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Some Catalytic Properties of ZSM-5, a New Shape Selective Zeolite

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The new zeolite is characterized by a series of diagnostic catalytic reactions. The molecular sieving effect among alkyl aromatics and aliphatics of varying length and degree of branching is described. The catalyst is remarkably free of deactivation problems in the absence of hydrogen or a hydrogenation component.

INTRODUCTION

Since the first article by Weisz and Frilette on molecular shape selective catalysis appeared in 1960 (*1*), more than 100 related technical papers and patents have been published in the literature (*2*).

Zeolites used in most of the past studies in shape selective catalysis have the largest pore openings consisting of eight-membered oxygen rings: Included in this group are zeolite A, chabazite, erionite, and stacking-faulted zeolites such as offretite, gmelinite, and ferrierite. The intracrystalline space in these zeolites is accessible to molecules having a critical dimension not larger than that of a normal paraffin molecule. Shape selective reactions involving larger molecules have been studied, though to a lesser extent, using large pore zeolites with pore openings consisting of twelve-membered oxygen rings: mordenite, faujasite, and fault-free synthetic offretite comprise this group.

We now report some studies with a new zeolite, ZSM-5 (*3*, *4*), which possesses pore openings intermediate in size between the small pore and the large pore zeolites. It sorbs at room temperature straight chain

TABLE 1

Chemical Composition of C_5–C_7 Hydrocarbon Mixture

Compound	Wt%
C_5s	
Isopentane	2.2
n-Pentane	2.7
Cyclopentane	0.9
C_6s	
n-Hexane	10.2
2-Methylpentane	9.7
3-Methylpentane	7.8
2,2-Dimethylbutane	1.8
2,3-Dimethylbutane	1.9
Methylcyclopentane	1.0
Benzene	21.5
C_7s	
n-Heptane	2.8
2-Methylhexane	3.0
3-Methylhexane	3.8
2,2-Dimethylpentane	0.5
2,3-Dimethylpentane	1.2
2,4-Dimethylpentane	0.5
3,3-Dimethylpentane	0.4
3-Ethylpentane	0.3
Toluene	25.8

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monomethyl-substituted paraffins and monocyclic hydrocarbons at significantly faster rates than those containing dimethyl-substituted or quaternary carbon atoms, and it excludes molecules with critical dimensions larger than that of 1,3,5-trimethylbenzene. Its catalytic behavior is described by the following test reactions.

EXPERIMENTAL

Experiments were conducted in two different types of apparatus with two feedstocks: (1) In an apparatus described previously (*5*) for the measurement of cracking activity based on *n*-hexane conversion and in the presence of helium at atmospheric pressure. In the present study, the reactant feed comprising an equi-weight mixture of *n*-hexane, 3-methylpentane, and 2,3-dimethylbutane, all Phillips research grade hydrocarbons, was metered into a flowing helium stream. (2) In a micropressure reactor also described previously (*6*), the reaction was carried out at 15 atm, 15/1 mole ratio of hydrogen to hydrocarbon, using the same hydrocarbon mixture as described in (1) above. (3) In the same micropressure reactor as in (2), a mixture of C_5 to C_7 hydrocarbons was passed over the catalyst at 315 and 340°C, 1.4 LSHV, and 35 atm. No hydrogen was used. The chemical composition of the hydrocarbon mixture is shown in Table 1.

