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The transformation of 1,2,4-trimethylbenzene A probe reaction to monitor external surface modifications of HZSM-5?

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Abstract

The transformation of 1,2,4-trimethylbenzene is proposed as a new probe reaction to monitor the catalytic effects of inertisation of the external surface of HZSM-5. The external surface has been modified by coating ZSM-5 crystallites with an inert silicalite shell. At 723 K and a WHSV of 0.6 h^{-1} it has been shown that the isomerisation products 1,2,3-trimethylbenzene and 1,3,5-trimethylbenzene reflect changes in external activity. The disproportionation products, 1,2,4,5-tetramethylbenzene and 1,2,3,5-tetramethylbenzene together are shown to indicate changes in overall activity and shape selective properties of the catalyst sample. The results correlate with those observed for the reaction of 1,3,5-triisopropylbenzene and n-hexane cracking.

Keywords: 1,2,4-Trimethylbenzene; HZSM-5; Probe reaction; External surface modification; Shape selectivity

1. Introduction

Examples of shape selective catalysis in zeolites were described more than 30 years ago by Weisz and coworkers [1–3]. Csicsery [4] categorised shape selectivity as follows:

(i) Reactant selectivity occurs when only a fraction of reactant molecules are small enough to diffuse through the catalyst pores.

(ii) Product selectivity occurs when some of the products formed within the pores are too bulky to diffuse out as observed products.

(iii) Restricted transition-state selectivity occurs when certain reactions are prevented because the corresponding transition state would require more space than is available in the cavities. Neither reactant nor potential product molecules are prevented from diffusing through the pores. Reactions requiring smaller transition states proceed unhindered.

Recently several authors [5–8] have suggested the activity of the external surface of the ZSM-5 zeolite as the cause of non-selective transformations. It has been shown that the removal, deactivation or coating of external acid sites improves shape selective properties of ZSM-5 [8,9]. Many techniques have been applied to modify the external surface of zeolites [10–14].

Namba et al. [12] suggested the conversion of

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1,3,5-triisopropylbenzene to monitor the external surface activity of HZSM-5. An alternative reaction, the conversion of 1,3,5-trimethylbenzene at 723 K was proposed by Gilson and Derouane [15]. Both reactants are too large to enter the pores of ZSM-5, therefore the rate of reactant consumption correlates directly with the activity of the external surface. The minimum Van der Waals diameters of some aromatic molecules are listed in Table 1.

However, it would be convenient to have a model reaction which reveals information about activity of the external surface and on shape selective properties simultaneously. The conversion of 1,2,4-TMB with the same kinetic diameter as *m*-xylene appears promising. Kikuchi et al. [18] have reported four competing reactions over acid catalysts: isomerisation, disproportionation, dealkylation and coke formation. In this reaction the reactant and the products are critically sized for the ZSM-5 pore system (Table 1). It may therefore be expected that this reaction is a sensitive test for shape selective properties and the external surface activity.

The mechanism of alkylbenzene disproportionation over ZSM-5 is still a matter of debate. Three different disproportionation mechanisms have been postulated viz. alkyl transfer [19], dissociative [20] and diphenylalkane mechanism [6].

Contradictory results in the reaction of 1,2,4-TMB over HZSM-5 have been observed. Gnep et al. [16] observed no transformation of 1,2,4-TMB at 623 K in a hydrogen atmosphere over ZSM-5. Meshram et al. [21] concluded that the transalkylation of trimethylbenzenes with toluene occurs mainly on the external surface of ZSM-5. In the alkylation of 1,2,4-TMB with methanol 1,2,3-TMB and 1,3,5-TMB (isomerisation products), 1,2,3,4-TeMB and 1,2,3,5-TeMB (alkylation products) and pentamethylbenzene (polyalkylation product) are reported as being produced only by reaction on the external surface of HZSM-5 crystallites [22]. However, trimethylbenzenes are not excluded from penetrating the intracrystalline pore space of ZSM-5 since a diffusion coefficient for 1,3,5-TMB of $D = 10^{-12}$ cm^2/s at 588 K has been determined [23,24]. 1,3,5-TMB is the largest of the three TMB-isomers and thus 1,2,4-TMB and 1,2,3-TMB can enter the intracrystalline pore space. However, if intracrystalline diffusion limitations are extremely high the activity of the intracrystalline pore space may be negligible compared to the activity of the external surface. This may be the case when 1,3,5-TMB is reacted over ZSM-5 in order to probe the catalytic activity of the external surface as suggested by Gilson and Derouane [15].

