Effect of the Crystal Size on the Activity of ZSM-5 Catalysts in Various Reactions

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ABSTRACT

To determine the effects of the crystal size of ZSM-5 catalysts on the reaction behaviour, eight ZSM-5 zeolites of various crystal size were synthesized and used in three different reactions. This showed a decrease in conversion with increasing crystal size for the catalysts synthesized with tetrapropylammonium bromide as the template. This leads to the conclusion that the volume of the zeolite crystals is not fully utilized. A possible reason, apart from the gradient of the Si/Al ratio in the zeolite crystal, is diffusion control, which may be expected from theoretical calculations.

INTRODUCTION

ZSM-5 was first synthesized in 1972 [1] and has since found various interesting industrial applications as a catalyst, including dewaxing, xylene isomerization, disproportionation of toluene and alkylation reactions. It is particularly suitable for the MTG (methanol to gasoline) process developed by Mobil Oil and its MTO (methanol to olefins) variant [2].

Apart from its high activity, ZSM-5 catalyst additionally has the advantage of a higher selectivity in the above reactions compared with conventional catalysts. Its low deactivation tendency compared with other zeolite types is another important factor. It is therefore a catalyst of particular interest, for which new applications in the organic intermediates field are being sought.

Earlier investigations on mordenite catalysts by a combination of secondary ion mass spectroscopy (SIMS) with reaction engineering measurements showed that the conversion of n-hexane proceeds preferentially in zones close
to the surface of the primary crystallites [3,4]. This work was intended to clarify whether the locus of the reaction in a ZSM-5 catalyst is also predominantly located in the regions close to the surface of the crystallites. In contrast to the publications quoted above, investigations were carried out on ZSM-5 catalysts of various crystal size. If the assumption that the locus of the reaction is located close to the surface of the crystallites is correct, it would be expected that large crystals would show lower activity than small crystals.

There are two different possible causes of the reaction proceeding preferentially in the regions close to the surface of the crystallites. On the one hand, the inhomogeneous structure of the crystallite (for example, the gradient of the Si/Al ratio) may be responsible. It is also conceivable that diffusion in the channels of the zeolites is impeded to such an extent that the reaction is controlled by diffusion.

Some studies have already been described in which the effect of the crystallite size on the catalyst activity was investigated. Haag et al. [5] found, on ZSM-5 catalysts at \(527^\circ\)C, no dependence of the cracking rate of n-hexane on the crystal size. Doelle et al. [6] reacted dimethyl ether at \(302^\circ\)C and found a Weisz number of 0.7, which indicates that intracrystalline diffusion has no effect on the reaction rate. The reaction rate also proved to be independent of the crystal size. Hölterich and Rieker [7] studied the cracking of n-hexane and 3-methylpentane on zeolite crystals of various size and found no indications of inhibition by diffusion. In contrast, Rajagopalan et al. [8] observed inhibition by diffusion in the cracking of West Texas heavy gas oil at \(500^\circ\)C on NaY with a particle size of 0.65 \(\mu\)m. Ratnasamy et al. [9] reported a decrease in ZSM-5 activity in xylene isomerization at \(300^\circ\)C with increasing crystal size and explained this observation by a diffusion theory in accordance with Wei [10] and Theodore and Wei [11].

To investigate the effect of crystal size on the activity of ZSM-5 catalysts, the hydrocracking of n-hexane, conversion of methanol to lower olefins and amination of methanol were carried out on eight catalysts of various crystal size. The three reactions differ in several important respects. Hexane conversion is a cracking reaction that is accompanied to a certain extent by the formation of carbonaceous deposits on the catalyst. In the conversion of methanol to lower olefins, a chain build-up takes place. In the amination of methanol with ammonia, two reactants are used, both of which can interact with the acidic centres of the zeolite. All three reactions are important because of their potential industrial applicability.

