3O_4

Right: Reduction profile of mixtures prepared by dry mixing, mixing in n-hexane, mixing in DIPE and mixing in hexanol and mixing in water

It might have been expected that the interaction between MoO₃ and Co₃O₄ is enhanced at elevated temperatures (thermal spreading), since the Tamman temperature of MoO₃ is 261°C [Knözinger and Taglauer, 1993] (for MoO₂, which will be present during reduction, the Tamman temperature was estimated from its melting point as 414°C). Therefore, the effect of temperature on the interaction, as measured by the reduction using TGA, was investigated by calcination of the dry physical mixture of Co₃O₄ and MoO₃ at 250°C for 3 hrs and at 500°C for 9 hrs in air. In both cases the reduction profile remained unaltered (see Figure 4.5). This indicates that thermal spreading was not significant in a loose mixture of the two solids. This does not exclude thermal spreading when MoO₃ and Al₂O₃ is in close contact.

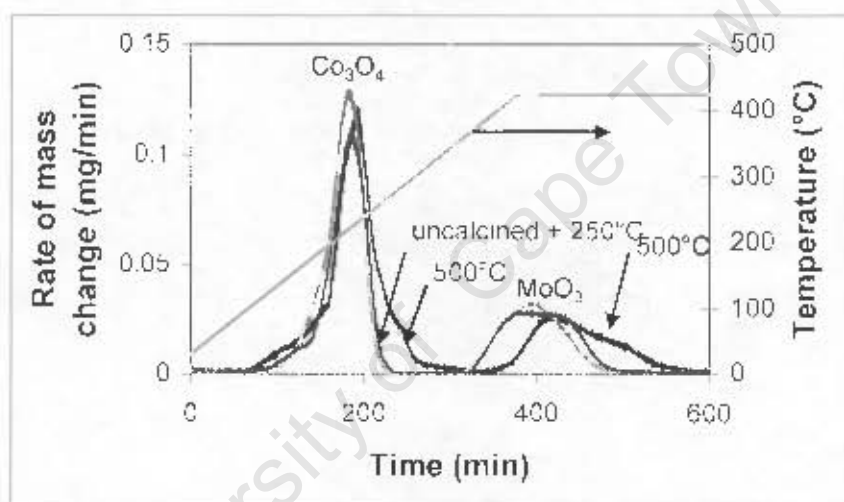


Figure 4.5: Reduction profile in hydrogen of loose mixtures of unsupported MoO₃ and Co₃O₄ calcined at 250 and 500°C

4.2.1 Physico-chemical characteristics of Co/MoO₃/γ-Al₂O₃

The Co/MoO₃/γ-Al₂O₃ catalysts calcined at 250°C were characterized using XRD (see Figure 4.6). After the addition of cobalt and calcination at 250°C, the MoO₃ and Al₂(MoO₄)₃ diffraction peaks disappeared. These diffraction lines were clearly visible in the XRD-pattern of the modified support. The calcined catalyst without MoO₃ on the support shows the presence of Co₃O₄. A Co₃O₄ crystallite size of 9nm was estimated by line broadening analysis, using the Debye-Scherrer equation [Ertl et al., 1997] for this catalyst. The Co₃O₄ diffraction peak at 2θ=59° was chosen for estimating β value because it was least influenced by γ-Al₂O₃ diffraction peaks

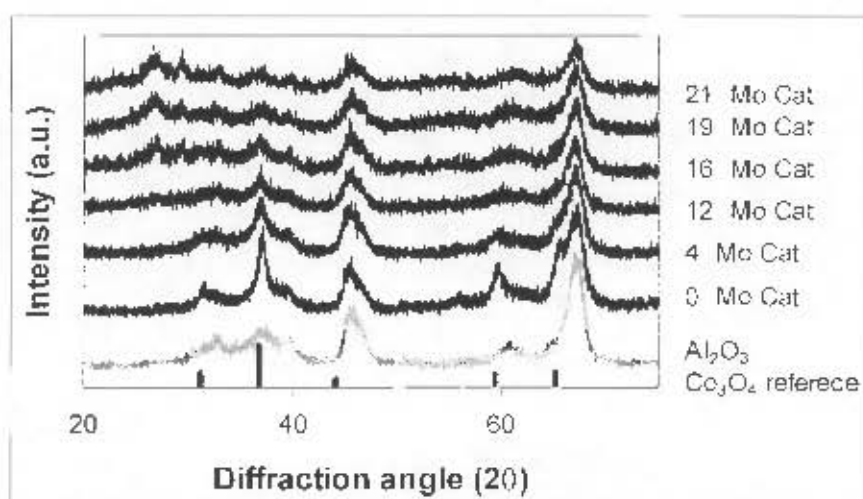


Figure 4.6: XRD-pattern of the calcined $\text{Co}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ -catalysts and Co_3O_4

The diffraction lines attributable to Co_3O_4 are absent when MoO_3 is present in the catalyst formulation. Catalyst containing more than 16wt.-% Mo show new diffraction lines at $2\theta=27.0^\circ$ and $2\theta=29.6^\circ$. A new crystalline phase is formed upon the introduction of cobalt accounting for the absence of the Co_3O_4 -diffraction lines and the disappearance of the MoO_3 and $\text{Al}_2(\text{MoO}_4)_3$ in the catalyst with a high MoO_3 -loading.

In order to gain more information on the unidentified diffraction peaks at $2\theta=27.0^\circ$ and $2\theta=29.6^\circ$, a catalyst with 19wt.-% MoO_3 -loading was calcined at 550°C for 12hrs. Some diffraction peaks disappeared and other became more intense in the range $2\theta=20\text{--}35^\circ$ (see Figure 4.7). These unidentified peaks can be attributed to two cobalt molybdate phases CoMoO_4 i.e. the low temperature modification α and the high temperature modification β [Arnoldy *et al.*, 1985b]. In the α -phase Mo^{6+} ions have an octahedral, whereas Mo^{6+} -ions are tetrahedrally surrounded in the β phase [Rodriguez *et al.*, 1998]. The transition $\alpha \rightarrow \beta$ starts between 330 and 410°C . Thus, the increase in the calcination temperature resulted in a partial phase transition, which confirms the presence of a mixture of β - CoMoO_4 and α - CoMoO_4 in the calcined catalyst sample.

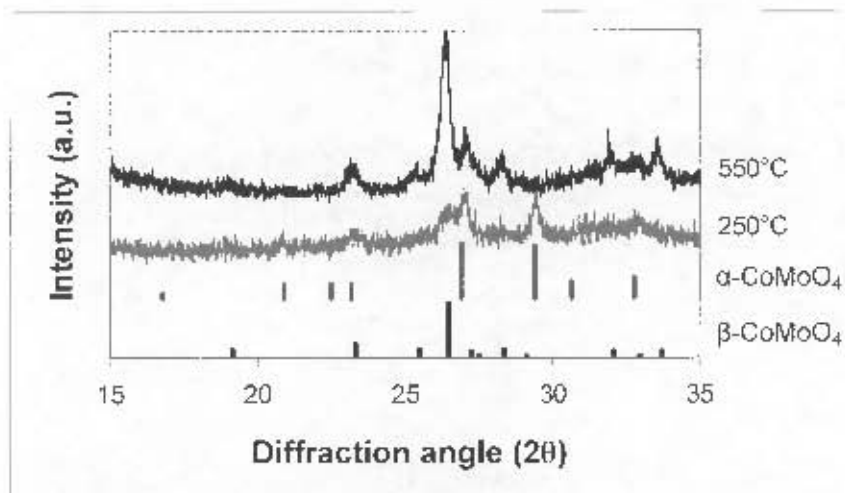


Figure 4.7: XRD spectrums of molybdenum oxide promoted catalysts containing 19wt.-% MoO₃ calcined at different temperatures

Table 4.1 shows the effect of the molybdenum loading on the BET-surface area, pore volume and average pore diameter in the calcined Co/MoO₃/γ-Al₂O₃ catalysts. The introduction of molybdenum in the catalyst formulation leads to a simultaneous reduction in the BET-surface area and the pore volume keeping the average pore diameter approximately constant.

Table 4.1: Influence of Mo-loading on the BET-surface area, pore volume and average pore diameter in the calcined Co/MoO₃/γ-Al₂O₃ catalysts

Catalyst	S _{BET} (m ² /g)	V _{pore} (cm ³ /g)	d _{pore} (nm)
0 Cat	160.7	0.42	10.4
4 Mo Cat	175.0	0.44	10.0
12 Mo Cat	145.0	0.37	9.8
16 Mo Cat	115.9	0.32	11.0
19 Mo Cat	98.3	0.26	10.6
21 Mo Cat	85.2	0.23	10.9

4.2.2 Reduction behaviour of Co/MoO₃/γ-Al₂O₃

The reduction behaviour of the calcined Co/MoO₃/γ-Al₂O₃ catalysts was characterized using temperature programmed reduction (TPR). The reduction behaviour of the catalyst was compared with the reduction behaviour of the

modified support material (see Figure 4.8). Molybdenum deposited on alumina can be reduced at elevated temperatures starting at ca 450°C . The various peak maximums observed between 500°C and 750°C observed might be ascribed to reduction of the various oxidation stages in the reduction of MoO_3 [Arnoldy *et al.*, 1985b], whereas the high temperature peak maximum might be attributed to the reduction of Al_2MoO_4 .

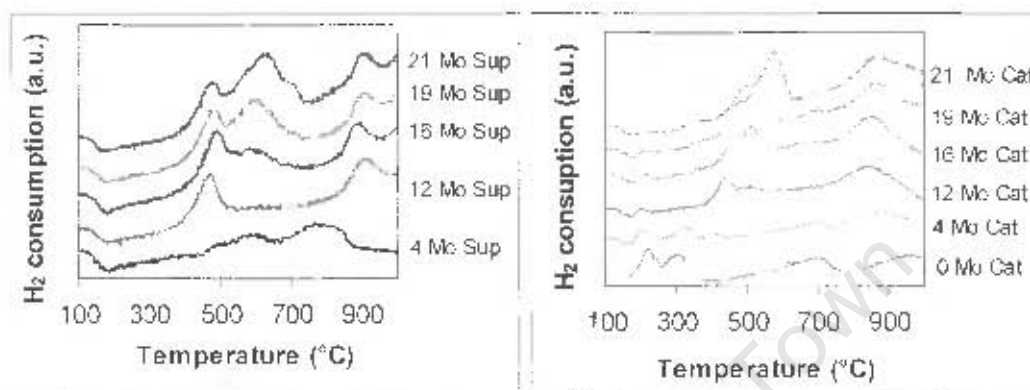


Figure 4.8: Temperature programmed reduction profile of the molybdenum modified support material (left) and the calcined $\text{Co}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts (right)

The TPR-profile of $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ shows two low temperature peak maximums and two high temperature peak maximums. The first peak between 190°C and 220°C might be ascribed to the reduction of Co_3O_4 to CoO and the second low temperature peak between 265°C and 305°C to the reduction of CoO to Co [Hilmen *et al.*, 1996]. However, the area of the first peak is $>25\%$ of the total area up till 400°C indicating that some reduction of CoO to Co may also be take place at these low temperatures. The reduction peak at temperature higher than 400°C may be due to cobalt in close interaction with alumina [Arnoldy and Moulijn, 1985]. The reduction peak at a temperature higher than 800°C may be due to cobalt aluminate [Arnoldy and Moulijn, 1985a; Arnoldy *et al.*, 1985b].

The low temperature peak maximum of the cobalt oxide shifts towards higher temperatures with the addition of molybdenum to the catalyst formulation. This was also observed by Arnoldy *et al.* [1985b] for the second cobalt reduction peak. This indicates that the rate of reduction of cobalt is decreased with the

addition of molybdenum oxide to the catalyst formulation, which may be due to coverage of cobalt with molybdenum oxide.

The reduction peak in the TPR between 600°C and 700°C might be assigned to the CoMoO₄ phase and the high temperature reduction peak (>750°C) to the reduction of cobalt aluminate and aluminium molybdate [Arnoldy *et al.*, 1985a]. The reduction of cobalt molybdate is more facile than the reduction of cobalt aluminate, since Al³⁺ polarises the Co-O bonds more than Mo⁵⁺ [Arnoldy *et al.*, 1985a].

Figure 4.9 shows the amount of hydrogen consumed for the reduction of the catalyst and for the reduction of the support. The molybdenum oxide and cobalt oxide was fully reduced at 1000°C. The hydrogen consumption increases with increasing molybdenum oxide loading. The amount of hydrogen consumed for the reduction of cobalt within the catalyst can be obtained by the difference of the amount of hydrogen consumed for the reduction of the catalyst and the amount of hydrogen consumed for the reduction of the support, and amounts to ca. 2mmol of H₂ per gram of catalyst. This corresponds to a cobalt loading of ca. 9-10 wt.-% depending on the oxidation state of cobalt in the calcined catalyst. This approximates well the intended cobalt loading.

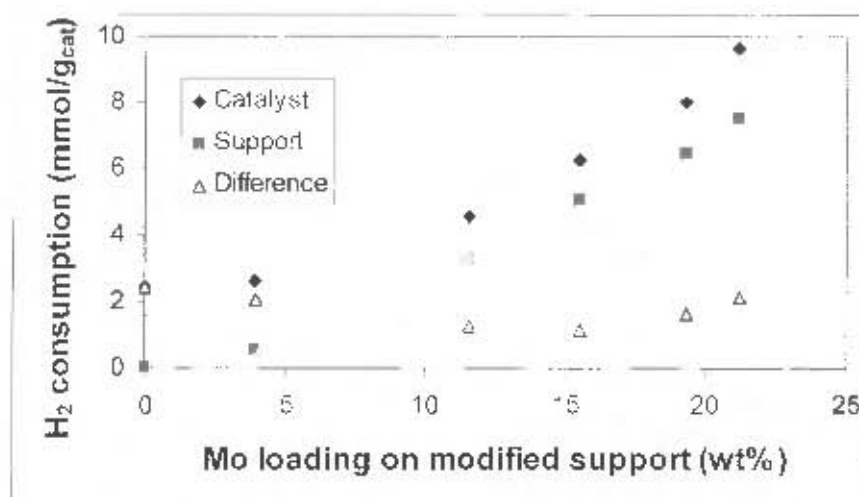


Figure 4.9: Integral hydrogen consumption (in mmol/g of catalyst) in the temperature programmed reduction (up to a temperature of 1000°C) of molybdenum modified alumina, $\text{Co/MoO}_3/\gamma\text{-Al}_2\text{O}_3$ and the difference attributable to the reduction of cobalt within the calcined catalyst

4.2.3 Characterization of reduced $\text{Co/MoO}_3/\gamma\text{-Al}_2\text{O}_3$

The cobalt-based catalysts supported on the molybdenum oxide modified alumina supports were calcined at 250°C in air followed by reduction at 425°C in pure hydrogen.

The reduction process eliminates the CoMoO_4 -phase present in the calcined catalyst. Figure 4.10 shows the XRD-pattern of the cobalt catalyst supported on alumina containing 19 wt.-% Mo in its calcined and in its reduced form (the reduced catalyst was covered with xylene to prevent re-oxidation). The diffraction peaks attributed to CoMoO_4 -phases (see Figure 4.7) disappeared indicating the decomposition of these phases in hydrogen at 425°C . It might be implied that the decomposition of the mixed cobalt molybdenum oxide phase is accompanied by the reduction of cobalt in this phase. The remaining diffraction peaks can be attributed to $\gamma\text{-Al}_2\text{O}_3$. Diffraction peaks attributable to metallic cobalt or MoO_x could not be detected implying that these phases are XRD-amorphous, i.e. the crystallites are either too small to be detected by XRD or contain too many defects.

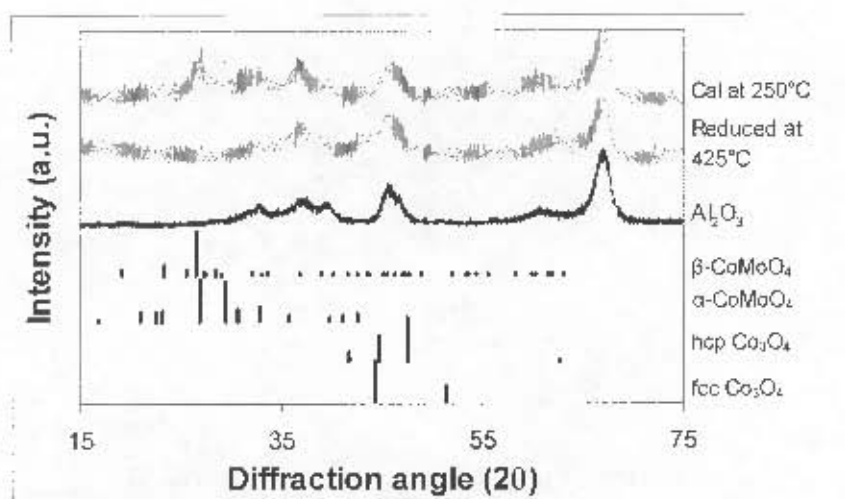


Figure 4.10: XRD patterns of $\text{Co/MoO}_3/\gamma\text{-Al}_2\text{O}_3$ with 19 wt.-% MoO_3 (19 Mo Cat) after calcination in air at 250°C (top) and after reduction at 425°C (bottom)

Degree of reduction

The degree of reduction of the catalysts was determined using thermal gravimetric analysis (TGA). The catalysts were reduced in pure hydrogen at 425°C overnight and oxidised in air at 350°C. The oxidation steps were done at 350°C to oxidise the cobalt to Co_3O_4 . If the cobalt is oxidised at a too high temperature, Co_3O_4 is converted to CoO [Sewell *et al.*, 1996]. The mass gain during the oxidative treatment was used to determine the degree of reduction of the catalyst.

The reduction of the catalyst may also lead to a partial reduction of the molybdenum on the support. Subsequent oxidation will also result in a mass gain. For instance, the oxidation of the reduced molybdenum oxide modified alumina, 21 Mo Sup yielded a mass gain of 32 mg/g. This indicates that the average oxidation state of molybdenum during the reduction was reduced to 4.1.

The degree of reduction of cobalt in the catalyst can be estimated by the difference of the mass gain of the reduced catalyst and the mass gain of the reduced support (see Figure 4.10 and Table 4.2). The implicit assumptions in this approach are that the molybdenum in the support reduces to the same

extent than in the catalyst containing molybdenum, and the interaction between cobalt and molybdenum does not hinder the full oxidation of cobalt to Co_3O_4 and molybdenum to the same state as in the re-oxidised reduced support. It was observed that the difference in the mass gain between the reduced catalyst and the reduced support remains fairly constant. Hence, it may be assumed that the interaction between the molybdenum and cobalt did not affect the degree of reduction of each other.

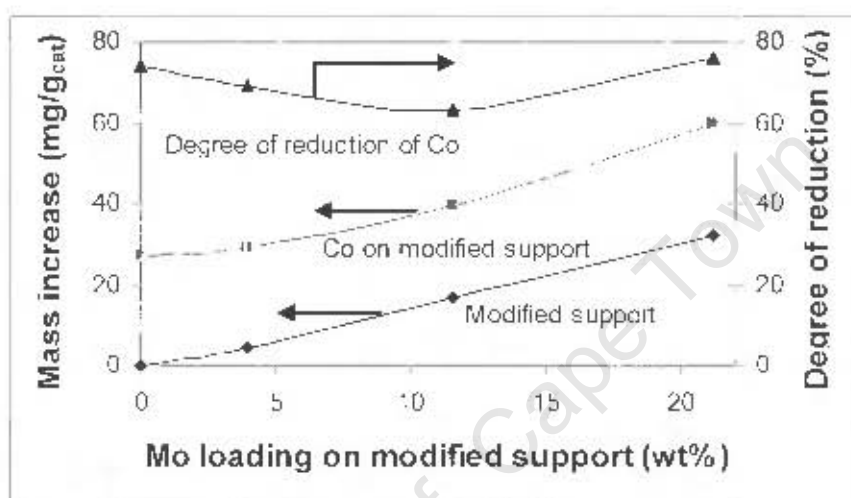


Figure 4.11: Mass gain during oxidation of the reduced $\text{Co}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ -catalysts and the molybdenum modified support and the degree of reduction of cobalt as estimated from the difference

Table 4.1: Degree of reduction of cobalt in $\text{Co}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ -catalysts as determined by the difference in the mass gain during the oxidation of the reduced catalyst and the reduced support ($T_{\text{reduction}} = 425^\circ\text{C}$ for 8hrs)

Catalyst	Degree of reduction (%)
0 Cat	74
4 Mo Cat	69
12 Mo Cat	63
21 Mo cat	76

Metal surface area

The activity of a catalyst in the Fischer-Tropsch synthesis over supported cobalt catalysts is believed to be proportional to the metal surface area

[Iglesia, 1993]. Static hydrogen chemisorption and CO TPD were used in attempt to quantify the metal surface area.

Static chemisorption was found to be of limited use to quantify the number of cobalt surface metal sites since both hydrogen and carbon monoxide can also chemisorb/adsorb on molybdenum oxide. IR showed CO adsorption on unreduced MoO₃/SiO₂ [Raskó and Kiss, 2003, Choi and Lee, 1997]. CO was found to adsorb on partially reduced molybdenum oxide (average oxidation state between 4+ and 6+) supported on alumina [Lombardo *et al.*, 1980]. MoO₂ has "metallic" functionality that can dissociate hydrogen that can bond to surface oxygens forming MoO₂(H_x)_{sc} [Al-Kandari *et al.*, 2005]. Partially reduced molybdenum supported on alumina (Mo oxidation state between +4 and +6) can chemisorb hydrogen [Jocono and Hall, 1977]. Figure 4.11 shows the hydrogen uptake in a static chemisorption experiment on the Co/γ-Al₂O₃ (0 Cat) without molybdenum added to the support and on Co/MoO₃/γ-Al₂O₃ with 12wt.-% Mo (12 Mo Cat). The hydrogen uptake on the catalyst without MoO₃ shows the typical dependency of the adsorbed volume on the pressure, with a strong increase in the adsorbed volume at very low pressures asymptotically approaching a constant value of ca. 0.3ml(STP)/g (see Figure 4.12). The metal surface area for this catalyst (0 Cat) can thus be estimated to be 1.1m²/g. The strong increase of the adsorbed volume at very low pressure indicates that the hydrogen adsorption is very strong under these conditions. The hydrogen uptake on Co/MoO₃/γ-Al₂O₃ with 12wt.-% Mo (12 Mo Cat) shows a different behaviour. It increases gradually with increasing pressure. A constant value is not approached at pressures up to 700mm Hg. This shows that hydrogen is likely to be chemisorbed on weaker sites, e.g. MoO_x as well as on metallic sites. It can also be speculated that hydrogen dissociates on the cobalt metal and spills over to form MoO₄(H_x)_{sc} [Al-Kandari *et al.*, 2005] or H_xMoO₃ [Marcq *et al.*, 1984]. At very low pressure the hydrogen uptake of the Co/MoO₃/γ-Al₂O₃ with 12wt.-% Mo (12 Mo Cat) is less than on Co/γ-Al₂O₃ (0 Cat). This might indicate that the exposed metallic cobalt surface area on the catalyst, to which molybdenum was added to the catalyst formulation, is less than the on the catalyst without molybdenum.

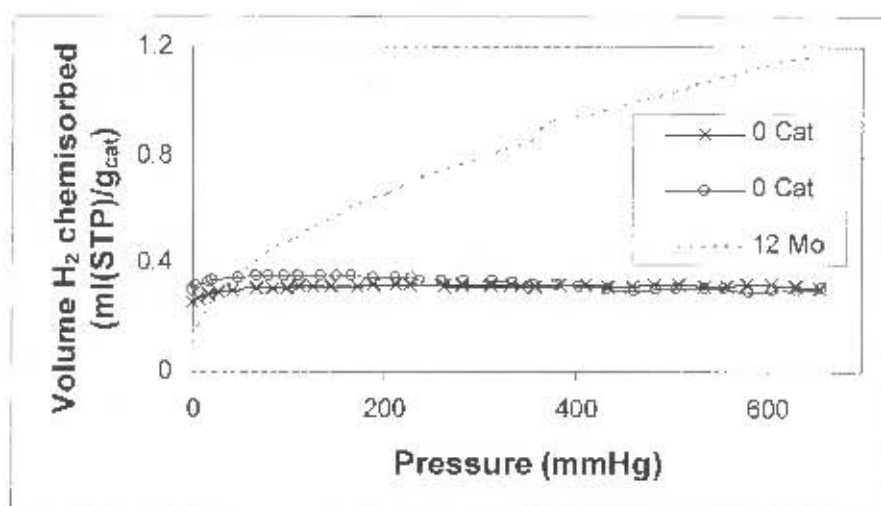


Figure 4.12: Static chemisorption of hydrogen at 125°C on $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (0 Cat) and on $\text{Co}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ with 12wt.-% Mo (12 Mo Cat)

Dynamic chemisorption measurements such as temperature programmed desorption (TPD) might be better suited to estimate the amount of material adsorbed on the different sites. Figure 4.13 shows the TPD-profiles obtained after adsorption of CO on the modified support materials and the molybdenum modified catalysts. The modified supports adsorb CO yielding a desorption peak at ca 150°C.

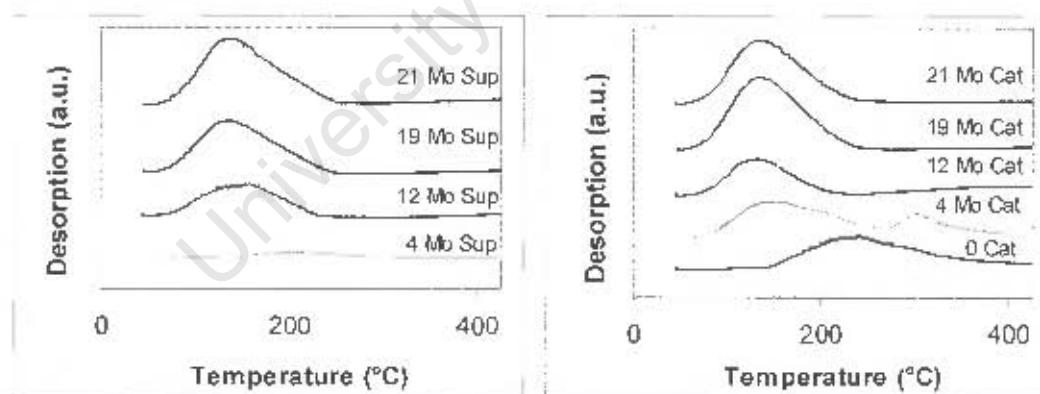


Figure 4.13: Temperature programmed desorption of CO (CO-TPD) of MoO_3 -modified support materials (left) and the $\text{Co}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts (both materials reduced in hydrogen at 425°C)

Table 4.2: Cobalt metal area determined from the CO desorption peak area between 250 and 425°C on reduced catalysts ($T_{\text{reduction}} = 425^\circ\text{C}$ for 8 hrs)

Catalyst	Temperature range of integration to obtain area of CO	CO desorption 250-425°C (ml(STP)/g _{cat})
	desorbed	
0 Cat	50-425°C	0.62
4 Mo Cat	270-425°C	0.25
12 Mo Cat	250-425°C	0.10
21 Mo cat	250-425°C	<0.05

CO desorbs from the unpromoted Co/γ-Al₂O₃ catalyst (0 Cat) at ca. 250°C. The amount of CO desorbed from this catalyst is 0.62ml(STP)/g_{catalyst}. The value obtained corresponds well with the amount of hydrogen chemisorbed at saturation (0.3ml(STP)/g_{catalyst}) implying associative CO-chemisorption and dissociative chemisorption of hydrogen.

A clear distinction between CO chemisorbed on cobalt, cobalt oxide and CO-chemisorbed on molybdenum oxide is not feasible at desorption temperatures below 250°C. It may be concluded that the cobalt metal area decreases with an increase in the molybdenum oxide loading in the catalyst formulation (see Table 4.3). This might be caused by a (partial) coverage of metallic cobalt with molybdenum oxide.

XPS-analysis of the reduced catalyst

The surface composition of the reduced catalysts and the oxidation state of the various elements were determined using XPS (see Table 4.4). However, it should be noted that XPS analyses may analyse layers up to 5 nm deep (N.N.7, 2006) in the catalyst and is thus not a true surface analysis. The near surface region of the catalyst Co/γ-Al₂O₃ (0 Cat) is enriched with cobalt. The amount of divalent cobalt seems to be surprisingly high seeing the high degree of reduction obtained with this catalyst (see Table 4.2). This can be rationalised by the presence of a highly dispersed cobalt oxide phase (e.g. cobalt aluminate) and larger crystallites of metallic cobalt.

Table 4.4: Elemental analysis of surface region in the reduced Co/MoO₃/γ-Al₂O₃ catalysts by XPS (analyses done by CSIR)

Catalyst	Element	Concentration (atom-%)	E _{binding} (eV)		
0 Cat	Al	14.7	74.5		Al ₂ O ₃
	C	3.0	284.7		
	Co	13.6	778.0	(8%)	Co
			781.3	(92%)	Cobalt oxide
	O	68.8	531.4		
12 Mo Cat	Al	14.5	74.5		Al ₂ O ₃
	Co	6.4	778.8	(75%)	Co
			782.2	(25%)	Cobalt oxide
	Mo	5.7	229.7	(52%)	MoO ₂
			231.7	(48%)	MoO ₃
	O	73.3	531.5		
21 Mo Cat	Al	14.8	75.0		Al ₂ O ₃
	C	2.6	284.9		
	Co	3.5	778.5	(22%)	Co
			781.4	(78%)	Cobalt oxide
	Mo	7.2	229.0	(36%)	MoO ₂
			231.6	(64%)	MoO ₃
	O	72.1	530.6		

The cobalt content in the near surface region of the molybdenum modified catalysts is significantly lower than in the catalyst without molybdenum. However the amounts of metallic cobalt metal for the molybdenum oxide promoted catalysts were 4.8atom-% and 0.8atom-%. The molybdenum content in the near surface region is increasing with increasing molybdenum loading, whereas the aluminium content remains approximately constant. The enrichment of the surface region with molybdenum is mainly due to the decrease in the surface concentration of cobalt.

The XPS analysis confirms that molybdenum in the catalyst is reduced as well and the surface near region consists of Mo⁴⁺ and Mo⁶⁺. It should however be noted that a lower oxidation state was expected based on the TGA-measurement of the modified support.

4.3 Characterisation of acidity in the reduced Co/MoO₃/γ-Al₂O₃ catalysts

The molybdenum modified catalysts are expected to have acidic properties [Petrakis and Kiviat, 1973, Ma *et al.*, 2004, Rajagopal *et al.*, 1995, Schrader and Cheng, 1983], which may affect the performance of these catalysts in the Fischer-Tropsch synthesis. The acidic properties of the reduced catalysts were probed using NH₃-TPD, the conversion of iso-propanol yielding propene and di-isopropyl-ether and the conversion of an olefin, 1-hexene.

4.3.1 NH₃-TPD over the reduced Co/MoO₃/γ-Al₂O₃ catalysts

The adsorption and subsequent temperature programmed desorption of ammonia is a well-described technique to characterize acidity in heterogeneous catalysts [Lowenthal *et al.*, 1995, Ma *et al.*, 2004, Rajagopal *et al.*, 1995]. The number of acid sites per gram of alumina was not strongly dependent on the molybdenum oxide loading (see Table 4.5). The number of acid sites decreases per unit of calcined mass when the catalysts were promoted with molybdenum oxide (see Table 4.5). The TPD spectra are similar for the Co/MoO₃/γ-Al₂O₃ catalysts (see Figure 4.14).

Table 4.5: Amount of NH₃ desorbed in NH₃-TPD experiments as measured by back-titration of the sulphuric acid trap

Support/Catalyst	Amount of NH ₃ adsorbed per g of Al ₂ O ₃ in support/catalyst (mmol/g Al ₂ O ₃)	Amount of NH ₃ adsorbed per gram of support/catalyst (mmol/g _{cat})
0 Sup	0.0606	0.0598
0 Cat	0.0576	0.0493
4 Mo Cat	0.0637	0.0548
12 Mo Sup	0.0610	0.0493
12 Mo Sup	0.0613	0.0501
12 Mo Cat	0.0638	0.0352
21 M Sup	0.0559	0.0384
21 M Sup	0.0607	0.0417
21 M Sup	0.0583	0.0397
21 M Cat	0.0674	0.0399

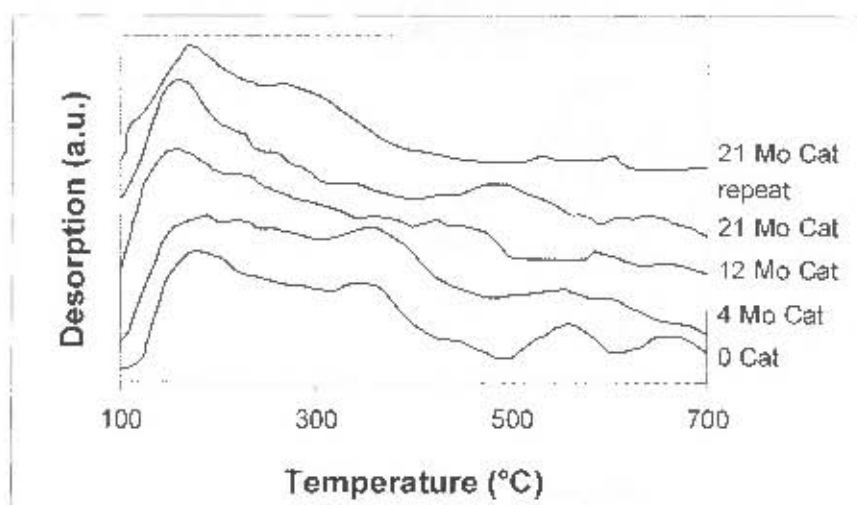


Figure 4.14: TCD signal as a result of ammonia and water desorption during TPD analyses

4.3.2 Probing acidity using conversion of iso-propanol

The acidic properties of catalysts can be probed using the dehydration of iso-propanol yielding propene and di-isopropylether (DIPE) [Bej *et al.*, 2003; Benadda *et al.*, 2003; Perez-Cadenas *et al.*, 2003]. Acetone can be formed from iso-propanol as well through dehydrogenation, which is mainly catalyzed by basic sites, but the reaction may also proceed over acidic sites [Bej *et al.*, 2003].

Figure 4.15 shows the yield of propene plus di-isopropylether (DIPE) in the conversion of iso-propanol (diluted in Ar) as a function of the space velocity. Even the reduced catalyst Co/γ-Al₂O₃ (0 Cat) is active for the conversion of iso-propanol to propene and di-isopropylether (DIPE) at relatively low space velocities. The activity of the reduced Co/MoO₃/γ-Al₂O₃ catalysts increases with increasing molybdenum content. This indicates an increase in the acidity of the reduced catalyst with increasing molybdenum content.

The yield of propene and di-isopropylether (DIPE) in the conversion of iso-propanol over the reduced, modified support (21 Mo Sup) is significantly higher than over the corresponding catalyst. This implies that the presence of (reduced) cobalt reduces the acidity of the support.

Some minor deactivation was observed in the iso propanol test. This was evidenced by the return to a lower space velocity after having performed the reaction at various space velocities. However, the deactivation seems to be minor and not affecting the conclusions in a major way.

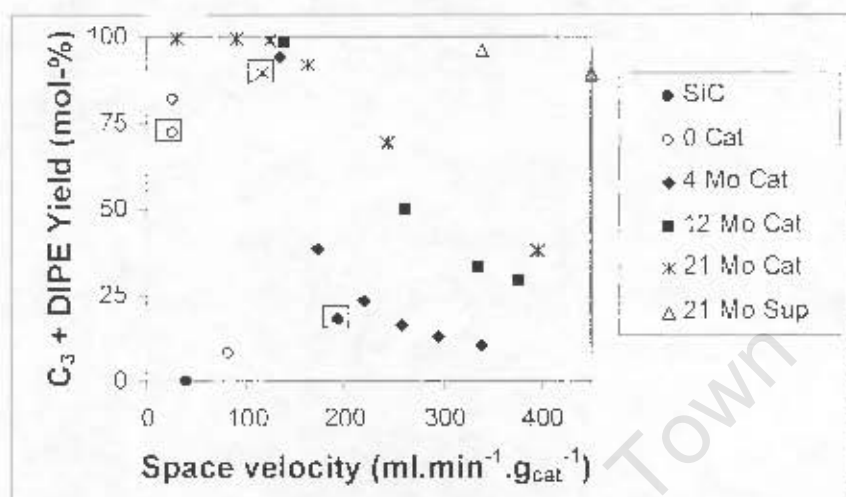


Figure 4.15: Yield of propene plus di-isopropylether (DIPE) in the conversion of iso-propanol at 220°C over the reduced catalysts (reduction in hydrogen at 425°C) as a function of space velocity (data-points in blocks are data-points obtained at the end of the run to check for catalyst deactivation)

4.3.2 Reactions of olefins over reduced $\text{Co}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts

Linear olefins, such as 1-hexene, may react over the supported cobalt molybdenum modified catalyst. These compounds may undergo double-bond isomerisation (both metal and acid catalysed), skeletal isomerisation (acid catalysed) or take part in metathesis (over MoO_x).

1-Hexene (diluted in argon) was passed over reduced 21 Mo Cat catalyst at 220°C to see whether and to which extent these side reactions may take place. A significant conversion of 1-hexene was observed, but the only products were the double bond isomers. Skeletal isomers and metathesis products were not observed. A conversion of 7% of n-heptane to skeleton isomers was observed at a temperature of 250°C for $\text{MoO}_3/\text{TiO}_2$ catalyst reduced at 400°C [Benadda *et al.*, 2003] Therefore the absence (or very low yield) of skeletal isomers might be attributed to the relative low temperature of

220°C for the acid catalysed skeletal isomerisation. The absence of any metathesis activity might indicate an over-reduction of molybdenum, since that will result in a reduction of the metathesis activity [Giordano *et al.*, 1975; Zhang *et al.*, 1991; Bartlett *et al.*, 1997].

4.4 Fischer-Tropsch synthesis over Co/MoO₃/γ-Al₂O₃ catalysts

The Fischer-Tropsch synthesis was mostly carried out in a fixed bed reactor at 220°C and 20 bar_a using a feed with H₂/CO=2mol/mol and a synthesis gas space velocity of 46ml/(min·g). In order to verify the obtained findings some experimental parameters, such as linear velocity, space velocity, pressure and temperature were varied for some of the catalysts. The possibility of poisoning the acidic sites in the Co/MoO₃/γ-Al₂O₃-Fischer-Tropsch catalyst was explored in a slurry reactor. A summary of the experimental results are given in Appendix D.

4.4.1 Catalyst activity

Figure 4.16 shows the conversion of carbon monoxide over Co/MoO₃/γ-Al₂O₃ as a function of time on stream at 220°C and 20 bar_a and a space velocity of 46ml(STP)/(min·g). All catalysts show a decline in the activity with time on stream. The catalyst without the addition of molybdenum to the catalyst formulation (0 Cat) showed the highest activity with a CO-conversion of ca. 40mol-% between 1000 and 5000 minutes on stream. The addition of a small amount of molybdenum to the catalyst formulation (4 Mo Cat) resulted in a strong decrease in the catalytic activity. The CO conversion of a Co/MoO₃/γ-Al₂O₃ catalyst tested at lower pressure and higher temperature was also lower than the Co/γ-Al₂O₃ catalyst (see Table 4.6). Thus, the addition of molybdenum has a detrimental effect on the catalytic activity. This might be attributed to the decoration and/or (partial) coverage of cobalt crystallites with MoO_x.

