

Reactions of Mixtures of Toluene and Methanol over ZSM-5

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Methanol, in the presence of toluene, was completely converted to hydrocarbons above 400°C. However, depending on the ratio of toluene to methanol in the feed mixture and the reaction severity, only a fraction of the methanol participated in the toluene alkylation reaction, with the remainder being converted to gaseous hydrocarbons. Alkylation is found to be *ortho/para*-directing over the small-crystal ZSM-5, similar to that found with aluminum chloride and amorphous silica/alumina catalysts, whereas the large crystals showed high *para* selectivity. The catalytic results are shown to be consistent with the diffusion characteristics of the zeolite. © 1988 Academic Press, Inc.

INTRODUCTION

The alkylation of toluene with methanol to produce xylenes was the subject of a number of articles in the sixties and early seventies using such catalysts as aluminum chloride (1) and different cationic forms of faujasites (2–4). With the discovery of the unique catalytic properties of ZSM-5 (5, 6) interest in the application of ZSM-5 for processing aromatics was initiated in the late sixties at the Mobil Research Laboratories. One of the significant findings of these early studies was the discovery of *para*-directed toluene disproportionation and alkylation reactions (7). These reactions signified the importance of controlling the interplay between the rate of intrazeolitic molecular diffusion and the rate of intrazeolitic chemical reactions to control the desired product selectivity. Details of the principles of the design of a *para*-selective catalyst have been elaborated by Olson and Haag (8) and a mathematical model incorporating the concept of diffusion-controlled product selectivity was proposed by Wei (9).

Kaeding and his group reported their studies on using ZSM-5 and ZSM-11 for the alkylation of toluene with methanol

(10–12). Most of these studies were concerned principally with the effect of catalyst modification on catalyst activity and product selectivity. Issues such as hydrogen-to-carbon balance and alkyl chain-to-aromatic ring balance, which determine the accuracy of the experimental results and the reaction stoichiometry, were not addressed.

Reported herein are the results of the experimental study, which addresses the specific question of reaction stoichiometry, the fate of methanol during the reaction, and the role of diffusion on *para* selectivity.

EXPERIMENTAL

Catalysts

The synthesis of the zeolite ZSM-5 has been described previously (13). Characteristics of the large and small crystals used in this study also have been reported earlier (7). Both samples have a SiO₂/Al₂O₃ ratio of 70. The large crystal sample has an average crystal size of 3 × 7 μm and the small crystal sample comprises loose aggregates of smaller than 0.1-μm crystals.

The as-synthesized zeolites were precalcined at 370°C and ammonium exchanged. NH₄-ZSM-5 was converted to H-ZSM-5 by

programmed calcination in air at 1°C/min to 538°C and held at 538°C for 10 h.

To determine the diffusive properties of these samples, the zeolites were also exchanged to the sodium form and a gas chromatographic method (14, 15) was used to determine the retention time of the xylene isomers.

This was carried out by packing 0.26 ml of 50/60-mesh zeolite in $\frac{1}{8}$ -in.-o.d. (1.75-mm-i.d.) stainless-steel tubing as the GC column. The length of the packed bed was about 11 cm, and the total length of the tubing between the injection port and the hydrogen flame detector was about 40 cm. Measurements were made at a series of temperatures by injecting 1- μ l samples of each of the xylene isomers between 150 and 400°C with the helium carrier gas flowing at a rate of 60 ml/min. Molecules that can diffuse through the intracrystalline pores desorb slowly to give broad peaks with a long retention time while those molecules that are too large to enter the pores appear as sharp peaks with short retention times.

To deactivate surface acid sites, the zeolite samples were treated either with a bulky nitrogen compound or with an organic silane compound. In the former case, the sample was treated by soaking in a 2% phenyl carbazole solution in acetone and dried. During the experiment, 1000 ppm of phenyl carbazole was added to the feed. Phenylcarbazole was selected for its molecular size which should poison only the external sites.

Silane treatment of H-ZSM-5 was carried out in reflux pyridine with dimethyl dichlorosilane (8 g catalyst, 50 ml of pyridine, 10 ml of DMCS) for 2 h. The catalyst was then filtered while hot, washed with pyridine (100 ml), chloroform (100 ml), and *n*-pentane (100 ml), pelleted, and screened to 30/50 mesh.

Feeds

Methanol and toluene were high-purity reagent-grade chemicals. They were used without further purification. The three xy-

lene isomers used in the sorption experiments were also high-purity reagent-grade chemicals.