Since the first commercialization of zeolitic cracking catalysts in fluidized catalytic cracking (FCC) plants in 1964, industrial research is now concentrated mainly on an increase in selectivity with respect to the motor fuel fraction, on a reduction in coke formation and on an improvement in the
TABLE 1

Synthesis conditions and crystal properties of the prepared catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Synthesis run</th>
<th>SiO$_2$/Al$_2$O$_3$</th>
<th>OH$^-$/SiO$_2$</th>
<th>Template</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>29</td>
<td>0.683</td>
<td>TPAOH</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>K2</td>
<td>75</td>
<td>0.213</td>
<td>TPAOH</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>K3</td>
<td>59</td>
<td>0.14</td>
<td>TPAOH</td>
<td>122</td>
<td></td>
</tr>
<tr>
<td>K4</td>
<td>29</td>
<td>0.683</td>
<td>TPAOH</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>K5</td>
<td>29</td>
<td>0.683</td>
<td>TPAOH</td>
<td>81</td>
<td></td>
</tr>
<tr>
<td>K6</td>
<td>59</td>
<td>0.1</td>
<td>TPAOH</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>K7</td>
<td>140</td>
<td>0.1</td>
<td>TPAOH</td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>K8</td>
<td>140</td>
<td>0.1</td>
<td>TPAOH</td>
<td>88</td>
<td></td>
</tr>
</tbody>
</table>

regeneration capacity of the catalysts. The cracking catalysts used are mainly wide-pore Y-zeolites in an amorphous silica/alumina matrix and also ZSM-5 catalysts.

As a depletion of the crude oil reserves must be expected in the long term, the Mobil process for converting methanol into hydrocarbons may play an important role in the future in safeguarding raw material supplies. In this process, methanol is converted on zeolitic catalysts, especially ZSM-5. With suitable selection of the reaction conditions and certain catalyst modifications, C$_2$–C$_4$ olefins are obtained preferentially.

In the field of organic intermediates production, it is hoped that the use of suitable zeolitic catalysts will improve the selectivity towards the desired products. Thus, in the amination of methanol to give mono-, di- and trimethylamine on conventional catalysts at high conversions, the undesirable trimethylamine is formed preferentially. By using shape-selective zeolite catalysts, it is hoped to favour the lower amines.

EXPERIMENTAL

The ZSM-5 zeolites were synthesized in a steel autoclave in our laboratories. The silicon source used was Ludox AS 40 (DuPont). Tetrapropylammonium ions were made available as the structure-directing cations in the form of the hydroxide (Fluka, catalysts K1, K4 and K5) or bromide (synthesized from tripropylamine and 1-bromopropane, Merck, catalysts K2, K3 and K6-K8). The synthesis charges also differed in the aluminium compound used, in the SiO$_2$/Al$_2$O$_3$ and OH$^-$/SiO$_2$ ratios of the gel used (Table 1) and in the addition of different alkali or alkali earth metal ions.

The shape and size of the crystals was determined from scanning electron micrographs (Philips Model 505). The crystals are usually prismatic and in
most instances show twinning or multiple twinning. Sometimes there is rounding of the faces, which can proceed to such an extent that spherical crystals are formed. Crystal size measurements were also carried out with a Coulter Counter TA II and, by Merck in Darmstadt, by means of laser light diffraction (Helos apparatus from Sympatec) (Table 2).

To decompose the tetrapropylammonium ions, the synthesized zeolites were calcined for 2.5 h at 540°C. They were then exchanged three times for 24 h with 5% ammonium nitrate solution under reflux and then calcined again at 500°C for 8 h each time. The volume composition was analysed after wet extraction by titrimetry. The crystallinities were determined from X-ray powder diagrams (Stoe PSD two-circle powder diffractometer) and referred to a Mobil standard (=100%) made available to us (Tables 1 and 3). The test reactions were carried out in conventional fixed-bed reactors with 0.52 g of zeolite catalyst.