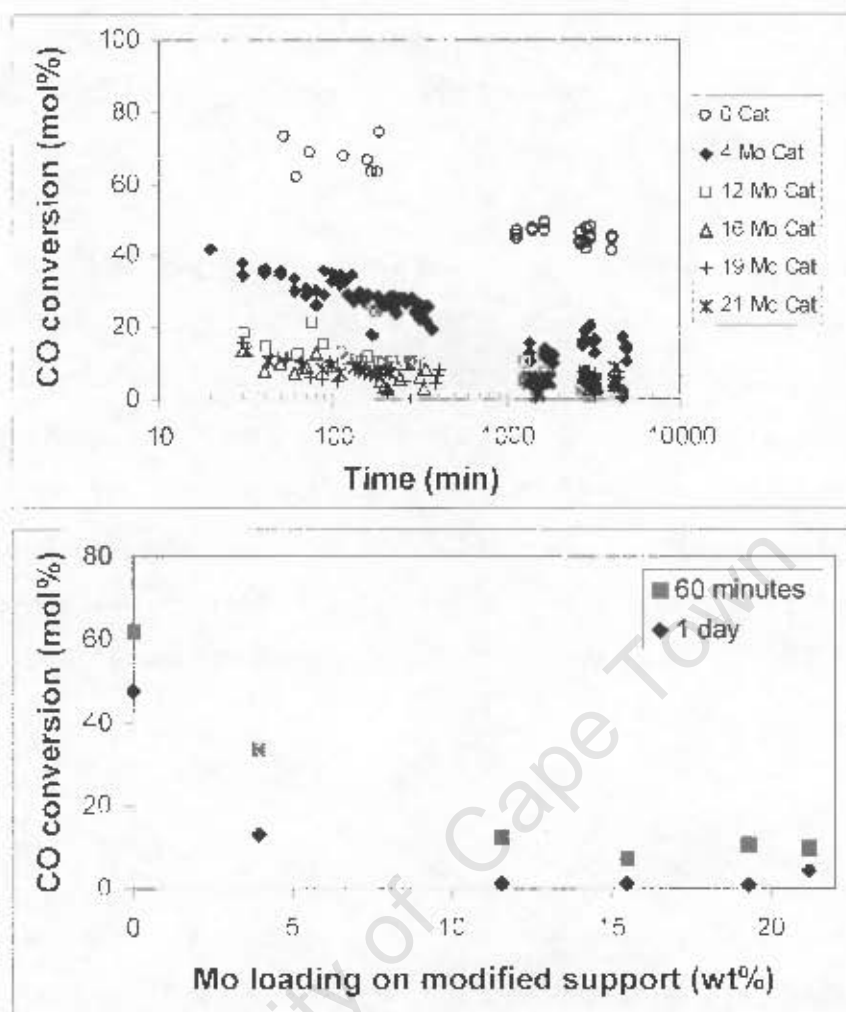


Figure 4.16: Conversion of CO over $\text{Co}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts tested at 220°C , 20bar_a , and a synthesis gas space velocity of $46\text{ml(STP)}/(\text{min g})$, $\text{H}_2/\text{CO}=2$ in a fixed bed reactor

Top: CO-conversion as a function of time on stream

Bottom: CO-conversion as a function of molybdenum loading after 60 minutes and 1000-2000 minutes (1 day) on stream

Table 4.6: Effect of reaction temperature and pressure on the obtained CO-conversion in the Fischer-Tropsch synthesis (220°C, synthesis gas space velocity: 23ml(STP)/(min.g), H₂/CO=2, fixed bed reactor, time on stream: 2-7 days)

Catalyst	T °C	P bar	X _{co} mol-%
Co/γ-Al ₂ O ₃ (0 Cat)	220	20	51
	220	5	27
	240	1	34
Co/MoO ₃ /γ-Al ₂ O ₃ with 12wt.-% Mo (12 Mo Cat)	220	20	16
	220	5	10
	240	1	25

4.4.2 Selectivity in the Fischer-Tropsch synthesis

The Fischer-Tropsch synthesis produces a wide product distribution with a strong regularity. Shifts in the product selectivity in the Fischer-Tropsch synthesis can be used as an indicator of the changes in the catalyst system.

Methane selectivity and chain growth probability

Figure 4.17 shows the possible reaction pathways in the Fischer-Tropsch synthesis according to the 'alkyl' mechanism for the formation of methane, olefins and paraffins. [Claeys and Van Steen, 2004]

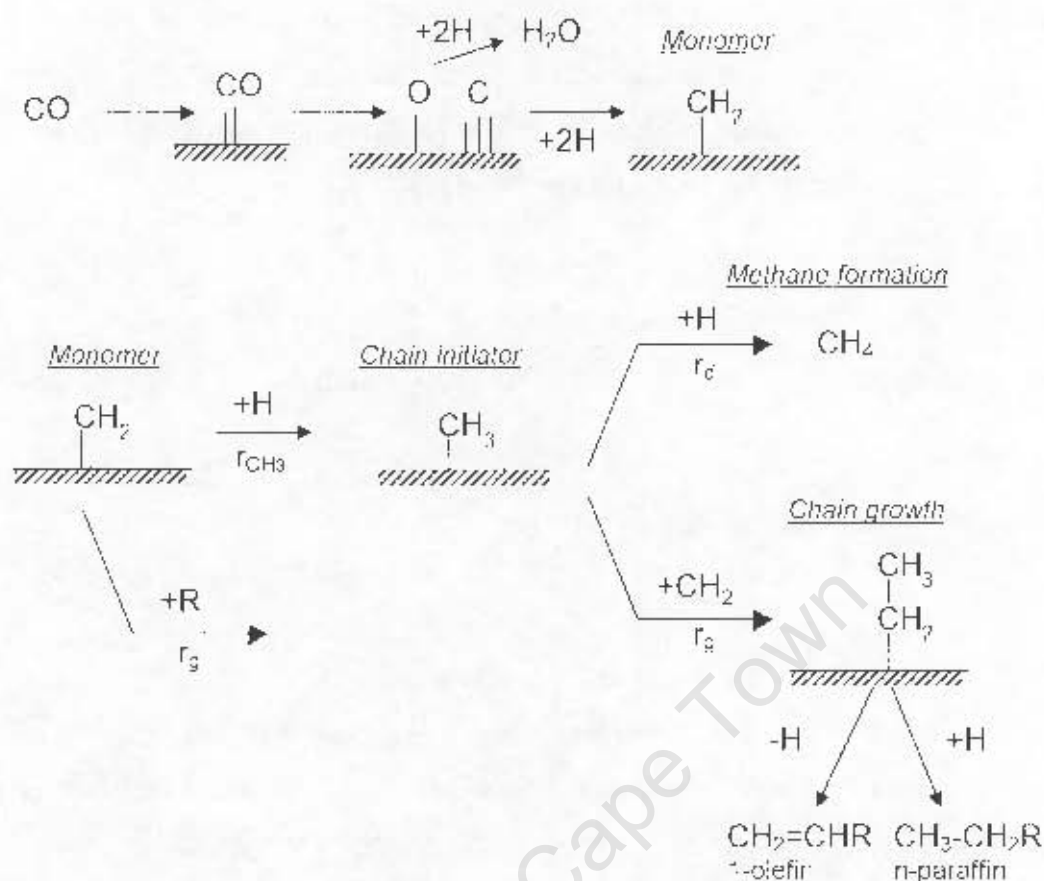


Figure 4.17: Possible reaction pathways in the Fischer-Tropsch synthesis according to the 'alkyl' mechanism [Claeys and Van Steen, 2004]

Figure 4.18 shows the chain growth probability ($\text{C}_1\text{-C}_{10}$) and the methane selectivity at 1-3 days on stream as a function of molybdenum loading. The methane selectivity was determined from an extrapolated FID-analysis (see Appendix E), since the determination of the methane selectivity from the inorganic and permanent gas analysis becomes inaccurate at low CO conversions. The chain growth probability decreases with increasing molybdenum loading from over 0.81 to less than 0.6 and the methane selectivity (in C-%) increases correspondingly (see Appendix A) for a functional relationship between chain growth probability and methane selectivity.

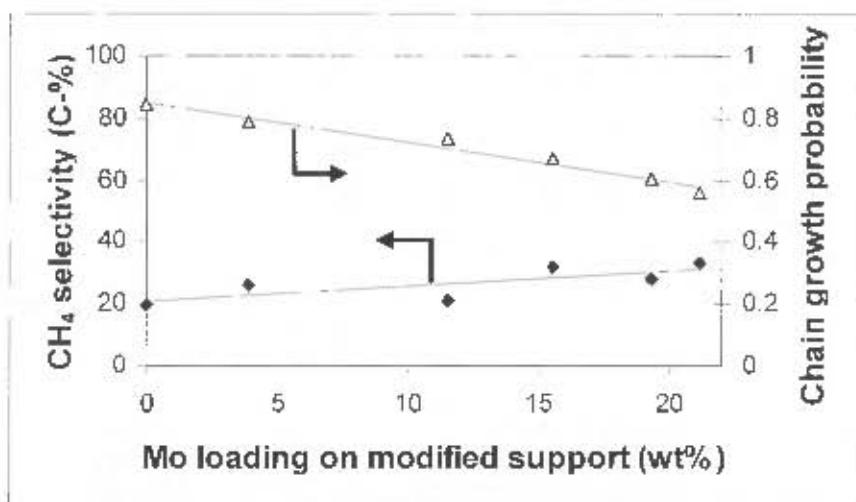


Figure 4.18: Influence of molybdenum loading on methane selectivity and chain growth probability (C_{3-10}) over Co/MoO₃/γ-Al₂O₃ ($T=220^{\circ}\text{C}$, $p=20\text{bar}_a$, synthesis gas space velocity= $46\text{ml(STP)/(min}\cdot\text{g)}$, $\text{H}_2/\text{CO}=2$, fixed bed reactor, time on stream: 1-3days)

The chain growth probability (C_{3-10}) did not change significantly with a change in the CO conversion over the catalyst without molybdenum in the catalyst formulation (0 Cat) (see Appendix F). The conversion of the unpromoted catalyst was varied by changing the space velocity between 23 and $736\text{ml(STP)}\text{min}^{-1}\text{g}_{\text{cat}}^{-1}$. The strong decrease in the chain growth probability with increasing molybdenum content in the catalyst at high molybdenum loading cannot be ascribed to a variation in the CO-conversion, since the level of CO-conversion was very similar for these catalysts. Similarly, the chain growth probability obtained with Co/MoO₃/γ-Al₂O₃ containing 4wt.-% Mo (4 Mo Cat) was independent of the space velocity (see Table 4.7). Hence, the observed decrease of the chain with increasing molybdenum loading is not likely to be an effect of the CO-conversion.

Table 4.7: Influence of space velocity in the CO-conversion in the Fischer-Tropsch synthesis and the chain growth probability (C₃-C₁₀) Co/MoO₃/γ-Al₂O₃ containing 4wt.-% Mo (4 Mo Cat) (220°C, 20bar_a, H₂/CO=2, fixed bed reactor)

SV, ml/(min.g)	23	23	46	46
Time on stream, days	1	2	1	3
X _{CO} , %	35	33	13	1
α	0.78	0.79	0.79	0.78

The catalysts were tested at lower pressures and higher temperature to see if the reaction conditions have an influence on the relative selectivities of the catalysts. At low pressure (1bar_a) and higher temperature (240°C) the chain growth probability of the molybdenum promoted catalyst were similar to the unpromoted catalysts (see Table 4.8).

Table 4.8: The influence of temperature and pressure on the chain growth probability of Co/γ-Al₂O₃ and Co/MoO₃/γ-Al₂O₃ containing 12wt% Mo (H₂/CO=2, fixed bed reactor, 23ml/(min.g)).

Catalyst		0	12
		Cat	Mo
		Cat	
P(Bar _a)	T(°C)	α	α
20	220	0.83	0.72
5	220	0.80	0.75
1	240	0.55	0.51

Olefin production in the Fischer-Tropsch synthesis

In the alkyl mechanism it is assumed that surface alkyl species may desorb by β-H-abstraction yielding 1-olefins and by H-addition yielding paraffins (see Figure 4.19) [Claeys and Van Steen, 2004].

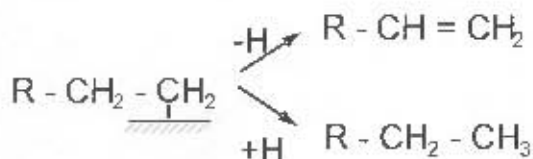


Figure 4.19: Formation of olefins and paraffins [Claeys and Van Steen, 2004; Schulz and Claeys, 1999]

1-Olefins are reactive product compounds which may re-adsorb on Fischer-Tropsch sites and undergo secondary hydrogenation yielding n-paraffins, double bond isomerisation yielding internal olefins or reincorporated into chain growth schemes (see Figure 4.20) [Schulz and Claeys, 1999]. Furthermore, olefins may undergo double bond isomerisation on acidic sites present in the catalyst (see 4.3.2).

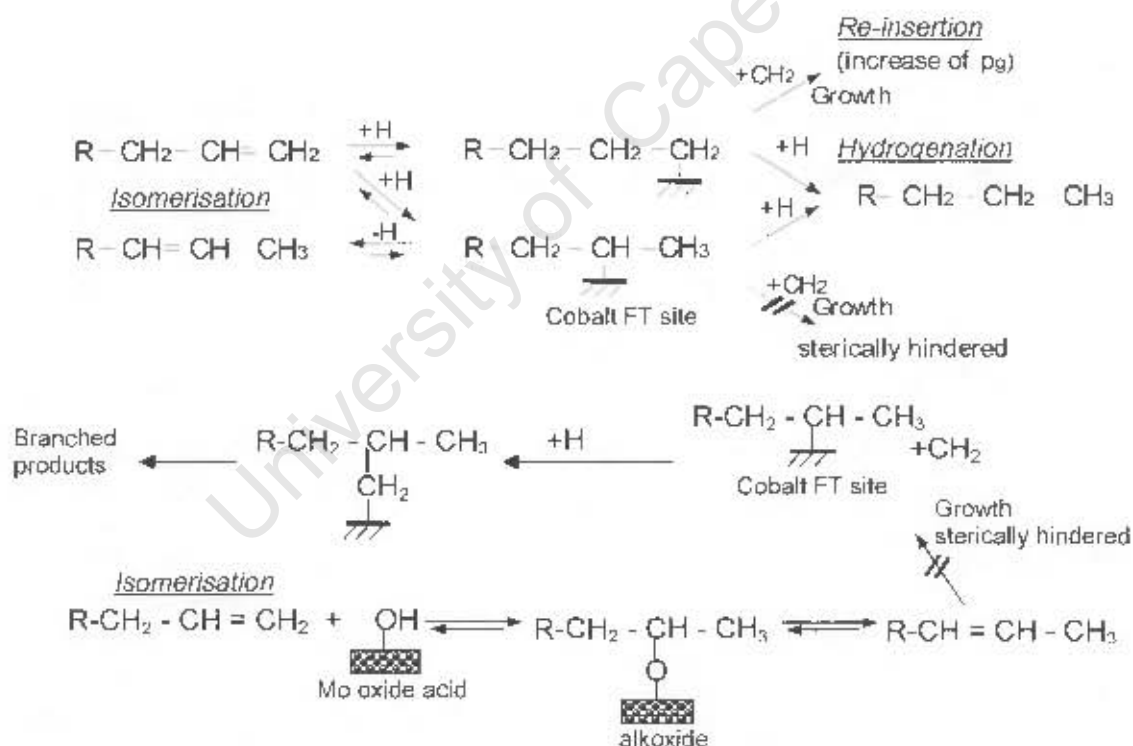


Figure 4.20: Schematic showing secondary reaction on a cobalt Fischer-Tropsch site [Claeys and Van Steen, 2004] and an acid molybdenum oxide site (see Chapter 2).

Figure 4.21 shows the olefin content in the fraction of linear hydrocarbons and the 1-olefin content as a function of carbon number after 3 days on stream.

The olefin content in the fraction of linear hydrocarbons is a measure for the extent of consumption of primary formed 1-olefins for the formation of n-paraffins or their re-incorporation into the chain growth scheme. The 1-olefin content in the fraction of linear olefins is a measure for the extent of primarily formed 1-olefins undergoing double bond isomerisation.

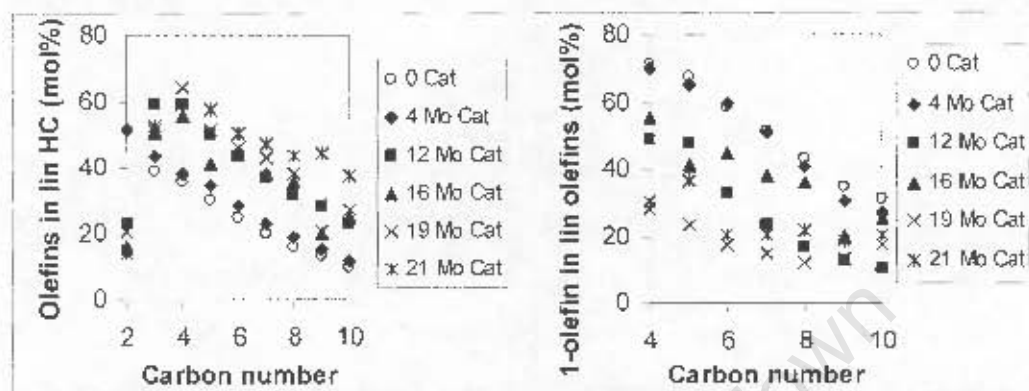


Figure 4.21: Olefin content in the fraction of linear hydrocarbons (left) and 1-olefin content in the fraction of linear olefins (right) as a function of carbon number (220°C , 20bar_a , synthesis gas space velocity $46\text{ml}(\text{STP})\text{min}^{-1}\cdot\text{g}_{\text{cat}}^{-1}$, $\text{H}_2/\text{CO}=2$, fixed bed reactor, time on stream: 3 days)

The olefin content in the fraction of linear hydrocarbons shows the expected behaviour of a low value in C_2 , passing through a maximum at C_3/C_4 , and decreasing with increasing carbon number. The low olefin content in the fraction of C_2 -hydrocarbons is attributed to the high reactivity in C_2 ; the reactivity of longer chain hydrocarbons is approximately constant, and the decrease as a function of carbon number is attributed to the concentration of these olefins near the catalytic active site [Schulz and Claeys, 1999].

The olefin content in the fraction of linear hydrocarbons increases with increasing molybdenum content in the catalyst indicating a reduced extent of secondary hydrogenation. Furthermore, the 1-olefin content in the fraction of linear olefins decreases with the addition of molybdenum oxide.

The observed increase in the olefin content in the fraction of linear hydrocarbons and the decrease in the 1-olefin olefin content in the fraction of

linear olefins might be attributed to the different CO-conversion, at which these catalysts were tested. Figure 4.22 shows the olefin content in the fraction of linear hydrocarbons and the 1-olefin content in the fraction of linear olefins as a function of the CO-conversion.

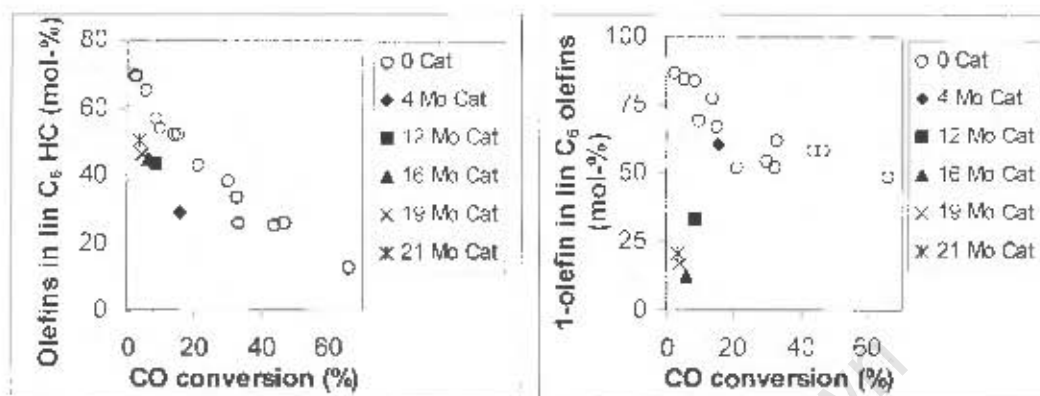


Figure 4.22: Olefin content in the fraction of linear hydrocarbons (left) and 1-olefin content in the fraction of linear olefins (right) as a function of carbon number (220°C, 20bar_a, synthesis gas space velocity 46ml(STP)/min/g_{cat} for the molybdenum promoted catalysts and gas space velocities between 23 and 736ml(STP)/min/g_{cat} for the unpromoted catalyst, H₂/CO=2, fixed bed reactor, time on stream: 3 days)

At a similar CO-conversion, the olefin content in the fraction of linear hydrocarbons for the catalyst without molybdenum is higher than the olefin content in the fraction of linear hydrocarbons for the catalysts containing molybdenum. A lower olefin content is attributed to the conversion of olefins to paraffins (secondary hydrogenation) or re-incorporation into the chain growth scheme. It should be noted, that the olefin content for the molybdenum containing catalysts increases with increasing molybdenum content, which is due to the decrease in the conversion. The 1-olefin content in the fraction of linear olefins decreases with increasing molybdenum content.

It might be postulated that molybdenum catalyses the double bond isomerisation much more rapidly than the production of olefins in the Fischer-Tropsch synthesis. The addition of molybdenum to the catalyst formulation led to the introduction of additional acidic sites in the catalyst capable of

catalysing the double bond-isomerisation leading to a lower 1-olefin content in the fraction of the linear olefins. Olefins with an internal double bond are less reactive for secondary reactions on Fischer-Tropsch sites than the corresponding 1-olefins [Schulz and Claeys, 1999]. However, molybdenum oxide can also catalyse hydrogenation of olefins [Jacono and Hall, 1977; Al-Kandari *et al.*, 2005]. For example hydrogenation of 1-pentene at 150°C was catalysed by unsupported MoO₃ reduced at 150°C in hydrogen [Al-Kandari *et al.*, 2005]. Higher reduction temperatures increased the hydrogenation activity. The authors attributed the hydrogenation function to molybdenum in the +5 and +4 (MoO₂) oxidation states. Hydrogen reduction of MoO₃ at temperatures between 380 and 400°C resulted in the formation of MoO₂(H_x)_{oc} that also can catalyse hydrogenation [Al-Kandari *et al.*, 2005]. Molybdenum supported on alumina with an average oxidation state between +4 and +6 catalysed hydrogenation of propene at 109°C [Jacono and Hall, 1977]. CO poisoned the hydrogenation reaction partially at a low reaction temperature of 25°C [Lombardo *et al.*, 1980]. The poisoning effect of CO may be less at higher temperatures. Molybdenum bronzes (H_xMoO₃) can also catalyse hydrogenation at reaction temperatures of 100 and 160°C [Marq *et al.*, 1984].

Figure 4.23 shows the olefin content in the fraction of linear hydrocarbons and the 1-olefin content in the fraction of linear olefins as a function of carbon number at two different space velocities obtained over the catalyst Co/MoO₃/γ-Al₂O₃ containing 4wt.-% Mo (4 Mo Cat). A decrease in the space velocity leads to an expected, but slight, decrease in the olefin content in the linear hydrocarbon fractions and the 1-olefin content in the fraction of linear hydrocarbons.

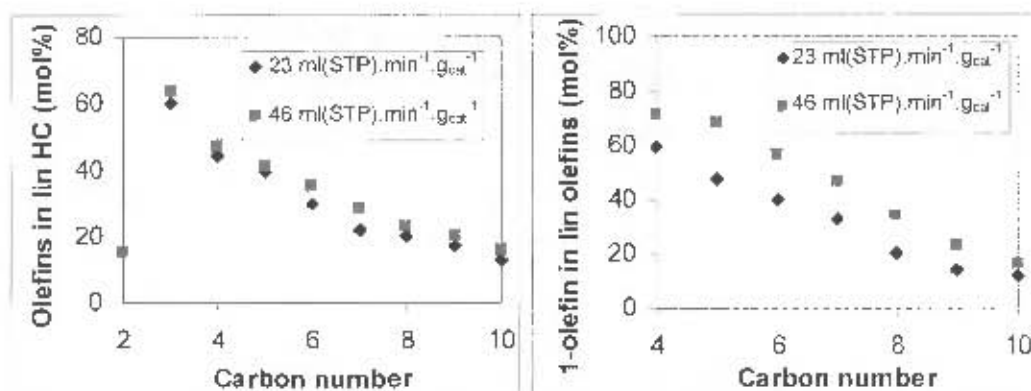


Figure 4.23: Olefin content in the fraction of linear hydrocarbons (left) and 1-olefin content in the fraction of linear olefins (right) as a function of carbon number over $\text{Co}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ containing 4wt.-% Mo (4 Mo Cat) (220°C , 20bar_a , $\text{H}_2/\text{CO}=2$, fixed bed reactor, time on stream: 1 day)

A decrease in the space velocity results in an increase in the extent of all secondary reactions. In the Fischer-Tropsch synthesis secondary hydrogenation and double bond isomerisation follow the same trend, since they take place on the same Fischer-Tropsch site [Schulz *et al.*, 1994]. In the molybdenum modified catalysts double bond isomerisation of primarily formed 1-olefins may take place on either Fischer-Tropsch sites or on acidic sites present in the catalyst. An increase in the content in double bond isomers caused by the presence of acidic sites in the catalyst may result in a decrease in secondary hydrogenation and olefin re-incorporation into the chain growth scheme, if the acid catalysed double bond isomerisation is much more rapid than double bond isomerisation on Fischer-Tropsch sites. A large extent of double bond isomerisation on acidic sites is expected to be accompanied by an increase in the olefin content. However, a decrease in the space velocity also results in an increase of the extent of secondary hydrogenation and re-incorporation of olefins. These effects may thus cancel each other and explain the slight change in the olefins in linear hydrocarbons as a function of the space velocity.

The rate of the double bond isomerisation over the molybdenum containing catalysts is best exemplified by varying the linear velocity through the catalyst

bed keeping the space velocity constant (see Figure 4.24). Any change in the product selectivity due to a change in the linear velocity must be attributed to mass transfer limitations in the product removal from the catalyst particle, since the CO-conversion is not affected by the linear velocity. The olefin content in the fraction of linear hydrocarbons is not affected by the linear velocity. This implies that the secondary reactions on the Fischer-Tropsch sites are slow in comparison to the product removal. The 1-olefin content in the fraction of linear olefins is however affected by the linear velocity. An increase in the linear velocity results in an increase in the 1-olefin content over the molybdenum containing catalyst. This implies that the double bond isomerisation in the molybdenum containing catalyst is rather fast and that it is affected by external mass transport limitations, i.e. removal of the product olefins from the catalyst particle.

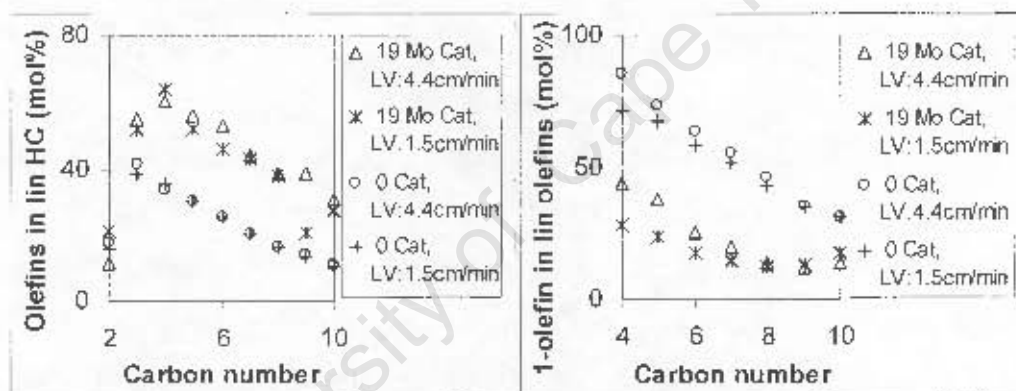


Figure 4.24: Olefin content in the fraction of linear hydrocarbons (left) and 1-olefin content in the fraction of linear olefins (right) as a function of carbon number over $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (0 Cat) and $\text{Co}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ containing 19wt.-% MoO_3 (19 Mo Cat) (220°C , 20bar_a , $\text{H}_2/\text{CO}=2$, fixed bed reactor, synthesis gas space velocity = $46\text{ml(STP)}/(\text{min g})$, time on stream: 3 days)

Production of branched compounds in the Fischer-Tropsch synthesis

The re-incorporation of internal olefins in the chain growth scheme may lead to the formation of branched compounds (see Figure 4.20 schematic) [Schulz *et al.*, 1994]. Acid sites may also catalyse skeletal isomerisation leading to the formation of branched hydrocarbons. However, skeletal isomerisation was not observed in the conversion of 1-hexene over the reduced, molybdenum modified catalyst at the same temperature making it unlikely to occur under Fischer-Tropsch conditions. Figure 4.25 shows the effect of molybdenum loading of the catalyst on the amount of branched hydrocarbons in the fraction of C₄, C₅ and C₆-hydrocarbons. Catalysts with a high molybdenum loading showed a significant increase in the amount of branched compounds in a hydrocarbon fraction. This might be interpreted as a result of re-adsorption of internal olefins yielding branched product compounds on Fischer-Tropsch sites.

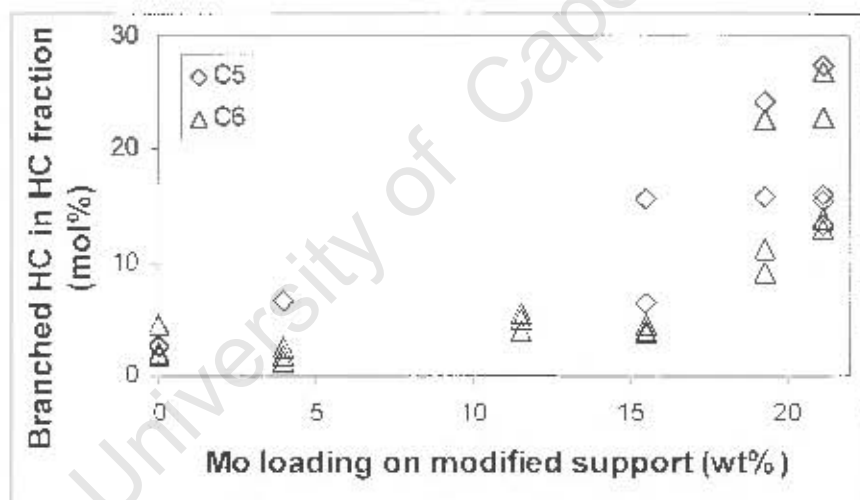


Figure 4.25: Amount of branched hydrocarbons in the fraction of C₅ and C₆ hydrocarbons as a function of the molybdenum loading (220°C, 20bar_a, synthesis gas space velocity 46ml(STP)/(min g), H₂/CO=2, fixed bed reactor, time on stream. 1-77h)

Poisoning acid sites in Co/MoO₃/γ-Al₂O₃

Acid sites present in a catalyst can be neutralised by co-feeding a base, such as ammonia. It was reported that ammonia poisoned the isomerisation reaction at 90°C by interacting with the acidic sites [Lombardo *et al.*, 1980]. Hence, ammonia co-feeding was investigated in the Fischer-Tropsch

synthesis over both the unpromoted Co/γ-Al₂O₃ (0 Cat) and Co/MoO₃/γ-Al₂O₃ containing 21wt.-% Mo (21 Mo Cat). The effect of ammonia co-feeding was investigated in a slurry reactor.

Ammonia may also adsorb on Fischer-Tropsch sites and cause poisoning [Bartholomew, 2001; Inga *et al.*, 2005]. Further more ammonia poisons the hydrogenation reaction on nickel, platinum, palladium [Bartholomew, 2001]. It was found that the heat of adsorption of ammonia on Pd and Ag was higher than the heats of adsorption of H₂ and CO [Stradella, 1992]. The stronger heat of adsorption of ammonia on metals relative to H₂ and CO may explain the poisoning effect of ammonia for the Fischer-Tropsch and hydrogenation reactions.

Figure 4.26 shows the CO-conversion as a function of time on stream. The CO conversion decreased rapidly with time for the unpromoted catalyst. The catalyst containing molybdenum showed a low conversion. In that case the yield of hydrocarbons as determined from the organic product analysis is a more accurate indication of the catalyst activity.

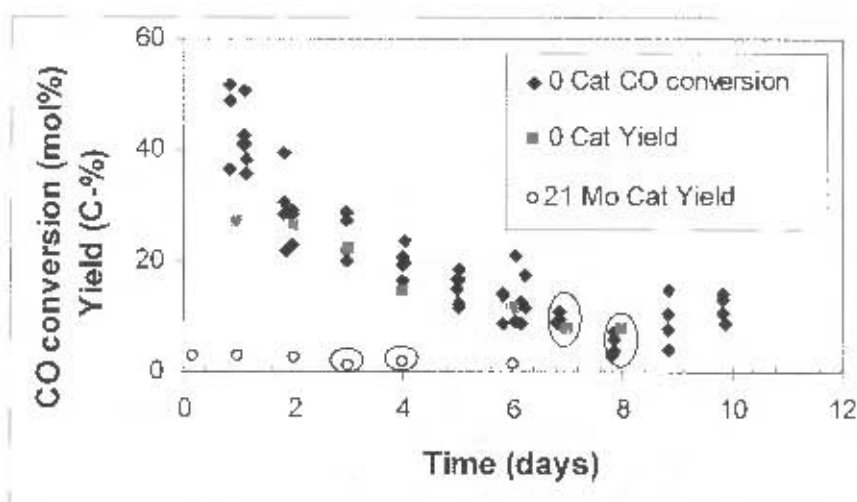


Figure 4.26: CO conversion and yield of organic product compounds in the Fischer-Tropsch synthesis over Co / γ -Al₂O₃ (0 Cat) and Co/MoO₃/γ-Al₂O₃ containing 21wt.-% MoO₃ (21 Mo Cat) in a slurry reactor (220°C, 20bar_a, synthesis gas space velocity= 20ml(STP)/(min·g), H₂/CO/NH₃=2.1:1:0 and H₂/CO/NH₃=2.1:1:0.0124 (4000vppm NH₃) for encircled data points)

The olefin content in the linear hydrocarbon fraction increased with the addition of NH₃ for both the promoted and unpromoted catalysts. The stronger adsorption of ammonia may have decreased the available hydrogen on the cobalt surface leading to a decrease in the hydrogenation. The similar effect of the ammonia on the olefin content in the linear hydrogenation fraction of the promoted and unpromoted catalyst may indicate that the hydrogenation was mostly on the cobalt metal surface.

The change in the 1-olefin content in the olefin fraction was insignificant for the unpromoted catalyst when NH₃ was co-fed (see Figure 4.27). The double bond isomerisation reaction was thus not significantly affected on the unpromoted catalyst. For the molybdenum oxide promoted catalyst (21 Mo Cat), the 1-olefin content in the olefin fraction increased significantly when NH₃ was co-fed. The double bond isomerisation reaction was thus partially poisoned by ammonia for the molybdenum oxide promoted catalyst. This

indicates that the additional double bond isomerisation observed when the catalyst was promoted with molybdenum was due to acid sites on the molybdenum oxide.

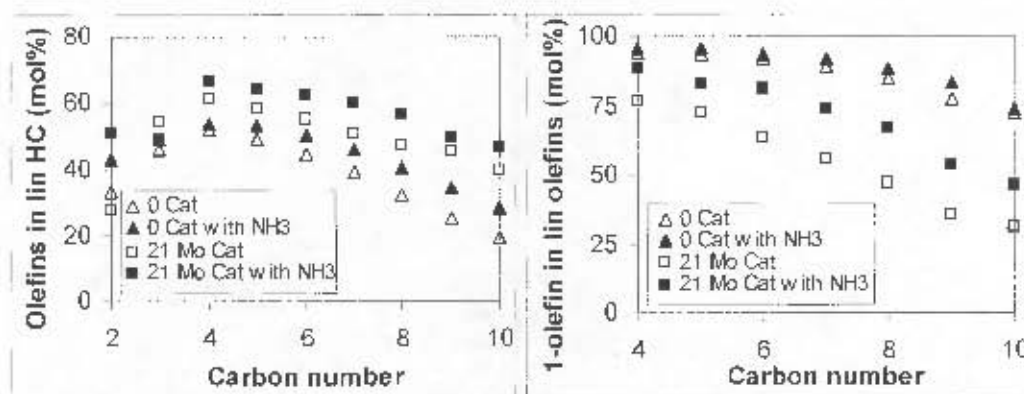


Figure 4.27: Influence on NH_3 co-feeding (0.8ml(STP)/min) on the olefin content in the fraction of linear hydrocarbons (left) and 1-olefin content in the fraction of linear olefins (right) as a function of carbon number over $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (0 Cat) and $\text{Co}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ containing 21wt.-% MoO_3 (21 Mo Cat) (220°C , 20bar_a , $\text{H}_2/\text{CO}=2.1$, slurry bed reactor, synthesis gas space velocity = $20\text{ml(STP)}/(\text{min}\cdot\text{g})$, stirring speed setting 30%)

The chain growth probability (C_3 to C_8) of the molybdenum oxide promoted catalyst (21 Mo Cat) was lower than that of the unpromoted (0 Cat) catalyst (Table 4.9). The chain growth probability decreased for both catalyst when NH_3 was co-fed (NH_3 flow = 0.8ml(STP)/min ; Total flow = 200ml(STP)/min). The decrease in the chain growth probability were slightly larger for the unpromoted catalyst (0 Cat) in comparison to the molybdenum oxide promoted catalyst (21 Mo Cat). This may indicate that the increase in the 1-olefin content when NH_3 was co-fed for the molybdenum oxide promoted catalyst, increased the readsorption of 1-olefins, resulting in the smaller decrease in the chain growth probability. Co-feeding NH_3 did not affect the amount of isomers in the C_5 hydrocarbon fraction significantly.

The decrease in the chain growth probability and increase in the olefin content in the linear hydrocarbon fractions may be explained by NH_3 adsorbing strongly on Fischer-Tropsch sites where the olefins would have re-adsorbed.

This would thus result in less olefins being re-adsorbed which will decrease the probability of further growth and hydrogenation.

Table 4.9: Influence of NH₃ on chain growth probability and the amount skeleton isomers in the C₅ hydrocarbon fraction

Time on stream	Unpromoted catalysts		2M MoO _x promoted catalyst	
	α	C ₅ s-isom (mol-%)	α	C ₅ s-isom (mol-%)
4hrs on stream			0.55	9.34
1 day	0.84	1.88	0.67	2.99
2 days	0.86	1.72	0.68	4.96
3 days	0.84	0.88		
4 days	0.83	1.58		
6 days	0.82	1.31		
after 1day of NH ₃ feeding	0.76 (day 7)	1.11	0.63 (day 3)	5.02
after 2 days of NH ₃ feeding	0.78 (day 8)	0.67	0.57 (day 4)	3.98
1 day after NH ₃ feeding			0.62	6.53

4.5 Summary and concluding remarks

The controlled of adsorption and deposition of the molybdenum oxide on the support alumina led to the formation of MoO₃ and Al₂(MoO₄)₃ as observed in XRD diffraction patterns. These phases disappeared when cobalt was added to the molybdenum modified support due to formation of CoMoO₄ phases. These phases are destroyed during reduction at 425°C.

The promotion of the cobalt catalyst with molybdenum did not affect the degree of reduction of the cobalt based on TGA results, decreased the rate of reduction of the cobalt as shown by TPR (attributed to the formation of CoMoO₄ and MoO₃-layers over the cobalt). The decrease in the rate of reduction was also supported by the mixing experiments of MoO₃ and Co₃O₄ in different solvent. This may be due to the formation of a MoO₃-layer covering the cobalt partially. The decrease in the cobalt metal surface area in

the molybdenum promoted catalyst as determined by CO TPD may also indicate the formation of a MoO_x-layer covering the cobalt partially, since the cobalt crystallites were XRD amorphous (Co₃O₄ crystallites were observed for the catalyst containing no molybdenum) and the cobalt degree of reduction were similar. The molybdenum reduces partially during reduction at 425°C.

The promotion of a cobalt Fischer-Tropsch catalyst with molybdenum oxide resulted in a decrease in the CO conversion and chain growth probability and increase in methane selectivity as tested at 220°C and 20bar_a. The change in selectivities cannot be ascribed to the change in the CO conversion, which may be explained by the decrease in the cobalt metal area as determined by CO chemisorption, e.g. by coverage of cobalt by a layer of molybdenum.

