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# NOTE

# Shape-Selectivity of Large and Small Crystals of Zeolite ZSM-5

We have shown recently (1) that the isomer distribution in the xylene resulting from the methylation of toluene by methanol on zeolite H-ZSM-5 is independent of conversion as long as reactant methanol is not exhausted, and that it depends *inter alia* on the size of the unmodified zeolite crystals. The interpretation of the observed isomer distribution as resulting from intracrystalline reaction and shape-selective diffusion led to the conclusion that only the *para* isomer should be generated on sufficiently large crystals of the unmodified zeolite, whereas with extremely small crystals (in the hypothetical limit consisting of only one unit cell) an isomer distribution should be observed which is not influenced by subsequent diffusion and isomerization of the primary product of alkylation. We now report briefly the results of experiments which have been conducted to test these conclusions.

Three samples of zeolite H-ZSM-5 of nearly identical composition (Si/Al = 24.0 ± 0.4) were synthesized as follows, aiming at one sample of rather large crystals and two samples of very small but intact crystals of different sizes. Following previously described studies on statistical factorial design for the alkaline-free synthesis of zeolites (3), samples were crystallized from a gel having a molar composition of 2.5 $(TPA)_2O$–2 $Al_2O_3$–96 $SiO_2$–1920 $H_2O$–192 $NH_3$. Tetrapropylammonium bromide (Fluka), colloidal silica (Ludox AS40), deionized water, aluminium triisopropylate (Merck), and an aqueous solution of ammonia (25% w/w) were sequentially mixed and vigorously stirred for 180 s. Crystallization was performed hydrothermally at 185°C for 168 h. Gels giving sample A (batch weight 23.5 kg) and sample B (batch weight 1.3 kg) were continuously stirred at 100 rpm, whereas sample C (batch weight 0.2 kg) was kept under static conditions. Crystalline products were filtered off, washed with deionized water, dried (110°C/24 h), and shallow-bed calcined (500°C/5 h).

The zeolites used as catalysts, their designations and their crystal sizes are listed in Table 1. The characteristic length $L$ is the ratio of the volume and the external surface of the crystals, which is to be considered as an average. Electron micrographs of the smallest (A) and the largest crystals (C) are shown in Fig. 1. Zeolites A and B were loosely agglomerated without binder to pellets with parti-

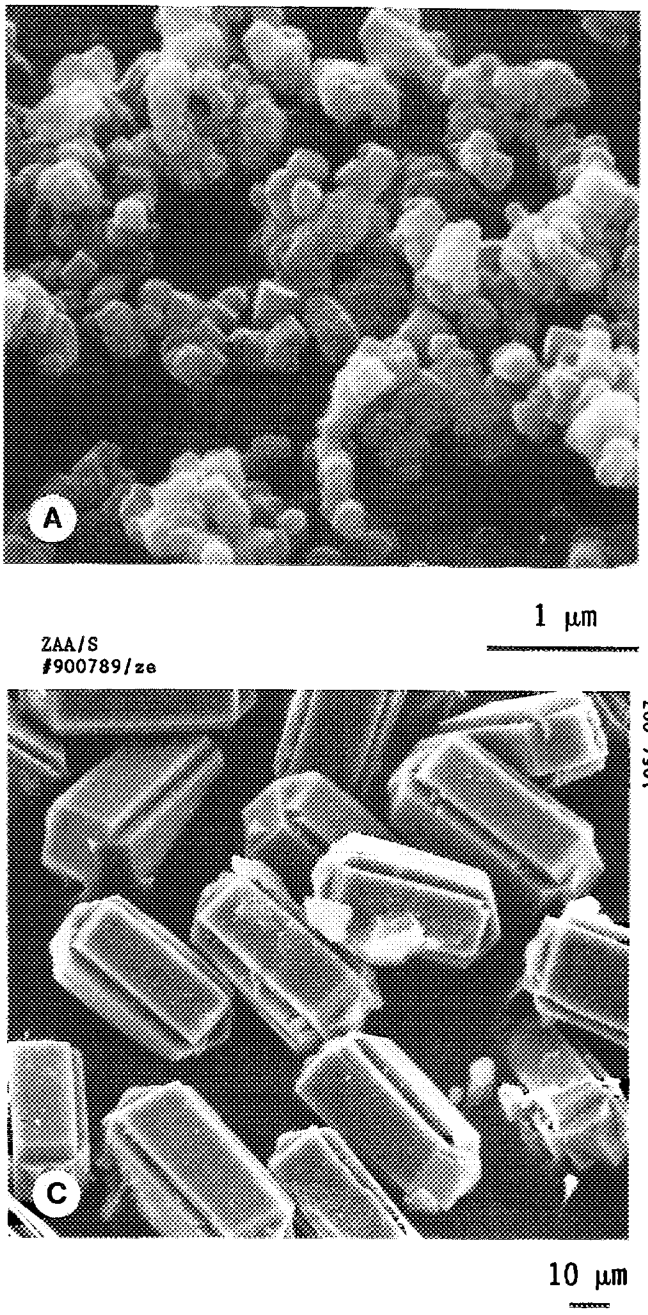

FIG. 1. SEM micrographs of zeolites A and C.