In the conversion of n-hexane on ZSM-5 catalysts, mainly C₁-C₅ cracking products are formed. To a smaller extent (<10%), n-hexane is also isomerized to dimethylbutanes and methylpentanes, and hydrocarbons with more than six carbon atoms are formed. In addition, carbonaceous deposits (coke) remain on the catalyst. The product mixture was separated in a gas chromatograph with a 100-m capillary column (squalane) with flame ionization detection.

The conversion of methanol to olefins gives a very wide product spectrum. Apart from lower olefins, alkanes and aromatics are observed. The products were analysed by gas chromatography using a two-column arrangement (80 cm OV-275 and 100 m squalane).

The amination of methanol leads above all to mono-, di- and trimethyl-
amine, with dimethyl ether and olefins as by-products. The mixture was separated by gas chromatography (25 m Carbowax 600 doped with potassium hydroxide).

All ZSM-5 catalysts used for the reactions were investigated by SIMS in the Surface Physics Department of Dornier System GmbH, Friedrichshafen, F.R.G. In this method, the samples are bombarded with argon ions (3 keV, 5·10^{-9} A on a 10 nm² spot) under an angle of 60°. The secondary ions produced were analysed by a quadrupole mass spectrometer (Balzers QMG 511) with a Balzers QRV 102 detector. The residual gas pressure in the SIMS apparatus was a few 10^{-9} mmHg during the measurement. The charging of the sample which occurs with the zeolites was compensated for by secondary electrons.

RESULTS AND DISCUSSION

Characterization of the ZSM-5 catalysts

The Si/Al atomic ratios in the volume, determined by titrimetry after digestion of the zeolites, are compared in Table 3 with the Si/Al atomic ratios determined on the crystal surface by SIMS analysis and with the average Si/Al atomic ratios determined at depths of 20 and 40 nm. In spite of considerable differences in the volume ratio (between 10 and 165), only slight differences in this ratio are seen at the surface (between 9 and 22). Generally, the ZSM-5 zeolites synthesized with tetrapropylammonium bromide (TPABr) as the template have a relatively high Si/Al ratio in the volume, whereas the zeolites synthesized with tetrapropylammonium hydroxide (TPAOH) as the template show markedly lower values. These results again indicate a considerable pH dependence of the zeolite synthesis and to various crystallization mechanisms when different components and templates are used [10-15]. The zeolites synthesized with TPABr generally also reach higher crystallinities than those synthesized with TPAOH.

Depth profiles of the Si/Al ratio, recorded by SIMS, show a slight decrease in the ratio in the region from the surface down to a depth of 100 nm for the zeolites synthesized with TPAOH, whereas a slight or even a considerable increase is observed for the zeolites synthesized with TPABr. The Si/Al ratios determined at depths of 20 and 40 nm were averaged and correlated with the surface value (Table 3). This quotient is less than 1 for the zeolites synthesized with TPAOH, but it is sometimes considerably above 1 for the zeolites synthesized with TPABr. This behaviour also indicates different crystallization mechanisms. The depth dependence of the Si/Al ratio has also been described previously [15-17], and such a dependence was observed in some instances. Depending on the synthesis charge, the Si/Al ratio can then decrease or increase towards the crystal centre.
TABLE 3