The 1-olefin content in linear olefins fractions for the molybdenum promoted catalysts were much less in comparison to that of the unpromoted catalyst if compared at the same level of CO conversion. The 1-olefin content in linear olefins fractions decreased with an increase in the molybdenum oxide loading. This indicates that more double bond isomerisation was taking place on the catalyst promoted with molybdenum oxide. This might be ascribed to catalysis by acid sites. The acidity increased with an increase in the molybdenum loading based on the iso-propanol test, which explains the increase in the double bond isomerisation with an increase in the molybdenum loading. Co-feeding of ammonia decreased the double bond isomerisation of the molybdenum oxide promoted catalyst, confirming the presence of acid sites on the molybdenum oxide was responsible for the increase in the double bond isomerisation during promotion.

Olefins with internal double bonds readsorb less readily than 1-olefins, and their reincorporation in the chain growth mechanism is thus less likely [Schulz and Claeys, 1999]. The increase in the double bond isomerisation may explain the decrease in the chain growth probability with an increase in the molybdenum loading. The fraction of branched hydrocarbons in hydrocarbons increased with an increase in the molybdenum loading. This may be

explained by the increase in the internal olefins as a function of the molybdenum loading, leading to a larger reincorporated of internal olefins.

The catalysts were tested at lower pressures and higher temperature to see if the reaction conditions have an influence on the relative selectivities of the catalysts. The chain growth probability of the molybdenum promoted and unpromoted catalyst were similar at higher temperature (240°C) and low pressure (1bar_a). The amount branched hydrocarbons also increased with a decrease in the pressure and increase in the temperature, indicating that the internal olefin were incorporated to a larger extent. This may be due to steric hindrance playing a smaller role at these operating conditions

The olefin content in linear hydrocarbon fractions increased with an increase in the molybdenum loading in the catalysts tested at the same space velocity, i.e. different conversions. The olefin content in linear hydrocarbon fractions for the molybdenum promoted catalysts were compared to the unpromoted catalyst as a function of the CO conversion (compared at different space velocities). Catalyst promoted with high loadings of molybdenum oxide showed slightly higher hydrogenation activity relative to the unpromoted catalyst. Therefore, the increase olefins in the linear hydrocarbon fractions with an increase in the molybdenum loading in the catalyst tested at the same space velocity was due to the decrease in the CO conversion. A decrease in the CO conversion leads to a decrease in secondary hydrogenation reactions.

It can be concluded that the use of molybdenum as a promoter at the investigated levels is not beneficial for the activity or selectivity of a cobalt catalyst. This study shows that the acidic properties of a promoter in the oxidation state present during the Fischer-Tropsch reaction should be evaluated when choosing a promoter.

5 Characterization and performance of $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$

5.1 Characterization of modified support materials

The $\gamma\text{-Al}_2\text{O}_3$ support was modified with vanadium by controlled adsorption of ammonium vanadate, $\text{NH}_4(\text{VO}_3)$, followed by deposition of the excess amount of vanadium. The deposition following the controlled adsorption step was needed to achieve larger vanadium loadings, since the adsorption capacity of alumina is limited (approximately 3 wt-% vanadium) [Wang and Hall, 1982].

Figure 5.1 shows the XRD-patterns of the calcined alumina support, on which various amount of vanadium has been put. All samples show the diffraction lines for $\gamma\text{-Al}_2\text{O}_3$. The intensity of the characteristic Al_2O_3 -diffraction peaks decreases with increasing vanadium content. The observed decrease in the peak intensity (40%) is stronger than expected based on the decreased alumina content in the catalyst (28%) for the 16 V Sup support (an even smaller decrease in the intensity is expected when taking the increase in density of the catalyst due to the addition of vanadium oxide into account).

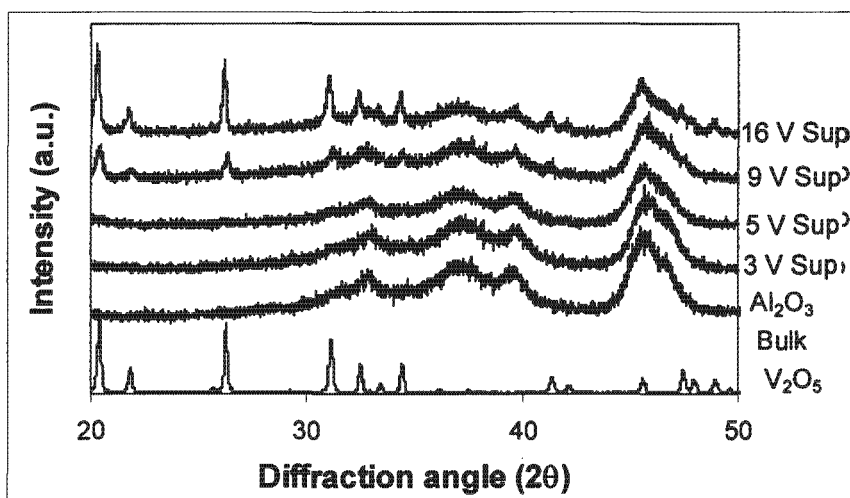


Figure 5.1: XRD spectrum of $\gamma\text{-Al}_2\text{O}_3$ -support (Pluralox SCCa 5-150) modified with vanadium (x V Sup supports) prepared using controlled adsorption-deposition technique and the diffraction lines of bulk V_2O_5 .

Additional diffraction lines are observed with increasing vanadium content and in particular for catalyst with a vanadium loading larger than 9wt.-% corresponding theoretically to 0.9 monolayers of V_2O_5 on this support. These diffraction lines can be ascribed to crystalline V_2O_5 . This indicates that evenly spread monolayer or multilayer of vanadium oxide is not formed with the employed synthesis technique. The intensity of the V_2O_5 diffraction peaks normalised relative to the alumina increased threefold increasing the vanadium content from 9wt.-% to 16wt.-%.

The morphology of the modified support changed significantly upon the addition of larger amounts of vanadium (see Figure 5.2). V_2O_5 can form needle like structures [Kim and Lee, 1999; Shin *et al.*, 2005]. The introduction of a large amount of vanadium onto the $\gamma\text{-Al}_2\text{O}_3$ -support may have resulted in V_2O_5 needles.

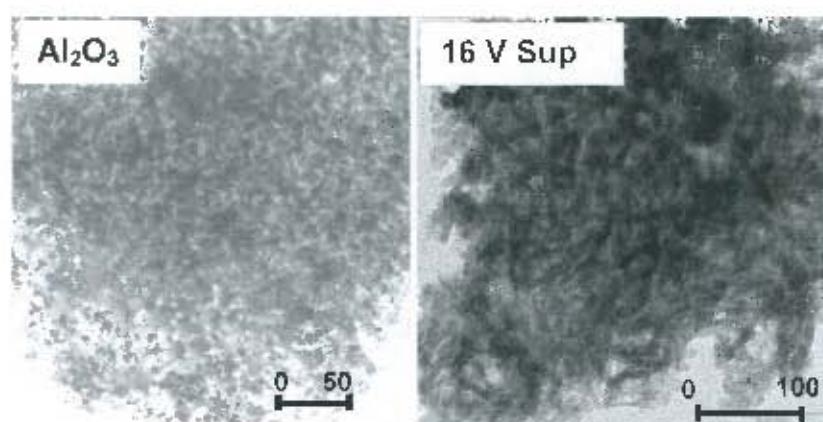


Figure 5.2: Change in support morphology as observed using TEM (scale in nm)

Left: TEM image of the unmodified support ($\gamma\text{-Al}_2\text{O}_3$, Pluralox SCCa 5-150) [Zwane, 2004]

Right: $\gamma\text{-Al}_2\text{O}_3$ -support (Pluralox SCCa 5-150) modified with 16wt.-% V by the controlled adsorption-deposition technique

5.2 Characterization of cobalt catalysts on the modified support materials

Cobalt was added to the V_2O_5 -modified $\gamma\text{-Al}_2\text{O}_3$ support material by colloidal impregnation. Cobalt was precipitated from a cobalt nitrate solution with ammonia as a precipitating agent and the precipitate was put on the support. The aim of this method was to form cobalt hydroxide crystals of which size are independent of the support.

The mixing of cobalt oxide (Co_3O_4) with V_2O_5 was investigated separately. Mixtures containing 50 wt% V_2O_5 and 50 wt% Co_3O_4 were prepared with and without water. The mixtures were left in water for 20 minutes before drying. Water was evaporated on a hot plate and the mixtures were further dried in an oven at 120°C for about 20min.

Figure 5.3 shows the reduction of unsupported V_2O_5 and Co_3O_4 as monitored using TGA and mixtures of Co_3O_4 and V_2O_5 . The reduction profile of the dry mixture was similar to reduction profile of the separate oxides. Mixing the oxides with water yielded an increase in the temperature at peak maximum of

the reduction peak for Co_3O_4 . The increase in the temperature at peak maximum of the Co_3O_4 reduction peak indicates some interaction between the cobalt and vanadium. Vanadium oxide can dissolve in water (0.8g per 100g of water at 20°C [Weast and Astle, 1982]). The dissolved V_2O_5 may be deposited on Co_3O_4 during the water removal step. This may retard the rate of reduction of cobalt. A similar effect might be expected in the prepared catalyst, since the catalyst preparation proceeds via an aqueous impregnation of the cobalt precipitate on the vanadium oxide modified support. Some V_2O_5 is present in the supports with a high V_2O_5 -loading (see Figure 5.1).

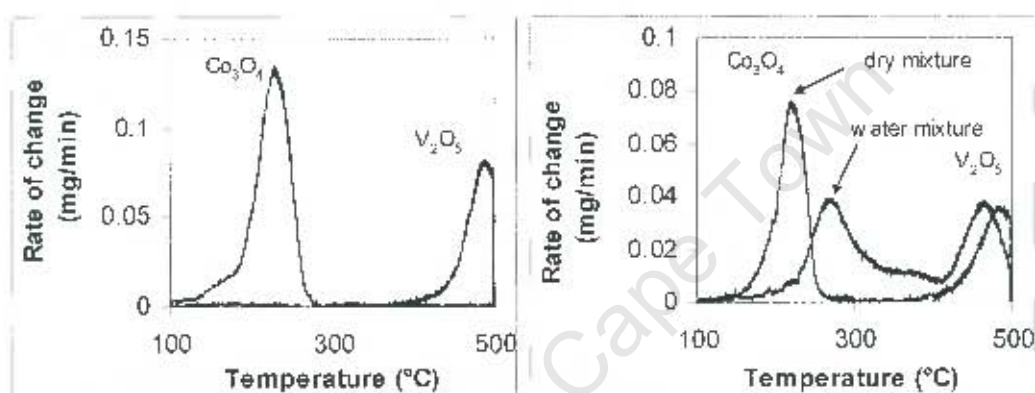


Figure 5.3: Reduction profile of mixtures of V_2O_5 (12.5mg) and Co_3O_4 (12.5mg) in hydrogen with a heating rate of 1°C/min

Left: Reduction profile of the separate oxides V_2O_5 (50mg) and Co_3O_4 (50mg)

Right: Reduction profile of mixtures prepared by dry mixing, mixing in water

5.2.1 Physico-chemical characteristics of $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$

The $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts calcined at 250°C were characterized using XRD (see Figure 5.4). The calcined catalyst without V_2O_5 on the support shows the presence of Co_3O_4 . A Co_3O_4 crystallite size of 9nm was estimated by line broadening analysis, using the Debye-Scherrer equation [Ertl et al., 1997] (using the Co_3O_4 diffraction peak at $2\theta=59^\circ$, since it was least influenced by $\gamma\text{-Al}_2\text{O}_3$ diffraction peaks). After the addition of cobalt and calcination at 250°C, the V_2O_5 diffraction peaks, which were clearly visible in the XRD-pattern of the modified support, disappeared in the 9 V Cat and became much less intense in the 16 V Cat catalyst. Furthermore, diffraction

lines attributable to Co_3O_4 became broader and less intense for the 3 V Cat and 5V Cat catalysts and were absent at higher V_2O_5 loadings. A Co_3O_4 crystallites size of 6nm were estimated for the 3 V Cat and 5V Cat catalysts.

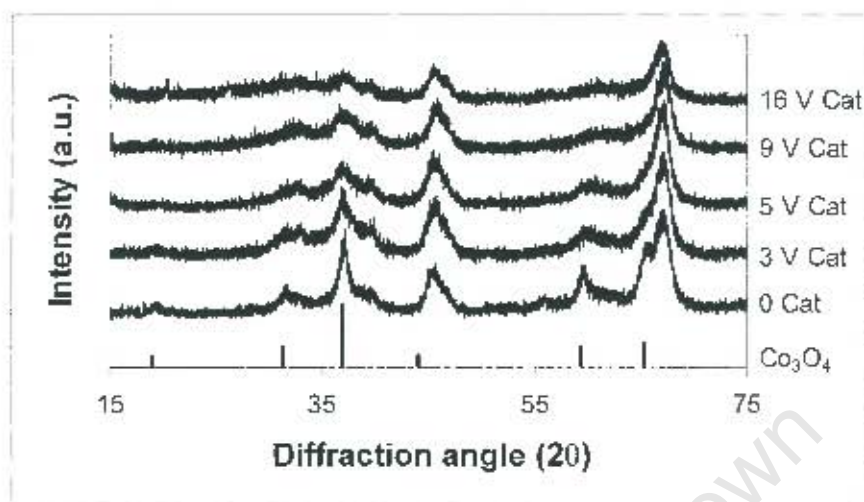


Figure 5.4: XRD-pattern of the calcined $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ -catalysts and Co_3O_4

Figure 5.5 shows the TEM-image of the $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ -catalysts containing 16wt% V (16 V Cat). Spherical crystallites/particles of ~12nm were observed after cobalt was added to the vanadium modified support. These crystallites are XRD amorphous possibly due to an amorphous structure or due to defects in the crystals.

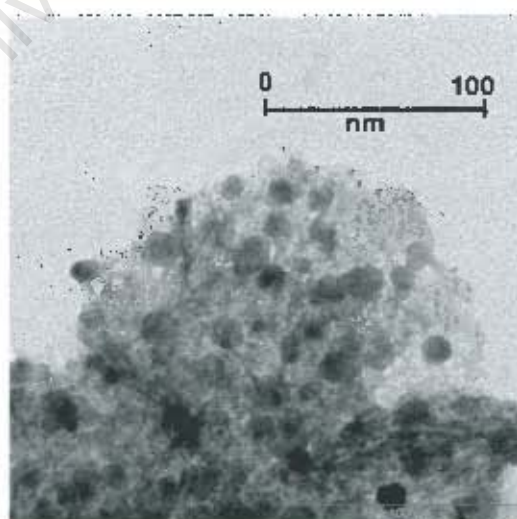


Figure 5.5: Change in $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ -catalysts containing 16wt% V (16 V Cat) morphology as observed using TEM

Table 5.1 shows the effect of the vanadium loading on the BET-surface area, pore volume and average pore diameter in the calcined $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts. The introduction of vanadium in the catalyst formulation leads to a reduction in the BET-surface area and the pore volume resulting in an approximately constant average pore diameter.

Table 5.1: Influence of V-loading on the BET-surface area, pore volume and average pore diameter in the calcined $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts

Catalyst	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	d_{pore} (nm)
0 Cat	160.7	0.42	10.4
3 V Cat	151.8	0.42	11.1
5 V Cat	154.5	0.39	10.0
9 V Cat	147.3	0.42	11.3
16 V Cat	118.8	0.31	10.3

5.2.2 Reduction behaviour of $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$

The reduction behaviour of the calcined $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts was characterized using temperature programmed reduction (TPR). The reduction behaviour of the catalyst was compared with the reduction behaviour of the modified support material (see Figure 5.6). Alumina supported vanadium oxide is easier reducible than bulk vanadium oxide. This was also observed by Reddy *et al.* [2004] and Koranne *et al.* [1994]. Reddy *et al.* [2004] explained it by a decrease in the diffusional limitation in the reduction of a thin layer of vanadia on a support. The vanadium oxide promoted support with the highest vanadium oxide loading (16 V Sup) still seems to have bulk V_2O_5 present, as observed in the XRD diffraction pattern (see Figure 5.1).

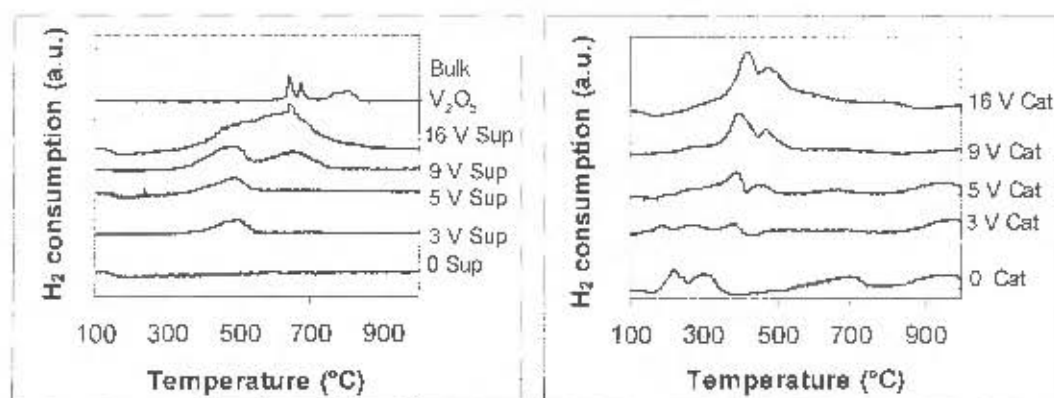


Figure 5.6: Temperature programmed reduction profile of the vanadium modified support material (left) and the calcined $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts (right)

The TPR-profile of $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ shows two low temperature peak maximums and two high temperature peak maximums. The first peak between 190°C and 220°C might be ascribed to the reduction of Co_3O_4 to CoO and the second low temperature peak between 265°C and 305°C to the reduction of CoO to Co [Hilmen *et al.*, 1996]. However, the area of the first peak is $>25\%$ of the total area up till 400°C indicating some reduction of CoO to Co at these low temperatures. The reduction peak at temperature higher than 400°C may be due to cobalt in close interaction with alumina [Arnoldy and Moulijn, 1985a]. The reduction peak at a temperature higher than 800°C may be due to cobalt aluminate [Arnoldy and Moulijn, 1985a; Arnoldy *et al.*, 1985b].

The low temperature peak maximum for the reduction of cobalt oxide shifts towards higher temperatures with the addition of vanadium to the catalyst formulation. This indicates that the rate of reduction of cobalt is retarded with the addition of vanadium oxide to the catalyst formulation, which may be due to a thin layer of vanadium oxide covering the cobalt. Guerrero-Ruiz *et al.* [1994] did not observe a temperature shift towards higher temperatures in the cobalt reduction peak maximum with the addition of vanadium.

The peak maximum for the reduction of vanadium oxide shifts towards lower temperatures with the addition of cobalt (see Figure 5.7). This was also

observed by Guerrero-Ruiz *et al.* [1994]. The formation of metallic cobalt may increase the rate of reduction of vanadium oxide by hydrogen spill-over.

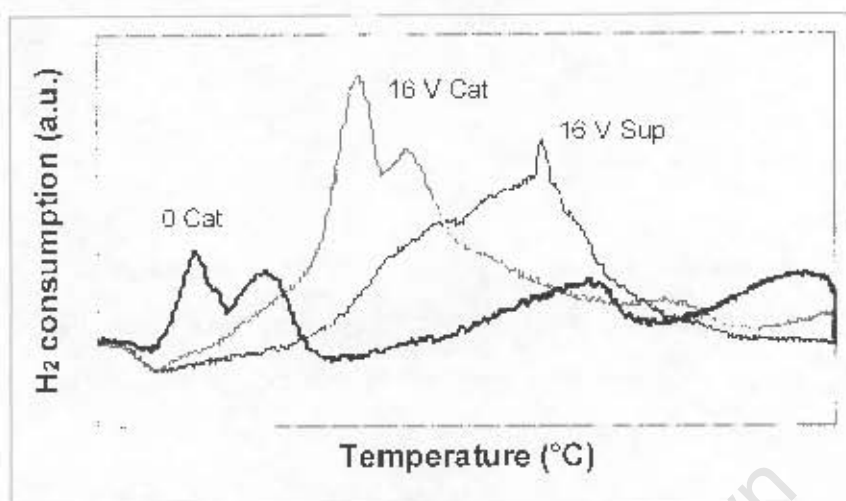


Figure 5.7: Influence of the addition of cobalt on the rate of reduction of vanadium oxide.

Figure 5.8 shows the amount of hydrogen consumed for the reduction of the catalyst and for the reduction of the support. The vanadium oxide and cobalt oxide was fully reduced at 1000°C. The hydrogen consumption increases with increasing vanadium oxide loading. The amount of hydrogen consumed for the reduction of cobalt within the catalyst can be obtained by the difference of the amount of hydrogen consumed for the reduction of the catalyst and the amount of hydrogen consumed for the reduction of the support, and amounts to ca. 2mmol of H₂ per gram of catalyst. This corresponds to a cobalt loading of ca. 9-10 wt.-% depending on the oxidation state of cobalt in the calcined catalyst and approximates well the intended cobalt loading.

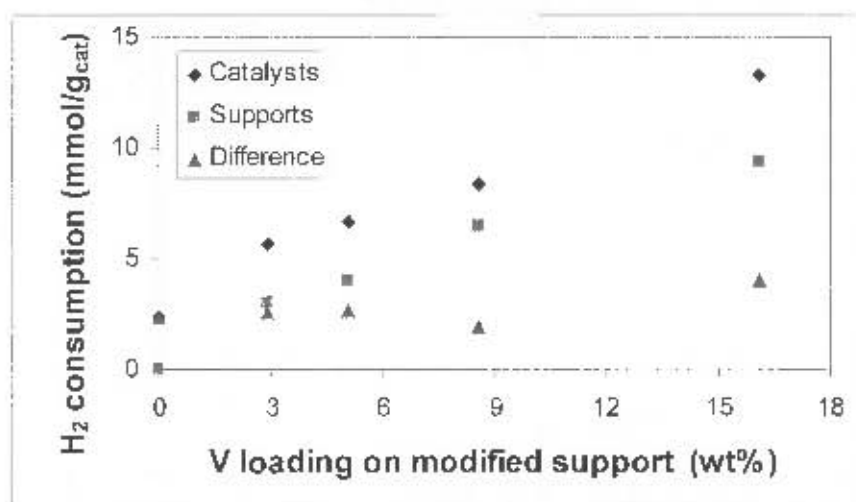


Figure 5.8: Integral hydrogen consumption (in mmol/g of catalyst) in the temperature programmed reduction (up to a temperature of 1000°C) of vanadium modified alumina, $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ and the difference attributable to the reduction of cobalt within the calcined catalyst

5.2.3 Characterization of reduced $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$

The cobalt-based catalysts supported on the vanadium oxide modified alumina supports were calcined at 250°C in air followed by reduction at 425°C in pure hydrogen.

The XRD analyses of the vanadium promoted cobalt catalysts (3 V Cat) and the unpromoted catalyst (0 Cat) (the reduced catalyst was covered with xylene to prevent re-oxidation) were performed. Diffraction peaks attributable to metallic cobalt or VO_x could not be detected implying that these phases are XRD-amorphous, i.e. the crystallites are either too small to be detected by XRD or contain too many defects.

Metal surface area

The activity of a catalyst in the Fischer-Tropsch synthesis over supported cobalt catalysts is believed to be proportional to the metal surface area [Iglesia, 1993]. Static hydrogen chemisorption and CO TPD were used in attempt to quantify the metal surface area.

Static chemisorption was found to be of limited use to quantify the number of cobalt surface metal sites since both hydrogen and carbon monoxide may also chemisorb/adsorb on vanadium oxide [Zwane, 2004]. Figure 5.9 shows the hydrogen uptake in a static chemisorption experiment on the $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (0 Cat) without vanadium added to the support and on $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ with 5wt.-% V (5 V Cat). The hydrogen uptake on the catalyst without V_2O_5 shows the typical dependency of the adsorbed volume on the pressure, with a strong increase in the adsorbed volume at very low pressures asymptotically approaching a constant value of ca. 0.3ml(STP)/g (see Figure 5.9). The metal surface area for this catalyst (0 Cat) can thus be estimated to be 1.1m²/g. The strong increase of the adsorbed volume at very low pressure indicates that the hydrogen adsorption is very strong under these conditions.

The hydrogen uptake on $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ with 5wt.-% vanadium (5 V Cat) shows a different behaviour. It increases gradually with increasing pressure. A constant value is not approached at pressures up to 700mm Hg. This shows that hydrogen is likely to be chemisorbed on weaker sites, e.g. VO_x as well as on metallic sites. It can also be speculated that hydrogen dissociates on the cobalt metal and spills over to form $\text{H}_x\text{V}_2\text{O}_5$ [Marcq *et al.*, 1984]. At very low pressure the hydrogen uptake of the $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ with 5wt.-% vanadium (5 V Cat) is less than on $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (0 Cat). This might indicate that the exposed metallic cobalt surface area on the catalyst, to which vanadium was added to the catalyst formulation, is only ca. 30% of that for the catalyst without vanadium.

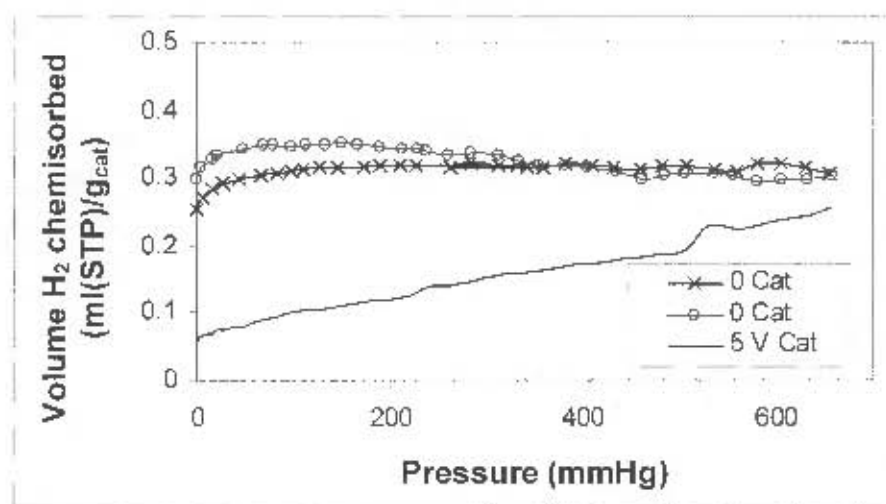


Figure 5.9: Static chemisorption of hydrogen at 125°C on $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (0 Cat) and on $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ with 5wt.-% V (5 V Cat)

Dynamic chemisorption measurements such as temperature programmed desorption (TPD) might be better suited to estimate the amount of material adsorbed on the different sites. Figure 5.10 shows the TPD-profiles obtained after adsorption of CO on the modified support materials and the vanadium modified catalysts. The modified supports adsorb CO yielding a desorption peak at ca. 150°C.

CO desorbs from the unpromoted $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ catalyst (0 Cat) at ca. 250°C. The amount of CO desorbed from this catalyst is 0.62ml(STP)/g_{catalyst}. The value obtained corresponds well with the amount of hydrogen chemisorbed at saturation (0.3ml(STP)/g_{catalyst}) implying associative CO-chemisorption and dissociative chemisorption of hydrogen.

From the CO-desorption on the modified support materials, it might be concluded that CO chemisorbed on oxides desorb below 200-250°C. The amount of CO, which desorbs at higher temperatures, might be ascribed to CO chemisorbed on metallic cobalt. It may then be concluded that the cobalt metal area decreases with an increase in the vanadium oxide loading in the catalyst formulation (see Table 5.2). This might be caused by a (partial) coverage of metallic cobalt with vanadium oxide.

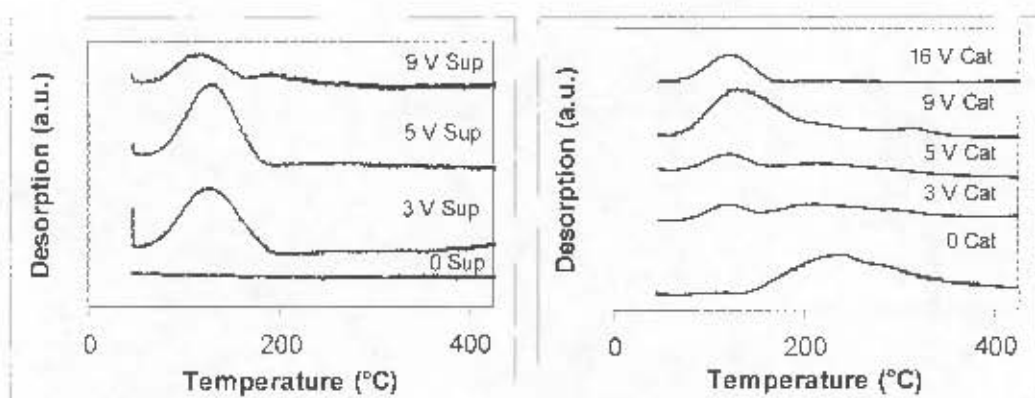


Figure 5.10: Temperature programmed desorption of CO (CO-TPD) of V_2O_5 -modified support materials (left) and the $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts (both materials reduced in hydrogen at 425°C)

Table 5.2: Cobalt metal area determined from the CO desorption peak area between 250 and 425°C on reduced catalysts ($T_{\text{reduction}} = 425^\circ\text{C}$ for 8hrs)

Catalyst	Temperature range of integration to obtain area of CO desorbed	CO desorption $250\text{-}425^\circ\text{C}$ (ml(STP)/g _{cat})
0 Cat	$50\text{-}425^\circ\text{C}$	0.62
3 V Cat	$160\text{-}425^\circ\text{C}$	0.19
5 V Cat	$170\text{-}425^\circ\text{C}$	0.21
9 V Cat	$200\text{-}425^\circ\text{C}$	0.18
16 V Cat	$180\text{-}425^\circ\text{C}$	0.07

XPS-analysis of the reduced catalyst

The surface composition of the reduced catalysts and the oxidation state of the various elements were determined using XPS (see Table 5.3). However, it should be noted that XPS analyses may analyse layers up to 5 nm deep (N.N.7, 2006) in the catalyst and is thus not a true surface analysis. The near surface region of the catalyst $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (0 Cat) is enriched with cobalt. The amount of divalent cobalt seems to be surprisingly high seeing the high degree of reduction obtained with this catalyst (see Table 5.3). This can be rationalised by the presence of a highly dispersed cobalt oxide phase (e.g. cobalt aluminate) and larger crystallites of metallic cobalt.

The amounts of metallic cobalt metal for the vanadium oxide promoted catalysts were 2atom-%, 4.7atom% and 0.2atom-%. The vanadium content in the near surface region is increasing with increasing vanadium loading.

The XPS analysis confirms that vanadium in the catalyst is reduced as well and the surface near region consists of V^{3+} , V^{4+} and V^{5+} . The amount of V^{5+} (relative to V^{3+} and V^{4+}) in the reduced catalyst samples increases with an increase in the vanadium loading.

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Table 5.3: Elemental analysis of surface region in the reduced Co/V₂O₅/γ-Al₂O₃ catalysts by XPS (analyses done by CSIR)

Catalyst	Element	Concentration (atom-%)	E _{binding} (eV)	
0 Cat	Al	14.7	74.5	Al ₂ O ₃
	C	3.0	284.7	
	Co	13.6	778.0	(8%) Co
			781.3	(92%) Cobalt oxide
	O	68.8	531.4	
5 V Cat	Al	17.1	74.4	Al ₂ O ₃
	Co	4.4	778.7	(46%) Co
			781.8	(54%) Cobalt oxide
	V	2.6	514.6	(18%) V(OH) ₃
			515.8	(40%) V ₂ O ₃
			516.4	(25%) VO ₂
			517.7	(17%) V ₂ O ₅
	O	69.6	530.6	
9 V Cat	Al	9.8	74.3	Al ₂ O ₃
	Co	7.8	778.1	(60%) Co
			781.6	(40%) Cobalt oxide
	V	7.2	514.3	(20%) V(OH) ₃
			515.5	(35%) V ₂ O ₃
			516.2	(25%) VO ₂
			517.4	(20%) V ₂ O ₅
	O	69.6	530.6	
16 V Cat	Al	9.8	74.9	Al ₂ O ₃
	Co	9.1	778.2	(2%) Co
			781.4	(98%) Cobalt oxide
	V	11.4	515.2	(28%) V ₂ O ₃
			515.7	(41%) VO ₂
			517.1	(31%) V ₂ O ₅
	O	64.0	531.1	

5.3 Characterisation of acidity in the reduced Co/V₂O₅/γ-Al₂O₃ catalysts

The vanadium modified catalysts are expected to have acidic properties [Gervasini *et al.*, 2004, Ishida, 1971, Khadar, 1995], which may affect the performance of these catalysts in the Fischer-Tropsch synthesis. The acidic

properties of the reduced catalysts were probed using NH_3 -TPD, the conversion of iso-propanol yielding propene and di-isopropyl-ether.

5.3.1 NH_3 -TPD over the reduced $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts

The adsorption and subsequent temperature programmed desorption of ammonia is a well-described technique to characterize acidity in heterogeneous catalysts [Lowenthal *et al.*, 1995; Ma *et al.*, 2004; Rajagopal *et al.*, 1995]. The TPD spectra are similar for the $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts whether V_2O_5 is present or not (see Figure 5.11).

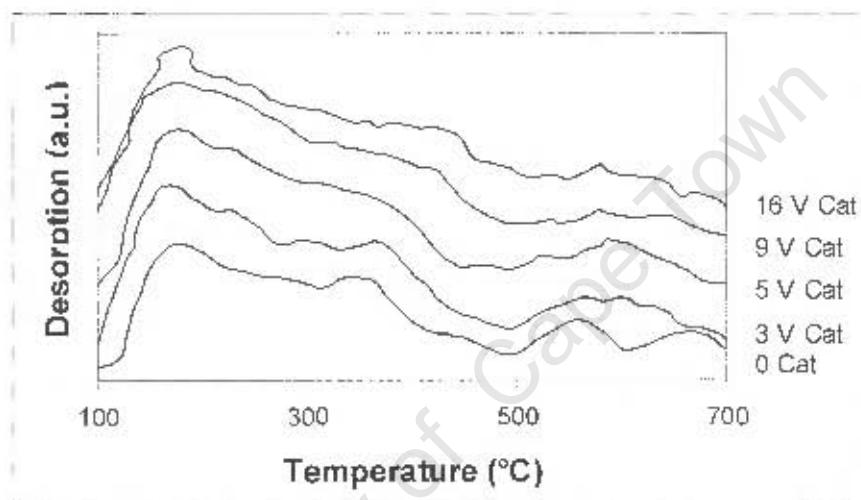


Figure 5.11: Ammonia desorption during TPD analyses on reduced catalysts (in each case the equivalent amount of catalyst corresponding to 0.25g of alumina was loaded; catalysts reduced for 16hrs at 425° in H_2)

The number of acid sites per gram of alumina and the number of acid sites decreases per unit of mass of calcined catalyst were not strongly dependent on the vanadium oxide loading (see Table 5.4). This may indicate that the addition of vanadium oxide to the catalyst did not increase the number of acid sites.

Table 5.4: Amount of NH_3 desorbed in NH_3 -TPD experiments as measured by back-titration of the sulphuric acid trap

Support/Catalyst	Amount of NH_3 adsorbed per gram of support or catalyst ($\text{mmol/g}_{\text{cat}}$)	Amount of NH_3 adsorbed per g of Al_2O_3 in support or catalyst ($\text{mmol/g Al}_2\text{O}_3$)
0 Sup	0.050	0.0606
0 Cat	0.049	0.0576
3 V Cat	0.053	0.0647
9 V Cat	0.057	0.0784
16 V Cat	0.042	0.0681

5.3.2 Probing acidity using conversion of iso-propanol

The acidic properties of catalysts can be probed using the dehydration of iso-propanol yielding propene and di-isopropylether (DIPE) [Bej *et al.*, 2003; Benadda *et al.*, 2003; Perez-Cadenas *et al.*, 2003]. Acetone can be formed from iso-propanol as well through dehydrogenation, which is mainly catalysed by basic sites, although this reaction may also proceed over acidic sites [Bej *et al.*, 2003].

Figure 5.12 shows the yield of propene plus di-isopropylether (DIPE) in the conversion of iso-propanol as a function of the space velocity. The order for the yield of propene plus di-isopropylether over the reduced catalysts was:

$$0 \text{ Cat} < 3 \text{ V Cat} < 16 \text{ V Cat} < 9 \text{ V Cat}$$

Thus, the unpromoted catalyst was the least acidic. The lower yield of propene on the 16 V Cat catalyst relative to the 9 V Cat catalyst may be due to the lower surface area (see BET results) of the 16 V Cat and lower number of acid sites per gram of catalyst as determined by the NH_3 -TPD (see Table 5.4).

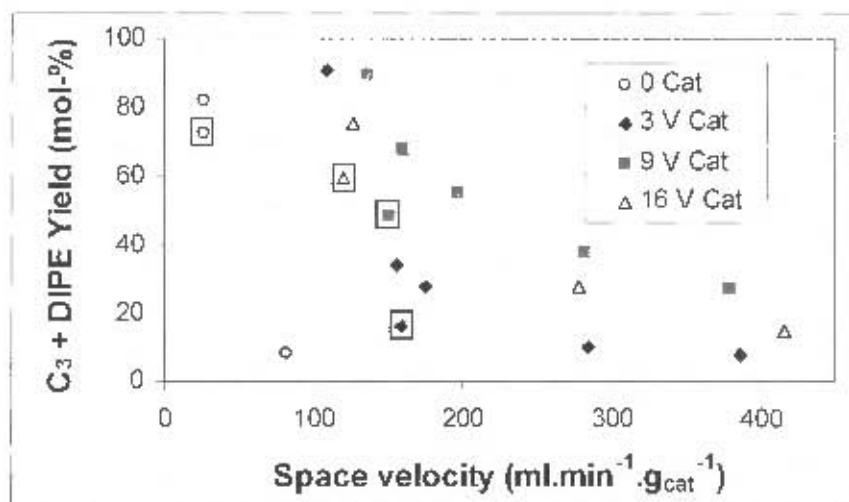


Figure 5.12: Yield of propene plus di-isopropylether (DIPE) in the conversion of iso-propanol at 220°C over the reduced catalysts (reduction in hydrogen at 425°C) as a function of space velocity (data-points in blocks are data-points obtained at the end of the run to check for catalyst deactivation)

Some minor deactivation was observed in the conversion of iso-propanol as evidenced by the return to a lower space velocity after having performed the reaction at various space velocities. However, the deactivation seems to be minor and not affecting the conclusions in a major way.

5.4 Fischer-Tropsch synthesis over $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts

The Fischer-Tropsch synthesis was carried out in a fixed bed reactor at 220°C and 20 bar_a using a feed with $\text{H}_2/\text{CO}=2\text{mol/mol}$ and a synthesis gas space velocity of 46ml/(min.g). In order to verify the obtained findings some experimental parameters, such as linear velocity, space velocity, pressure and temperature were varied for some of the catalysts. A summary of the experimental results are given in Appendix D.

5.4.1 Catalyst activity

Figure 5.13 shows the conversion of carbon monoxide over $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ as a function of time on stream at 220°C and 20 bar_a and a space velocity of 46ml(STP)/(min.g). The catalyst without the addition of vanadium to the

catalyst formulation (0 Cat) showed the highest activity with a CO-conversion of ca. 40mol-% between 1000 and 5000 minutes on stream. The activity decreased with an increase in the vanadium loading (see Figure 5.13). The addition of vanadium has a detrimental effect on the catalytic activity. The influence of vanadium oxide on the activity also had a detrimental effect at lower pressures and higher temperatures (see Figure 5.14 and Table 5.5). This might be attributed to the decoration and/or (partial) coverage of cobalt metal surface area VO_x .