This paper discusses the transformation of 1,2,4-TMB over HZSM-5 and HZSM-5* in which the external surface has been inertised using a silicalite shell. The objective was to relate the rates of product formation to the activity of the external surface and the shape selective properties of HZSM-5. n-Hexane and 1,3,5-TiPB cracking were carried out to characterise the external activity and the overall activity.

Table 1
Minimum Van der Waals diameters of alkyl aromatics [16,17] and pore diameters of ZSM-5

Alkyl aromatic	Abbreviation	Minimum Van der Waals diameter (Å)
m-Xylene		7.4
1,2,3-Trimethylbenzene	1,2,3-TMB	7.9
1,2,4-Trimethylbenzene	1,2,4-TMB	7.4
1,3,5-Trimethylbenzene	1,3,5-TMB	8.6
1,2,3,4-Tetramethylbenzene	1,2,3,4-TeMB	7.9
1,2,3,5-Tetramethylbenzene	1,2,3,5-TeMB	8.6
1,2,4,5-Tetramethylbenzene	1,2,4,5-TeMB	7.4
1,3,5-Triisopropylbenzene	1,3,5-TIPB	9.4
ZSM-5, straight		5.2 × 5.7
Sinusoidal		5.3 × 5.6
Intersection cavities		≈9

2. Experimental

2.1. Materials

1,2,4-trimethylbenzene (purity >98%), 1,3,5-triisopropylbenzene (purity >97%) and n-hexane (purity >96%) were used without further purification. The parent HZSM-5 was prepared according to Argauer and Landolt [25]. The synthesis conditions were the same as described in Webers work

[26], except that the synthesis time was 24 h instead of 72 h.

2.2. Coating of HZSM-5

HZSM-5 was coated according to the method described by Rollmann [13].

This procedure provides a crystalline zeolite having an aluminum free outer shell of crystalline SiO_2 (HZSM-5*). The shell of SiO_2 has the same crystal structure as ZSM-5. To obtain this modification 4 g of the parent zeolite were reimmersed into a secondary synthesis mixture which contained no $Al(OH)_3$, but was otherwise of identical composition to the primary synthesis mixture. The sample was prepared using non-detemplated and non-ion-exchanged parent crystals. The modification synthesis time was 72 h at 160°C. During the secondary synthesis the catalyst mass increased 4.5 times. All samples were washed and dried, detemplated and ion-exchanged after modification.

2.3. Characterization of physicochemical properties

Powder X-ray diffractometry was done using Cu-Kα radiation. Electron micrographs were obtained using a Cambridge S200 Scanning Electron Microscope (SEM). The bulk Si/Al ratio was determined by Atomic Absorption Spectroscopy (AA) using a Varian DS-15 spectrometer.

2.4. Catalytic experiments

The cracking of 1,3,5-triisopropylbenzene, the cracking of n-hexane and the conversion of 1,2,4-trimethylbenzene were carried out in a downflow tubular reactor at atmospheric pressure. The catalyst was diluted with 5 g quartz sand and calcined over night at 773 K in air. The mass of HZSM-5 and HZSM-5* was 137 mg and 500 mg, respectively. This ratio of catalyst masses was based on AA results to keep the number of aluminum constant. The reactants were fed by passing nitrogen (99.99%) as carrier gas through a thermostated saturator. The reaction conditions are listed in Table 2. Reaction products were sampled using evacuated glass ampoules [27] and analyzed by gas chromatography using a Supelcowax® 10 fused silica capillary column (30 m × 0.2 mm) and a PONA column (50 m × 0.2 mm). Cyclohexane of 99.5% purity was used as internal standard.

Table 2
Reaction conditions

Parameter	n-C6	1,3,5-TIPB	1,2,4-TMB
Temperature (K)	811	543	723
Pressure (bar)	1	1	1
$P_{reactant}$ (mbar)	100	1.5	13
WHSV [a] (h^{-1})	5.4	0.35	0.6
Time-on-stream (min)	10	10	0–300

[a] The WHSVs are based on the mass of parent catalyst for all experiments, i.e. constant Al content.

3. Results and discussion

3.1. Catalyst characterization

The Si/Al ratio as measured by AA increased from 26 to 100 due to the formation of a silicalite layer. SEM photographs showed that there was no amorphous material. The crystal size of the parent ranged from 1–3 μm. A change in crystal size due to the modification process could not be detected by means of SEM. A theoretical increase of 60% of the crystal diameter can be calculated, if it is assumed that all the material is deposited on the parent crystals, all crystals have grown with the same mass ratio and all crystals have a diameter of 2 μm. XRD verified that the crystals observed were in fact ZSM-5.