Experimental Procedures

The experiments were carried out in a microreactor system containing about 0.5 to 1 g of 30/50-mesh catalyst. The reaction conditions, unless otherwise stated, were 260 to 500°C, 4–16 LHSV at atmospheric pressure. A liquid feed containing a mixture of methanol/toluene (2/1 to 1/1 mole ratio) was passed over the catalyst. The reactor effluent passed through an ice-water condenser to a gas holder. The condensed liquid was weighed and then separated into two phases and analyzed by gas chromatography. For the organic phase a 35-ft 10% polyphenyl ether on Gas Chrom R column was used. The column was held at 95°C until appearance of the *o*-xylene peak; then, the temperature was raised at 8°C/min to 180°C and held for 30 min. A Poropak QS column was used for the aqueous phase.

RESULTS AND DISCUSSIONS

Sorption and Diffusion Characteristics

The effect of crystal size and cationic form of ZSM-5 on the gas chromatographic retention time of each of the xylene isomers is presented in Figs. 1 and 2 as peak height versus temperature. While the total peak area for a given size sample injected into the GC column should be the same, the retention time and the peak heights are quite different. Those isomers not sorbed by the zeolite have peak heights close to that found with an empty GC column; while those isomers sorbed by the zeolite elute slowly from the column and have much lower peak heights at low temperatures. As the temperature is raised, rate of desorption increases and the peak heights generally increase gradually. Thus the relative peak heights give an indication of the sorption and diffusion characteristics of the zeolites under near-reaction conditions.

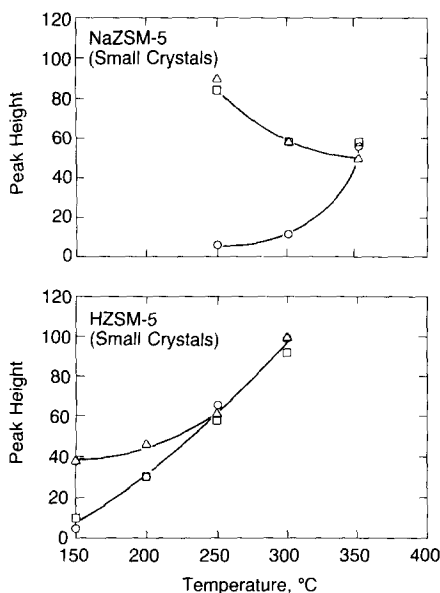


FIG. 1. GC peak height versus temperature: ○, *para*; □, *ortho*; △, *meta*.

As shown in Fig. 1, our data indicate that for the small-crystal Na-ZSM-5, at 250°C, the peak height from *m*- and *o*-xylenes approached that found with an empty GC column (peak height 120), indicating that the *m*- and *o*-xylene isomers are nearly completely excluded by the zeolite below 250°C. *p*-Xylene, on the other hand, is sorbed and held strongly by the zeolite below 250°C. Above 350°C, all three xylene isomers had about the same retention time and peak height, suggesting that they are sorbed and then desorbed from the zeolite at these higher temperatures.

The same zeolite sample after ammonium exchange and air calcination showed a significant change in sorption and diffusion characteristics. Note that all three xylene isomers were sorbed and desorbed at temperatures almost 100°C lower compared with the results for Na-ZSM-5, thus suggesting that the hydrogen form has a larger intracrystalline channel than the sodium form. This more open structure not only allows all three xylene isomers to enter the pores, but also increases the rate of desorption as we note that at 300°C the peaks are

much sharper in the hydrogen form than in the sodium form, approaching that found with an empty GC column. Also of interest is that at lower temperatures (below 200°C), both *ortho o*- and *p*-xylene became strongly sorbed, with only *m*-xylene being partially excluded.

Figure 2 shows that for the large-crystal Na-ZSM-5 there is a distinct shape-selective effect between the *para* isomer and the *ortho*, *meta* isomers throughout the temperature range studied. However, the peak height of the *p*-xylene was much higher than that observed with the small crystals; furthermore, instead of becoming sharper with increasing temperature, the peaks in fact decreased in height at 350°C. The higher peak heights found with the larger crystals at lower temperatures could be due to overloading of the GC column when too large a pulse of xylene was injected. Exchange to the hydrogen form again, as in the case of the small crystals, appeared to open up the channels. However, unlike the small crystals, the large crystals exclude *ortho* and *meta* isomers completely at temperatures as high as 400°C. It is noted that