Table 5.5: Effect of reaction temperature and pressure on the obtained CO-conversion in the Fischer-Tropsch synthesis (synthesis gas space velocity: $23\text{ml(STP)}/(\text{min.g})$, $\text{H}_2/\text{CO}=2$, fixed bed reactor, time on stream: 2-7 days)

Catalyst	T °C	P bar	X _{co} mol-%
$\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (0 Cat)	220	20	51
	220	10	41
	220	5	27
	220	1	22
	230	1	28
	240	1	34
$\text{Co}/\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ with 9wt.-% V (9 V Cat)	220	20	19
	220	10	17
	220	5	14
	220	1	13
	230	1	16
	240	1	19

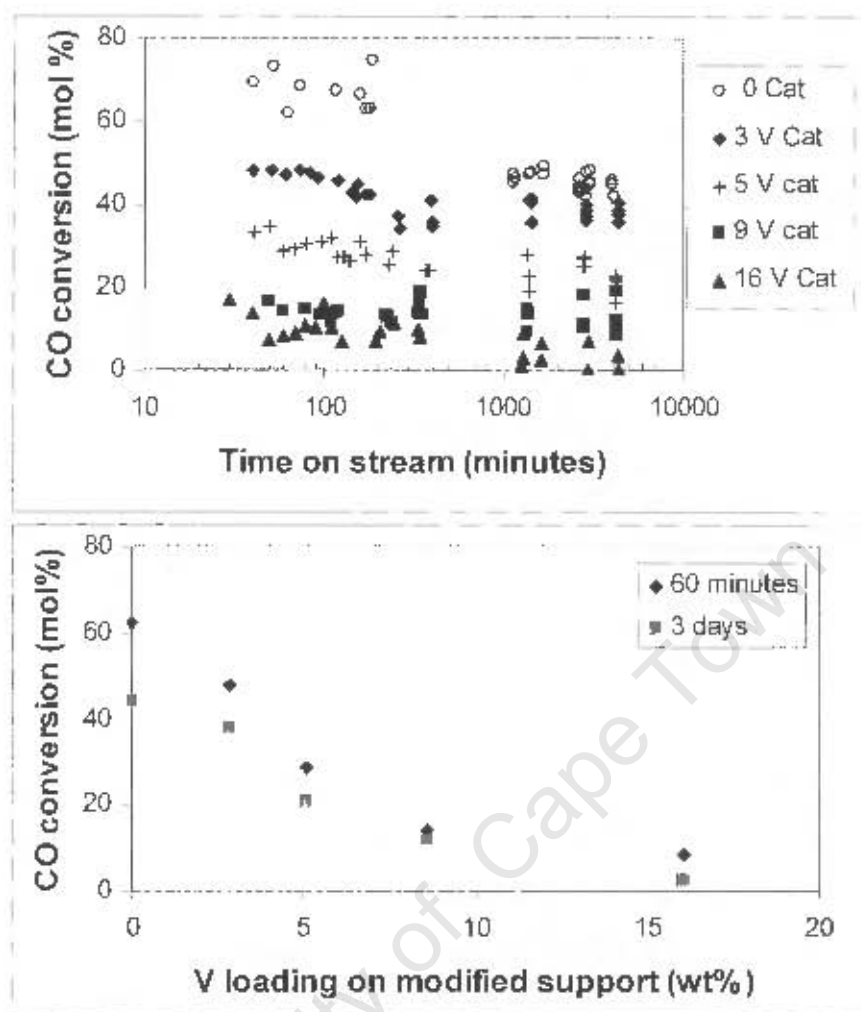


Figure 5.13: Conversion of CO over $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ tested at 220°C , 20bar_a , and a synthesis gas space velocity of $46\text{ml(STP)}/(\text{min g})$, $\text{H}_2/\text{CO}=2$ in a fixed bed reactor

Top: CO-conversion as a function of time on stream

Bottom: CO-conversion as a function of vanadium loading after 60 minutes and 4000-5000 minutes (3 days) on stream

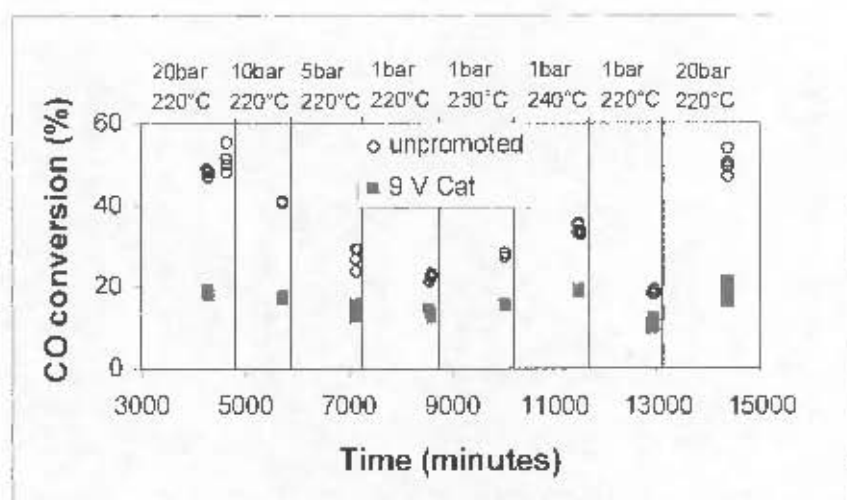


Figure 5.14: Influence of vanadium on the activity of a cobalt catalyst (9 V Cat) at different temperatures and pressures (synthesis gas space velocity: $23\text{ml(STP)}/(\text{min.g})$, $\text{H}_2/\text{CO}=2$, fixed bed reactor)

5.4.2 Selectivity in the Fischer-Tropsch synthesis

The Fischer-Tropsch synthesis produces a wide product distribution with a strong regularity. Shifts in the product selectivity in the Fischer-Tropsch synthesis can be used as an indicator of the changes in the catalyst system.

Methane selectivity and chain growth probability

Figure 5.15 shows the chain growth probability ($\text{C}_3\text{-C}_{10}$) and the methane selectivity at 1-3 days on stream as a function of vanadium loading. The methane selectivity was determined from an extrapolated FID-analysis (see Appendix E), since the determination of the methane selectivity from the inorganic and permanent gas analysis becomes inaccurate at low CO conversions. The chain growth probability decreases from 0.84 to 0.7 with increasing vanadium loading up to a vanadium loading of 9wt.-%. With a further increase in the vanadium loading the chain growth probability did not decrease. The methane selectivity (in C-%) did not increase significantly with an increase in the vanadium loading (see Figure 5.15)

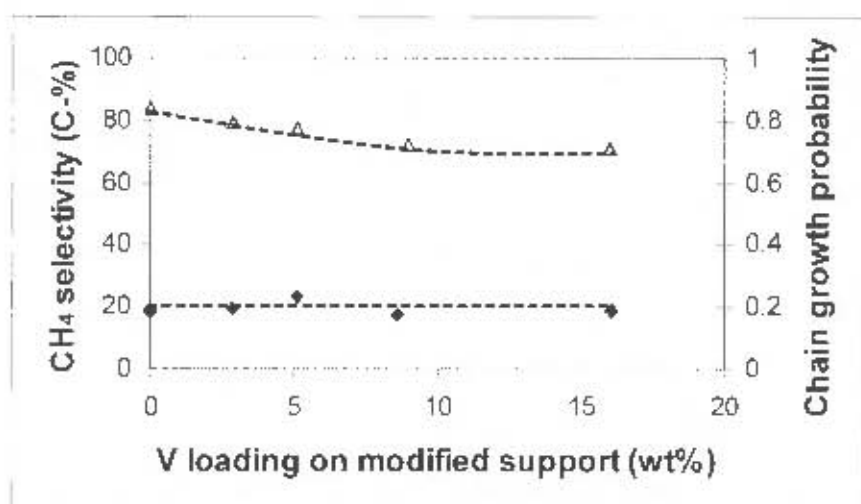


Figure 5.15: Influence of vanadium loading on methane selectivity and chain growth probability (C₃-C₁₀) over Co/V₂O₅/γ-Al₂O₃ (T=220°C, p=20bar_a, synthesis gas space velocity=46ml(STP)/(min.g), H₂/CO=2, fixed bed reactor, time on stream: 1-3days)

The chain growth probability (C₃₋₁₀) was not affected by the change in the CO conversion over the catalyst without vanadium in the catalyst formulation (0 Cat) (see Appendix F). Similarly, the chain growth probability obtained with Co/V₂O₅/γ-Al₂O₃ containing 9wt.-% vanadium (9 V Cat) was independent of the space velocity (see Table 5.6). Hence, the observed decrease of the chain with increasing vanadium loading is not likely to be an effect of the CO-conversion.

Table 5.6: Influence of space velocity (same linear velocity) in the CO-conversion in the Fischer-Tropsch synthesis and the chain growth probability (C₃-C₁₀) Co/V₂O₅/γ-Al₂O₃ containing 9wt.-% vanadium (9 V Cat) (220°C, 20bar_a, H₂/CO=2, fixed bed reactor, 1-3 days on stream)

SV, ml/(min.g)	15	23	46	46
X _{CO} , %	31	19	12	12
Time on stream	(3 days)	(3 days)	(3 days)	(1 day)
α	0.73	0.74	0.69	0.75

The catalysts were tested at lower pressures and higher temperatures to see if the reaction conditions have an influence on the relative selectivities of the

catalysts. The methane selectivity increased and the chain growth probability decreased with a decrease in the pressure and an increase in the temperature for the $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts (see Figure 5.16 and Figure 5.17). With a decrease in pressure and an increase in temperature the difference in the chain growth probabilities between the promoted and unpromoted catalyst decreased (see Figure 5.16). At 1bar and 240°C , the chain growth probabilities are similar for the $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts.

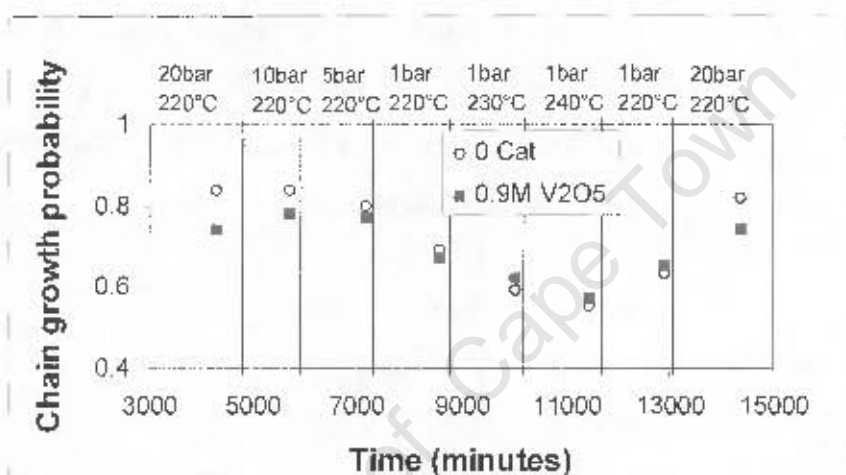


Figure 5.16: Influence of temperature and pressure chain growth probability (C_{3-10}) over $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (0 Cat) and $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ (9 V cat) (synthesis gas space velocity= $23\text{ml(STP)}/(\text{min}\cdot\text{g})$, $\text{H}_2/\text{CO}=2$, fixed bed reactor)

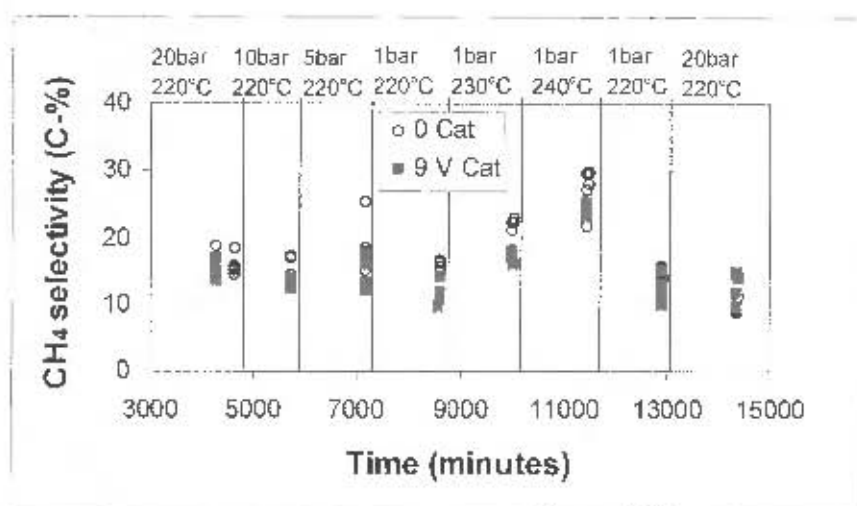


Figure 5.17: Influence of temperature and pressure on the methane selectivity over $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (0 Cat) and $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ (9 V cat) (synthesis gas space velocity=23ml(STP)/(min.g), $\text{H}_2/\text{CO}=2$, fixed bed reactor)

Olefin production in the Fischer-Tropsch synthesis

In the alkyl mechanism it is assumed that surface alkyl species may desorb by β -H-abstraction yielding 1-olefins and by H-addition yielding paraffins (see Figure 5.18) [Claeys and Van Steen, 2004].

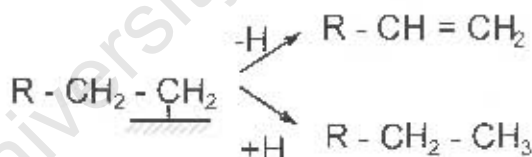


Figure 5.18: Formation of olefins and paraffins in the Fischer-Tropsch synthesis [Claeys and Van Steen, 2004; Schulz and Claeys, 1999]

1-Olefins are reactive product compounds which may re-adsorb on Fischer-Tropsch sites and undergo secondary hydrogenation yielding n-paraffins, double bond isomerisation yielding internal olefins or reincorporated into chain growth schemes (see Figure 5.19) [Schulz and Claeys, 1999]. Furthermore, olefins may undergo double bond isomerisation on acidic sites present in the catalyst (see 5.3.2 and Figure 5.19).

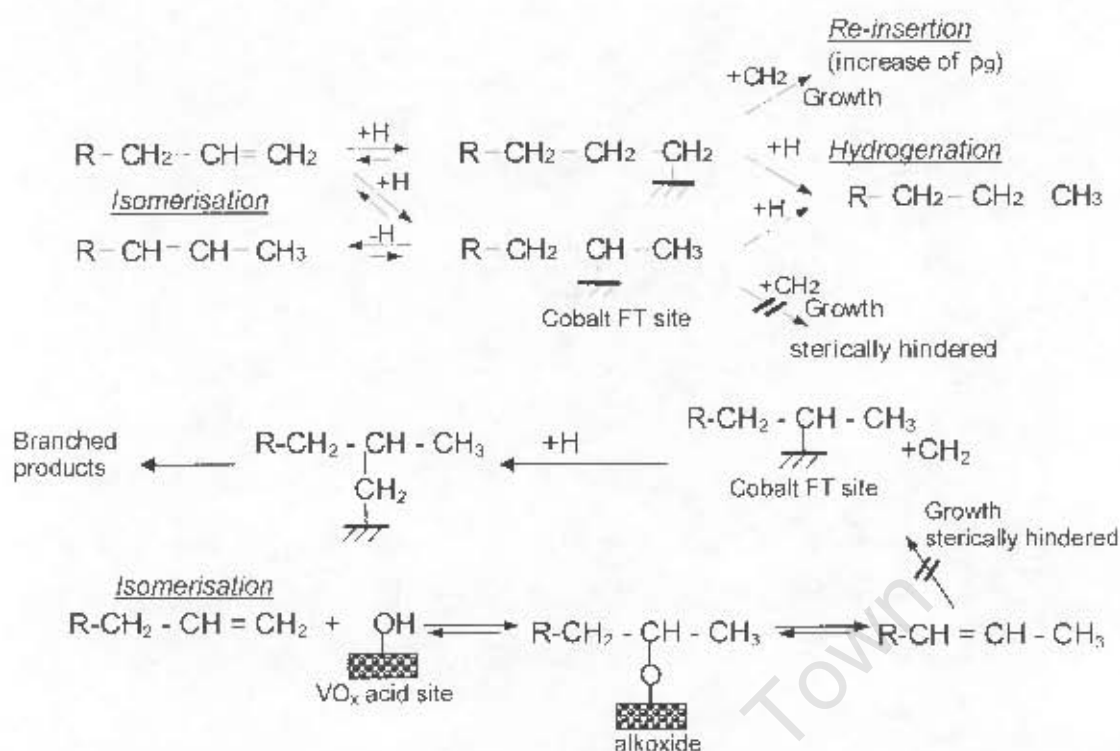


Figure 5.19: Schematic showing secondary reaction on a cobalt Fischer-Tropsch site [Claeys and Van Steen, 2004] and an acid vanadium oxide site (see Chapter 2).

Figure 5.20 shows the olefin content in the fraction of linear hydrocarbons and the 1-olefin content as a function of carbon number after 3 days on stream. The olefin content in the fraction of linear hydrocarbons is a measure for the extent of consumption of primary formed 1-olefins for the formation of *n*-paraffins or their re-incorporation into the chain growth scheme. The 1-olefin content in the fraction of linear olefins is a measure for the extent of primarily formed 1-olefins undergoing double bond isomerisation.

The olefin content in the fraction of linear hydrocarbons shows the expected behaviour of a low value in C_2 , passing through a maximum at C_3/C_4 , and decreasing with increasing carbon number. The low olefin content in the fraction of C_2 -hydrocarbons is attributed to the high reactivity in C_2 ; the reactivity of longer chain hydrocarbons is approximately constant, and the decrease as a function of carbon number is attributed to the concentration of these olefins near the catalytic active site [Schulz and Claeys, 1999].

The olefin content in the fraction of linear hydrocarbons increases with increasing vanadium content in the catalyst indicating a reduced extent of secondary hydrogenation (see Figure 5.20). Furthermore, the 1-olefin content in the fraction of linear olefins decreases with the addition of vanadium oxide (see Figure 5.20).

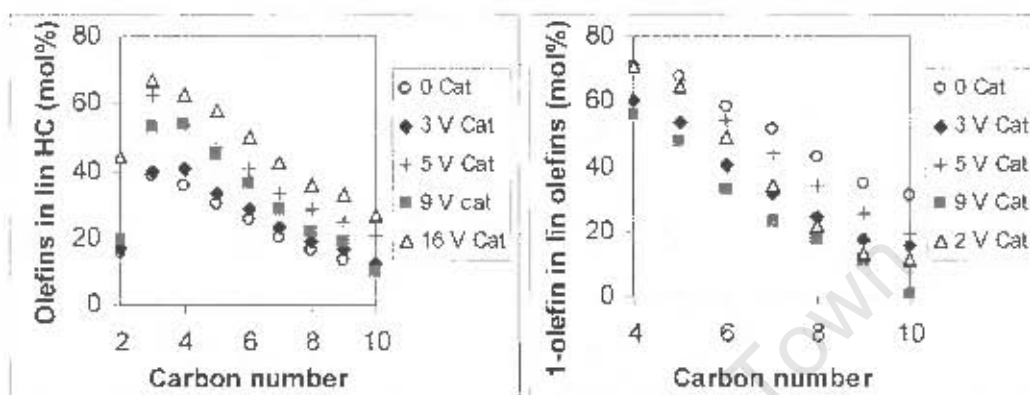


Figure 5.20: Olefin content in the fraction of linear hydrocarbons (left) and 1-olefin content in the fraction of linear olefins (right) as a function of carbon number (220°C, 20bar_a, synthesis gas space velocity 46ml(STP)min⁻¹g_{cat}⁻¹, H₂/CO=2, fixed bed reactor, time on stream: 3 days)

The observed increase in the olefin content in the fraction of linear hydrocarbons and the decrease in the 1-olefin olefin content in the fraction of linear olefins might be attributed to the different CO-conversion, at which these catalysts were tested. Figure 5.21 shows the olefin content in the fraction of linear hydrocarbons and the 1-olefin content in the fraction of linear olefins as a function of the CO-conversion.

At a similar CO-conversion, the olefin content in the fraction of linear hydrocarbons for the catalyst without vanadium is higher than the olefin content in the fraction of linear hydrocarbons for the catalysts containing high loadings of vanadium. The catalysts with low loadings of vanadium (5V Cat and 3V Cat) have similar olefin content in the fraction of linear hydrocarbons when compared at similar levels of CO conversion. A lower olefin content is attributed to the conversion of olefins to paraffins (secondary hydrogenation)

or re-incorporation into the chain growth scheme. This might be ascribed to a hydrogenation activity on vanadia within the catalyst. The hydrogenation ability of V_2O_3 at 250°C [Komarewsky and Erikson, 1953], of reduced supported vanadium oxide (average oxidation state between +3 and +4) at 70°C [Ishida, 1971] and vanadium hydrogen bronze, $\text{H}_x\text{V}_2\text{O}_5$, between 60 and 160°C [Marcq *et al.*, 1984] have been reported earlier.

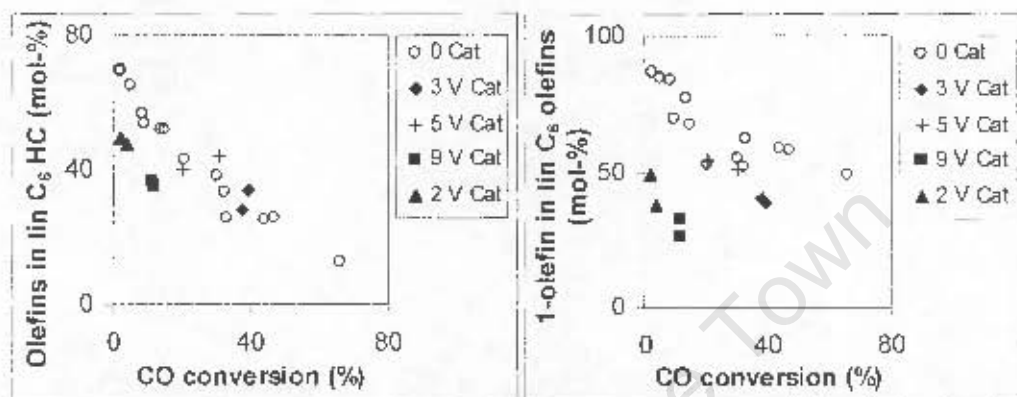


Figure 5.21: Olefin content in the fraction of linear hydrocarbons (left) and 1-olefin content in the fraction of linear olefins (right) as a function of carbon number (220°C , 20bar_a , synthesis gas space velocity $46\text{ml}(\text{STP})/\text{min}/\text{g}_{\text{cat}}$ for the vanadium promoted catalysts and gas space velocities between 23 and $736\text{ml}(\text{STP})/\text{min}/\text{g}_{\text{cat}}$ for the unpromoted catalyst, $\text{H}_2/\text{CO}=2$, fixed bed reactor, time on stream: 1-3 days)

The 1-olefin content in the fraction of linear olefins is lower for the catalyst containing vanadium relative to the catalyst without vanadium.

Figure 5.22 shows the olefin content in the fraction of linear hydrocarbons and the 1-olefin content in the fraction of linear olefins as a function of carbon number at different space velocities, constant linear velocity, obtained over the catalyst $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ containing 9wt.-% vanadium (9 V Cat). The olefin content in the linear hydrocarbon fractions and the 1-olefin content in the fraction of linear hydrocarbons was not a strong function of the space velocity.

The rate of the double bond isomerisation over the vanadium containing catalysts is best exemplified by varying the linear velocity through the catalyst bed keeping the space velocity constant (see Figure 5.23). Any change in the product selectivity due to a change in the linear velocity must be attributed to external mass transfer limitations in the product removal from the catalyst particle, since the CO-conversion is not affected by the linear velocity. The olefin content in the fraction of linear hydrocarbons is not affected by the linear velocity for the unpromoted catalyst. This implies that the secondary reactions on the Fischer-Tropsch sites are slow in comparison to the product removal. The olefin content in the fraction of linear hydrocarbons increased with an increase in the linear velocity for the catalyst containing vanadium. This indicates that secondary hydrogenation taking place on the additional sites in the vanadium promoted catalyst is much faster than secondary hydrogenation on the metallic cobalt sites in the unpromoted catalyst.

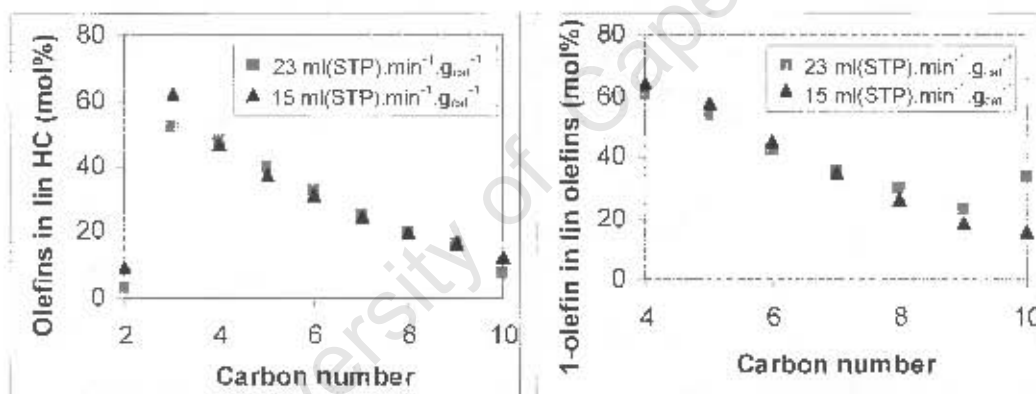


Figure 5.22: Olefin content in the fraction of linear hydrocarbons (left) and 1-olefin content in the fraction of linear olefins (right) as a function of carbon number over $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ containing 9wt.-% vanadium (9 V Cat) (220°C , 20bar_a , $\text{H}_2/\text{CO}=2$, fixed bed reactor, linear velocity 1.5cm/min , time on stream: 3 days)

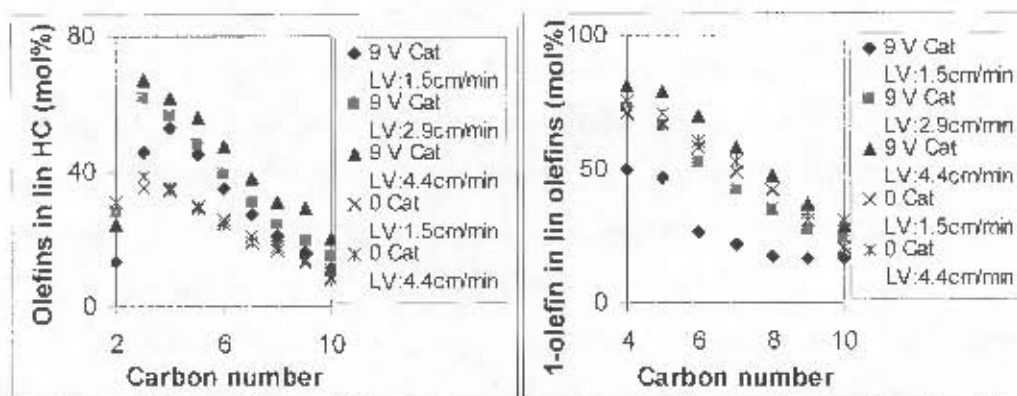


Figure 5.23: Olefin content in the fraction of linear hydrocarbons (left) and 1-olefin content in the fraction of linear olefins (right) as a function of carbon number over $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (0 Cat) and $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ containing 9wt.-% vanadium (9 V Cat) (220°C , 20bar_a, $\text{H}_2/\text{CO}=2$, fixed bed reactor, synthesis gas space velocity = $46\text{ml(STP)}/(\text{min g})$, time on stream: 3 days)

The 1-olefin content in the fraction of linear hydrocarbons is not affected by the linear velocity for the unpromoted catalyst. An increase in the linear velocity results in an increase in the 1-olefin content over the vanadium containing catalyst. This implies that the double bond isomerisation in the vanadium containing catalyst is rather fast and that it is affected by external mass transport limitations, i.e. removal of the product olefins from the catalyst particle. This indicates a fast secondary double bond isomerisation in the promoted catalysts, e.g. over the vanadia present in the catalyst, compared to the double bond isomerisation on metallic cobalt sites in the unpromoted catalyst.

The 1-olefin content in the fraction of linear hydrocarbons over the catalyst containing vanadium was even more affected by the linear velocity than the olefin content in the fraction of linear hydrocarbons. This indicates that secondary isomerisation is faster than secondary hydrogenation on the vanadium oxide catalyst.

Production of branched compounds in the Fischer-Tropsch synthesis

The re-incorporation of internal olefins in the chain growth scheme may lead to the formation of branched compounds (see Figure 5.19 schematic) [Schulz *et al.*, 1994]. Acid sites may also catalyse skeletal isomerisation leading to the formation of branched hydrocarbons. Figure 5.24 shows the effect of vanadium loading of the catalyst on the amount of branched hydrocarbons in the fraction of C_5 and C_6 -hydrocarbons. The amount of branched compounds in a hydrocarbon fraction did not increase significantly with an increase in the vanadium loading.

The amount branched hydrocarbons increased with a decrease in the pressure (see Figure 5.25). At low pressure, steric hindrance plays a smaller role and therefore internal olefins can readsorb and grow further resulting in branched hydrocarbons. The amount branched hydrocarbons increased with an increase in the temperature.

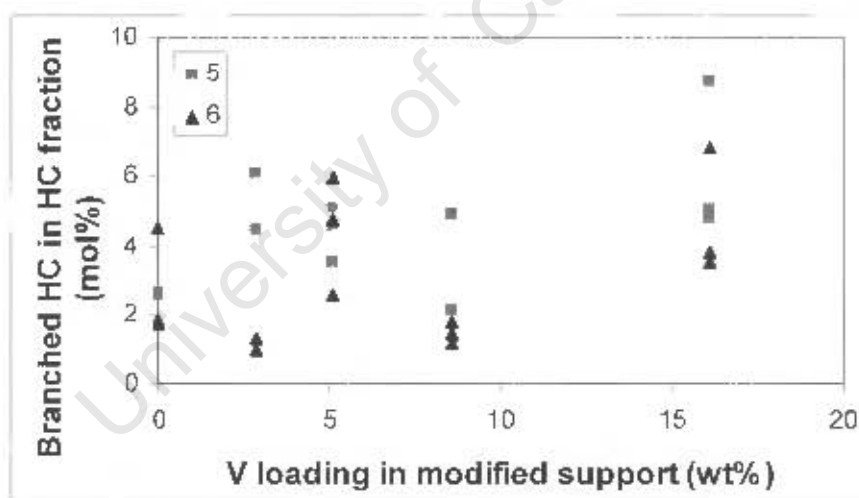


Figure 5.24: Amount of branched hydrocarbons in the fraction of C_5 and C_6 hydrocarbons as a function of the vanadium loading (220°C , 20bar_a , synthesis gas space velocity $46\text{ml(STP)}/(\text{min}\cdot\text{g})$, $\text{H}_2/\text{CO}=2$, fixed bed reactor, time on stream: 1-77h)

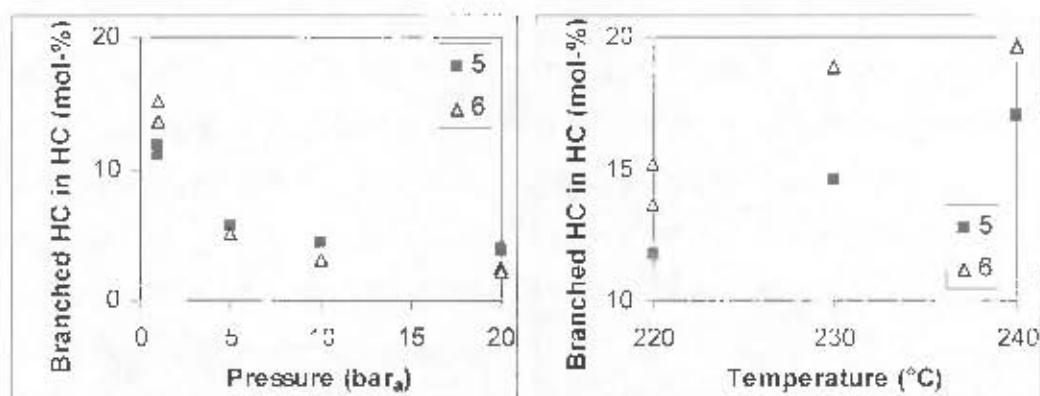


Figure 5.25: Amount of branched hydrocarbons in the fraction of C_6 and C_5 hydrocarbons as a function of the pressure at 220°C (left) and temperature at 1 bar_a (right) for $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ containing 9wt.-% vanadium (9 V Cat) (synthesis gas space velocity $23\text{ ml(STP)/(min.g)}$, $\text{H}_2/\text{CO}=2$, fixed bed reactor, time on stream: 1-77h)

5.5 Summary and concluding remarks

The controlled adsorption and deposition of the vanadium oxide on the support alumina did not lead to the formation of vanadium oxide thin multilayers at high vanadium loadings. The formation of V_2O_5 was observed in XRD diffraction patterns at high vanadium loadings. The intensity of the V_2O_5 diffraction peaks decreased and disappeared when cobalt was added to the vanadium modified support.

The addition of vanadium oxide to the cobalt catalyst decreased the rate of reduction of the cobalt as shown by TPR. The decrease in the rate of reduction was also supported by the mixing experiments of V_2O_5 and Co_3O_4 in water. This may be due to the formation of a thin layer of V_2O_5 covering the cobalt partially. The decrease in the cobalt metal surface area in the vanadium promoted catalyst as determined by CO TPD may also indicate the formation of a thin layer of VO_x covering the cobalt partially. The vanadium reduces partially during reduction at 425°C as determined by XPS. The addition of cobalt to the vanadium promoted supports increased the rate of reduction of the vanadium oxide.

The promotion of a cobalt Fischer-Tropsch catalyst with vanadium oxide decreased the CO conversion and decreased the chain growth probability tested at 220°C and 20bar_a. The methane selectivity did not increase significantly with an increase in the vanadium loading. The decrease in the CO conversion may be explained by the decrease in the cobalt metal area as determined by CO chemisorption.

The 1-olefin content in linear olefins fractions for the vanadium promoted catalysts were less in comparison to that of the unpromoted catalyst when compared at the same CO conversion. The 1-olefin content in linear olefins fractions was not a strong function of the vanadium oxide loading.

Double bond isomerisation can be catalysed by acid sites. The acidity increased with the addition of vanadium to the catalyst formulation based on the iso-propanol test, which explains the increase in the double bond isomerisation with the addition of vanadium to the catalyst formulation.

Olefins with internal double bonds readsorb less readily than 1-olefins, and their reincorporation in the chain growth mechanism is thus less likely [Schulz and Claeys, 1999]. The increase in the double bond isomerisation may explain the decrease in the chain growth probability with an increase in the vanadium loading. The acidity of the 9 V Cat and 16 V Cat catalysts were similar, which may explain the similar chain growth probabilities of these catalysts.

The catalysts were tested at lower pressures and higher temperatures to see if the reaction conditions have an influence on the relative selectivities of the catalysts. The chain growth probability of the vanadium promoted catalyst was similar to the unpromoted catalysts at low pressure (1bar_a) and higher temperature (240°C). The fraction branched hydrocarbons in hydrocarbons also increased with a decrease in the pressure and increase in the temperature, indicating that the internal olefin were incorporated to a larger

extent. This may be due to steric hindrance playing a smaller role at these operating conditions.

The olefin content in linear hydrocarbon fractions increased with an increase in the vanadium loading in the catalysts tested at the same space velocity, i.e. different conversions. The olefin content in linear hydrocarbon fractions for the vanadium promoted catalysts were compared to the unpromoted catalyst as a function of the CO conversion (compared at different space velocities). Slightly more hydrogenation took place on the catalyst promoted with high loadings of vanadium oxide relative to the unpromoted catalyst. Therefore, the increase olefins in the linear hydrocarbon fractions with an increase in the vanadium loading in the catalyst tested at the same space velocity was due to the decrease in the CO conversion. A decrease in the CO conversion leads to a decrease in secondary hydrogenation reactions.

6 Discussion

6.1 Characterisation of acidic properties of the catalysts

The addition of vanadium oxide and molybdenum oxide increased the acidity of the catalysts. The average turnover frequencies as calculated from the yield of propene and di-isopropylether during the iso-propanol test reaction and number of acid sites from NH_3 TPD titrations (see Table 6.1) can be used to estimate the average acid strength of the sites. The strength of the acid sites is much higher on the $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co/MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts than on the $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ catalyst. This is in agreement with the DFT molecular modelling calculations where it was found that the deprotonation energy for an Al-Al-O-cluster is much higher than that of Al-Mo-O-clusters and Al-V-O-clusters.

Table 6.1 Average turnover frequencies per acid sites as determined from iso-propanol test reaction and NH_3 TPD titrations

Catalyst	Yield of C_3 at -300ml.min.g ⁻¹ .cat ⁻¹ (mol%)	Turn over frequencies (mol.min ⁻¹ . acid site ⁻¹)
0 Cat	0.02	8.8×10^{-4}
3 V Cat	0.10	1.8×10^{-3}
9 V Cat	0.36	4.7×10^{-3}
16 V Cat	0.26	4.9×10^{-3}
4 Mo Cat	0.13	2.2×10^{-3}
12 Mo Cat	0.42	7.4×10^{-3}
21 Mo Cat	0.58	1.1×10^{-2}

The $\text{Co/MoO}_3/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts with high vanadium and molybdenum loadings have higher strength of acidity than the catalysts with low loadings of vanadium and molybdenum. At low loadings the molybdenum oxide and vanadium oxide molecules may exist as highly dispersed monomeric species with low levels of (or without) polymeric species. With an increase in the molybdenum and vanadium loadings the amount of polymeric species will increase [Benirez *et al.*, 2003; Hu *et al.*, 1995; Wachs and Deo,

1991; Weckhuysen and Keller, 2003]. DFT-calculations indicated that an increase in the number of molybdenum and vanadium atoms in the clusters decreased the deprotonation energy. This corresponds to an increase in the strength of the acid site with an increase in the molybdenum and vanadium loadings.

The strength of the acid sites of the $\text{Co/MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts is higher than the strength of the acid sites of the $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalyst (even more so considering that there are more moles of vanadium in the 16 V Cat catalyst than moles of Mo in the 21 Mo Cat catalyst). DFT-calculations showed that the deprotonation energy is lower for an Al-Mo-O-cluster with Mo in the +6 formal oxidation state relative to the deprotonation energy for a Al-V-O-cluster with vanadium in the +5 formal oxidation state. DFT-calculations also indicated that the strength of the acid sites decreases with a decrease in the formal oxidation state. XPS analyses showed a higher average formal oxidation state of molybdenum in the cobalt catalyst compared to that of vanadium in the cobalt catalyst. This indicates that the $\text{Co/MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts will have acid sites with higher average strength than the acid sites in the $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts.

DFT-calculations showed that the strength of the acid sites may be correlated to the activation energy of double bond isomerisation. The activation energy for double bond isomerisation increases with a decrease in the formal oxidation state of the molybdenum and vanadium. Since the highest formal oxidation states of vanadium and molybdenum have the lowest activation energy it may be assumed that highest oxidation states of vanadium and molybdenum present in the catalyst are mostly responsible for double bond isomerisation.

The activation energy for double bond isomerisation was estimated to be lower for the low coordination Al-Mo-O-cluster with molybdenum in the +6 oxidation state (100kJ/mol) in comparison to the low coordination Al-V-O-cluster with vanadium in the +5 oxidation state (120kJ/mol), using DFT. Thus,

the double bond isomerisation is expected to take place to a larger extent on the Co/MoO₃/γ-Al₂O₃ catalyst relative to the Co/V₂O₅/γ-Al₂O₃ catalyst during the Fischer-Tropsch synthesis.

6.2 Fischer-Tropsch synthesis

6.2.1 Catalyst activity

Both vanadium and molybdenum oxide decreased the conversion of the cobalt Fischer-Tropsch catalysts, which may be due to the decrease in the cobalt surface area (see Figure 6.2). It has been suggested in literature that molybdenum oxide and vanadium oxides may cover metals like Ni, Pd and Rh [Aksoylu *et al.*, 1998; Beutel *et al.*, 1997; Juan *et al.*, 1997; Shen *et al.*, 1994]. The following results may indicate that vanadium oxide and molybdenum oxide are covering the cobalt:

- The rate of reduction of cobalt decreased due to the presence of vanadium and molybdenum in Co/V₂O₅/γ-Al₂O₃ and Co/MoO₃/γ-Al₂O₃ catalysts in comparison with the Co/γ-Al₂O₃ catalyst as determined by TPR.
- Mixing Co₃O₄ and MoO₃ or V₂O₅ with water also showed a decrease in the rate of reduction of cobalt as determined by TGA.
- The addition of vanadium and molybdenum decreased the cobalt metal surface area for the Co/V₂O₅/γ-Al₂O₃ and Co/MoO₃/γ-Al₂O₃ catalysts as determined by CO TPD.