Si/Al atom ratios for the catalysts used

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Crystallite diameter (μm)</th>
<th>Si/Al (volume)</th>
<th>Si/Al (20–40 nm)</th>
<th>Si/Al (surface)</th>
<th>Si/Al (20–40 nm)/(Si/Al (surface))</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>14.8</td>
<td>13</td>
<td>12.1</td>
<td>14.2</td>
<td>0.85</td>
</tr>
<tr>
<td>K2</td>
<td>10.5</td>
<td>53</td>
<td>20.1</td>
<td>9.2</td>
<td>2.18</td>
</tr>
<tr>
<td>K3</td>
<td>21.0</td>
<td>165</td>
<td>20.2</td>
<td>17.2</td>
<td>1.17</td>
</tr>
<tr>
<td>K4</td>
<td>5.4</td>
<td>11</td>
<td>15.5</td>
<td>22.0</td>
<td>0.70</td>
</tr>
<tr>
<td>K5</td>
<td>5.2</td>
<td>10</td>
<td>18.1</td>
<td>19.7</td>
<td>0.92</td>
</tr>
<tr>
<td>K6</td>
<td>17.7</td>
<td>43</td>
<td>14.3</td>
<td>11.2</td>
<td>1.27</td>
</tr>
<tr>
<td>K7</td>
<td>6.2</td>
<td>86</td>
<td>22.3</td>
<td>22.2</td>
<td>1.00</td>
</tr>
<tr>
<td>K8</td>
<td>4.5</td>
<td>101</td>
<td>45.6</td>
<td>20.7</td>
<td>2.20</td>
</tr>
</tbody>
</table>

*Crystal size determination*

Table 2 lists the crystal sizes of the zeolites used, as determined by the various methods. Crystal lengths determined visually from scanning electron micrographs are given first. For comparison, the crystal sizes of three selected samples were also determined by laser light diffraction and with a Coulter counter. In this method, the diameter of a sphere of equal volume is determined. The value at which 50% by weight passed through a screen was assumed to be the average.

Fig. 1 shows a typical particle size distribution curve from measurements.
with a Coulter counter. For the Coulter counter measurements, a statistical average was also formed in accordance with the equation

$$\log \bar{x} = \frac{\sum \log x \, d\theta}{\sum d\theta}$$

where $\bar{x}$ is the average crystal size and $x$ is the crystal size within the weight interval $d\theta$ of screenings. There is good agreement between the determination of the averages by the different methods. There are deviations from the figures determined by scanning electron microscopy, especially as fairly large crystals usually have an elongated shape, so that generally higher figures were found for the length under the microscope. As the breadth of the crystal size distribution is also important, the measure taken from the latter in the last column is the difference between the diameters at 90% and 10% by weight passing through a screen divided by the diameter at 50% by weight passing through a screen. The smaller this parameter, the narrower is the crystal size distribution. The results of the measurements with the Coulter counter and with laser light diffraction disagree on this point.

*n-Hexane isomerization*

As the various zeolites were prepared by different methods, the catalysts showed differences not only in crystal size but also in other properties such as modulus and crystallinity, so that varying catalyst activities were to be expected. To enable the effect of the crystal size of ZSM-5 on its catalytic activity to be studied, all eight catalysts were used under the same conditions for conversion of n-hexane. The catalyst loading (weight hourly space velocity, WHSV) was 7.9 g of n-hexane/(g of catalyst × hour). The reaction was carried out at 300°C under a pressure of 40 bar. In addition to the n-hexane, 11 times the molar amount of hydrogen was fed in.

Fig. 2, in which the yield of cracked products at the start of the reaction is plotted against the ZSM-5 crystal size, shows that the activity of the catalyst, independent of its other properties, increases sharply with decrease in crystal size. It can also be seen that the catalysts synthesized with TPAOH give a slightly higher yield of cracked products in the conversion of n-hexane than the ZSM-5 zeolites prepared with TPABr. Catalyst K1 does not fit this picture. On the other hand, the X-ray analysis of this catalyst shows that it has a relative crystallinity of only 39%.

*Conversion of methanol to olefins*

The conversion of methanol to hydrocarbons (the conversion to dimethyl ether was disregarded) at 340°C and 6 bar pressure were determined for catalysts K1, K2, K3 and K8 at various catalyst loadings with a constant running
Fig. 2. Yield of cracking products as a function of crystallite size for n-hexane conversion. ZSM-5 catalysts synthesized with (♦) TPABr or (■) TPAOH.

time of 5 h. For a catalyst loading WHSV of 10 g of methanol/(g of catalyst × hour), the conversions were interpolated and plotted against the crystal size (Fig. 3). Here again, the ZSM-5 catalysts synthesized with TPABr showed a decrease in conversion with increasing crystal size, in spite of the otherwise different properties. As in the cracking of n-hexane, catalyst K1 prepared with TPAOH does not fit this picture but gives a particularly low conversion.