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TABLE 1

Designation and Properties of Zeolites H-ZSM-5

| Designation | Si/Al | Crystal size ($\mu$m) | $L$($\mu$m) |
|---|---|---|---|
| A | 24.0 | cubes, $a \times a \times a$<br>$a = 0.15 \pm 0.05$ | 0.025 |
| B | 23.7 | cubes<br>$a = 0.25 \pm 0.1$ | 0.045 |
| C | 24.3 | $50 \times 20 \times 20$ | 4.5 |

cle size of (0.4 ± 0.1) mm, whereas the large crystals C were used as a catalyst without agglomeration.

Kinetics and product composition in the methylation of toluene with methanol were observed in a well-mixed batch reactor as described previously (1). The fractions $x_p$ of the *para* and $x_m$ of the *meta* isomer in the xylene produced are shown in Fig. 2 as a function of methanol conversion $X_M$ for 350°C (623 K) and initial partial pressures of 10 mbar for toluene, 20 mbar for methanol; by definition we have $x_p + x_m + x_o = 1$. Less than 25% of the toluene converted had reacted to other products such as ethylbenzene and trimethylbenzene. The large crystals C were found to be 100% *para*-selective up to full conversion of methanol, whereas the integral *para*-selectivity drops off after about 60% conversion of methanol on the much smaller crystals A and B, due to the concomitant isomerization of xylene. Isomerization is restricted to the near-surface region of the crystals (1), whose extent is proportional to $1/L$, and thus is in the ratio of 1 : 180 if unit masses of zeolites A and C are compared. Rates of formation of xylene (sum of all three isomers) depend also on crystal size under otherwise identical conditions (see Table 2). Under the conditions specified there the intracrystalline effectiveness of zeolite C for xylene formation appears to be around 5%, assuming the mass specific rates of xylene formation on crystals of given composition but different size to be proportional to intracrystalline effectiveness. The initial isomer distributions in the product xylene (constant up to at least 50% conversion of methanol) on zeolites A, B, and C are listed in Table 3 for three temperatures. The result $x_p = 1.00$ (100% *para* selectivity) means that the fraction of the other isomers (*meta* plus *ortho*) amounted to less than 0.002%.

The interpretation of isomer distribution as resulting from diffusion-mediated shape-selectivity requires that only *para*-xylene be observed in the products if sufficiently large unmodified crystals of ZSM-5 are used as catalysts (2). This expectation from theory is clearly fulfilled.

The fraction of the *para*-xylene in the products at limited conversion of methanol exceeds the value at equilibrium ($(x_p)_{eq} \approx 0.24$) even on the smallest crystals used here (A). It is not possible to infer the primary isomer

TABLE 2

Initial Rates $r_m$ of Xylene Formation per Unit Mass of Zeolite at 623 K, $p_{CH_3OH}$ = 20 mbar, $p_{Tol}$ = 10 mbar.

| Zeolite: | A | B | C |
|---|---|---|---|
| $r_m \times 10^6$ (mol g$^{-1}$ s$^{-1}$) | 15 | 19 | 0.51 |

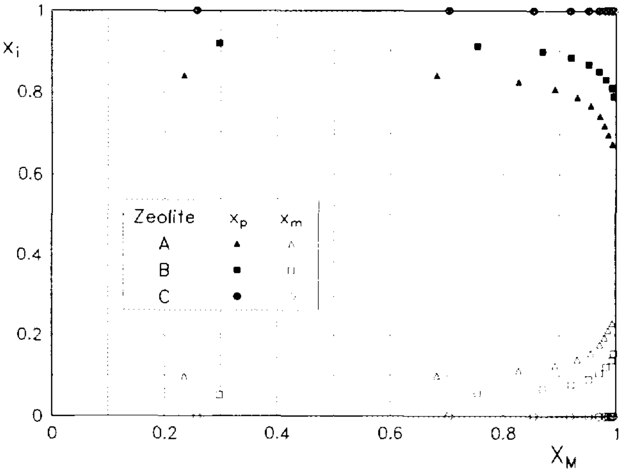

FIG. 2. Isomer distribution in xylene from toluene methylation as a function of conversion $X_m$ of methanol. $T$ = 623 K; $(p_{CH_3OH})_0$ = 20 mbar; $(p_{Tol})_0$ = 10 mbar; $x_p + x_m + x_o = 1$.

TABLE 3

Isomer Distribution in Xylene from Toluene Methylation[a] on Catalysts A, B, and C

| Temperature (K) | Zeolite | $x_p$ | $x_m$ | $x_o$ |
|---|---|---|---|---|
| 548 | A | .63 | .18 | .19 |
| | B | .75 | .13 | .12 |
| | C | 1.00 | 0 | 0 |
| 573 | A | .75 | .12 | .13 |
| | B | .85 | .08 | .07 |
| | C | 1.00 | 0 | 0 |
| 623 | A | .84 | .10 | .06 |
| | B | .91 | .06 | .03 |
| | C | 1.00 | 0 | 0 |

[a] $(p_{CH_3OH})_0$ = 20 mbar, $(p_{Tol})_0$ = 10 mbar; conversion of methanol <50%.

distribution of the alkylation reaction in the zeolite from our observations, because no limiting values of $x_i$ (which would have to be independent of crystal size) have been obtained with very small crystals of different size (A vs B).

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