Different metal oxides, MoO₂, MoO₃, V₂O₃, V(OH)₃ and V₂O₅ are present in the Co/V₂O₅/γ-Al₂O₃ and Co/MoO₃/γ-Al₂O₃ catalysts as determined by XPS. The surface free energies as shown in Table 6.2, indicate that the surface energies for MoO₃ and V₂O₅ are lower than that of cobalt metal. The coverage of the metallic cobalt surface by molybdenum and vanadium oxide species is therefore thermodynamically feasible. Thermal spreading may have occurred during reduction at 425°C, since the Tammann temperatures of MoO₃ and V₂O₅ are 261 and 209°C respectively [Knötzinger and Taglauer, 1993]. Figure 6.1 is a schematic illustration of how the catalyst surface is perceived to look like.

Table 6.2: Surface free energies [Knötzing and Taglauer, 1993]

Compound	Surface free energy (mJ/m ²)
Co	2550
Mo	2950
MoO ₃	50-70
V	2600
V ₂ O ₅	80-90

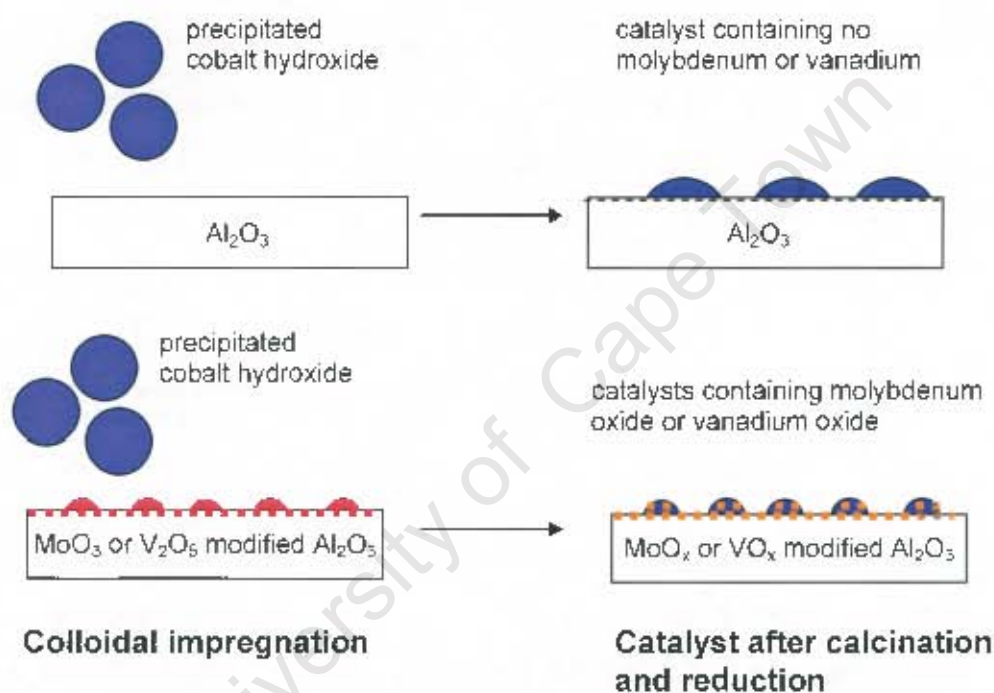


Figure 6.1: Schematic illustration of the catalyst surface (light blue: cobalt hydroxide; red: molybdenum and vanadium in the highest oxidation state; dark blue: cobalt metal; orange: reduced molybdenum oxide and vanadium oxide; black --- on alumina surface: cobalt oxide with strong alumina interaction)

The catalysts containing molybdenum deactivated more than the catalyst containing vanadium. A decrease of ~23% in the CO conversion from 1hr to 1 day on stream were observed for the Co/ γ -Al₂O₃ catalyst and the Co/V₂O₅/ γ -Al₂O₃ catalysts (see Figure 6.2). For the same time period, the CO conversion decreased on average 76% for the Co/MoO₃/ γ -Al₂O₃ catalysts.

Catalyst deactivation may be due to poisoning, sintering or fouling [Bartholomew, 2001]. The formation of alkoxide species during the Fischer-Tropsch reaction may aid thermal spreading of vanadium oxide and molybdenum oxide [Wachs and Cai, 2001; Wang *et al.*, 1999]. The heat of formation for vanadium alkoxide is similar to that of molybdenum alkoxide for the low coordination clusters as determined by DFT. Maximum thermal spreading may have already taken place during reduction since most of the $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts did not deactivate faster than the $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ catalyst. Hence, this is not likely to be the cause.

Poisoning due to impurities in the feed would have resulted in the same amount of deactivation for all the catalysts. Deactivation due to oxidation by water [Van Berge *et al.*, 2000; Schanke *et al.*, 1995] would have had the largest impact on the catalyst containing no vanadium or molybdenum since the CO conversion was the highest if it is assumed that the cobalt crystallite sizes for all the catalysts were identical. However, at a crystallite size of 9 nm (XRD of calcined catalyst) and $\text{H}_2\text{O}/\text{H}_2$ ratio of 0.4, no oxidation may be expected [Van Steen *et al.*, 2005]. The cobalt crystallite sizes may be smaller for the catalyst containing molybdenum and vanadium since Co_3O_4 diffraction peaks were observed for the $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ catalyst and not for the $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co/MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts. The catalyst containing molybdenum and vanadium had a lower activity resulting in lower $\text{H}_2\text{O}/\text{H}_2$ ratios. Since the crystallite size is not known, deactivation due to oxidation by water cannot be estimated.

Oligomerisation or carbon formation on molybdenum oxide [Grupp *et al.*, 1991, Jacobs, 2002] causing fouling of the cobalt sites may have attributed to the faster deactivation of the $\text{Co/MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts. The strength of adsorption of CO on the catalyst containing molybdenum is higher than that of the catalysts without molybdenum. The higher strength of adsorption may result in an increase in the dissociation of CO leading to carbon formation.

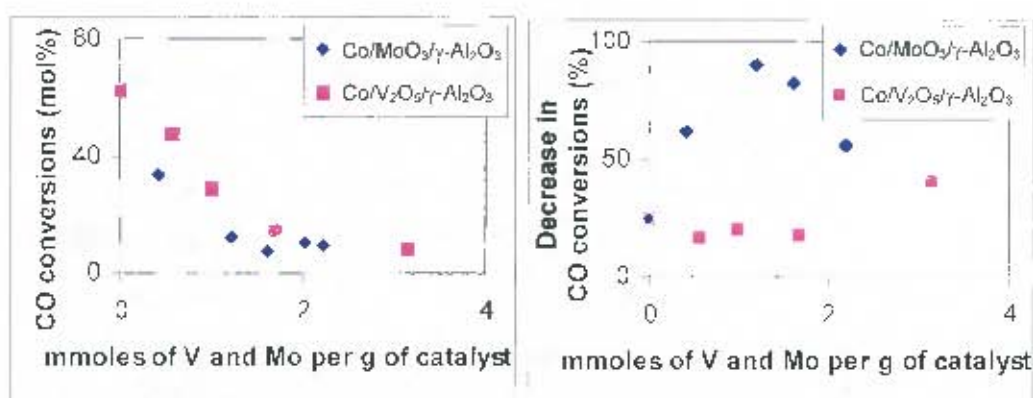


Figure 6.2: Influence of molybdenum and vanadium on the CO conversion of a cobalt catalyst (220°C, 20bar_s, synthesis gas space velocity 46ml(STP)/(min·g), H₂/CO=2, fixed bed reactor, time on stream: 1-77hrs)

Left: CO conversion after 1 hr on stream

Right: Decrease in CO conversion from 1hr on stream to 1 day on stream

Figure 6.3 shows the effect of reactor pressure on the observed CO-conversion. The increase in CO conversion with reactor pressure could be expected based on the rate expressions published for cobalt-based Fischer-Tropsch synthesis. The dependency of the CO conversion on the reactor pressure was used to estimate the effect of molybdenum and vanadium on the intrinsic reaction kinetic parameters. The rate expression proposed by Yates and Satterfield [1991] was used to describe the CO conversion as a function of reactor pressure assuming perfect plug flow in the reactor. The fits shown in Figure 6.3 were done between 5 and 20 bar_s to compare the different catalysts over the same pressure ranges. The obtained kinetic parameters are given in Table 6.3. A statistical analysis of the data evaluation is given in Appendix J.

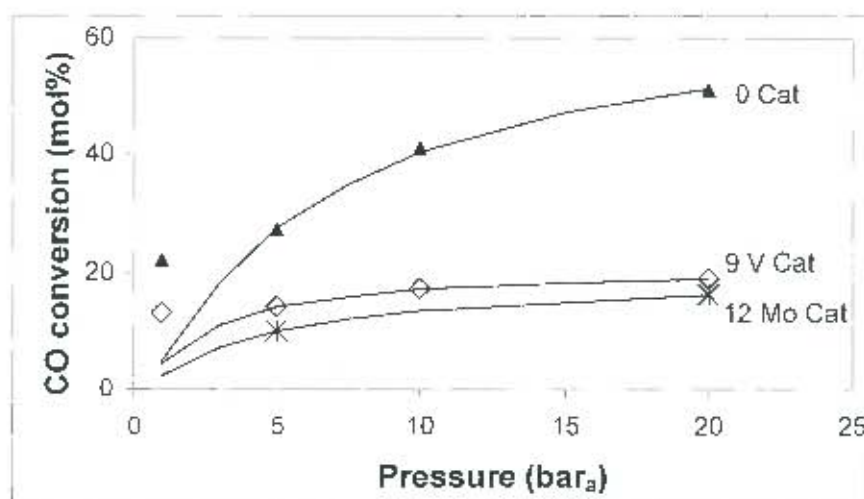


Figure 6.3: Influence of pressure on the obtained CO-conversion in the Fischer-Tropsch synthesis in a fixed bed reactor (220°C, synthesis gas space velocity: 23ml(STP)/(min.g), H₂/CO=2, time on stream: 3-8 days). Solid lines indicate fit to model using the rate expression proposed by Yates and Satterfield [1991]

Table 6.3: Estimated kinetic parameters in the rate expression proposed by Yates and Satterfield [1991] based on the work of Wojciechowski, [1988] as obtained by fitting the obtained CO-conversion as a function of reaction pressure assuming plug flow behaviour (synthesis gas space velocity: 23ml(STP)/(min.g), H₂/CO=2, time on stream: 3-8 days)

$$-r_{\text{CO}} = \frac{a \cdot p_{\text{CO}} \cdot p_{\text{H}_2}}{(1 + b \cdot p_{\text{CO}})^2}$$

Catalyst	a (5-20 bar _a) mmol/(min bar ² g)	b (5-20 bar _a) bar ⁻¹	a (1-20 bar _a) mmol/(min bar ² g)	b (1-20 bar _a) bar ⁻¹
Co/γ-Al ₂ O ₃ (0 Cat)	0.14	1.09	1.60	4.46
Co/MoO ₃ /γ-Al ₂ O ₃ with 12wt.-% Mo (12 Mo Cat)	0.08	2.63	Not measured	Not measured
Co/V ₂ O ₅ /γ-Al ₂ O ₃ with 9wt.-% V (9 V Cat)	0.25	1.57	7.53	15.98

The order for the inhibition term, b , was: 0 Cat < 9 V Cat < 12 Mo Cat. This may be due to the increase in the strength of adsorption of CO deduced from the increase in the desorption temperature of CO from cobalt metal sites (see Figure 6.4).

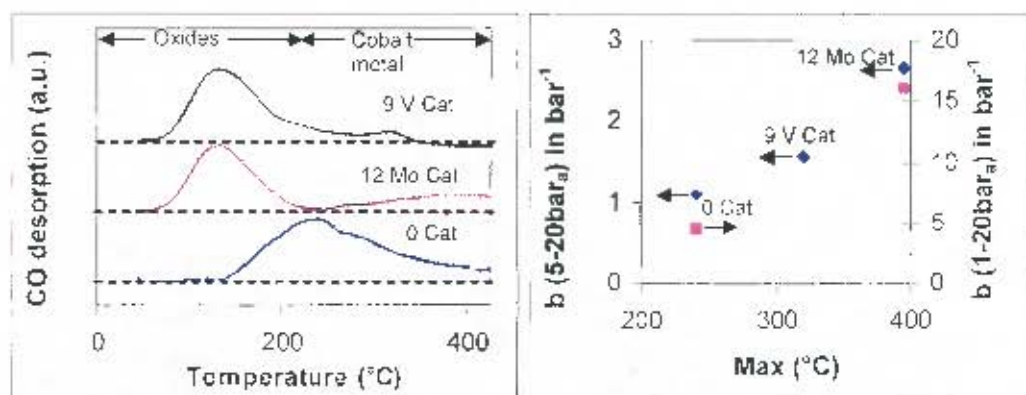


Figure 6.4: Left: Temperature programmed desorption of CO (CO-TPD) of Co/V₂O₅/γ-Al₂O₃ (9 V Cat), Co/MoO₃/γ-Al₂O₃ (12 Mo Cat) and Co/γ-Al₂O₃ catalysts (0 Cat) (catalyst reduced in hydrogen at 425°C)

Right: Correlation between maximum temperature of CO desorption from CO-TPD and kinetic parameter b

The kinetic parameter, a , contains the number of cobalt Fischer-Tropsch sites. Thus the parameter, a , can be normalised relative to the number of cobalt sites as determined from CO-TPD (see Table 6.4). The order for activity of the cobalt sites are then 0 Cat << 12 Mo Cat < 9 V Cat. Based on the cobalt metal surface area a decrease in the CO-conversion was expected with a factor of 6.2 and 3.4 with the addition of molybdenum and vanadium respectively. A factor decrease of 3.2 with the addition of molybdenum and a factor decrease of 2.7 for the addition of vanadium was observed. Thus, the CO conversion decreased less than expected based on the cobalt metal surface areas with the addition of molybdenum or vanadium. It must therefore be concluded that the activity of the cobalt Fischer-Tropsch sites increased with the addition of molybdenum or vanadium. The kinetic parameter, a , may be partially dependent on adsorption coefficient K_{CO} depending on which reaction, during the Fischer-Tropsch synthesis, is taken as the rate limiting step [Wojciechowski, 1988]. An increase in the adsorption strength of CO may thus increase the rate. Alternatively the parameter, a , may contain the coefficient K_C , which is the dissociation constant for CO. It has been proposed in literature that the addition of vanadium and molybdenum to Fischer-Tropsch catalyst may increase the dissociation of CO leading to an increase

in the activity of the sites [Guerrero-Ruiz *et al.*, 1994; Mori *et al.*, 1986; Sachtler *et al.*, 1985].

Table 6.4: Cobalt metal area determined from the CO desorption peak area between 250 and 425°C on reduced catalysts ($T_{\text{reduction}} = 425^\circ\text{C}$ for 8hrs) and the kinetic parameter, a , per cobalt site

Catalyst	T-range of CO desorption from Co-metal	CO desorption (ml(STP)/g _{cat})	$a/\text{Co}_{\text{site}}$ (min bar ²) ⁻¹
0 Cat	50-425°C	0.62	5
12 Mo Cat	250-425°C	0.10	18
9 V Cat	200-425°C	0.18	31

Molybdenum oxide and vanadium oxide can be introduced in the catalyst chemical formulation in three ways:

- (a) as a support
- (b) as a support modifier
- (c) promoter

The addition of molybdenum and vanadium increases the activity of cobalt sites and simultaneously cover some cobalt sites. Thus, the activity may be expected to go through a maximum with the addition of molybdenum or vanadium. This indicates that modifying an alumina support with the aim to cover it with molybdenum or vanadium or using molybdenum or vanadium as support is not beneficial for the overall activity of a cobalt catalyst. Using molybdenum or vanadium as promoter at low levels might be beneficial for the overall activity of a cobalt catalyst.

A lower measured activation energy was determined for the Fischer-Tropsch reaction at 1 bar_a in the temperature range 220 to 240°C using the Co/V₂O₅/γ-Al₂O₃ catalyst (109 kJ/mol) relative to the activation energy using the Co/γ-Al₂O₃ catalyst (125 kJ/mol). A decrease in the observed activation energy may be attributed to an increase in the intrinsic activity or due to an increase in the strength of adsorption.

6.2.2 Catalyst selectivity

Figure 6.5 shows that the chain growth probability decreases with an increase in the molybdenum loading in the $\text{Co/MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts when tested at 220°C and 20bar_a . The chain growth probability decreases and levels off with an increase in the vanadium loading in the $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ catalysts when tested at 220°C and 20bar_a .

The following three factors were evaluated as possible causes for the observed changes in the chain growth probabilities with the addition of vanadium and molybdenum to the cobalt catalyst:

- CO conversion
- Acidity of catalysts
- Hydrogenation characteristics of catalyst

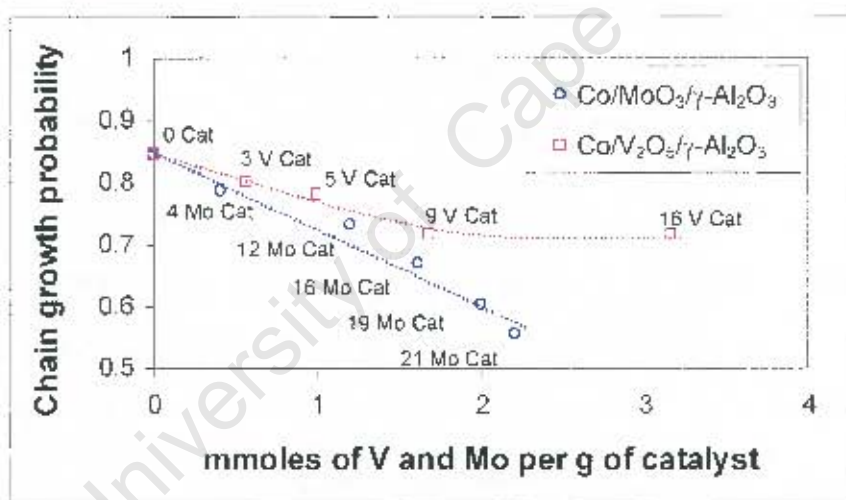


Figure 6.5: Comparison of the influence of vanadium and molybdenum on the chain growth probability of a cobalt catalyst (catalysts: 0 Cat, 16 V Cat and 21 Mo Cat, 220°C , 20bar_a , synthesis gas space velocity $46\text{ml}(\text{STP})/(\text{min g}_{\text{cat}})$, $\text{H}_2/\text{CO}=2$, fixed bed reactor, time on stream: 1-77hrs)

CO conversion

The CO conversion is a function of the number of cobalt metal sites and activity of the sites. The decrease in the CO conversion as a function of the loading of vanadium oxide and molybdenum oxide in the cobalt catalysts may indicate that the probability of the olefin readsorption and further growth will

decrease leading to a decrease in the chain growth probability. It can be argued that the number and activity of cobalt sites may not have been the key parameter influencing the chain growth probability in this study based on the following observations:

- The CO conversion of the 16 V Cat catalyst was lower than that of the 9 V Cat catalyst, but the catalysts had similar chain growth probabilities
- The Co/MoO₃/γ-Al₂O₃ catalysts with high molybdenum loadings (i.e., 16 Mo Cat, 19 Mo Cat and 21 Mo Cat) had similar CO conversions but different chain growth probabilities.

Acidity of catalysts

High loadings of vanadium oxide and all loadings of molybdenum oxide in the cobalt catalyst decreased the 1-olefin content in the olefins fractions when compared at the same conversion with the cobalt catalyst containing no vanadium oxide and molybdenum oxide. A larger decrease in the 1-olefin content in the olefins fractions for the Co/MoO₃/γ-Al₂O₃ catalyst (21 Mo Cat) relative to the Co/V₂O₅/γ-Al₂O₃ catalyst (16 V Cat) was observed when compared at high molybdenum and vanadium loadings at similar CO conversions (see Figure 6.6). This indicates that double bond isomerisation was taking place to a larger extent on the Co/MoO₃/γ-Al₂O₃ catalyst than on the Co/V₂O₅/γ-Al₂O₃ catalyst. This may be explained by the higher strength of acidity of the Co/MoO₃/γ-Al₂O₃ catalyst (21 Mo Cat) relative to the Co/V₂O₅/γ-Al₂O₃ catalyst (16 V Cat) with high molybdenum and vanadium loadings (see Table 6.1).

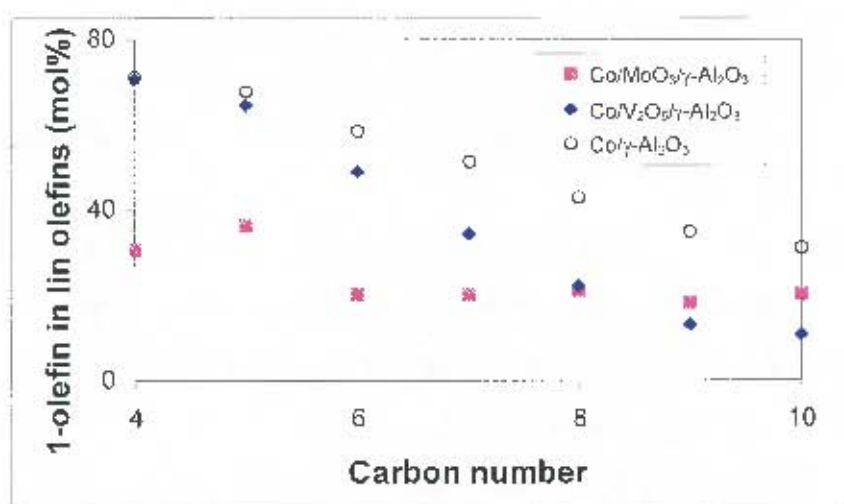


Figure 6.6: Comparison of the influence of vanadium and molybdenum on the 1-olefin content in the fraction of linear olefins as a function of carbon number (220°C, 20bar_a, synthesis gas space velocity 46ml(STP)min⁻¹.g_{cat}⁻¹, H₂/CO=2, fixed bed reactor, time on stream: 3 days, catalysts: 0 Cat, 16 V Cat and 21 Mo Cat)

Olefins with internal double bonds readsorb less readily than 1-olefins, and their reincorporation in the chain growth mechanism is thus less likely [Schulz and Claeys, 1999]. As a result of the increased double bond isomerisation (see Figure 6.6), the chain growth probability will decrease (see Figure 6.5). The DFT molecular modelling calculation showed that the strength of the acid sites can be linked to the activation energy of double bond isomerisation and thus the rate of double bond isomerisation. It may thus be argued that if the strength of the acid sites is a key parameter influencing the chain growth probability, the strength of the acid sites can be directly linked to the chain growth probability. The following examples are given to support this argument:

- The strength of acid sites increased and levelled off with an increase in the vanadium loading in the Co/V₂O₅/γ-Al₂O₃ catalysts. This may explain the levelling off in the chain growth probability with an increase in the vanadium loading in the Co/V₂O₅/γ-Al₂O₃ catalysts.
- The strength of the acid sites of the Co/MoO₃/γ-Al₂O₃ catalysts increased with an increase in the molybdenum which may explain the decrease in the chain growth probability. No levelling off in the chain

growth probability with an increase in the molybdenum loading was observed.

- The higher strength of the acid sites of the 21 Mo Cat catalyst may explain the lower chain growth probability relative to the 16 V Cat catalyst.

Hydrogenation characteristics of catalysts

Vanadium oxide and molybdenum oxide in the cobalt catalyst decreased the olefin content in the fraction of linear hydrocarbons, when compared at the same conversion with the cobalt catalyst containing no vanadium oxide and molybdenum oxide. The olefin contents in the fraction of linear hydrocarbons of the catalyst containing high loadings of vanadium and molybdenum (i.e. 16 V Cat and 21 Mo Cat) were similar (see Figure 6.7). The CO conversions for the catalysts (16 V Cat and 21 Mo Cat) were similar, and therefore the olefin contents in the fraction of linear hydrocarbons can be directly compared (see Figure 6.7). The chain growth probabilities of the catalysts were very different (see Figure 6.5), indicating that hydrogenation was not the key parameter influencing the chain growth probability in this study.

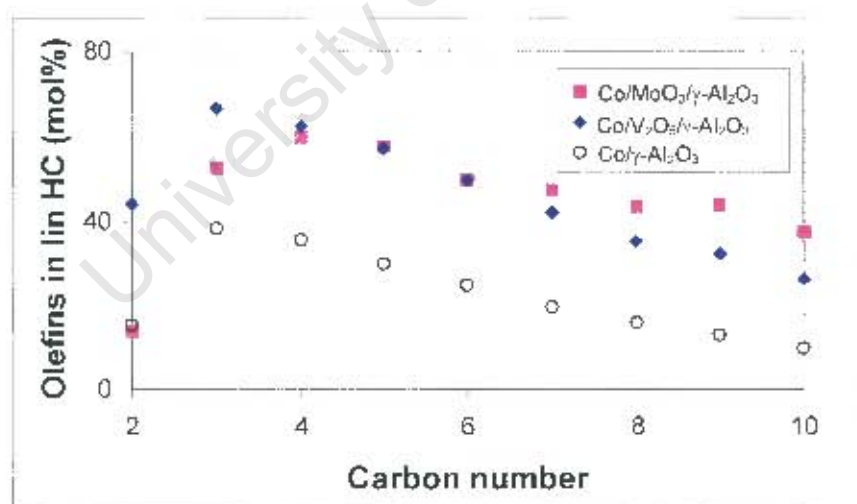


Figure 6.7: Comparison of the influence of vanadium and molybdenum on the olefin content in the fraction of linear hydrocarbons as a function of carbon number (220°C, 20bar_a, synthesis gas space velocity 46ml(STP)min⁻¹.g_{cat}⁻¹, H₂/CO=2, fixed bed reactor, time on stream: 3 days, catalysts: 0 Cat, 16 V Cat and 21 Mo Cat)

Comparison of possible factors influencing selectivity

The qualitative ranking of the factors considered at 220°C and 20bar_g influencing the chain growth probability with the addition of molybdenum and vanadium to a cobalt catalyst are as follows:

Acidity of the catalyst >> hydrogenation on MoO_x and VO_x $\equiv$ number/activity of cobalt sites.

Acidity of the catalyst has been identified as the key parameter influencing the selectivity of the catalysts, thus the selectivity may be directly correlated with the strength of the acid sites as shown in Figure 6.8. The relative rate of double bond isomerisation (see Appendix H) increases with an increase in the strength of the acid sites (see Figure 6.8). Due to the increase in the rate of isomerisation, less olefins are re-incorporated in the hydrocarbon chains leading to a decrease in the chain growth probability. Thus the chain growth probability decreases with an increase in the strength of the acid sites (see Figure 6.8). Zhang *et al.* [2003] and Soares *et al.* [1993] also ascribed the difference in selectivity in cobalt catalysts to the acidity of the catalyst and similar trends as in this study can be deduced from their data as shown in Figure 6.9.

Therefore, when selecting a support or promoter for a catalyst, the impact of the chosen promoter on the acidity characteristics of the reduced catalyst should be considered.

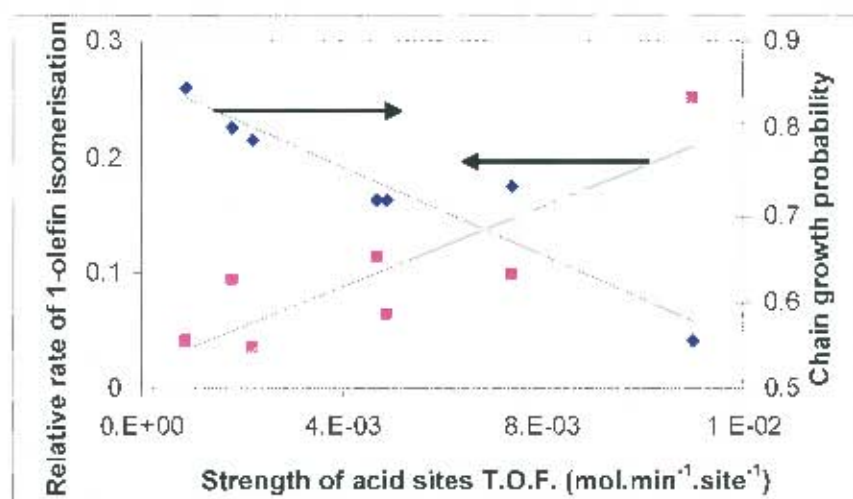


Figure 6.8: Influence of strenght of the acid sites on the selectivity of the catalysts (calculation of relative rate of isomerisation of C₆ are shown in Appendix H)

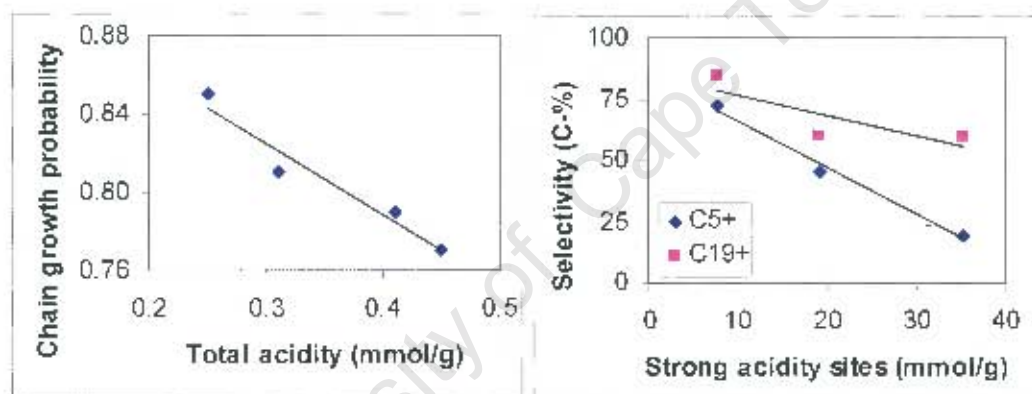


Figure 6.9: Influence of strenght of the acid sites on the selectivity of the catalysts.

Left: Graph drawn from data of Zhang et al. [2003]

Right: Graph drawn from data of Soares et al., [1993]

6.3 Impact of operating conditions on importance of acidity influencing the selectivity

With a decrease in the pressure and an increase in the temperature, the chain growth probabilities of the catalysts decreased. With a decrease in the pressure and an increase in the temperature, the difference in chain growth probabilities between the Co/ γ -Al₂O₃ catalyst and the Co/MoO₃/ γ -Al₂O₃ and the Co/V₂O₅/ γ -Al₂O₃ catalysts decreased. At a temperature of 240°C and atmospheric pressure the chain growth probabilities of Co/ γ -Al₂O₃ catalyst and

the Co/MoO₃/γ-Al₂O₃ and the Co/V₂O₅/γ-Al₂O₃ catalysts were similar. The CO conversions were also lower for the Co/MoO₃/γ-Al₂O₃ and the Co/V₂O₅/γ-Al₂O₃ catalysts relative the Co/γ-Al₂O₃ catalyst at these conditions.

The relative proportion of branched hydrocarbons increased with an increase in the temperature and a decrease in the pressure. This may be explained by a lower surface coverage by olefins, thus the steric hindrance of internal olefins has a lower influence on the relative amount of adsorbed internal olefins to adsorbed 1-olefins. Therefore an increase in double bond isomerisation due to acid sites, has a lower or negligible impact on the chain growth probability at high temperatures and low pressures.

It may be concluded that the effect of vanadium oxide and molybdenum oxide on a cobalt catalyst's selectivity may be temperature and pressure dependent and may explain to some extent the differences in the selectivities reported by various authors [Aksoylu and Önsan, 1998; Chen and Adocina, 1994; Guerrero-Ruiz *et al.*, 1994; Takahashi *et al.*, 1986].

7 Conclusions

7.1 Characterization of modified support materials

A $\gamma\text{-Al}_2\text{O}_3$ support was modified with molybdenum or vanadium by controlled adsorption of ammonium heptamolybdate or ammonium vanadate followed by deposition of the excess amount of molybdenum or vanadium. The deposition following the controlled adsorption step was needed to achieve larger molybdenum loadings, since the adsorption capacity of alumina is limited [Wang and Hall, 1982]. The modified supports were calcined at 550°C. XRD indicated that in both $\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ and $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ supports, V_2O_5 and MoO_3 formed. This indicates that at high molybdenum or vanadium loadings, thin layers of V_2O_5 or MoO_3 were not formed, but crystallites. Aluminium molybdate also formed with the molybdenum oxide modified supports. Crystallites were also observed in TEM for the vanadium oxide or molybdenum oxide modified supports.

7.2 Characterization of cobalt catalysts on the modified support materials

Cobalt was added to the MoO_3 -modified $\gamma\text{-Al}_2\text{O}_3$ support material by colloidal impregnation [Roy *et al.*, 2001]. Cobalt was precipitated from a cobalt nitrate solution with ammonia as a precipitating agent and the precipitate was put on the support. The aim of this method was to form cobalt hydroxide crystals of which the size were independent of the support.

Mixing the Co_3O_4 with MoO_3 or V_2O_5 in water yielded an increase in the temperature at the maximum of the reduction peak for Co_3O_4 during temperature programmed reduction in a TGA. The increase in the temperature at the maximum of the Co_3O_4 reduction peak indicates some interaction between the cobalt and molybdenum or vanadium. Dissolved MoO_3 or V_2O_5 may dissolve and subsequently deposit on the surface of Co_3O_4

during the drying step resulting in a retardation of the rate of reduction of cobalt. A similar effect might be expected in the prepared catalyst, since the catalyst preparation proceeds via an aqueous impregnation of the cobalt precipitate on the molybdenum oxide modified support, since MoO_3 and V_2O_5 are present on the supports with a high MoO_3 or V_2O_5 loading.

7.2.1 Physico-chemical characteristics of cobalt on modified alumina supports

The calcined catalyst without MoO_3 or V_2O_5 on the support shows the presence of Co_3O_4 . A Co_3O_4 crystallite size of 9nm was estimated by line broadening analysis, using the Debye-Scherrer equation [Ertl *et al.*, 1997]. The diffraction lines attributable to Co_3O_4 are absent when MoO_3 is present in the catalyst formulation. The diffraction lines attributable to Co_3O_4 are less intense and broader for low levels of V_2O_5 and absent for high levels of V_2O_5 present in the catalyst formulation. A new crystalline phase, CoMoO_4 is formed upon the introduction of cobalt, accounting for the absence of the Co_3O_4 -diffraction lines and the disappearance of the MoO_3 and $\text{Al}_2(\text{MoO}_4)_3$ in the catalyst with a high MoO_3 -loading.

The introduction of molybdenum or vanadium in the catalyst formulation leads to a reduction in the BET-surface area and the pore volume resulting in an approximately constant average pore diameter.

7.2.2 Reduction behaviour of cobalt on modified alumina supports

The low temperature peak maximum for the reduction of cobalt oxide in the TPR spectrums shifts towards higher temperatures with the addition of molybdenum or vanadium to the catalyst formulation. This indicates that the rate of reduction of cobalt is retarded with the addition of molybdenum or vanadium oxide to the catalyst formulation, possibly due to a thin layer of molybdenum or vanadium oxide covering the cobalt and the formation of cobalt molybdate.

Conclusions

The peak maximum for the reduction of vanadium oxide shifts towards lower temperatures with the addition of cobalt. The formation of metallic cobalt may increase the rate of reduction of vanadium oxide by hydrogen spill-over.

The hydrogen consumption increases with increasing molybdenum oxide or vanadium oxide loading. The cobalt, vanadium and molybdenum was completely reduced at 1000°C. The amount of hydrogen consumed for the reduction of cobalt within the catalyst can be obtained by the difference of the amount of hydrogen consumed for the reduction of the catalyst and the amount of hydrogen consumed for the reduction of the support, and amounts to ca. 2mmol of H₂ per gram of catalyst. This corresponds to a cobalt loading of ca. 9-10 wt.-% depending on the oxidation state of cobalt in the calcined catalyst and approximates the intended cobalt loading well.

7.2.3 Characterization of reduced cobalt on modified alumina supports

The XRD analyses of the cobalt catalysts containing molybdenum or vanadium (19 Mo Cat or 3 V Cat) and the unpromoted catalyst (0 Cat) (the reduced catalyst was covered with xylene to prevent re-oxidation) were performed. Diffraction peaks attributable to metallic cobalt, MoO_x or VO_x could not be detected implying that these phases are XRD-amorphous, i.e. the crystallites are either too small to be detected by XRD or contain too many defects.

There was a constant difference in the mass increase as measured by TGA during oxidation between the reduced catalyst and reduced support. This may indicate that the addition of molybdenum did not affect the degree of reduction of the cobalt.

The hydrogen uptake in a static chemisorption experiment on the reduced catalyst without MoO₃ or V₂O₅ shows the typical dependency of the adsorbed volume on the pressure, with a strong increase in the adsorbed volume at very low pressures asymptotically approaching a constant value of ca. 0.3ml(STP)/g (see Figure 5.9). The metal surface area for this catalyst (0 Cat) can thus be estimated to be 1.1m²/g. The strong increase of the adsorbed

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volume at very low pressure indicates strong hydrogen adsorption under these conditions.

The hydrogen uptake on $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ with 5wt.-% vanadium (5 V Cat) and on $\text{Co/MoO}_3/\gamma\text{-Al}_2\text{O}_3$ with 12wt.-% molybdenum (12 Mo Cat) show a different behaviour. It increases gradually with increasing pressure. A constant value is not approached at hydrogen pressures up to 700mm Hg. This shows that hydrogen is likely to be chemisorbed on weaker sites, e.g. MoO_x or VO_x as well as on metallic sites. Hydrogen might dissociate on the cobalt metal and spills over to form $\text{MoO}_4(\text{H}_x)_{\text{ac}}$, H_xMoO_3 or $\text{H}_x\text{V}_2\text{O}_5$ [Al-Kandari *et al.*, 2005; Marcq *et al.*, 1984].

At very low pressure the hydrogen uptake of the $\text{Co/MoO}_3/\gamma\text{-Al}_2\text{O}_3$ with 12wt.-% molybdenum (12 Mo Cat) and $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ with 5wt.-% vanadium (5 V Cat) is less than on $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (0 Cat). This may indicate that the exposed metallic cobalt surface area on the catalyst, to which molybdenum or vanadium was added in the catalyst formulation, is less than the cobalt metal surface area on the catalyst without molybdenum or vanadium.

CO desorbs from the unpromoted $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ catalyst (0 Cat) at ca. 250°C. The amount of CO desorbed from this catalyst is 0.62ml(STP)/g_{catalyst}. The value obtained corresponds well with the amount of hydrogen chemisorbed at saturation (0.3ml(STP)/g_{catalyst}) implying associative CO-chemisorption and dissociative chemisorption of hydrogen.

From the CO-desorption on the modified support materials, it might be concluded that CO chemisorbed on oxides desorbs below 200-250°C. The amount of CO, which desorbs at higher temperatures, can be ascribed to CO chemisorbed on metallic cobalt. It may then be concluded that the cobalt metal area decreases with an increase in the molybdenum oxide or vanadium oxide loading in the catalyst formulation. This might be caused by a (partial) coverage of metallic cobalt with molybdenum or vanadium oxide. The strength of CO adsorption increased with the addition of molybdenum or

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vanadium to the catalyst as visualised by the increase in the desorption peak maximum.

The surface composition of the reduced catalysts and the oxidation state of the various elements were determined using XPS. However, it should be noted that XPS analyses may analyse layers up to 5 nm deep in the catalyst and is thus not a true analysis of the surface (N.N. 7). The near surface region of the catalyst $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ (0 Cat) is enriched with cobalt. The amount of divalent cobalt seems to be surprisingly high in view of the high degree of reduction obtained with this catalyst. This can be rationalised by the presence of a highly dispersed cobalt oxide phase (e.g. cobalt aluminate) and larger crystallites of metallic cobalt.