Fig. 3. Conversion of methanol as a function of crystallite size. ZSM-5 catalysts synthesized with (♦) TPABr or (■) TPAOH.
Fig. 4. Yield of amines for amination of methanol as a function of crystallite size for ZSM-5 catalysts synthesized with (+) TPABr or (■) TPAOH.

Amination of methanol

Methanol was reacted on catalysts K1–K8 with ammonia at 370°C, 3 bar pressure and a WHSV loading of 3.8 g of methanol/(g of catalyst x hour). The three amines were formed with a total selectivity between 55 and 90%. A plot of the yield of the three amines against crystal size (Fig. 4) again shows a decrease in this yield with increasing crystal size for the catalyst prepared with TPABr. In this reaction also, the other catalysts prepared with TPAOH show higher yields.

DISCUSSION

Eight ZSM-5 catalysts of different crystal size were prepared by varying the synthesis conditions. All these catalysts were used in three very different test reactions (only four catalysts in the methanol conversion). It has been shown that the catalysts can be classified into two groups according to the template used. Even the SIMS depth profiles show that there are fundamental differences in the crystal structure. However, different behaviour was also observed in the reaction investigations. It was shown for all the reactions investigated that, for the catalysts synthesized with TPABr, the reactivity decreases with increasing crystal size independent of the other catalyst properties. This leads to the assumption that the crystal volume is not fully utilized for the catalyst reaction in the three reactions investigated.

There are two possible explanations. On the one hand, the ZSM-5 zeolites prepared with TPABr have a silicon-rich core, which presumably contains only
TABLE 4

Diffusion coefficients of various molecules in ZSM-5 crystal according to the literature

<table>
<thead>
<tr>
<th>Substance</th>
<th>Temperature (°C)</th>
<th>Diffusion coefficient (cm²/s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Methylpentane</td>
<td>23</td>
<td>2.6·10⁻¹⁰-7.0·10⁻¹²</td>
<td>20</td>
</tr>
<tr>
<td>Benzene</td>
<td>28</td>
<td>1.6·10⁻¹⁰-6.6·10⁻¹²</td>
<td>20</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>28</td>
<td>1.4·10⁻⁹-5.6·10⁻¹¹</td>
<td>20</td>
</tr>
<tr>
<td>n-Hexene</td>
<td>538</td>
<td>3.0·10⁻⁴</td>
<td>5</td>
</tr>
<tr>
<td>3-Methylpentene</td>
<td>538</td>
<td>4.0·10⁻⁵</td>
<td>5</td>
</tr>
<tr>
<td>2,2-Dimethylbutane</td>
<td>538</td>
<td>2.0·10⁻⁸</td>
<td>5</td>
</tr>
<tr>
<td>2,2-Dimethylbutene</td>
<td>538</td>
<td>7.0·10⁻⁸</td>
<td>5</td>
</tr>
<tr>
<td>2,2-Dimethylheptane</td>
<td>538</td>
<td>3.0·10⁻⁸</td>
<td></td>
</tr>
<tr>
<td>Dimethyl ether</td>
<td>20</td>
<td>1.2·10⁻⁹</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.5·10⁻⁹</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>20</td>
<td>2.3·10⁻¹⁰</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.5·10⁻¹⁰</td>
<td></td>
</tr>
<tr>
<td>m-Xylene</td>
<td>20</td>
<td>2.2·10⁻¹⁰</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.4·10⁻¹⁰</td>
<td>6</td>
</tr>
<tr>
<td>n-Butane</td>
<td>24, 61</td>
<td>5.7·10⁻⁸, 1.1·10⁻⁷</td>
<td>21</td>
</tr>
<tr>
<td>Isobutane</td>
<td>24, 61</td>
<td>1.9·10⁻⁸, 5.5·10⁻⁸</td>
<td>21</td>
</tr>
</tbody>
</table>