3.1.1. Cracking of 1,3,5-TIPB

When comparing the cracking of 1,3,5-TIPB over HZSM-5 and HZSM-5* it was found that the conversion decreased from 90% to 10% respectively as shown in Table 3. As this reaction can only occur on the external surface [12] this indicates that the external surface has been deactivated, however not to the expected 100% inertisation. A blank run showed that the residual conversion observed on HZSM-5* was not due to thermal cracking. Alternatively, trace quantities of Al may have either been incorporated into the inert silical-

Table 3
Catalyst activities as measured by conversion at equal temperature and WHSV for each reaction

Reactant	Conversion [a] over HZSM-5, (C%)	Conversion [a] over HZSM-5*, (C%)	Ratio HZSM-5*/ HZSM-5
n-C6	25	12	0.48
1,3,5-TIPB	90	10	0.11
1,2,4-TMB	23	5	0.22

[a] Conversion after 10 min of time on stream.

ite shell or migrated from HZSM-5 seeds during or after synthesis. It is also possible that dissolution of the HZSM-5 seeds during the secondary synthesis could provide Al for the incorporation in the silicalite layer. Nevertheless, a significant change was observed in the activity. If a first order rate equation can be assumed for this reaction, the rate constant decreased by a factor of 22. This is to say that there is 22 times less active external surface on HZSM-5* when compared to HZSM-5. It was therefore assumed that the external surface of HZSM-5* can be considered deactivated.

3.1.2. Cracking of n-hexane

Table 3 shows that the conversion of hexane was reduced from 25% over HZSM-5 to 12% over HZSM-5*. This represents a decrease in the first order rate constant by a factor of 2, which is less than the decrease observed for 1,3,5-TIPB cracking. The hexane cracking reaction is widely used to measure relative activities of cracking catalysts [28]. For HZSM-5 it has also been shown that diffusion limitations are negligible for crystal sizes smaller than 40 μm at 773 K [29–31]. The results suggest that this was not the case for the 3μm crystals of the modified sample in this work, as it is highly unlikely that the external surface can contribute 50% to the observed reaction rate in HZSM-5. In addition to that the number of aluminum atoms was kept the same in both catalyst beds. Therefore a decrease in the total activity is not due to a lower number of aluminum atoms. It is of course possible that the growth of a silicalite layer over the HZSM-5 seeds may not be as defect free and crystalline as would be expected. Thus it is possible that the silicalite layer may introduce diffusional resistances which are influencing the reaction in HZSM-5*.

3.2. Transformation of 1,2,4-TMB

Molecules with a minimum Van der Waals diameter larger than the pore diameter are not necessarily excluded from the pore system. However, when comparing the molecule sizes in Table 1, it is expected that the diffusivity decreases in the sequence:

$$m\text{-xylene} = 1,2,4\text{-TMB} = 1,2,4,5\text{-TeMB} > 1,2,3\text{-TMB} = 1,2,3,4\text{-TeMB} > 1,3,5\text{-TMB} = 1,2,3,5\text{-TeMB}.$$

It would therefore be expected that the rate of product formation in the conversion of 1,2,4-TMB may be used to distinguish between products formed on the external surface to those formed within the pores. Thus this reaction might form the basis for the evaluation of changes in activity and selectivity observed during inertisation of the external surface of HZSM-5. It must be pointed out that all these molecules will fit into the pores of ZSM-5, particularly in the channel intersections, and thus it is possible to make all the reaction products within the pore system. However, the largest of these products cannot diffuse or diffuse very slowly such that if a product is observed it will have to have been formed on the external surface. Additionally large molecules formed within the pores will have to undergo further reaction to smaller products before they are observed in the product stream.

Figs. 1 and 2, which plot the rates of formation of 1,2,3-TMB, 1,3,5-TMB, 1,2,3,5-TeMB and 1,2,4,5-TeMB, show that both catalysts deactivate with time on stream at 723 K. However, the deactivation is slow enough to allow reproducible results. Table 3 shows that the conversion of 1,2,4-TMB is reduced from 23 to 5% over HZSM-5 and HZSM-5* respectively notwithstanding that the number of aluminum atoms in the catalyst bed was kept constant. If ZSM-5 would not show any significant diffusion or external surface effects for this reaction, a decrease in conversion similar