The XPS analysis confirms that molybdenum or vanadium in the catalyst is reduced as well and region near the surface consists of Mo^{4+} and Mo^{6+} or V^{3+} , V^{4+} and V^{5+} .

7.3 Characterisation of acidity in the reduced cobalt on modified alumina supports

The TPD spectra are similar for the $\text{Co}/\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts. The addition of molybdenum oxide or vanadium oxide to the catalyst did not increase the number of acid sites as measured by back-titration of the sulphuric acid trap. The addition of molybdenum oxide or vanadium oxide to the catalyst increased the strength of the acid sites as shown by iso-propanol test reaction turnover frequencies. This is in agreement with the DFT molecular modelling calculations where it was found that the deprotonation energy for an Al-Al-O-cluster is much higher than that of Al-Mo-O-clusters and Al-V-O-clusters.

The strength of the acid sites of the $\text{Co}/\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts is higher than that of the $\text{Co}/\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$. It was further observed that the deprotonation energy is lower for an Al-Mo-O-cluster with Mo in the +6 formal oxidation state

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relative to the deprotonation energy for a Al-V-O-cluster with vanadium in the +5 formal oxidation state. DFT molecular modelling calculations indicated that the strength of the acid sites decreases with a decrease in the formal oxidation state. XPS analyses shows that the average formal oxidation state of the molybdenum in the cobalt catalyst is higher than that of the vanadium in the cobalt catalyst, indicating acid sites of a higher average strength in the Co/MoO₃/γ-Al₂O₃ catalysts compared to those in the Co/V₂O₅/γ-Al₂O₃ catalysts.

The Co/MoO₃/γ-Al₂O₃ and Co/V₂O₅/γ-Al₂O₃ catalysts with high vanadium and molybdenum loadings have higher strength of acidity than the catalysts with low loadings of vanadium and molybdenum. At low loadings the molybdenum oxide and vanadium oxide molecules may exist as highly dispersed monomeric species with (or without) low levels of polymeric species. With an increase in the molybdenum and vanadium loadings the amount of polymeric species will increase [Benirez *et al.*, 2003, Hu *et al.*, 1995, Wachs and Deo, 1991, Weckhuysen and Keller, 2003]. DFT molecular modelling calculations indicated that an increase in the number of molybdenum and vanadium atoms in the clusters, decreased the deprotonation energy which corresponds to an increase in the strength of the acid site. This may explain the increase in the strength of the acid sites with an increase in the molybdenum and vanadium loadings.

The reaction of an olefin, 1-hexene, passed over reduced 21 Mo Cat catalyst at 220°C showed double bond isomerisation. Skeletal isomers and metathesis products were not observed. The absence (or very low yield) of skeletal isomers might be attributable to the relatively low temperature of 220°C for the acid catalysed skeletal isomerisation [Benadda *et al.*, 2003]. The absence of any metathesis activity might indicate an over-reduction of molybdenum, since that will result in a reduction of the metathesis activity [Giordano *et al.*, 1975; Zhang *et al.*, 1991; Bartlett *et al.*, 1997].

7.4 Fischer-Tropsch synthesis

7.4.1 Catalyst activity

The addition of molybdenum or vanadium (3-21 wt-%) to a cobalt catalyst decreased the CO conversion of the Fischer-Tropsch reaction. This is attributed to the decrease in the cobalt surface area due to the molybdenum or vanadium partially covering the cobalt. Estimated kinetic parameters in the rate expression proposed by Yates and Satterfield [1991] showed the addition of molybdenum or vanadium increased the activity of the cobalt sites. This may indicate that lower levels of molybdenum or vanadium than that used in this study may be beneficial for greater catalyst activity.

The catalyst containing molybdenum and high levels of vanadium deactivated faster than the corresponding catalyst which did not contain molybdenum or had low levels of vanadium. An increase in the rate of deactivation may be due to oxidation, sintering and carbon formation. No definite conclusion can be made on the additional deactivation mechanism causing the faster rate of deactivation for the catalyst containing molybdenum and high levels of vanadium.

7.4.2 Selectivity in the Fischer-Tropsch synthesis

At a similar CO-conversion, the olefin content in the fraction of linear hydrocarbons for the catalyst without molybdenum or vanadium is higher than the olefin content in the fraction of linear hydrocarbons for the catalysts containing molybdenum or high loadings of vanadium. A lower olefin content is attributed to the conversion of olefins to paraffins (secondary hydrogenation). Additional hydrogenation may have taken place on partially reduced molybdenum oxide and vanadium oxide, since these oxides can adsorb as indicated by the static H₂-chemisorption.

At a similar CO-conversion, the 1-olefin content in the fraction of linear olefins for the catalyst without molybdenum or vanadium is higher than the 1-olefin content in the fraction of linear olefins for the catalysts containing

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molybdenum or vanadium. This is attributed to the acid catalysed double bond isomerisation on molybdenum and vanadium oxide occurring much more rapidly than the production of olefins in the Fischer-Tropsch synthesis. When the acid sites of a catalyst containing high loadings of molybdenum were poisoned with ammonia, the 1-olefin content in the fraction of linear olefins increased significantly, which indicates that acid sites on molybdenum oxide were responsible for the increase in observed double bond isomerisation.

DFT-calculations indicated that the strength of the acid sites may be correlated to the activation energy of double bond isomerisation. The activation energy for double bond isomerisation increases with a decrease in the formal oxidation state of the molybdenum and vanadium. XPS analyses showed a higher average formal oxidation state of molybdenum in the cobalt catalyst compared to that of vanadium in the cobalt catalyst. This explains the larger extent of double bond isomerisation on the Co/MoO₃/γ-Al₂O₃ catalyst relative to the Co/V₂O₅/γ-Al₂O₃ catalyst during the Fischer-Tropsch synthesis.

The addition of molybdenum or vanadium (3-21 wt-%) to a cobalt catalyst increased the acidity of the catalyst. The increased acidity led to an increase in double bond isomerisation that resulted in a decrease in the chain growth probability during Fischer-Tropsch synthesis at 220°C and 20bar_a. The decrease in the chain growth probability was more for the catalyst containing molybdenum, relative to the catalyst containing vanadium. This may be explained by the higher acidity and the larger extent of double bond isomerisation of the catalyst containing molybdenum. A significant increase in the methane selectivity was observed for the catalyst containing molybdenum. The methane selectivity did not increase significantly for the catalysts containing vanadium.

Catalysts with a high molybdenum loading showed a significant increase in the amount of branched compounds in a hydrocarbon fraction. This might be interpreted as a result of re-adsorption of internal olefins yielding branched product compounds on Fischer-Tropsch sites and not on acidic sites since it

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was shown that acid catalysed skeletal isomerisation did not occur. Catalysts containing vanadium did not increase the amount of branched compounds in the hydrocarbon fraction significantly.

The qualitative ranking of the factors considered at 220°C and 20bar_a influencing the chain growth probability with the addition of molybdenum and vanadium to a cobalt catalyst are as follows:

Acidity of the catalyst >> hydrogenation on MoO_x and VO_x $\cong$ number/activity of cobalt sites.

The influence of the increased acidity on the Fischer-Tropsch selectivity at 1bar_a and 240°C was negligible since the chain growth probabilities of the cobalt catalysts containing vanadium or molybdenum were similar to the cobalt catalyst containing no vanadium or molybdenum. The relative proportion of branched hydrocarbons increased with an increase in the temperature and a decrease in the pressure. This may be explained by a lower surface coverage by olefins, thus the steric hindrance of internal olefins has a lower influence on the relative amount of adsorbed internal olefins to adsorbed 1-olefins. Therefore an increase in double bond isomerisation due to acid sites, has a lower or negligible impact on the chain growth probability at high temperatures and low pressures.

7.5 Concluding remarks

The addition of molybdenum and vanadium increases the activity of cobalt sites and simultaneously cover some cobalt sites. Thus, the activity may be expected to pass through a maximum with the addition of molybdenum or vanadium. The molybdenum catalysts deactivated more than the catalyst without molybdenum. The vanadium catalysts deactivated to the same extent relative to the catalyst without vanadium. Therefore, a study using low levels of vanadium at commercially realistic conditions ($P \sim 20\text{bar}_a$ and $T = 210\text{-}240^\circ\text{C}$) may be interesting.

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This study indicates that modifying an alumina support with the aim to cover it with molybdenum or vanadium or using molybdenum or vanadium as support is not beneficial for the overall activity of a cobalt catalyst. This is mainly due to dissolution and deposition of these oxides on the cobalt surface during catalyst preparation and thermal spreading. The modification of the support with molybdenum or vanadium increased the acidity of the catalyst. Using molybdenum oxide and vanadium oxide as supports will also result in an increase in the acidity. The increased acidity was found not to be beneficial for the chain growth probabilities and methane selectivities of the catalysts. When alternative supports and the modification of supports are considered, the dissolution behaviour during catalyst preparation, the thermal mobility and the acidity properties should all be taken into account.

When using vanadium or molybdenum as promoters at low levels, the acidity may be low enough not to influence the chain growth probability of the cobalt catalyst negatively.

Molecular modelling is an useful characterisation technique to study the acidity properties of metal oxides during a screening process for alternative metal oxides. The formal oxidation state influences the acidic characteristics of transition state metal oxides. Therefore the acidity characteristics of the metal oxide in the formal oxidation state present during Fischer-Tropsch synthesis should be considered.

The operating conditions influenced the magnitude of the effect of molybdenum and vanadium on the selectivity of the cobalt Fischer-Tropsch catalyst. The implication is therefore that realistic commercial operating conditions should be used when catalysts are tested.

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Appendix A

Methane selectivity and readsorption of olefins: Carbon % vs. Mole %

The alkyl mechanism is presently the most widely accepted mechanism for the chain growth in the Fischer-Tropsch synthesis (see Figure A.1). Chain initiation is envisaged to take place via dissociative CO chemisorption, by which surface carbon and surface oxygen species are generated. Surface oxygen is removed from the surface by reaction with adsorbed hydrogen yielding water. According to this reaction scheme, surface carbon species is converted into a surface CH_2 -species, which can either react with surface hydrogen yielding a surface CH_3 -species or act as the monomer in the Fischer-Tropsch polymerization reaction. The surface CH_3 -species is regarded as the chain initiator in this polymerisation reaction, which can either desorb by reacting with surface hydrogen yielding methane or grow by reaction with a monomeric species. Product formation is envisaged to take place by β -hydrogen abstraction yielding 1-olefins or by hydrogen addition yielding n-paraffins as primary products.

The probability of desorption of a product containing N number of carbons can be defined by:

$$p_{dN} = \frac{r_{dN}}{r_{dN} + r_{gN}} \dots\dots\dots (A1)$$

The probability of desorption, p_d , of the surface species CH_3 (Sp_1) equals the molar content (mole %) of CH_4 (Pr_1) in the organic products, since each mole of product has only one CH_3 group coming from the surface species CH_3 .

According to the reaction scheme in Figure A.1 all carbon in the organic product compounds originates from a CH_2 -species. Thus, the selectivity for methane in C-% is equal to the probability that a CH_2 -species is converted into methane. The probability that a CH_2 -species reacts to form a CH_3 -surface species can be defined as:

$$P_{\text{CH}_2 \rightarrow \text{CH}_3} = \frac{r_{\text{CH}_3}}{r_{\text{CH}_3} + r_g} \dots\dots\dots (A2)$$

Thus the methane selectivity is given by the likelihood that a CH_2 species is converted into a CH_3 -species and the likelihood that a CH_3 -species is converted into methane

$$\text{CH}_4 \text{ carbon\%} = P_d * P_{\text{CH}_2 \rightarrow \text{CH}_3} \dots\dots\dots (A3)$$

Assuming that these reactions are all elementary reactions, the reaction probability can be written in terms of surface coverage, θ (see formula 4 and 5).

$$p_{d,1} = \frac{k_{d1} \theta_H}{k_{d1} \theta_H + k_{g1} \theta_{\text{CH}_2}} \dots\dots (4)$$

$$P_{\text{CH}_2 \rightarrow \text{CH}_3} = \frac{k \theta_H}{k \theta_H + k_{gr} \theta_R} \dots\dots (5)$$

When readsorption becomes significant in the Fischer-Tropsch synthesis, θ_R will increase, but (up to a certain level) without significantly affecting θ_H and θ_{CH_2} . Thus readsorption may lead to a decrease in $P_{CH_2 \rightarrow CH_3}$ and thus methane selectivity in C-% without affecting methane selectivity in mol-%.

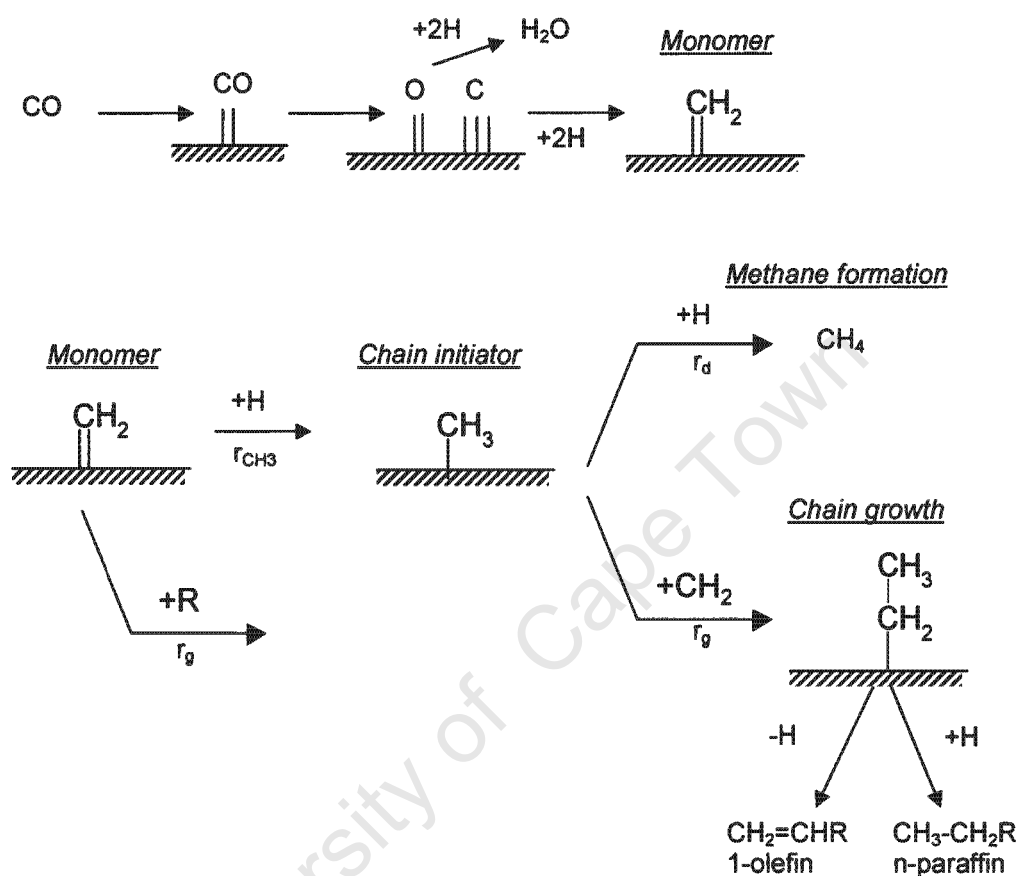


Figure A.1: Possible reaction pathways in the Fischer-Tropsch synthesis according to the 'alkyl' mechanism [Claeys and van Steen, 2004]

Appendix B

Verification of DFT calculations

B.1 Density Functional Theory (DFT)

The basic idea in DFT is that the ground state total energy of a system depends on its electronic density, ρ . The constituents of the total energy can be written [N.N.3, 2002; Phala, 2004]:

$$E[\rho] = T[\rho] + U[\rho] + E_{\text{ex}}[\rho] \dots\dots\dots (B.1)$$

with $T[\rho]$ kinetic energy
 $U[\rho]$ classical electrostatic energy due to Coulombic interaction
 E_{ex} exchange correlation energy.

The exchange correlation energy is all the other interactions that are required to reproduce the total energy exactly. This exchange correlation is not known and can be approximated with various functions as proposed by various researchers. The various functions give similar but not identical results. These proposed functions can be divided into two groups, (1) Local density Approximation (LDA) and (2) Generalised Gradient Approximations (GGA). The functions of the first group, LDA functions, underestimate the exchange correlation in the low electron density regions [MSc course notes, 2004]. The LDA functions overestimate the bond energies [N.N.3, 2002]. Functions of the second group, GGA, are thus preferred. In this study the function BLYP (Becke exchange functional (B88) in conjunction with the Lee-Yang-Parr correlation functional) from the GGA group is typically used.

The derivative of the exchange-correlation energy with respect to the electron density gives the exchange-correlation potential, μ_{ex} [N.N.3, 2002; Phala, 2004]

$$\mu_{\text{ex}} = \frac{\partial E_{\text{ex}}[\rho]}{\partial \rho} \dots\dots\dots (B.2)$$

which is added into the Hamiltonian operator in the Schrödinger equation.

$$\left(-\frac{\hbar}{m} \nabla^2 + V + \mu_{\text{ex}}(r) \right) \cdot \Psi(r) = E \cdot \Psi(r) \dots\dots\dots (B.3)$$

The Schrödinger equation can be solved for the one-electron orbitals, from which the electron density, ρ , at any given point, r , can be calculated by

$$\rho(r) = \sum_{i=1}^N |\Psi_i(r)|^2 \dots\dots\dots (B.4)$$

Solving the DFT equations is an iterative procedure starting from 'guess' wave functions [Phala, 2004]. The self-consistent field (SCF) procedure in DFT consists essentially of 1) choosing an initial set of coefficients to expand basis sets, 2) construct a set of molecular orbitals (wave functions), 3) using the trial set to construct the electron density according to equation (4), 4) using the density to calculate the Coulomb and the exchange-correlation potentials, a new set of molecular orbitals and the electron density. This procedure is repeated until the input and the output densities agree to some tolerance value. This density is then used to evaluate the total energy (see Equation 1). In this study DMol³ - a density functional theory quantum mechanical package are used to do the calculations.

B.2 Vibrational frequencies (Infra red spectroscopy)

DMol³ can calculate the vibrational frequencies, by using a matrix of Cartesian second derivatives (Hessian matrix). A minimum in energy is given by the first derivative is zero and the second derivative is positive. For a saddle point, the second derivative is negative [Frisch, 2004]. It is therefore necessary to check for negative frequencies (also known as imaginary frequencies) after geometry optimisation. If all the calculated frequencies are positive, it is still possible that a local minimum has been obtained. The starting geometry should be changed and optimisation should be done again to check whether a local minimum had not been obtained.

B.3 Verification of molecular modelling calculations

The molecular modelling calculations were verified using known compounds containing molybdenum, such as Mo, MoO₃, Mo(CO)₆

B.3.1 Verification of spin multiplicity using Mo(g) and Moⁿ⁺(g)

The number of possible orientations, of the spin angular momentum calculated as $2S + 1$, relates to a given total spin quantum number (S), for the same spatial electronic wavefunction [N.N.4, 2004]. S is the number of unpaired electrons divided by 2.

During the molecular modelling calculations various spin multiplicities may be selected with the preferred multiplicity the one having the lowest energy. This was tested by an energy calculation for neutral molybdenum in the gas phase. Considering the ground state of molybdenum with 6 unpaired electrons, a septet multiplicity state is expected to have the lowest energy. Energy calculations on gaseous Mo including all electrons in the calculation using a double numerical base set with d-functions (DND) were performed. It was found (see Table B.1) that singlet and septet multiplicity gave the lowest and identical energie values. This was observed both when using the BLYP or the VWN-BP function from the GGA-group. It can be further observed that the calculated energy using the BLYP-functional is slightly higher than the energy calculated using the VWN-BP function

The auto-setting in the DMOL³ program can be used to find automatically the correct multiplicity.

Appendix B

Table B.1: Energies (in Ha) of various multiplicity states of neutral Mo (calculations performed including all electrons using a double numerical base set with d-functions (DND))

Functional (GGA)	Multiplicity	Energy (Ha)
BLYP	Auto	-3977.6111
BLYP	Singlet	-3977.6111
BLYP	Triplet	-3977.5092
BLYP	Quintet	-3977.5760
BLYP	Septet	-3977.6111
VWN-BP	Auto	-3977.8821
VWN-BP	Singlet	-3977.8821
VWN-BP	Triplet	-3977.7491
VWN-BP	Quintet	-3977.8245
VWN-BP	Septet	-3977.8821

To confirm the finding of the correct multiplicity using the auto-setting, calculations on gas phase Mo^{n+} -ions ($n=1-3$) were performed including all electrons in the calculation using a double numerical base set with d-functions (DND) using the VWN-BP functional from the GGA-group.

Removing one electron from Mo yields Mo^+ with 5 unpaired electrons. Thus, a sextet multiplicity is expected to be the most stable. The calculations showed that the sextet multiplicity gave the lowest energy (see Table B.2). Similarly, the calculations for Mo^{2+} and Mo^{3+} yielded with the expected multiplicity the lowest energy. The 'auto'-setting also yielded the lowest energy. Thus auto setting for the multiplicity may be used with confidence.

Table B.2: Energies (in Ha) of various multiplicity states of charged $\text{Mo}^{n+}(\text{g})$ (calculations performed including all electrons using a double numerical base set with d-functions (DND) and the VWN-BP functional in GGA-group)

Mo⁺		Mo²⁺		Mo³⁺	
Multiplicity	Energy (Ha)	Multiplicity	Energy (Ha)	Multiplicity	Energy (Ha)
Auto	-3977.6218	Auto	-3977.0074	Auto	-3975.9581
Doublet	-3977.4772	Singlet	-3977.0074	Doublet	-3975.8957
Quartet	-3977.5246	Triplet	-3976.9238	Quartet	-3975.9581
Sextet	-3977.6218	Quintet	-3977.0074	Sextet	-3974.7311
Octet	-3976.3939	Septet	-3975.8507	Octet	-3973.5508

B.3.2 Verification of different functionals

Gas phase Mo

Different functionals were tested to calculate the energy of gas phase Mo to find the most suitable one, i.e. the one with the lowest energy (see Table B.3). The lowest energy was obtained for the VWN-BP functional for the Mo with a singlet multiplicity.

Table B.3: Energies of neutral Mo calculated including all electrons with an DND basis set and singlet multiplicity with varying functional

Functional	Energy (Ha)
BLYP	-3977.61110
BOP	-3977.54110
BP	-3977.86446
HCTH	- ¹
PBE	-3977.12943
PW91	-3977.81570
RPBE	-3977.39535
VWN-BP	-3977.88212

¹ no convergence after 1000 iterations

Ionisation energy of Mo

The ionisation energies were calculated using different functionals by comparing the energy of neutral gas phase Mo and gas phase Mo^{n+} . The calculations included all electrons using a double numerical base set with d-functions (DND).

Figure B.1 shows the error obtained in the calculated value for the ionisation energy relative to the reported values [N.N. 2, 2004]. Table B.4 shows the calculated values for the functional BLYP. The ionisation energy for the generation of most Mo^{n+} -states are determined with reasonable accuracy, with the exception for the 4+-oxidation state, for which the error in the ionisation energy is ca. 10%. On average the BLYP-functional seems to predict the ionisation energy for all oxidation states the best, but the differences are marginal.

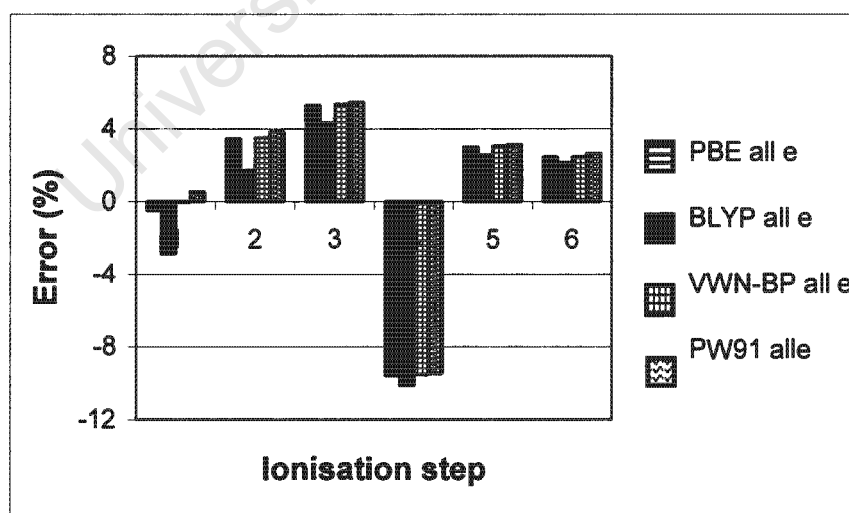


Figure B.1: Error (in %) between the calculated ionisation step and the reported ionisation energies [N.N., 2, 2004] using various functionals (calculations performed including all electrons using a double numerical base set with d-functions (DND))

Table B.4: Ionisation energy for the formation of Mo^{n+} (calculations performed including all electrons using a double numerical base set with d-functions (DND) and the BLYP functional) and compared with reported ionisation energies [N.N. 2, 2004]

Oxidation state	$E_{\text{calculated, kJ/mol}}$	$E_{\text{reported, kJ/mol}}$	Error (%)
1+	664.7	684.3	-2.9
2+	1586.8	1560.0	1.7
3+	2731.0	2618.0	4.3
4+	4026.1	4480.0	-10.1
5+	5391.5	5257.0	2.6
6+	6781.9	6640.8	2.1

Geometry of $\text{MoO}_2(\text{g})$

The geometry of MoO_2 was optimized using the various functionals including all electrons in the calculation using a double numerical base set with d-functions (DND) (see Table B.5). The calculated bond lengths, the O-Mo-O angle, and the calculated IR-adsorption bands were compared with results published.

Table B.6: Calculated bond length, O-Mo-O angle for MoO_2 (calculations performed including all electrons using a double numerical base set with d-functions (DND))

Functional	$R_{\text{Mo-O, calc. (Å)}}$	$\theta_{\text{O-Mo-O, calc. (°)}}$	$\nu_{\text{calc. (cm}^{-1}\text{)}}$	$\nu_{\text{calc. (cm}^{-1}\text{)}}$
BLYP	1.747	115.4	886	922
BOP	1.747	115.6	885	921
BP	1.734	115.3	903	939
PBE	1.733	115.1	902	939
PW 91	1.733	115.0	904	941
RBPE	1.739	115.5	890	927
VWN-BP	1.734	115.3	903	939

The calculated bond lengths and bond angles compare well with the calculated values using Jaquar 4.1 [Sniatynsky and Cedeno, 2004] and GAUSSIAN 94 [Zhou and Andrews 1999; Bare *et al.*, 1998]. The calculated bond angle differs however significantly from the experimentally reported value of $122 \pm 4^\circ$ [Bare *et al.*, 1998].

The experimentally obtained IR-adsorption bands for MoO_2 are reported to be at 903 and 951 cm^{-1} [Zhou and Andrews, 1999]. Calculated vibrational frequencies are typically larger than the frequencies observed experimentally [Scott and Radom, 1996]. Scaling factors are used. The scaling factors to be used are dependent on the choice of exchange functional and correlation functional [Scott and Radom, 1996].

Heat of dissociation of MoO₂ yielding MoO

The molecular modelling calculations were further tested by calculating the heat of dissociation of MoO₂:



The reported heat of dissociation is given as 560.2 ±20.9kJ/mol [N.N. 2, 2004] or calculated as 596.341kJ/mol from data from Knacke *et al.* [1991]

The calculated reaction enthalpy ($\Delta H_{\text{calc}}^{\text{rxn}}$) was obtained from the energy of the reaction (products-reactants) corrected for zero point energy (ZPE) and thermal energy from 0 to 298K:

$$\Delta H_{\text{calc}}^{\text{rxn}} = (\Delta E + \Delta \text{ZPE} + \Delta E_{\text{th}}) + \Delta(\text{PV}) \dots\dots\dots(\text{B.6})$$

where $\Delta E = E[\text{M}(\text{CO})_6(\text{g})] - 2E[\text{O}_2(\text{g})] - 3E[\text{C}_2(\text{g})] - E[\text{MoO}_2(\text{g})]$
 $\Delta(\text{PV}) = RT$

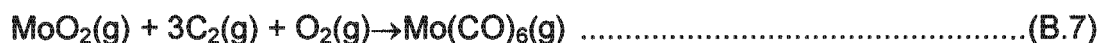
Table B.7: Calculated heat of dissociation of MoO₂ including all electrons in the calculation performed using double numerical base set with d-functions (DND) (Error calculated based on the reported value of 560.2 ±20.9kJ/mol [N.N. 2, 2004])

Functional	$\Delta H_{\text{calc}}^{\text{rxn}}$ (kJ/mol)	Error (%)
BLYP	555.3	-0.8
PB	529.5	-5.4
PBE	529.9	-5.4
PW 91	535.5	-4.4
VWN-BP	509.2	-9.1

The BLYP-functional seems to yield the most correct result, but in general the error obtained in the calculated heat of dissociation is less than 10%.

Heat of formation of Mo(CO)₆

The molecular modelling calculations were also tested by calculating the formation energy of molybdenum hexacarbonyl according to following reaction [Sniatynsky and Cedeno, 2004]:



The calculated reaction enthalpy ($\Delta H_{\text{calc}}^{\text{f}}$) was obtained from the energy of the reaction (products-reactants) corrected for zero point energy (ZPE) and thermal energy from 0 to 298K:

$$\Delta H_{\text{calc}}^{\text{f}} = (\Delta E + \Delta \text{ZPE} + \Delta E_{\text{th}}) + \Delta(\text{PV}) \dots\dots\dots(\text{B.8})$$

where $\Delta E = E[\text{M}(\text{CO})_6(\text{g})] - 2E[\text{O}_2(\text{g})] - 3E[\text{C}_2(\text{g})] - E[\text{MoO}_2(\text{g})]$
 $\Delta(\text{PV}) = -4RT$

A similar study was performed by Sniatynsky and Cedeno [2004], who studied the functionals BLYP, B3LYP, BP86, B3P86, PWP91, B3PW91 with Jaguar 4.1 software. Effective core potential was used to describe the innermost

core electrons of the metal atoms and a basis set of Gaussian functions was used to describe the outermost core electrons and the valence electrons. A triple zeta basis set was used to describe the non-metal atoms. They reported that the BLYP function corresponded best to the reported experimental value. The error in the calculated heat of formation varied between 1.4-10.2%.

Table B.6 shows the computed heat of formation of $\text{Mo}(\text{CO})_6$ in comparison to the reported experimental value. All electrons were included in the calculation using a double numerical base set with d-functions. The error in the calculated heat of formation varies between 1.5-7.5%. The PW91-functional yielded the lowest error.

Table B.8: Calculated heat of formation of $\text{Mo}(\text{CO})_6$ including all electrons in the calculation performed using double numerical base set with d-functions (DND) (Error calculated based on the reported value of 3416.654kJ/mol [Sniatynsky and Cedeno, 2004])

Functional	$\Delta H_{\text{calc}}^{\text{f}}$ (kJ/mol)	Error (%)
BLYP	-3211.0	6.0
BOP	-3160.1	7.5
BP	-3281.0	4.0
PBE	-3346.3	2.1
PRBE	-3194.4	6.5
PW91	-3367.2	1.4
VWN-BP	-3280.2	4.0

B.3.3 Conclusions

The multiplicity of the spin can be selected with confidence by the DMol³-program. However, there were no clear best performing functional. For a particular investigation an error of up to 10% can be expected depending on the choice of the functional. Taking this into account the study was performed using the functional GGA with BLYP was used for all further calculations.

Appendix C

Optimised structures

Table C1: Optimised structures for the Al-Mo-Al-clusters

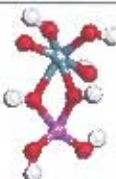
Oxidation state	Low coordination	High coordination
6		
5		
4		
3		

Table C2: Optimised structures for the Al-V-Al-clusters

Oxidation state	Low coordination	High coordination
5		
4		
3		

Table C3: Optimised structures for the Al-Mo-Al-clusters with adsorbed NH_3

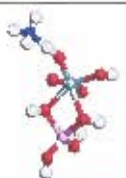
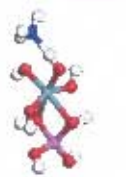
Oxidation state	Low coordination	High coordination
6		
5		
4		
3		

Table C4: Optimised structures for the Al-V-Al-clusters with adsorbed NH_3

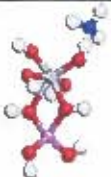
Oxidation state	Low coordination	High coordination
5		
4		
3		

Table C5: Optimised structures for the Al-Mo-Al-clusters with adsorbed propene

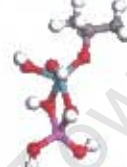
Oxidation state	Low coordination	High coordination
6		
5		
4		
3		

Table C6: Optimised structures for the Al-V-Al-clusters with adsorbed propene

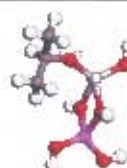
Oxidation state	Low coordination	High coordination
5		
4		
3		

Table C7: Transition state structures (alkoxide as intermediate) for the Al-Mo-Al-clusters

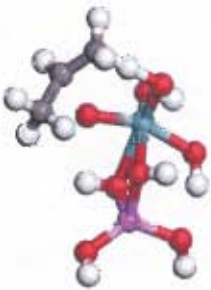
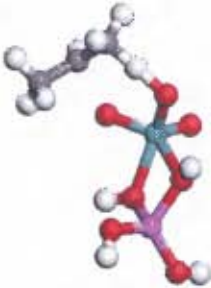
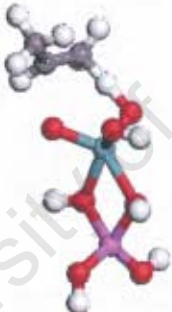
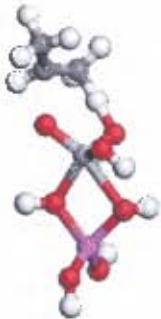
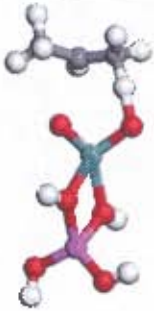
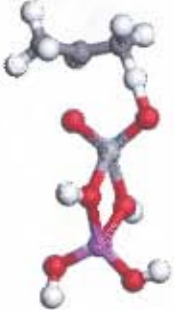
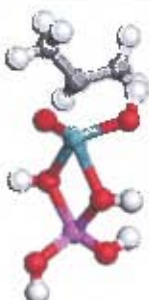
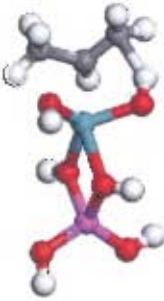
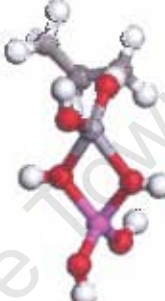
Oxidation state	Molybdenum	Vanadium
+6 high coordination		
+6 low coordination		
+5 low coordination		
+4 low coordination		

Table C8: Transition state structures (alkyl as intermediate) for the Al-Mo-Al-clusters

Oxidation state	Molybdenum	Vanadium
+4 low coordination		
+3 high coordination		

Appendix D

The following are saved on a CD at the back of the thesis

Summary of experimental FT results (FID and TCD)

XPS (raw data)

XRD (raw data)

Thesis in electronic format

University of Cape Town

FID analyses

The methane selectivity can also be calculated using the FID data as shown below. The methane selectivity calculated from the FID analyses are more accurate than that from the TCD analyses when the CO-conversion is very low.

Calculation of yield from FID data

$$Y = \frac{\text{mass products}}{\text{mass CO fed}}$$

$$Y = \frac{\sum \text{area FID}_{\text{all}}}{\text{area FID}_{\text{C6}}} \times \frac{m_{\text{C6}}}{m_{\text{CO}}} \text{ with } m \text{ defined as mass flow rate}$$

$$Y = \frac{\sum \text{area FID}_{\text{all}}}{\text{area FID}_{\text{C6}}} \times \frac{6n_{\text{C6}}}{n_{\text{CO}}}$$

$\sum \text{area FID}_{\text{all}}$ calculated by extrapolation of chain growth probability as shown above.

Calculation of CH₄ selectivity from FID data

$$S_{\text{CH}_4} = \frac{\text{CH}_4 \text{ area}}{\sum \text{area FID}_{\text{all}}} \times 100$$

$\sum \text{area FID}_{\text{all}}$ calculated by extrapolation chain growth probability as shown above.