A few active centres. On the other hand, it would be conceivable that the diffusion of the substances participating in the reaction is slow compared with the reaction, that is, reaction control by diffusion comes into play. In both instances, only the regions close to the surface of the crystallites would be effective as reaction centres. The larger the zeolite crystals used, the greater is the proportion of non-utilized catalyst and therefore the lower is the catalyst activity.

In contrast to this behaviour, the zeolites synthesized with TPAOH generally reach higher conversions. However, it was not possible to prove a dependence of the activity of these catalysts on the crystal size, as zeolite catalysts of different crystal size were not available in sufficient numbers for such an investigation.

In order to assess the influence of diffusion on the reaction behaviour, an estimate may be made here for the amination of methanol. The data used for this purpose come from reaction studies which were carried out in a separate measurement series on a ZSM-5 catalyst not used in this work [18]. One important parameter is here the Weisz number, \( W_z \):

\[
W_z = \frac{R^2}{D_{0f} C_0} (-r_{\text{net,m}})
\]
where $R$ is half the crystal diameter, $D_{\text{eff}}$ is the effective diffusion coefficient, $c_0$ is the inlet concentration of methanol and $r_{\text{het.m}}$ is the measured reaction rate.

Entering the reaction rate into the equation for the Weisz number:

$$W_z = \frac{R^2 \rho_k d(1-U)}{D_{\text{eff}} d W C_0 F_0}$$

and estimating the differential quotients allowed Weisz numbers to be determined. $U$ is the methanol conversion, $\rho_k$ is the catalyst density, $W$ is the catalyst weight and $F_0$ is the methanol loading. The critical parameters in determining the Weisz number are the crystal diameter and the effective diffusion coefficient. The crystallite size of 2 $\mu$m had been determined for this catalyst by scanning electron micrographs. In contrast, measurements with a Coulter counter gave a length of 5 $\mu$m.

The determination of diffusion coefficients in zeolites is a problem. There is still disagreement in the literature as to their order of magnitude, as shown in Table 4. Seidel [19] investigated the diffusion coefficients of various molecules in ZSM-5 zeolites and gave diffusion coefficients of the order of $10^{-10}$ cm$^2$/s at 25°C and activation energies of diffusion of about 25 kJ/mol. For a first estimate, these values should also be assumed for methanol. A diffusion coefficient of $2.3 \cdot 10^{-8}$ cm$^2$/s at 370°C is then calculated according to the equation

$$D = D_0 e^{-\frac{E_{\text{diff}}^A}{RT}}$$

On the basis of these figures, the data used here from reaction studies [18] for a low catalyst loading of 3.1 g/g·h give, even assuming a crystal length of 5 $\mu$m, a Weisz number of 5.0, which does not indicate a significant contribution of diffusion control. At high catalyst loadings (51.5 g/g·h) lower conversions are observed, so that there is a higher average concentration in the reactor. The Weisz numbers calculated under these conditions are markedly higher, so that a lower degree of catalyst utilization due to diffusion control is to be expected. As these studies were carried out on catalysts of different crystal sizes at low loadings (3.8 g/g·h), diffusion control as the cause of the decrease in activity with increasing crystal size cannot be proved by these data. In addition, however, it must be taken into account that there is also some uncertainty in the estimation of the diffusion coefficient.

In conclusion it may be said that the cause of the decrease in activity of the catalysts prepared with TPABr with increase in crystal size cannot be proved with certainty. Evidently, only the outer crystal zones are utilized for the cat-
alytic reaction. However, both diffusion control and a silicon-rich inner core with hardly any active centres are conceivable causes.

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