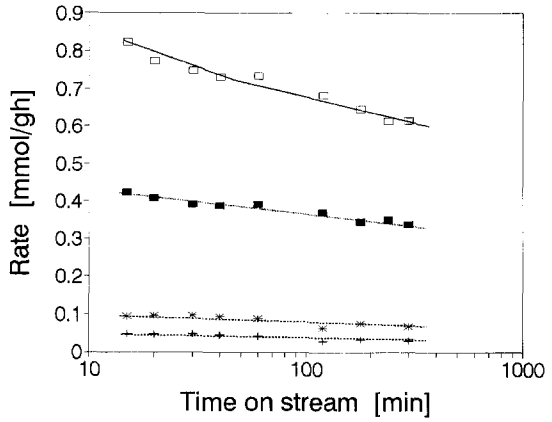

Fig. 1. Rates of formation of the respective products versus time on stream in the reaction of 1,2,4-TMB over HZSM-5 and HZSM-5* at $T=723$ K, $p(1,2,4\text{-TMB})=13$ mbar and WHSV = 0.6 h^{-1}. ■, 1,2,3-TMB/HZSM-5; □, 1,3,5-TMB/HZSM-5; +, 1,2,3-TMB/HZSM-5*; ×, 1,3,5-TMB/HZSM-5*.

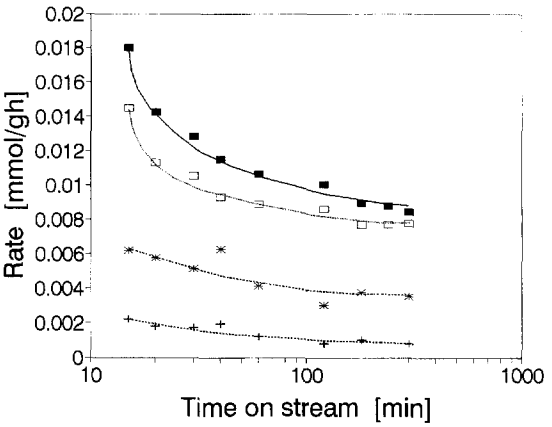

Fig. 2. Rates of formation of the respective products versus time on stream in the reaction of 1,2,4-TMB over HZSM-5 and HZSM-5* at $T=723$ K, $p(1,2,4\text{-TMB})=13$ mbar and WHSV = 0.6 h^{-1}. ■, 1,2,3,5-TeMB/HZSM-5; □, 1,2,4,5-TeMB/HZSM-5; +, 1,2,3,5-TeMB/HZSM-5*; ×, 1,2,4,5-TeMB/HZSM-5*.

to that of hexane cracking might have been expected.

In the isomerisation reaction (Fig. 1), 1,3,5-TMB is formed over both catalysts with a higher rate than 1,2,3-TMB. This could be explained if the distribution of TMB-isomers would be thermodynamically controlled, since 1,3,5-TMB is the thermodynamically favoured isomer. However, the distribution of TMBs is not at equilibrium, thus the rate of formation is kinetically controlled. In that case however, the shape selective, intracrystalline pore space would be expected to isomerise 1,2,4-TMB rather into 1,2,3-TMB than into 1,3,5-TMB, as 1,2,3-TMB has a smaller minimum Van der Waals diameter than 1,3,5-TMB. Since this is not the case, it may be concluded that the activity of the intracrystalline pore space in the isomerisation reaction is negligible. Thus the isomerisation reaction of 1,2,4-TMB occurs primarily on the external surface of HZSM-5 crystallites.

Fig. 2 shows that amongst the disproportionation products 1,2,3,5-TeMB is formed with the highest rate over HZSM-5. However, when the external surface is coated 1,2,4,5-TeMB is formed with the highest rate. According to the minimum Van der Waals diameters shown in Table 1 the formation of 1,2,4,5-TeMB is favoured within the pore system. Additionally, the primary disproportionation reaction is far from equilibrium for both catalysts, while the consecutive isomerisation reaction between the TeMB isomers is close to equilibrium over HZSM-5 but *not* over HZSM-5*. It is therefore possible that the 1,2,4,5-TeMB formed within the pore system is consecutively isomerised on the external surface. Therefore the formation of 1,2,3,5-TeMB occurs mainly on the outside while the formation of 1,2,4,5-TeMB occurs to a significant extent within the pores of HZSM-5.