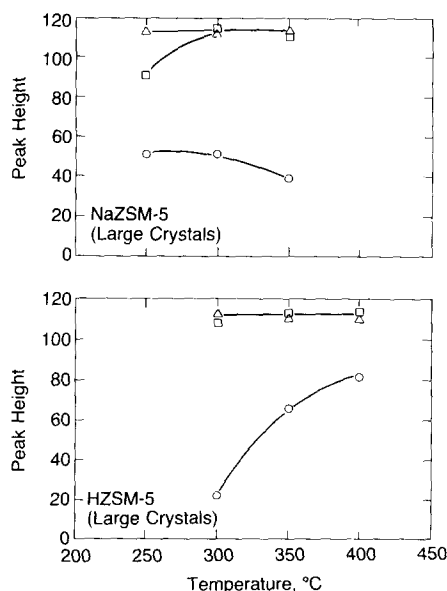


FIG. 2. GC peak height versus temperature: ○, *para*; □, *ortho*; △, *meta*.

TABLE I
 Experimental Results

| Run: | D-1A | D-1B | R-1A | R-1B | R-2 | R-3 | R-4A | R-4B |
|-----------------------------|----------------|-------|-----------|-------|----------------|-------|-----------|-------|
| Catalyst: | Small crystals | | | | Large crystals | | | |
| Conditions: | N-poisoned | | Silylated | | Untreated | | Silylated | |
| Temperature (°C) | 260 | 315 | 400 | 300 | 500 | 400 | 500 | 500 |
| Toluene/methanol (mol) | 1.04 | 1.04 | 2 | 2 | 2 | 2 | 2 | 2 |
| LHSV | 4 | 4 | 6.6 | 6.6 | 6.6 | 6.6 | 6.6 | 16.4 |
| Time on stream (h) | 1 | 2 | 1 | 2.5 | 1 | 1 | 0.7 | 1.3 |
| Conversion (wt%) | | | | | | | | |
| Toluene | 17.5 | 32.9 | 56.7 | 19.0 | 41.8 | 19.2 | 34.3 | 24.6 |
| Methanol | 45.6 | 57.8 | 100.0 | 37.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Organic products (wt%) | | | | | | | | |
| C ₆ ⁻ | 2.7 | 1.4 | 13.4 | 7.1 | 19.0 | 20.7 | 19.4 | 20.6 |
| Benzene | 0 | .2 | 0 | 0 | 1.6 | 0.1 | 0.4 | 0.1 |
| Toluene | 77.4 | 61.9 | 33.2 | 72.8 | 44.6 | 62.0 | 50.4 | 57.8 |
| <i>p</i> -Xylene | 2.8 | 4.9 | 9.0 | 4.2 | 14.7 | 6.1 | 19.0 | 15.8 |
| <i>m</i> -Xylene | 2.9 | 12.1 | 14.9 | 3.8 | 11.6 | 3.8 | 5.6 | 1.9 |
| <i>o</i> -Xylene | 5.5 | 4.5 | 10.5 | 8.1 | 5.8 | 2.8 | 2.2 | 1.8 |
| Ethylbenzene | 0 | 0 | 0 | 0 | 0 | 0.1 | 0 | 0 |
| C ₈ aromatics | 11.2 | 21.5 | 34.4 | 16.1 | 32.1 | 12.8 | 26.8 | 19.5 |
| Trimethyl benzenes | 8.7 | 15.0 | 19.0 | 4.0 | 2.7 | 4.4 | 3.0 | 2.0 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

the *ortho* and *meta* peaks were as sharp as those obtained with an empty GC column; while the *para* peaks were very broad below 300°C, indicating strong sorption, and became sharper when the rate of desorption increased as the temperature increased.

The sorption and diffusion characteristic of these samples provided the incentive to investigate their shape-selective catalytic properties.

Catalytic Reactions

Experimental results. Shown in Table I are the experimental data for toluene alkylation over four different catalysts, viz., phenyl carbazole-treated small-crystal ZSM-5, surface-silanized small-crystal ZSM-5, large-crystal ZSM-5, and surface-silanized large-crystal ZSM-5. The composition of the organic phase as shown includes the gas products and the unconverted toluene. Material balances including the organic phase, the aqueous phase, and the gases for these runs were better than 98 wt%.

Reaction severity was varied by changing either temperature or space velocity. For example, the temperature was increased between runs D-1A and D-1B and lowered between runs R-1A and run R-1B; and the liquid hourly space velocity was raised between runs R-4A and R-4B. After each change, the reactor was allowed to reach a steady state in about 30 min before the sample for the material balance was taken. It was noted that as the reaction severity was increased, the conversion of toluene to higher aromatics increased. However, C₁₀⁺ aromatics were not found as was reported by Kaeding *et al.* (10), who used more severe reaction conditions. As was also noted by Kaeding *et al.* (10), when the mole ratio of methanol to toluene was increased, increasing amounts of C₆⁻ light gases were produced from methanol instead of the conversion of more toluene to xylenes. Therefore, a compromise must be reached between maximizing single-pass toluene conversion and the efficient use of methanol as an alkylating agent.