Extrapolation of chain growth probability

The chain growth probability is extrapolated where the hydrocarbons could not be measured to be able to calculate the total FID area which is used to calculate the yield and methane selectivity.

$$P_{gC10} = \frac{r_g}{r_g + r_{dpar C10} + r_{dolC10}}$$

$$P_{gC10} = \frac{r_g}{r_g + r_{dpar} \left(1 + \frac{r_{dolC10}}{r_{dpar C10}} \right)}$$

$$\frac{1}{P_{gC10}} = \frac{r_g + r_{dpar} \left(1 + \frac{r_{dolC10}}{r_{dpar}} \right)}{r_g} \dots \dots \dots \text{Equation A}$$

$$r_{dolC11} = f \times r_{dolC10}$$

$$\frac{r_{dolC11}}{r_{dpar}} = f \frac{r_{dolC10}}{r_{dpar}}$$

$$\frac{r_{dolC12}}{r_{dpar}} = f^2 \frac{r_{dolC10}}{r_{dpar}}$$

$$P_{gC11} = \frac{r_g}{r_g + r_{dpar} \left(1 + \frac{r_{dolC11}}{r_{dpar C11}} \right)}$$

$$P_{gC11} = \frac{r_g}{r_g + r_{dpar} \left(1 + f^1 \frac{r_{dolC10}}{r_{dpar C10}} \right)}$$

Appendix E

$$P_{gCN} = \frac{r_g}{r_g + r_{dpar} \left(1 + f^{N-10} \frac{r_{dolC10}}{r_{dparC10}} \right)}$$

$$ol\ content_{C10} = \frac{r_{dolC10}}{r_{dolC10} + r_{dparC10}}$$

$$\frac{1}{ol\ content_{C10}} = \frac{r_{dolC10} + r_{dparC10}}{r_{dolC10}}$$

$$\frac{1}{ol\ content_{C10}} = 1 + \frac{r_{dparC10}}{r_{dolC10}}$$

$$\frac{1}{ol\ content_{C10}} - 1 = \frac{r_{dparC10}}{r_{dolC10}}$$

$$\frac{\frac{1}{ol\ content_{C10}} - 1}{1} = \frac{r_{dparC10}}{r_{dolC10}}$$

$$\frac{\frac{1}{ol\ content_{C10}} - 1}{1} = \frac{r_{dparC10}}{r_{dolC10}} \quad \text{multiply top and bottom with } ol\ content\ to\ give$$

$$\frac{ol\ content_{C10}}{1 - ol\ content_{C10}} = \frac{r_{dolC10}}{r_{dparC10}} \quad \text{..... Equation B}$$

$$\frac{1}{P_{gC10}} = 1 + \frac{r_{dparC10}}{r_g} \left(1 + \frac{r_{dolC10}}{r_{dparC10}} \right) \quad \text{.....Equation C (Equation A rearranged)}$$

$$\frac{\frac{1}{P_{gC10}} - 1}{\left(1 + \frac{r_{dolC10}}{r_{dparC10}} \right)} = \frac{r_{dparC10}}{r_g} \quad \text{combine with equation B to give}$$

$$\frac{\frac{1}{P_{gC10}} - 1}{\left(1 + \frac{\text{ol content}_{C10}}{1 - \text{ol content}_{C10}}\right)} = \frac{r_{d \text{ par } C10}}{r_g} \text{ put in Equation C to give}$$

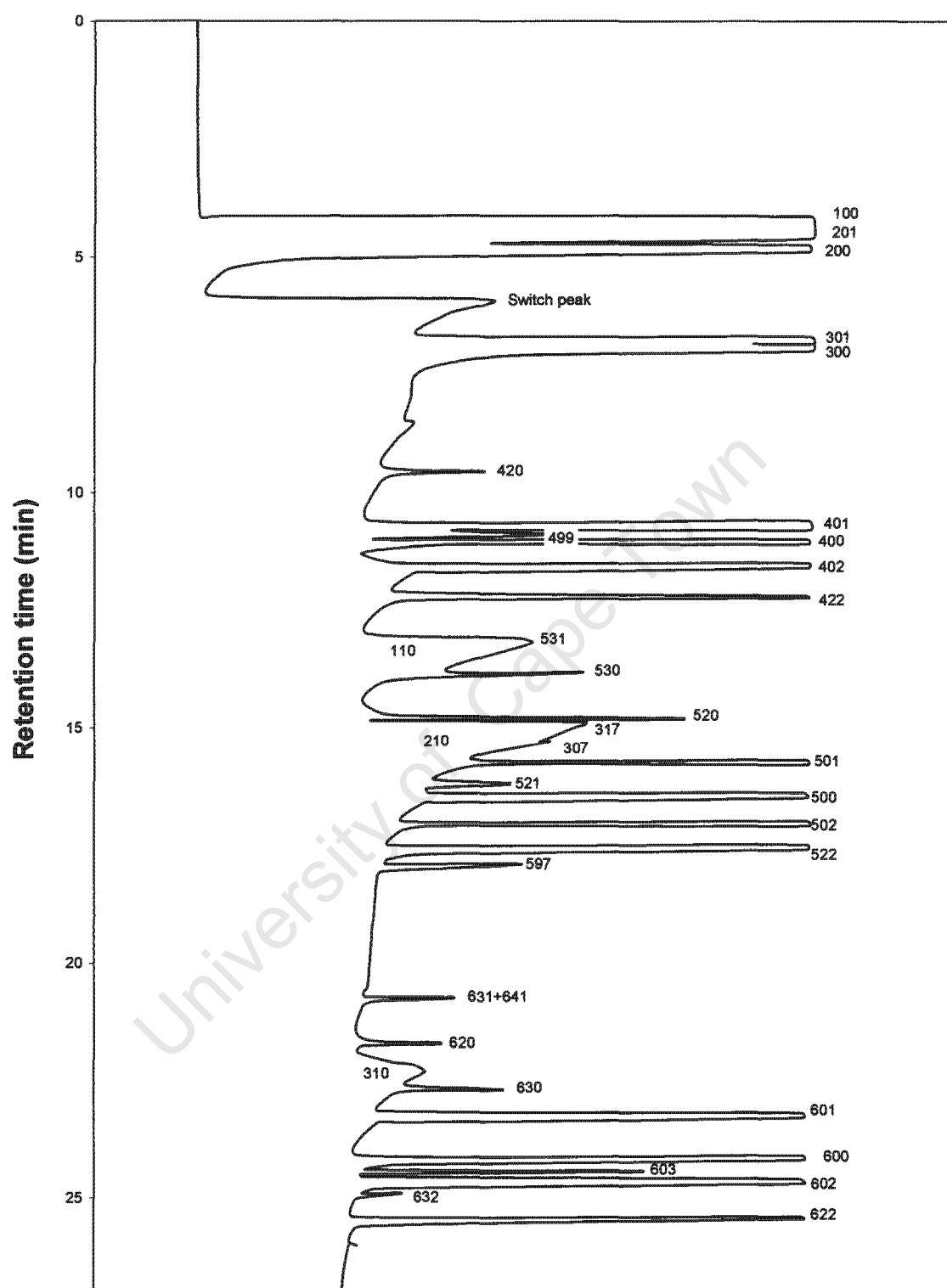
$$\frac{1}{P_g} = 1 + \left[\frac{\frac{1 - P_{gC10}}{P_{gC10}}}{\left(1 + \frac{\text{ol content}_{C10}}{1 - \text{ol content}_{C10}}\right)} \right] \left(1 + \frac{r_{d \text{ ol } C10}}{r_{d \text{ par } C10}} \right)$$

$$\frac{1}{P_{gN}} = 1 + \left[\frac{\frac{1 - P_{gC10}}{P_{gC10}}}{\left(1 + \frac{\text{ol content}_{C10}}{1 - \text{ol content}_{C10}}\right)} \right] \left(1 + f^{N-10} \frac{r_{d \text{ ol } C10}}{r_{d \text{ par } C10}} \right) \text{ combine with Equation B to}$$

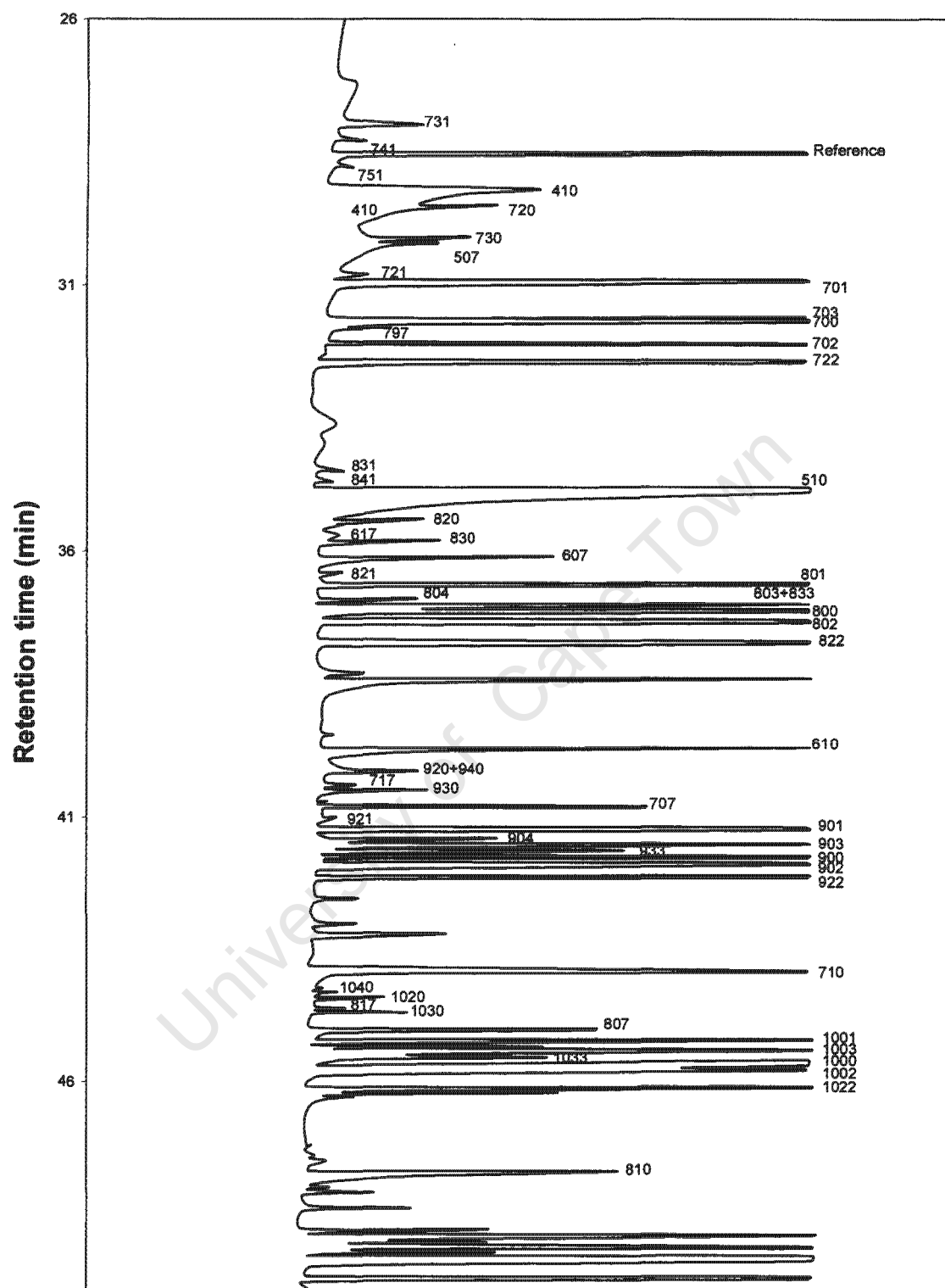
give

$$\frac{1}{P_{gN}} = 1 + \left[\frac{\frac{1 - P_{gC10}}{P_{gC10}}}{\left(1 + \frac{\text{ol content}_{C10}}{1 - \text{ol content}_{C10}}\right)} \right] \left(1 + f^{N-10} \frac{\text{ol content}_{C10}}{1 - \text{ol content}_{C10}} \right)$$

FID Spectrum, peak identification



Appendix E



Appendix E

Compound	Code	Response Factor
Methane	100	1
Methanol	110	0.55
Ethane	200	2
Ethene	201	2
Ethanol	210	1.55
Ethanal	207	1
Propane	300	3
Propene	301	3
Propanol(-1)	310	2.55
Propanal	307	2
Propanol(-2)	315	2.55
Propanon	317	2
n-Butane	400	4
Butene-(1)	401	4
tr.-Butene-(2)	402	4
cis-Butene-(2)	422	4
Butadiene(1,3)	499	4
Butanol(-1)	410	3.55
Butanal	407	3
Butanol(-2)	415	3.55
Butanone(2)	417	3
2-Me-Propan	420	4
2-Me-Propen (1)	421	4
n-Pentane	500	5
Pentene-(1)	501	5
tr.-Pentene-(2)	502	5
cis-Pentene-(2)	522	5
Pentanol(-1)	510	4.55
Pentanal	507	4
Pentanone(2)	517	4
2-Me-Butane	520	5
2-Me-Butene (1)	521	5
3-Me-Butene (1)	531	5
2-Me-Butene (2)	597	5
n-Hexan	600	6
Hexen-(1)	601	6
tr.-Hexen-(2)	602	6
cis-Hexen-(2)	622	6
tr.-Hexen-(3)	603	6
cis-Hexen-(3)	633	6
Hexanol(-1)	610	5.55

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Hexanal	607	5
Hexanone(2)	617	5
2-Me-Pentane	620	6
3-Me-Pentane	630	6
2-Me-Pentene (1)	621	6
3-Me-Pentene (1)	631	6
4-Me-Pentene (1)	641	6
2-Me-Pentene (2)	697	6
3-Me-Pentene (2)	632	6
4-Me-Pentene(2), cis and trans	642	6
2,3 Di-Me-Butane	623	6
2,4 Di-Me-Butane	624	6
2,3 Di-Me-Butene(1)	664	6
Cyclohexane	reference	6
n-Heptane	700	7
Heptene-(1)	701	7
tr.-Heptene-(2)	702	7
cis-Heptene-(2)	722	7
tr.-Heptene-(3)	703	7
cis-Heptene-(3)	733	7
Heptanol(-1)	710	6.55
Heptanal	707	6
Heptanone(2)	717	6
2-Me-Hexane	720	7
3-Me-Hexane	730	7
2-Me-Hexene (1)	721	7
3-Me-Hexene (1)	731	7
4-Me-Hexene (1)	741	7
5-Me-Hexene (1)	751	7
2-Me-Hexene (2)	797	7
3-Me-Hexene (2)	732	7
2,3 Di-Me-Pentane	723	7
3-Et-Pentane	780	7
n-Oktane	800	8
Oktene-(1)	801	8
tr. -Oktene-(2)	802	8
cis-Oktene-(2)	822	8
tr. Oktene-(3)	803	8
cis-Oktene-(3)	833	8
tr.-Oktene-(4)	804	8
Oktanol(-1)	810	7.55
Oktanal	807	7
Oktanone(2)	817	7
2-Me-Heptane	820	8
3-Me-Heptane	830	8
4-Me-Heptane	840	8
2-Me-Heptene (1)	821	8
3-Me-Heptene (1)	831	8

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4-Me-Heptene (1)	841	8
5-Me-Heptene (1)	851	8
n-Nonane	900	9
Nonene-(1)	901	9
tr.-Nonene-(2)	902	9
cis-Nonene-(2)	922	9
tr.-Nonene-(3)	903	9
cis-Nonene-(3)	933	9
Nonene-(4)	904	9
Nonanol(-1)	910	8.55
Nonanal	907	8
Nonanone(2)	917	8
2-Me-Oktane	920	9
3-Me-Oktane	930	9
4-Me-Oktane	940	9
2-Me-Oktene (1)	921	9
2,4 Di-Me-Heptane	924	9
2,5 Di-Me-Heptane	925	9
3-Et-Oktane	980	9
n-Decane	1000	10
Decene-(1)	1001	10
tr.-Decene-(2)	1002	10
cis-Decene-(2)	1022	10
tr.-Decene-(3)	1003	10
cis-Decene-(3)	1033	10
tr.-Decene-(4)	1004	10
cis-Decene-(4)	1044	10
Decene-(5)	1005	10
Decanol(-1)	1010	9.55
Decanal	1007	9
Decanone(2)	1017	9
2-Me-Nonane	1020	10
3-Me-Nonane	1030	10
4-Me-Nonane	1040	10
5-Me-Nonane	1050	10

Appendix F

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Results and discussion on unpromoted catalyst: base case study

F.1 Physio-Chemical Characterisation

F.1.1 XRD

Figure F.1 shows the XRD spectrum of the calcined and the reduced catalysts. A Co_3O_4 crystallite size of 9nm was estimated by line broadening analysis, using the Scherrer equation (β estimated from the width at half the height of the Co_3O_4 peak). The Co_3O_4 diffraction peak at $2\theta=59^\circ$ was chosen for estimating β value because it was least influenced by $\gamma\text{-Al}_2\text{O}_3$ diffraction peaks.

The XRD spectrum of the reduced catalyst (covered by xylene to prevent oxidation) showed no cobalt metal diffraction peaks. Either the crystallites were very small, XRD amorphous or the crystallites were not detected due to stacking faults. CoO diffraction peak was observed.

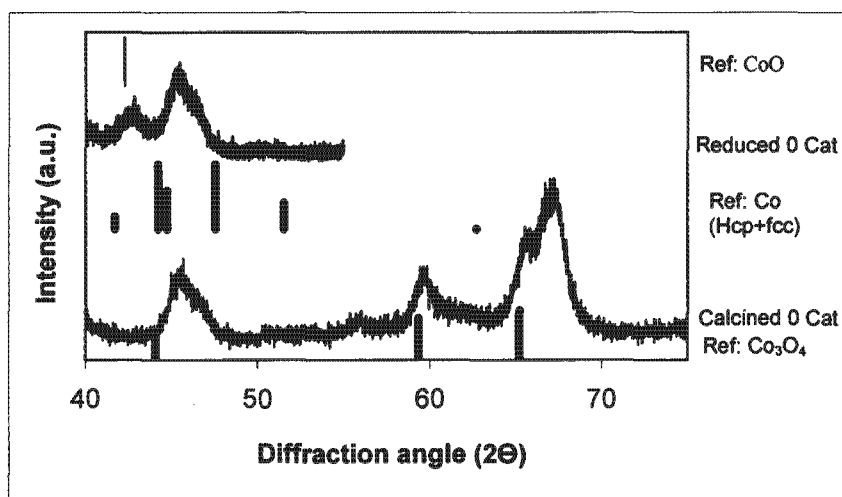


Figure F.1: XRD spectrum of reduced (at 425°C in H₂, heating rate 2°C) and calcined catalyst

F.1.2 Influence of reduction temperature on the degree of reduction

The degree of reduction increases with an increase in the reduction temperature for the unpromoted catalysts (0 Cat) (see Figure F.2). The oxidation steps in all cases were done at 350°C to ensure oxidation of cobalt is oxidised to the same oxidation state and comparable degrees of reduction. If the cobalt is oxidised at a too high temperature Co₃O₄ is converted to CoO [Sewell *et al.*, 1996]. A degree of reduction of 25% may be obtained without the formation of cobalt metal if the reduction of Co₃O₄ is assumed to be in two consecutive steps, i.e. (1) reduction to CoO (2) reduction to Co. Different batches of the catalyst showed similar trends.

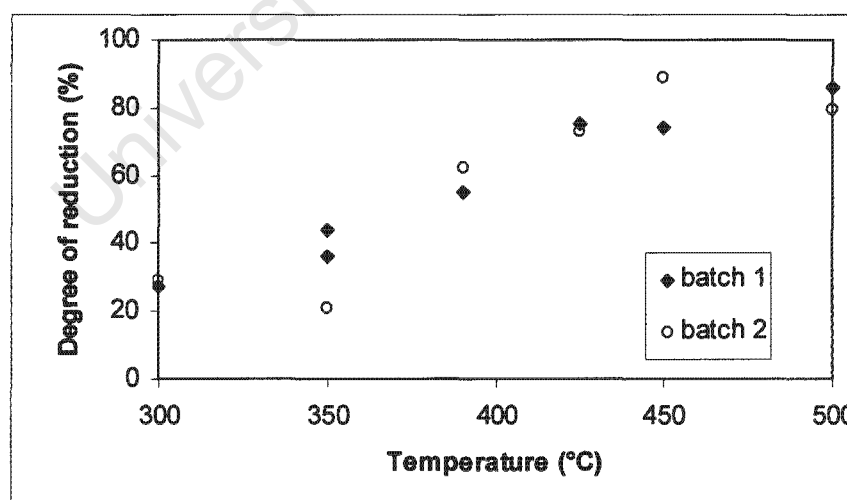


Figure F. 2: The influence of the reduction temperature on the degree of reduction of the cobalt of two batches of unpromoted catalyst. The catalyst (50mg) was reduced at 425°C in pure hydrogen (37ml (STP)/min) for 8 to 10hrs. A heating rate of 1°C/minute was used

F.1.3 Temperature programmed reduction (TPR)

The temperature programmed reduction of three batches of unpromoted catalyst were done (See Figure F.3). This shows the amount of scatter due to catalyst preparation and analyses may be present when catalyst containing different amounts of promoters are tested and compared. The first peak between 190°C and 220°C may be due to the reduction of Co_3O_4 to CoO . The second peak between 265°C and 305°C may be due to the reduction of CoO to Co . However, the area of the first peak is >25% of the total area up till 400°C indicating that reduction of CoO to Co may also be part of the first reduction peak. The reduction peak at temperature higher than 400°C may be due to cobalt in close interaction with alumina [Arnoldy and Moulijn, 1985]. The reduction peak at a temperature higher than 800°C may be due to cobalt aluminate [Arnoldy and Moulijn, 1985; Arnoldy *et al.*, 1985].

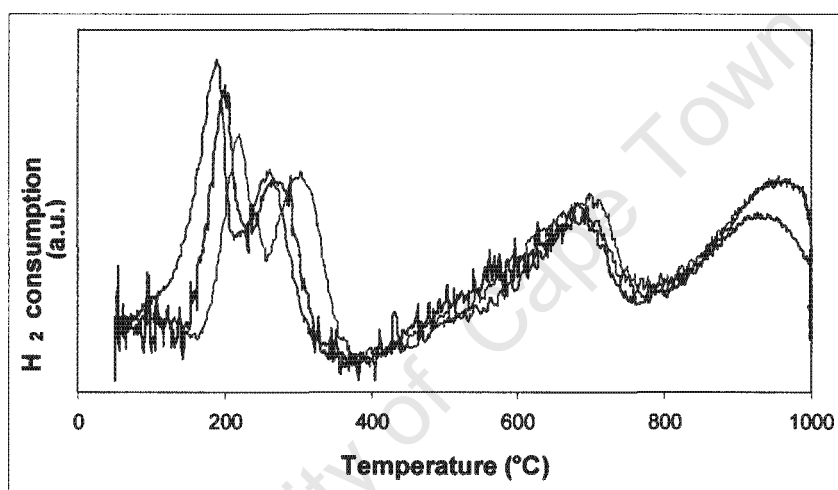


Figure F. 3: TPR of different batches of unpromoted (0 Cat) catalysts. Hydrogen (5.6 vol%) in argon with a total flow of 46ml(STP)/min was used as the reducing gas. The temperature was ramped at 10°C/min from ~50°C to 1000°C and was kept at this temperature for 1 hour

F.1.4 Influence of reduction temperature on CO TPD analyses

CO and H_2 chemisorptions were done by Backman *et al.*, (2001) on a cobalt supported on silica catalysts containing different amounts of cobalt which reduced to different extents (see Figure F.4). CO chemisorptions were also done on the unreduced catalysts. The total CO uptakes (at 30°C) during CO chemisorption by the unreduced catalysts were more than that on the reduced catalysts, indicating that CO also adsorbs on cobalt oxide. The irreversible CO was less on the unreduced catalyst relative to the reduced catalyst. This may indicate that CO adsorbs less strongly on oxidised cobalt than the cobalt metal. The amount of irreversible CO and H_2 chemisorption increased with an increase in the degree of reduction which was in turn a function of the metal loading (see Figure F.4).

Appendix F

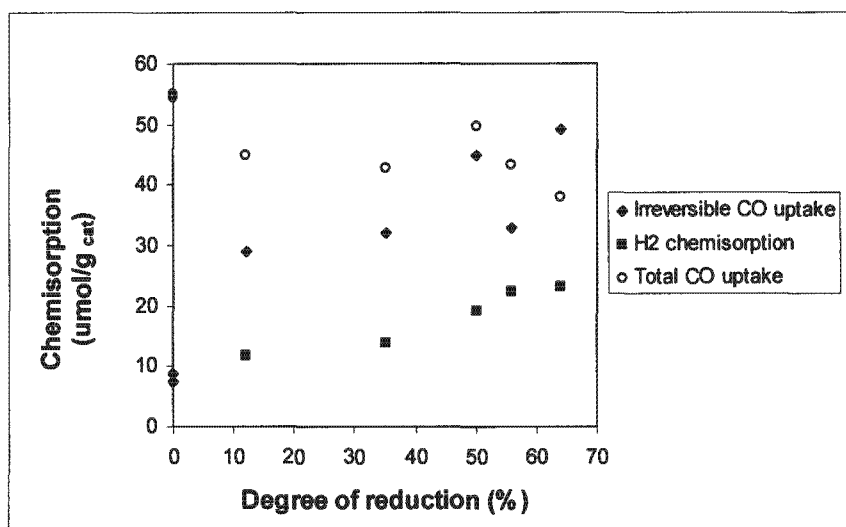


Figure F. 4: The influence of the degree of reduction on H₂ and CO chemisorption (the graph was drawn from data obtained from Backman *et al.*, (2001). CO chemisorption at 30°C and H₂ chemisorption at 100°C

Temperature programmed desorption (TPD) of CO was performed on the unpromoted catalyst reduced at different temperatures (see Figure F.5). At a low reduction temperature of 100°C, cobalt metal may not be expected, based on the degree of reduction and TPR results. Even though no cobalt metal may be present, CO was still adsorbed by the catalyst. This may indicate that CO was also adsorbed on cobalt oxide. This correlates with the results of Backman *et al.* (2001) that CO adsorbed on cobalt oxide. The strength of the CO adsorption increased as the temperature of reduction increases. This may indicate that CO adsorbs less strongly on cobalt oxide than on cobalt metal which correlates with the interpretation (see above) of results of Backman *et al.* (2001). Not only CO desorbs from the catalysts during a TPD analyses, since the unreduced unpromoted catalyst which was not exposed to CO also gave a signal at a temperature higher than 275°C (see Figure F.5). This was not due to a signal from water desorption since dried zeolite was used as a trap between the reactor part with the catalyst and the TCD.

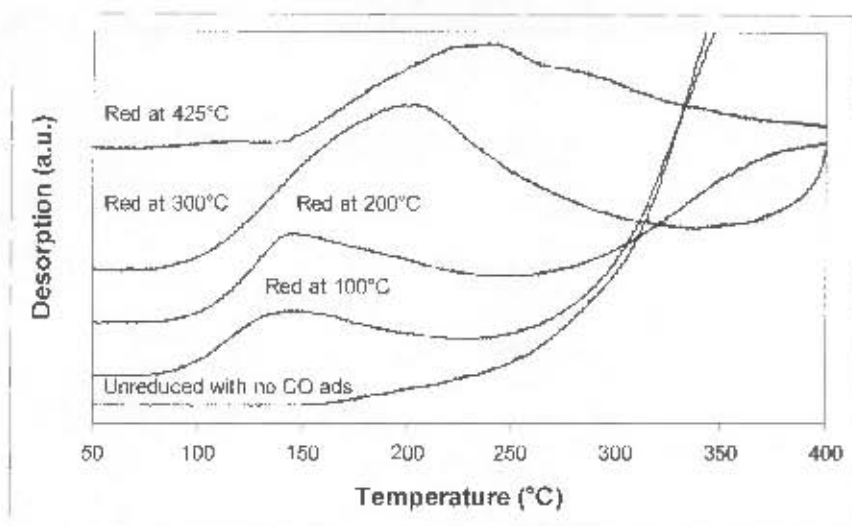


Figure F. 5: CO TPD of the unpromoted catalyst (0M) reduced at different temperatures. (The unreduced catalyst and catalyst reduced at 100°C were pre-calcined at 250° in He. The catalyst reduced at 200, 300 and 425°C were not pre-calcined.)

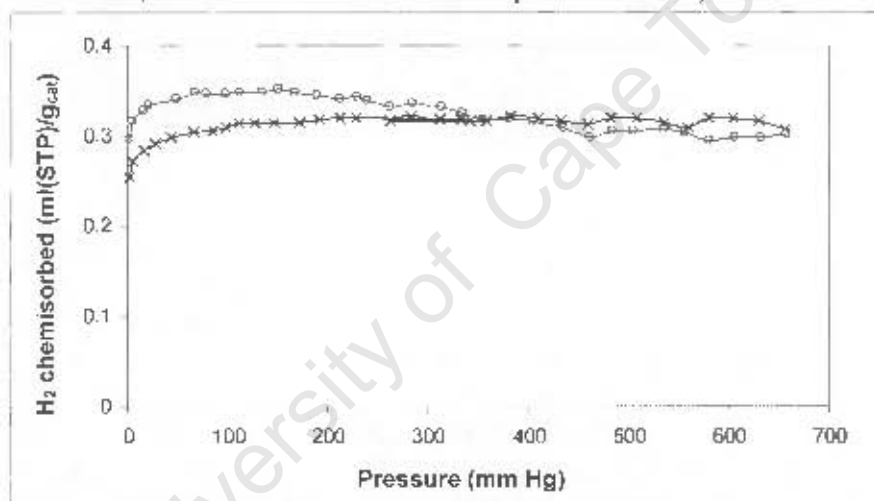


Figure F. 6: Static chemisorption on the unpromoted catalyst after reduction at 425°C

A volume of $\sim 0.3 \text{ ml(STP)/g}_{\text{catalyst}}$ of hydrogen was adsorbed on the unpromoted catalysts (see Figure F.6). The volume (determined from peak area between 120°C and 425°C and calibration with injection of known volumes) of desorbed CO of the unpromoted was $0.62 \text{ ml(STP)/g}_{\text{catalysts}}$. The volumes corresponds well if non dissociative CO chemisorption and dissociative H_2 chemisorption on the same sites are assumed.

F.1.4 XPS analyses

After reduction at 425°C, 8% of the cobalt on the surface was cobalt metal (binding energy 778.0 eV for Co(0) and 781.3 eV for 'CoO'). The amount of divalent cobalt seems to be surprisingly high seeing the degree of reduction obtained with catalyst with TGA. XPS is a surface technique where as TGA is a bulk technique. This can be rationalised by the presence of highly

dispersed cobalt oxide phase (e.g. cobalt aluminate) and larger crystallites of metallic cobalt.

Table F. 1: XPS analyses (analyses and interpretation in this table done by CSIR)

Catalyst name	Element	Atomic concentration (%)	Binding energy (eV)	Probable compounds
0 Cat	Al	14.7	74.5	Al ₂ O ₃
	C	3.0	284.7	
	Co	13.6	778.0 (8%)	Co
			781.3 (92%)	Cobalt oxide
	O	68.8	531.4	Oxide Hydroxides

Relating physio-chemical analyses

The crystallite size of the Co₃O₄ peak in the calcined catalyst determined by XRD was 8.6nm. TEM analyses of the calcined catalyst yielded an average crystallite size of 11nm [Zwane, 2004].

The H₂ and CO chemisorption giving the cobalt metal surface area together with the degree of reduction was used to calculate the cobalt metal crystallite size of 44nm for the reduced unpromoted catalyst (0 Cat). XRD analyses showed no cobalt metal diffraction peaks. This may be explained that the crystallites contained stacking faults making it XRD amorphous.

No mass transfer limitation were expected during the reduction of the catalyst for the XRD analyses since a high flow (380ml(STP)/min) of hydrogen flowing through the catalyst were used. During the reduction of the catalyst for the chemisorption and XPS analyses, mass transfer limitations may have been present since the hydrogen did not flow through the catalyst. This may have resulted in different amounts of sintering due to a higher partial pressure of water being present. If different amounts of sintering took place, different crystallite sizes may have resulted.

F.2 Fischer-Tropsch synthesis

F.2.1 Influence of reduction temperature on synthesis performance of the catalyst

The initial CO conversion of the unpromoted catalyst (0 Cat) reduced at 425°C is higher than the unpromoted catalyst reduced at 350°C (see Figure F.7). The stabilised CO conversion is however identical. This may indicate that the cobalt that reduced additionally at the higher reduction temperature deactivated during the first day on stream. The CO conversions for the different runs at 350°C after 1 day on stream indicates that the Fischer-

Tropsch runs can be done repeatable. The Fischer-Tropsch synthesis seems to be at steady state after 1 day on stream based on the CO conversions.

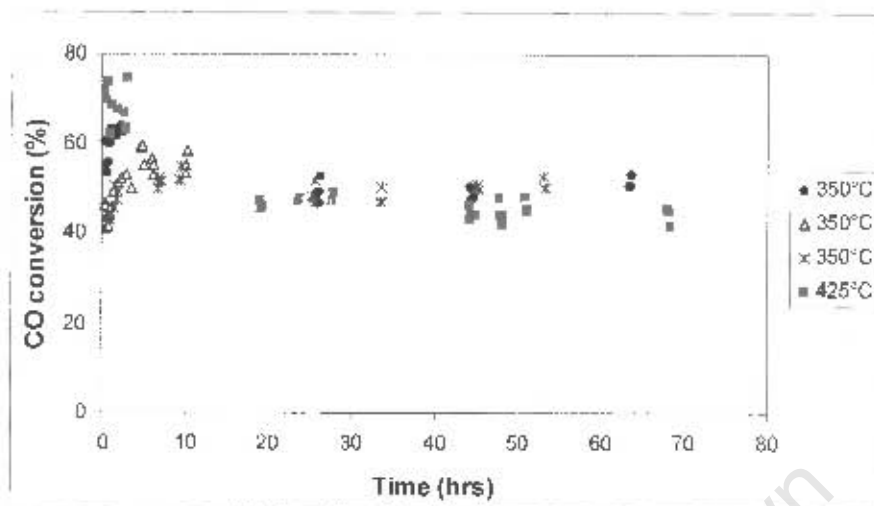


Figure F.7: Influence of reduction temperature on CO conversion and stability of the catalyst during the Fischer-Tropsch synthesis with the unpromoted catalyst (0.5g) tested at 220°C, 20bar_a, and a synthesis gas flow rate of 23ml(STP)/min, H₂/CO=2 in a fixed bed reactor.

F.2.2 Influence of time on stream on selectivity

The olefin in the linear hydrocarbon fraction decreased for the unpromoted catalyst as a function of time (see Figure F.8). The 1-olefin in the olefins fraction increased as a function of time (see Figure F.9). These changes in the selectivity may be due to a changing catalyst surface [Schulz *et al.*, 2002]. After 1 day on stream the olefin content in the linear hydrocarbon fraction and the 1-olefin content in the olefins fraction did not change. The Fischer-Tropsch synthesis seems to be at steady state after 1 day on stream based on the selectivity data.

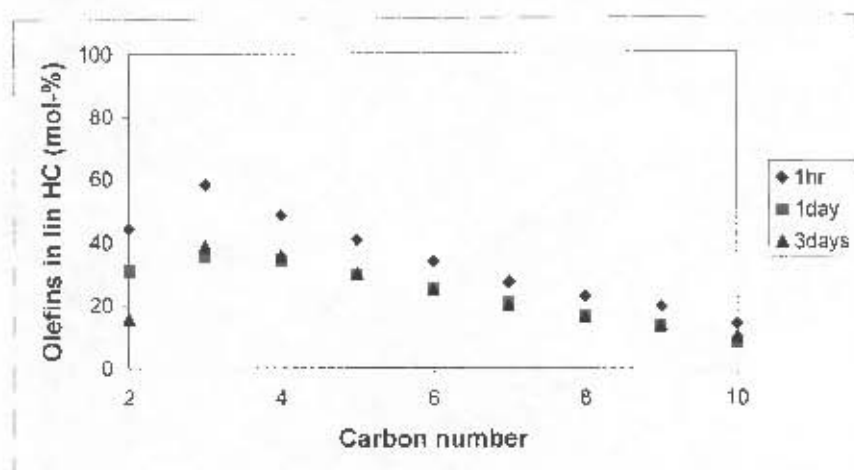


Figure F.8: Olefin content in linear hydrocarbons as a function of the time for the unpromoted catalyst. The Fischer-Tropsch syntheses were done with 0.5g catalyst at 220°C, 20bar_a, and a synthesis gas flow rate of 23ml(STP)/min, H₂/CO=2 in a fixed bed reactor.

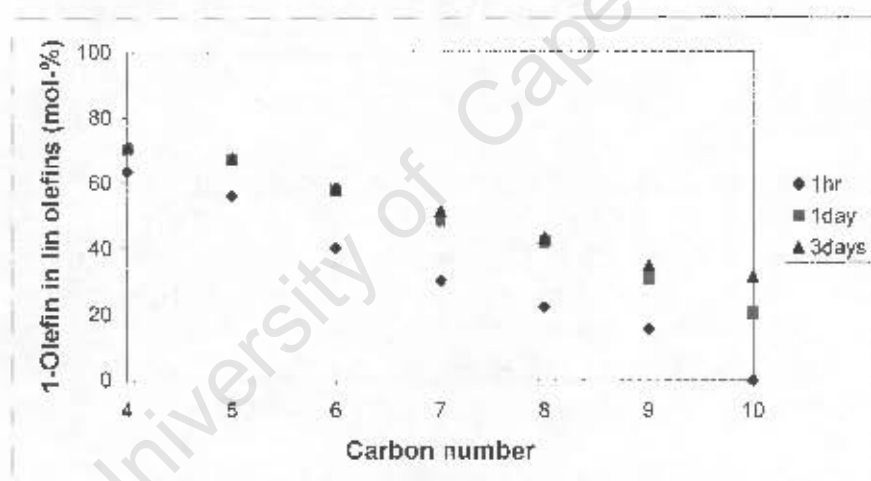


Figure F.9: 1-Olefin content in linear olefins (lin olefins) as a function of the time for the unpromoted catalyst. The Fischer-Tropsch syntheses were done with 0.5g catalyst at 220°C, 20bar_a, and a synthesis gas flow rate of 23ml(STP)/min, H₂/CO=2 in a fixed bed reactor.

F.2.3 Influence of linear velocity on the CO conversion and selectivity

The linear velocity (keeping the space velocity constant by loading more catalysts) was changed by increasing the flow rate from 23 ml(STP)/min to 69 ml(STP)/min to test whether a boundary layer was present resulting in mass transfer limitations affecting the CO conversion and selectivity. The CO conversion, methane selectivity (see Figure F.10), chain growth probability (see Table F.4), olefin content in linear hydrocarbon fractions (Figure F.11 and Figure F.13) and 1-olefin content in olefin fractions (Figure F.12 and Figure F.14) after 1 day and 3 days on stream were not significantly influenced by an increase in the linear velocity. It may thus be concluded that external mass transfer limitations are not playing a significant role. C_8 hydrocarbon fraction will be useful to study the olefin and 1-olefin selectivity at different conversions for the promoted and unpromoted catalysts.

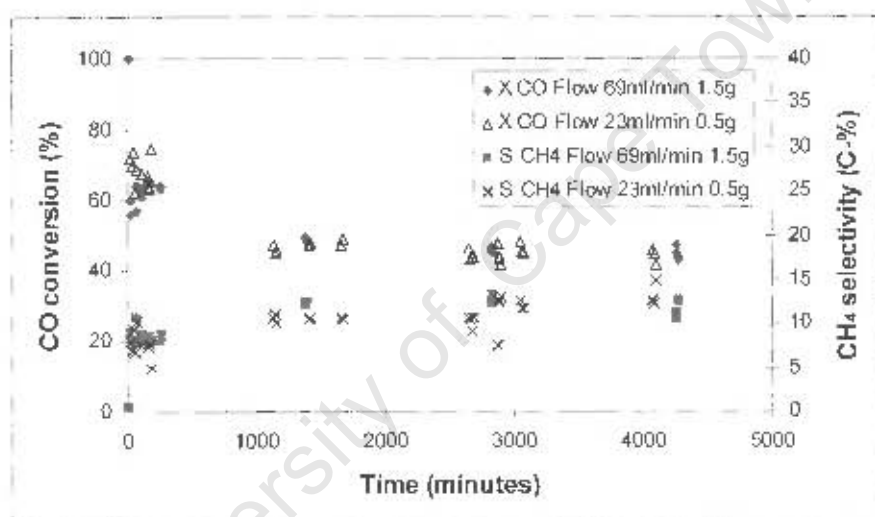


Figure F.10: Influence of linear velocity on CO conversion and CH_4 selectivity of the catalyst during the Fischer-Tropsch synthesis with the unpromoted catalyst (0M C) (0.5 to 1.5g) tested at 220°C , 20bar_a , and a synthesis gas flow rate of 23 to 69ml(STP)/min , $H_2/CO=2$ in a fixed bed reactor.

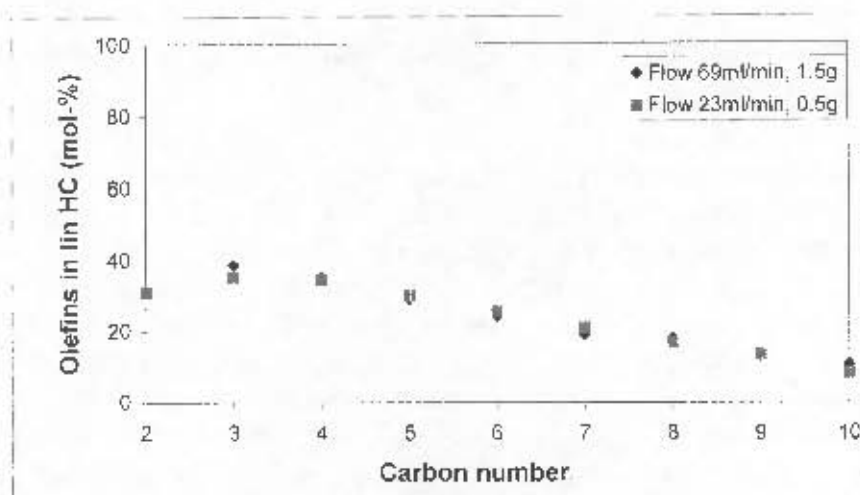


Figure F.11: Comparison of the olefins content in the linear hydrocarbon fraction at different linear velocities and the same space velocity. The Fischer-Tropsch syntheses were done with 0.5 and 1.5g unpromoted catalyst, and a synthesis gas flow rate of 23 and 69 ml(STP)/min, $H_2/CO=2$ in a fixed bed reactor. Analyses after 1 day on stream.