To compare the influence of the silicalite coating on each product a rate ratio RR(i) is formed, which is defined by Eq. 1:

$$\mathrm{RR}(i)=\frac{\text{rate of formation of product } i \text{ over HZSM}-5^*}{\text{rate of formation of product } i \text{ over HZSM}-5}\cdot 100\% \quad (1)$$

Figs. 3 and 4 show that the ratio RR(i) decreased by a factor of 10, except for 1,2,4,5-TeMB which decreased by a factor of 2. These results may be explained by considering the two extreme cases of 1,3,5-TIPB and n-hexane cracking reactions. The reduction in the 1,2,3-TMB, 1,3,5-TMB and 1,2,3,5-TeMB rate of formation is similar to that observed for the

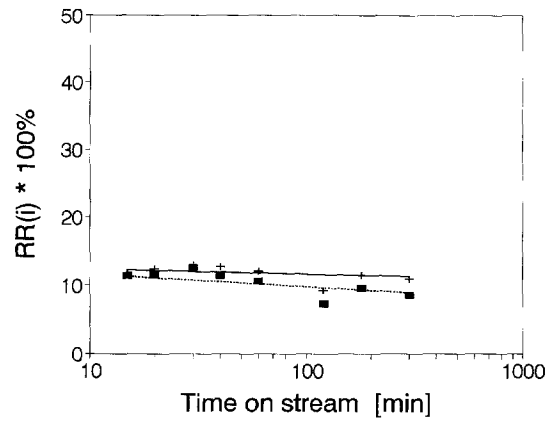

Fig. 3. Rate ratio RR(i) versus time on stream at $T=723$ K, p(1,2,4-TMB)=13 mbar and WHSV=0.6 h^{-1}. ■, 1,2,3-TMB; +, 1,3,5-TMB.

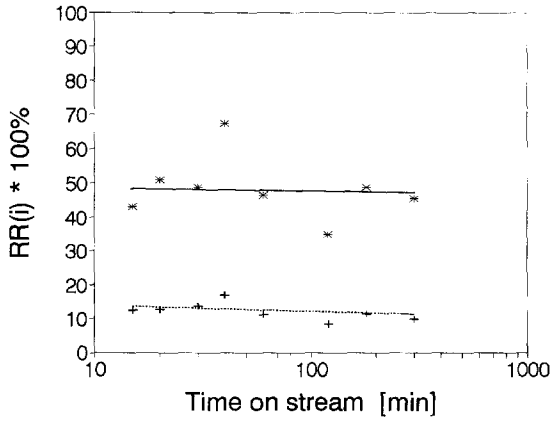

Fig. 4. Rate ratio RR(i) versus time on stream at $T=723$ K, p(1,2,4-TMB)=13 mbar and WHSV=0.6 h^{-1}. +, 1,2,3,5-TeMB; ×, 1,2,4,5-TeMB.

1,3,5-TIPB reaction which occurs only on the external surface. Thus 1,2,3-TMB, 1,3,5-TMB and 1,2,3,5-TeMB originate mainly from the external surface. Therefore, these reaction products can be used to indicate how successful inertisation of the external surface has been. In the case of 1,2,4,5-TeMB, the decrease in the rate of formation is similar to that obtained for n-hexane cracking and proves that the formation of 1,2,4,5-TeMB occurs mainly within the pores. Thus 1,2,4,5-TeMB can be used to probe the activity of the catalyst after modification.

It may be argued that the isomerisation products are small enough to show similar behaviour to 1,2,4,5-TeMB. However, the rate of formation of isomerisation products is of the order of 50 times greater than the disproportionation products. All the 1,2,4-TMB reaction molecules are large enough to undergo diffusion restriction within the ZSM-5 pores. Thus fast reactions occurring within the pores will be severely diffusion limited and thus the products of this reaction come mainly from the external surface. Note: it is possible that the isomerisation reaction could still be faster than disproportionation within the pores, but this contribution to the overall reaction is negligible and not quantified. It is due to the slow formation of TeMB isomers that the internal surface contributes significantly to the overall rate of formation of 1,2,4,5-TeMB.

Thus the conversion of 1,2,4-TMB over HZSM-5 presents a good model reaction for evaluating the effect that inertisation of the external surface area has on the performance of the catalyst. With this reaction it is possible to probe the effectiveness of the inertisation, the change in external activity, the change in overall activity *and* the change in selectivity. Activities of catalysts however, cannot be compared simply using rates of product formation. Due to consecutive reactions rates of product formation might decrease with increasing activity of a catalyst. A reasonable measure to compare activities is the rate of a primary reaction at equal reactor conditions. In order to correlate reaction rates with rates of product formation it is necessary to minimise consecutive reactions. Therefore it is clear that there is a need to understand the reaction network. This will be the subject of a subsequent paper.

4. Conclusions

It has been shown that the conversion of 1,2,4-TMB can be used to probe the effects of inertisation of the external surface of HZSM-5. The isomerisation products are shown to reflect changes in external activity, while the disproportionation products, 1,2,4,5-TeMB and 1,2,3,5-TeMB together indicate changes in overall activity and selectivity. The results are shown to correlate

well with those observed for the reactions of 1,3,5-TiPB and n-hexane cracking over HZSM-5.

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