TABLE 2
Fate of Methanol

| Run: | D-34 | D-35 | R-39 | R-40 | R-37 | R-38 | R-25 | R-26 |
|------------------------|----------------|------|-----------|------|----------------|------|-----------|------|
| Catalyst: | Small crystals | | | | Large crystals | | | |
| Conditions: | N-poisoned | | Silylated | | Untreated | | Silylated | |
| Temperature (°C) | 260 | 315 | 400 | 300 | 500 | 400 | 500 | 500 |
| Toluene/methanol (mol) | 1.04 | 1.04 | 2 | 2 | 2 | 2 | 2 | 2 |
| LHSV | 4 | 4 | 6.6 | 6.6 | 6.6 | 6.6 | 6.6 | 16.4 |
| Time on stream (h) | 1 | 2 | 1 | 2.5 | 1 | 1 | 0.7 | 1.3 |
| Light gases | 54.1 | 22.1 | 57.3 | 70.0 | 81.4 | 88.7 | 83.0 | 88.4 |
| Alkyl groups | 45.5 | 77.1 | 39.2 | 30.0 | 18.6 | 11.3 | 17.0 | 11.6 |
| New rings | 0.4 | 0.8 | 3.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

Fate of methanol. As shown by the data in Table 1, methanol, in the presence of toluene, was completely converted to hydrocarbons above 400°C, over all the catalysts tested. However, as shown in Table 2, only a fraction of the methanol participated in the toluene alkylation reaction. Depending on the ratio of toluene to methanol in the feed mixture and the reaction severity, alkylation represented between 11 and 77% of the methanol converted. Chain-to-ring calculations of the present data showed that the formation of new aromatic rings from methanol was in evidence only in the case of surface-poisoned small crystals at 400°C; in all the other cases, methanol was converted either to alkyl groups or to gaseous hydrocarbons.

Xylene isomer distribution. As could be expected from the diffusion characteristics of the small-crystal ZSM-5, inactivation of the surface acid sites did not show *para* selectivity. Shown in Fig. 3 is a trilinear plot of the xylene isomer distribution obtained in the present study. Also shown are the data reported by Allen and Yats (1) over aluminum chloride and those reported by Yashima and his co-workers (3, 4) over amorphous silica/alumina. Alkylation over the small-crystal H-ZSM-5 is shown to be similarly *ortho/para*-directing and the xylene isomer distribution moved toward the equilibrium composition as the reaction se-

verity was increased. The xylene isomer distribution followed a distinctly different pathway with either the large-crystal or the silylated large-crystal ZSM-5 catalysts. The pathway appears to begin at the apex (100% *p*-xylene) and moves toward the equilibrium composition at higher reaction severity. Thus, it leaves no doubt that the diffusion characteristics of the large-crystal ZSM-5 play a major role in altering the xylene isomer distribution. It is interesting to note that most *para*-selective catalysts reported by Kaeding and his co-workers (12) gave xylene isomer distributions that also fall on the same line.

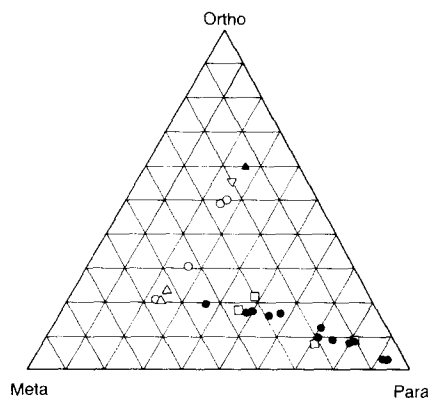


FIG. 3. Xylene isomer distribution. ○, This study (small crystals); □, this study (large crystals); △, equilibrium; ▲, AlCl₃ (1); ▽, SiO₂/Al₂O₃ (3); ●, P-modified ZSM-5 (10).

CONCLUSIONS

Mixtures of toluene and methanol react over ZSM-5 to form C_8^+ alkyl benzenes and light hydrocarbon gases. In the absence of diffusion constraints, the alkylation reaction is *ortho/para*-directing, similar to that of aluminum chloride and amorphous silica/alumina catalysts. When severely diffusion constrained, as in the case of large crystals or surface silylated large crystals, the alkylation reaction takes a distinctly *para*-directing pathway.

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