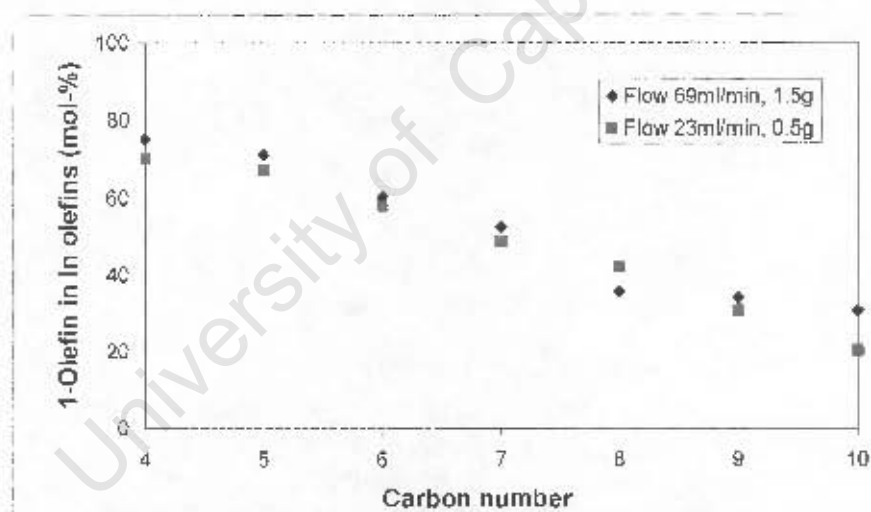


Figure F.12: Comparison of the 1-olefin content in the linear olefins fraction at different pressures. The Fischer-Tropsch syntheses were done with 1g unpromoted catalyst, and a synthesis gas flow rate of 23ml(STP)/min, $H_2/CO=2$ in a fixed bed reactor. Analyses after 1 day on stream.

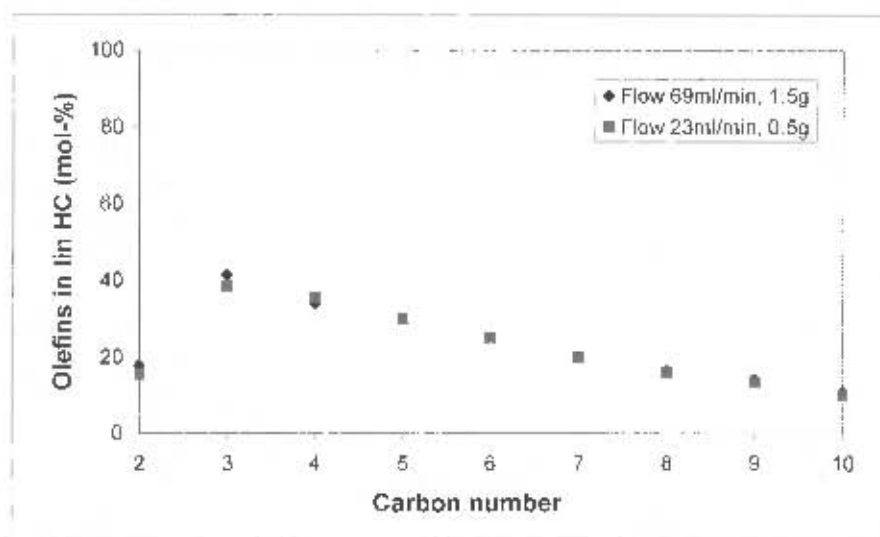


Figure F.13: Comparison of the olefins content in the linear hydrocarbon fraction at different linear velocities and the same space velocity. The Fischer-Tropsch syntheses were done with 0.5 and 1.5g unpromoted catalyst, and a synthesis gas flow rate of 23 and 69 ml(STP)/min, $H_2/CO=2$ in a fixed bed reactor. Analyses after 3 days on stream.

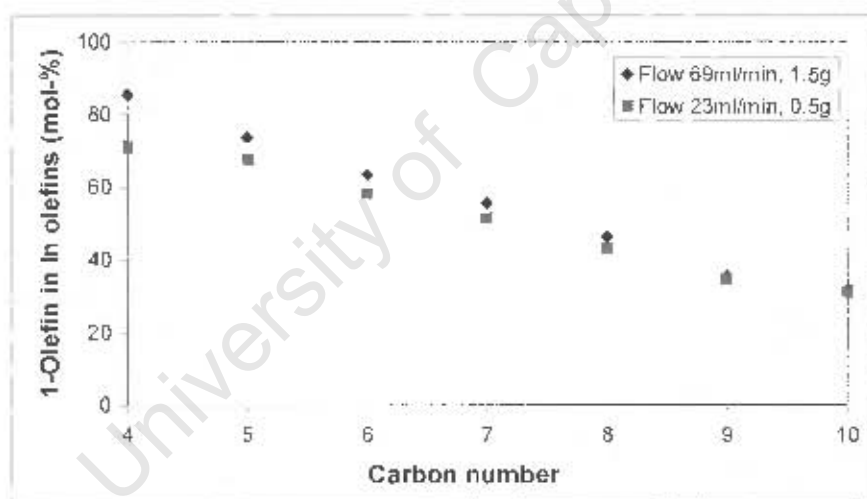


Figure F.14: Comparison of the 1-olefin content in the linear olefins fraction at different pressures. The Fischer-Tropsch syntheses were done with 1g unpromoted catalyst, and a synthesis gas flow rate of 23ml(STP)/min, $H_2/CO=2$ in a fixed bed reactor. Analyses after 3 days on stream.

F.2.4 Influence of conversion on selectivity

The olefins in the linear hydrocarbon fractions and 1-olefins in the olefins fractions may be expected to increase with a decrease in conversion due to a decrease in the extent of secondary reactions like hydrogenation and double bond isomerisation.

The water partial pressure decreases as the conversion decreases which will have the opposite effect on the olefins than the conversion. Water inhibits secondary reactions like hydrogenation and isomerisation [Schulz *et al.*, 1997, Iglesia *et al.*, 1993]. The olefin content in linear hydrocarbons increased slightly as a function of the water partial pressure for a 100Co/15ZrO₂/0.66Ru catalyst at 190°C [Schulz *et al.*, 1997]. The 1-olefin content in linear olefins increase significantly as the water partial pressure increased [Schulz *et al.*, 1997].

Iglesia *et al.* (1993) reported a decrease in the olefin to paraffin and 1-olefin to paraffin ratios with an increase in the residence time with a corresponding increase in the conversion and water partial pressure for a ruthenium catalysts. An increase in the C₆₊ and decrease in the CH₄ selectivity with an increase in the residence time was observed.

Both the mass catalyst loaded and the gas flow were changed in order to change the space velocity and the conversion (see Figure F.15). After 1 day on stream the CO conversion (see Figure F.7) and selectivity of the unpromoted catalyst were stable (see Figure F.8 and Figure F.9) therefore the gas flow could be changed to change the conversion. The conversion had no effect on the chain growth probability in the range C₂-C₁₀ (Table F.2 and Figure F.16). The methane selectivity was not significantly influenced by conversion (see Figure F.17). A decrease in the CO conversion resulted in a strong increase in the olefin content in the linear hydrocarbon fraction and an increase in the 1-olefin content in the linear olefin fraction (see Figure F.18; Figure F.19 Figure F. and Figure F.20Figure F.). Scatter was observed in the data (especially C₂ and C₃), however a clear trend was still observed.

The catalyst has a lower CO conversion compared at the same space velocity after it had been exposed to higher conversions, i.e. higher water partial pressure See Figure F.15 and Table F.4). Deactivation may have occurred due to an increase in the water partial pressure.

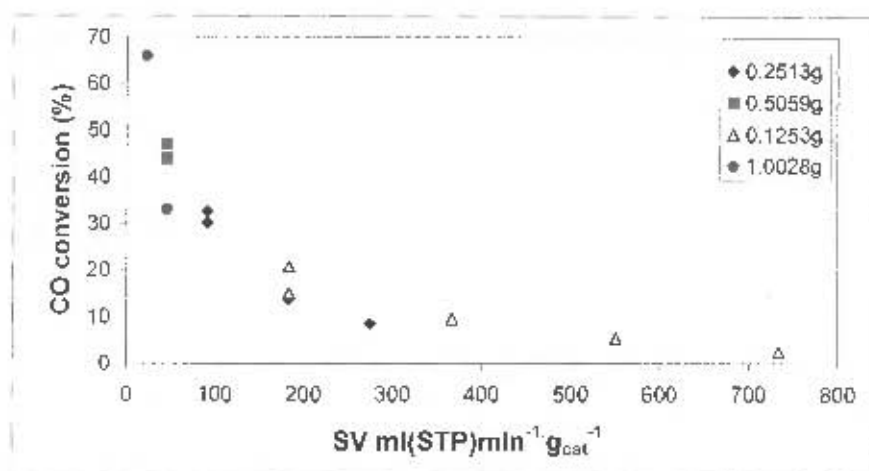


Figure F.15: Influence of the space velocity on the CO conversion. The Fischer-Tropsch syntheses were performed at 220°C, 20bar_a, and H₂/CO=2 in a fixed bed reactor.

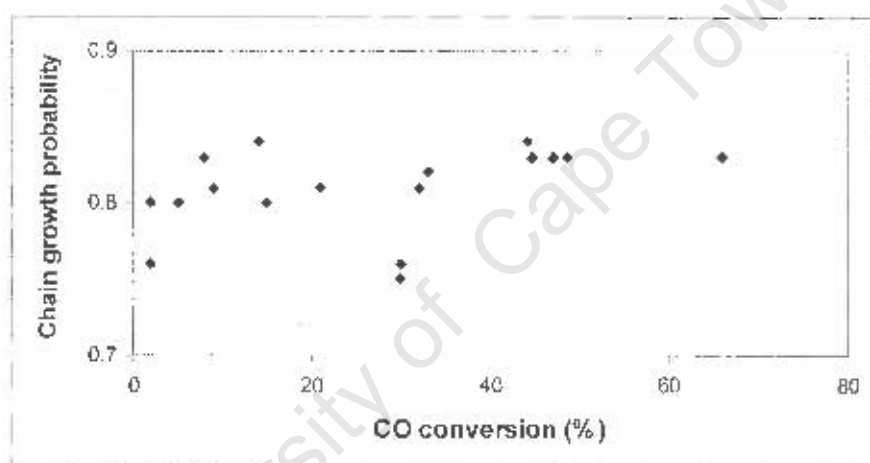


Figure F.16: Influence of CO conversion on the chain growth probability (C₃-C₁₀) of an unpromoted catalyst. The Fischer-Tropsch syntheses were performed at 220°C, 20bar_a, and H₂/CO=2 in a fixed bed reactor.

Table F. 2: Influence of CO conversion on chain growth probability

Catalyst mass (g)	Flow (ml/min)	CO conversion (%)	Time on stream	Chain growth probability (C3-C10)
1.5056	69	49	1day	0.83
1.5056	69	45	3days	0.83
1.0028	23	66	1day	0.83
1.0028	46	33	2days	0.82
0.5059	23	47	1day	0.83
0.5059	23	44	3days	0.84
0.2513	23	30	1day	0.75
0.2513	23	30	1day	0.76 (repeat FID analyses)
0.2513	23	32	2days	0.81
0.2513	23	32	2days	0.81 (repeat FID analyses)
0.2513	46	14	3days	0.84
0.2513	69	8	4days	0.83
0.1253	23	21	1day	0.81
0.1253	23	15	5days	0.80
0.1253	46	9	2days	0.81
0.1253	69	5	3days	0.80
0.1253	92	2	4days	0.76
0.1253	92	2	4days	0.80(repeat FID analyses)

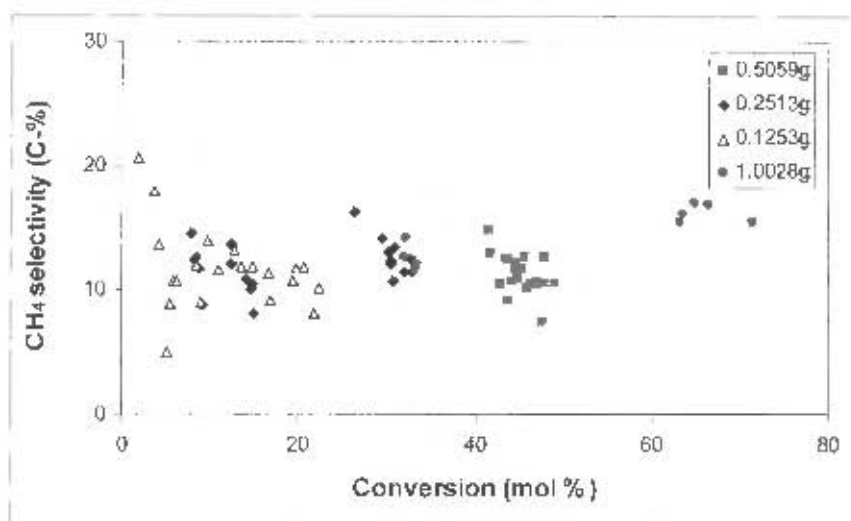


Figure F.17: Influence of CO conversion on the CH₄ selectivity of the unpromoted catalysts. The Fischer-Tropsch syntheses were performed at 220°C, 20bar_a, and H₂/CO=2 in a fixed bed reactor.

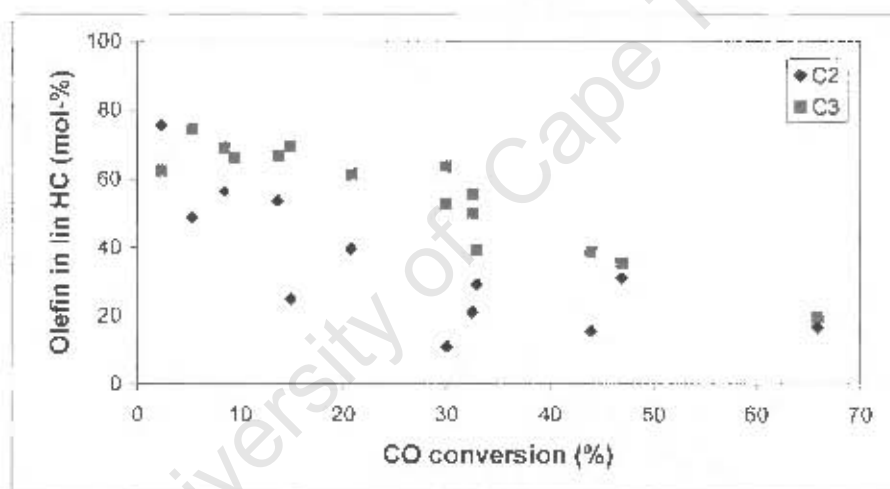


Figure F.18: Influence of CO conversion on the C₂ and C₃ olefin in hydrocarbon fraction selectivity of the unpromoted catalysts. The Fischer-Tropsch syntheses were performed at 220°C, 20bar_a, and H₂/CO=2 in a fixed bed reactor.

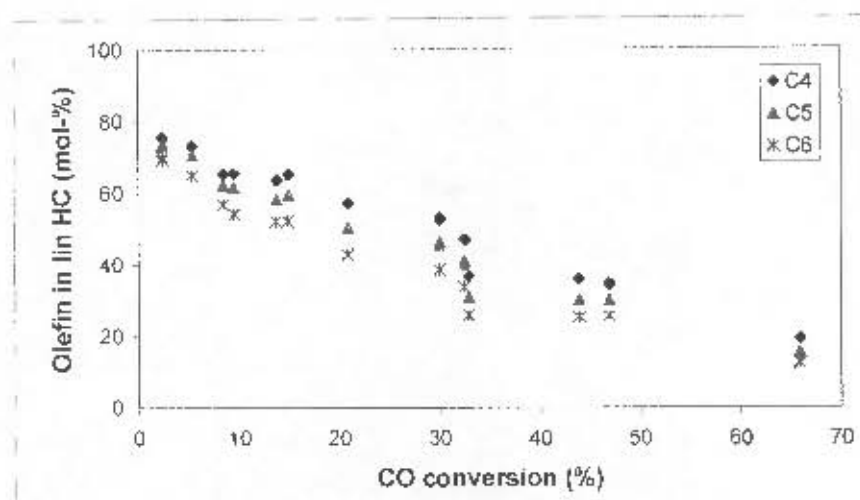


Figure F.19: Influence of CO conversion on the C₄ to C₆ olefins in linear hydrocarbon fraction selectivity of the unpromoted catalysts. The Fischer-Tropsch syntheses were performed at 220°C, 20bar_a, and H₂/CO=2 in a fixed bed reactor.

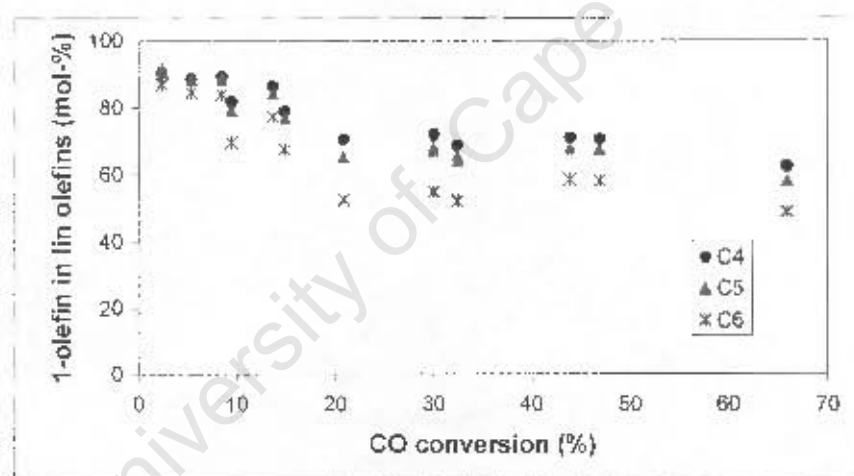


Figure F.20: Influence of CO conversion on the C₄ to C₆ 1-olefins in linear olefin fraction selectivity of the unpromoted catalysts. The Fischer-Tropsch syntheses were performed at 220°C, 20bar_a, and H₂/CO=2 in a fixed bed reactor.

F.2.5 Influence of pressure and temperature on the selectivity

The pressure was decreased to study the effect of pressure on the selectivity. After the pressure decrease, the pressure was increased again to check if time on stream played a role in the selectivities. A decrease in pressure increased the olefin content in the linear hydrocarbon fraction (see Figure F.22). This could be a conversion effect since the conversion decreased (see Figure F.21) with a decrease in the pressure and a decrease in the conversion is expected to increase the olefin content in the linear hydrocarbon fraction. A decrease in pressure decreased the 1-olefin content in the linear olefins fraction (see Figure F.23). This is not due to the decrease in the

conversion since an increase in the 1-olefin content in the linear olefins is expected with a decrease in the conversion. The amount branched hydrocarbons increased with a decrease in the pressure (see Figure F.24). At low pressure steric hindrance may play a smaller role and therefore internal olefins can readsorb and grow further resulting in branched hydrocarbons.

The temperature was increased to study the effect of temperature on the selectivity. A increase in the temperature decreased the C_2 olefin in the linear hydrocarbon fraction, decreased the 1-olefin content in the linear olefins fraction, decreased the chain growth probability in the range C_3 - C_{10} and increased the branched hydrocarbons content in the hydrocarbon fraction, CO conversion and CH_4 selectivity (see Figure F.21, Figure F.25, Figure F.26, Figure F.27 and Table F.3). All the secondary reactions have increased with an increase in the temperature. This may be due to an increase in the conversion as the temperature increased. After the temperature was increased, the temperature was decreased again to check if time on stream played a role in the selectivities. The 1-olefin selectivities for the repeat at 220°C were significantly higher (see Figure F.26). If time on stream did not play a role, then a larger decrease in the 1-olefin selectivities may have been observed with an increase in the temperature.

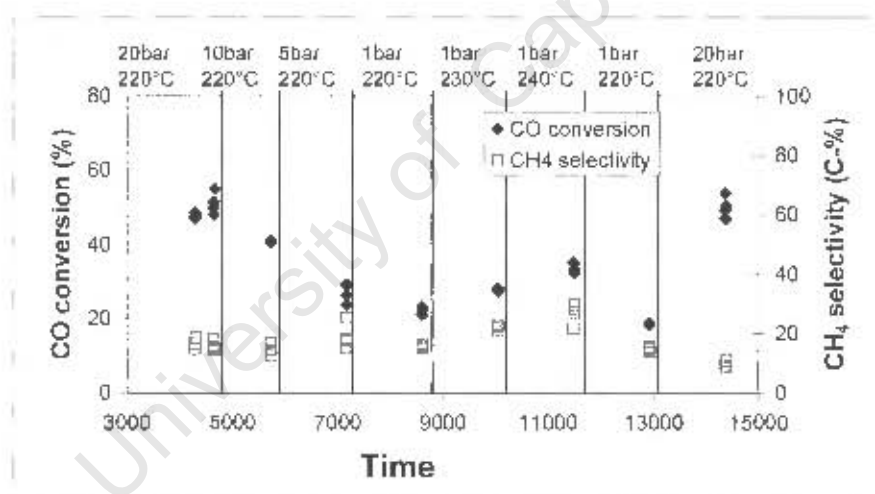


Figure F.21: Influence of pressure and temperature on the CO conversion and CH_4 selectivity. The Fischer-Tropsch syntheses were done with 1g unpromoted catalyst, and a synthesis gas flow rate of 23ml(STP)/min, $H_2/CO=2$ in a fixed bed reactor.

Appendix F

Table F.3: Influence of pressure and temperature on the chain growth probability

Temperature (°C)	Pressure (bar _a)	Chain growth probability (C ₃₋₁₀)
220	20	0.84
220	10	0.84
220	5	0.80
220	1	0.69
230	1	0.59
240	1	0.55
220	1	0.63
220	20	0.82

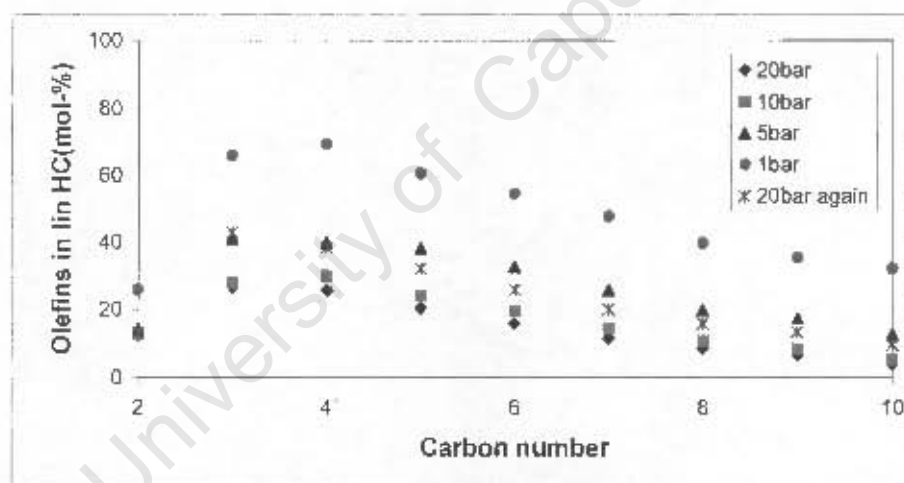


Figure F.22: Comparison of the olefins content in the linear hydrocarbon fraction at different pressures. The Fischer-Tropsch syntheses were performed with 1g unpromoted catalyst, and a synthesis gas flow rate of 23ml(STP)/min, H₂/CO=2 in a fixed bed reactor at 220°C.

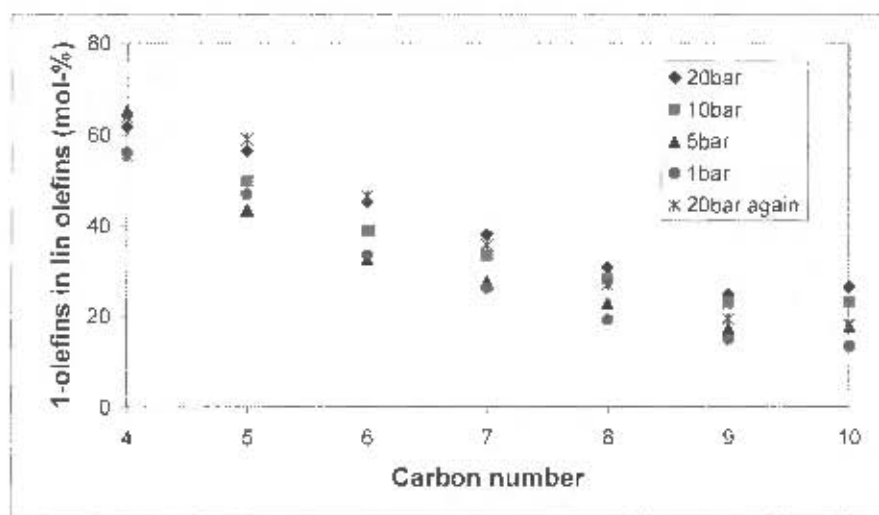


Figure F.23: Comparison of the 1-olefin content in the linear olefins fraction at different pressures. The Fischer-Tropsch syntheses were performed with 1g unpromoted catalyst, and a synthesis gas flow rate of 23ml(STP)/min, $H_2/CO=2$ in a fixed bed reactor at 220°C.

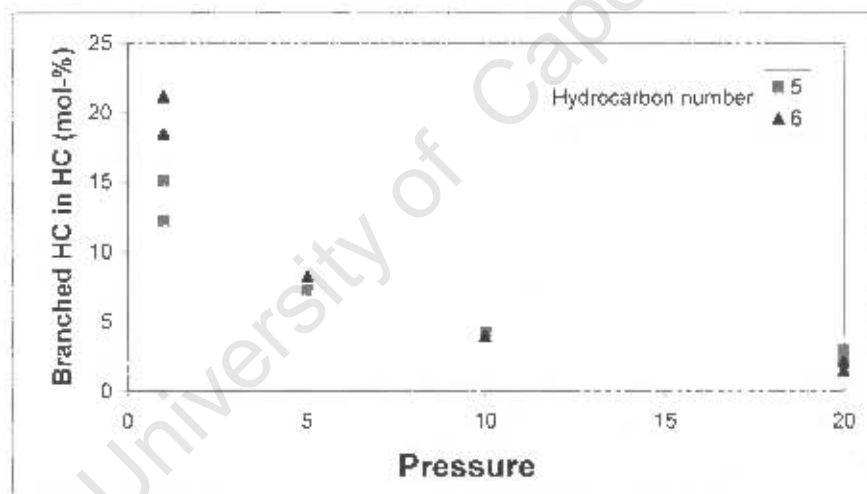


Figure F.24: Comparison of branched material content in the hydrocarbon fraction at different pressures. The Fischer-Tropsch syntheses were performed with 1g unpromoted catalyst, and a synthesis gas flow rate of 23ml(STP)/min, $H_2/CO=2$ in a fixed bed reactor at 220°C.

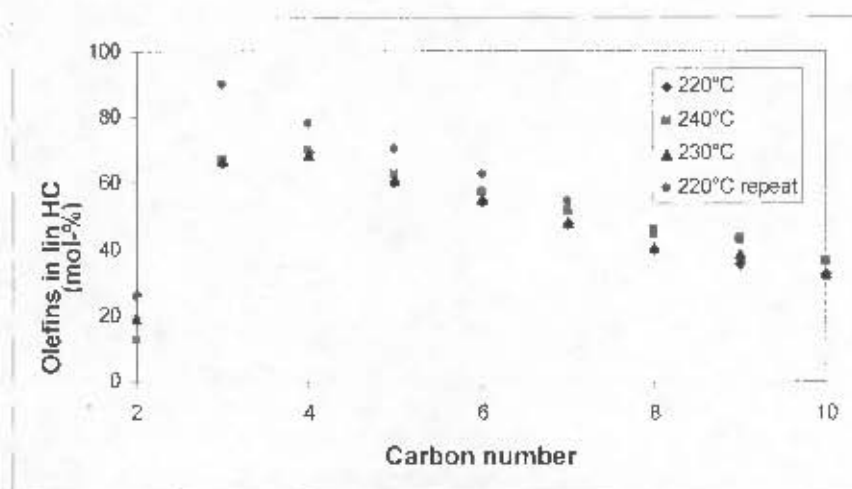


Figure F.25: Comparison of the olefins content in the linear hydrocarbon fraction at different temperatures. The Fischer-Tropsch syntheses were performed with 1g unpromoted catalyst, and a synthesis gas flow rate of 23ml(STP)/min, $H_2/CO=2$ in a fixed bed reactor at atmospheric pressure.

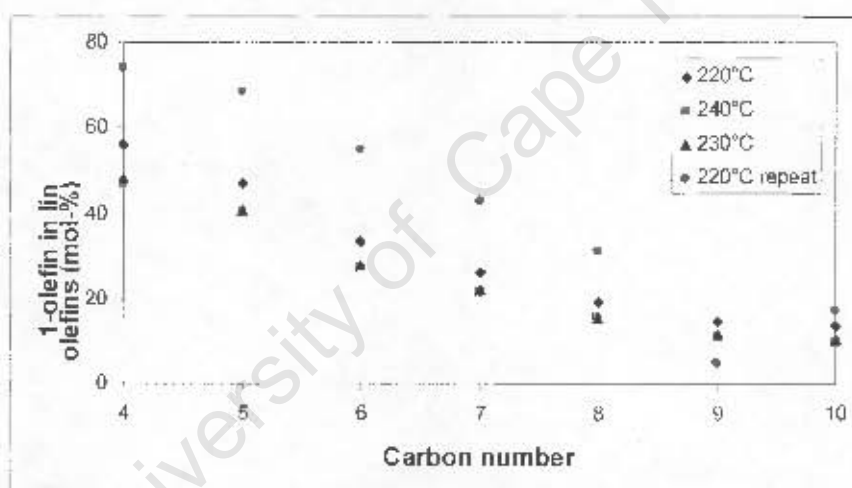


Figure F.26: Comparison of the 1-olefin content in the linear olefins fraction at different temperatures. The Fischer-Tropsch syntheses were performed with 1g unpromoted catalyst, and a synthesis gas flow rate of 23ml(STP)/min, $H_2/CO=2$ in a fixed bed reactor at atmospheric pressure.

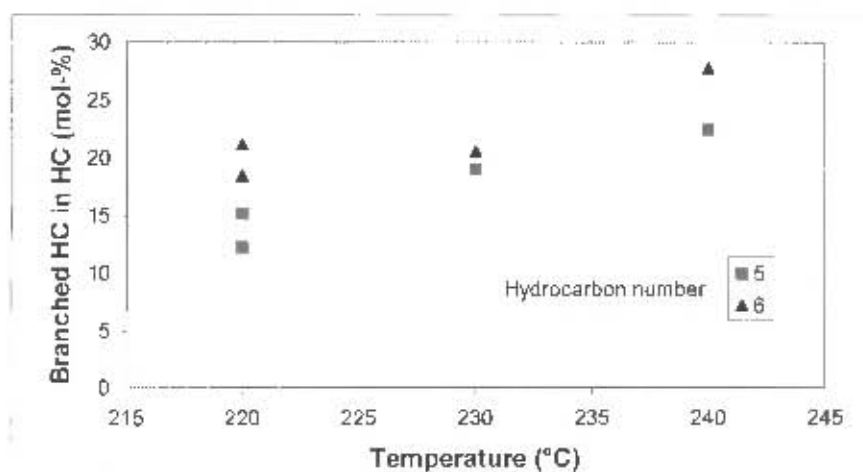


Figure F.27: Comparison of branched material content in the hydrocarbon fraction at different temperatures. The Fischer-Tropsch syntheses were performed with 1g unpromoted catalyst, and a synthesis gas flow rate of 23ml(STP)/min, $H_2/CO=2$ in a fixed bed reactor atmospheric pressure.

Appendix G

Influence of the stirring speed in the reactor

For the Fischer-Tropsch synthesis in the slurry reactor the influence of the stirring speed on the CO conversion was investigated. An increase of the stirring speed from 10% to 20% increased the CO conversion (see Figure H1). A further increase did not change the CO conversion. This indicates that mass transfer of the reagents through a boundary layer around the catalyst particle was present at low stirring speeds. A stirring speed of 30% is adequate at low CO conversions which may not necessarily be the case at higher CO conversions.

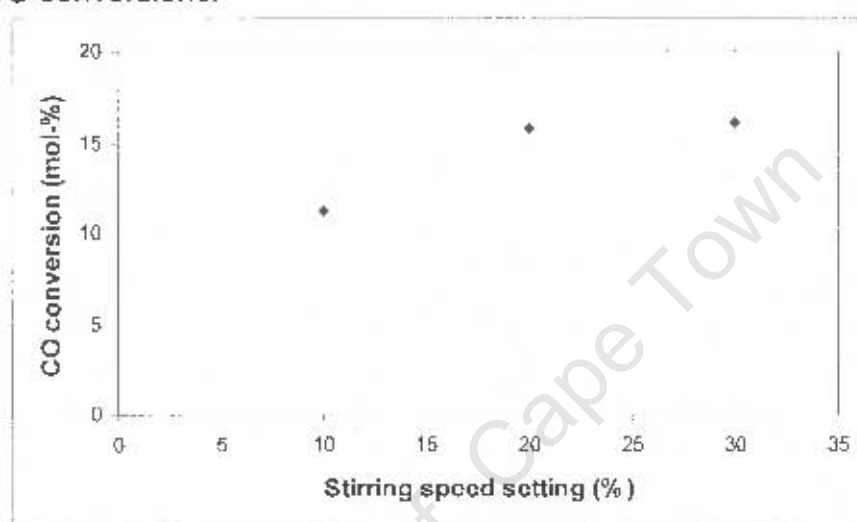


Figure H1: The influence of the stirring speed on the CO conversion (each data point is the average of 4 TCD analyses). The Fischer-Tropsch synthesis was performed at 220°C, 20bar_a, synthesis gas flow rate of 200ml(STP)/min and 10g of unpromoted catalyst.

Appendix H

Relative rate of double bond isomerisation

rate of formation of internal olefin = $k \cdot C_{1\text{-olefin}}$

$$\frac{r_{i\text{-olefin}}}{C_{1\text{-olefin}}} \approx k \frac{Y_{i\text{-olefin}}}{C_{1\text{-olefin}}} \text{ assuming a first order reaction}$$

$$\frac{r_{i\text{-olefin}}}{C_{1\text{-olefin}}} \approx k \left[\frac{\frac{\text{Area}_{i\text{-olefin}} \cdot \dot{n}_{\text{ref}}}{\text{Area}_{\text{ref}}}}{\frac{\text{Area}_{1\text{-olefin}} \cdot \dot{n}_{\text{ref}}}{\text{Area}_{\text{ref}} \cdot \text{Total flow}}}} \right]$$

$$\frac{r_{i\text{-olefin}}}{C_{1\text{-olefin}}} \approx k \frac{A_{i\text{-olefin}}}{A_{1\text{-olefin}}} \times \text{total flow out}$$

Total flow out = $3 - (2 - 1/n)X_{\text{CO}} \cdot V_{\text{CO in}}$ where n is the average carbon number

Total flow calculation:

Compound	In	Out
H ₂	2	$F_{\text{in}} (2 - 2X_{\text{CO}})$
CO	1	$F_{\text{in}} (1 - X_{\text{CO}})$
-(CH ₂)-	0	$1/n F_{\text{in}} X_{\text{CO}}$
H ₂ O	0	$F_{\text{in}} X_{\text{CO}}$
Total flow	3	$F_{\text{in}} (3 - 2 + 1/n) X_{\text{CO}}$

Total flow out = In - Out

Total flow out = $3 - (2 - 1/n)X_{\text{CO}} \cdot V_{\text{CO}}$

Appendix I

With 100 μ m catalyst particles with an average pore diameter of 10nm, Knudsen diffusion may be the operating diffusion mechanism. A diffusion coefficient of $2 \times 10^{-6} \text{ m}^2/\text{s}$ was estimated. For diffusion in liquids a diffusion rate of $\sim 1 \times 10^{-9} \text{ m}^2/\text{s}$ may be assumed [Levenspiel, 1979]. Base on a CO-conversion of 40% at the given reaction conditions ϕ^2 is estimated to be between 3.6×10^{-6} and 7×10^{-3} , i.e. smaller than 0.01. External mass transfer limitations may be neglected based on the Weisz-Prater criterion [Weis and Prater, 1954].

$$\phi^2 = \frac{R^2 (-r_{\text{CO}}) \rho}{9 \cdot C_{\text{CO}} D_{\text{CO}}}$$

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Appendix J

Statistical analyses

The interdependence of the kinetic parameters was tested by calculating $\frac{b}{\sqrt{a}}$.

The ratio of kinetic parameters, 2.9, for the 0 Cat was much smaller than the ratios of 5.6 and 5.3 for the 12 Mo Cat and 9 V Cat respectively. This indicates that the kinetic parameter b increased significantly when molybdenum or vanadium is added to the catalyst.

The rate expression was linearised:

with the y-intercept equal to $-\frac{1}{b}$ and

the slope equal to $\frac{(a \cdot g_{cat})^{0.5}}{b}$ — assuming plug flow behaviour.

The average between the inlet and out partial pressures were used in the kinetic expression. The results of the statistical analyses (regression function of Excel) on the data of the $\text{Co/V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$ and $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ catalysts in the linearised format (see Figure K.1) are shown in Table K.1.

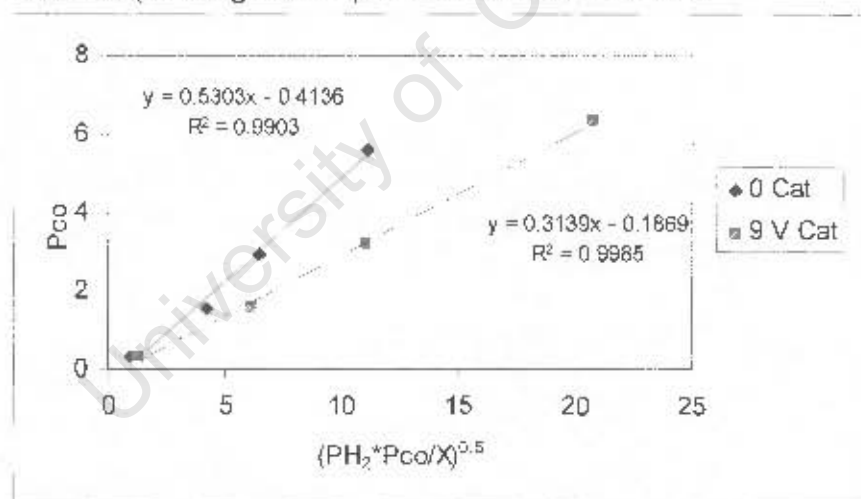


Figure K.1: Data plotted using the linearised rate equation

Table K.1: Statistical analyses of the data plotted using the linearised rate equation

Catalyst	intercept	Standard deviation	Slope	Standard deviation
0 Cat (all)	-0.41	0.25	0.530	0.037
9 V Cat (all)	-0.19	0.11	0.314	0.009
0 Cat (excl 1bar)	-0.91	0.06	0.588	0.007
9 V Cat (excl 1bar)	-0.37	0.01	0.325	0.0004

The standard deviation improves significantly when the 1 bar data are excluded. The effect of one standard deviation on the intercept and slope on

the kinetic parameters a and b (see Table 6.6) may indicate that the kinetic parameter b is not statistically different for the catalysts considered.

Table K.2: Effect of one standard deviation on the intercept and slope on the kinetic parameters a and b (all data included)

Catalyst	a	Range of one standard deviation	b	Range of one standard deviation
0 Cat	0.55	0.48-0.63	2.4	1.5-6.2
9 V Cat	0.94	0.89-1.00	5.4	3.4-12.4

A test of significance were done on the intercept which has a ~20% probability for the nul hypothesis when all the data points were used.

The following hypotheses were set up to test if the intercept of the line on the 0 Cat data is statistically significantly smaller than the intercept of the line on the 9V Cat data:

$$H_0: \mu = -0.19$$

$$H_a: \mu \leq -0.19$$

Test statistics using z (Moore, 1995):

$$z = \frac{\bar{x} - \mu_0}{\sigma / \sqrt{n}}$$

$$z = \frac{-0.41 + 0.19}{0.25/2} = -1.76$$

This corresponds to a P value of 0.0392 (obtained from a statistical table, Moore, 1995). This means that there is 4% probability that the intercept of the line on the 0 Cat data is not statistically significantly smaller than the intercept of the line on the 9V Cat.

Alternatively the following hypotheses could be set up:

$$H_0: \mu = -0.19$$

$$H_a: \mu \neq -0.19$$

Test statistics using z (Moore, 1995):

$$z = \frac{\bar{x} - \mu_0}{\sigma / \sqrt{n}}$$

$$z = \frac{-0.41 + 0.19}{0.25/2} = -1.76$$

$$P = 2P(Z \geq 1.76) = 2(1 - 0.9608) = 0.078$$

There is an 8% probability for the intercept for the 9V Cat to be as small as the intercept of the 0 Cat.