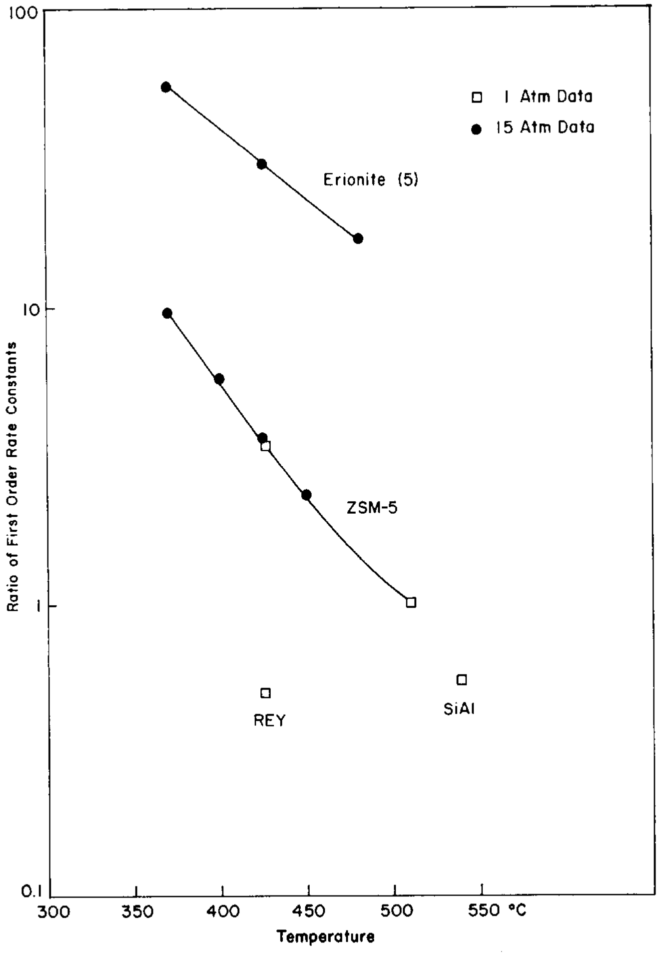

Fig. 1. Shape selectivity between *n*-hexane and 3-methylpentane.

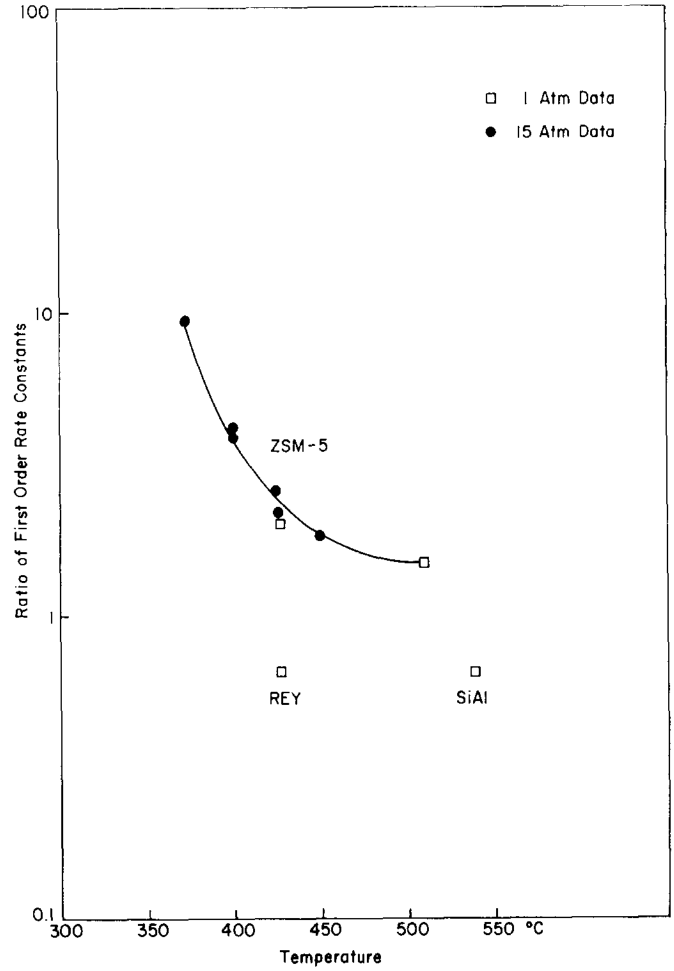

FIG. 2. Shape selectivity between 3-methylpentane and 2,3-dimethylbutane.

RESULTS AND DISCUSSION

1. Shape Selectivity among Hexane Isomers

The selectivity in the conversion of hexane isomers may be expressed in terms of the ratio of the first-order rate constants, k(*n*-hexane)/k(3-methylpentane) and k(3-methylpentane)/k(2,3-dimethylbutane). Figure 1 shows the selectivity between *n*-hexane and 3-methylpentane as a function of reaction temperature. Figure 2 shows the selectivity between 3-methylpentane and 2,3-dimethylbutane. These data include both the atmospheric and the 15 atm results for ZSM-5, erionite, RE-Y, and amorphous silica–alumina.

The observed relative rate constants for converting hexane isomers over the amorphous silica–alumina catalyst indicated that in the absence of steric constraints, 2,3-dimethylbutane is about four times more reactive than *n*-hexane and twice as reactive as 3-methylpentane. As expected, the large pore zeolite, rare earth exchanged zeolite Y, did not show preference for either isomer and has a selectivity corresponding to the intrinsic reactivity of these molecules. Furthermore, it was noted that these ratios of relative rate constants were approximately constant over a range of temperatures.

Earlier studies on erionite, a small pore zeolite (*6*), showed its shape selectivity to be sharply divided between a *n*-hexane molecule and its branched isomers. The rate of conversion of branched isomers, while negligible at below 400°C, increased faster with increasing temperature than that of *n*-hexane. The observed apparent activation energy for the conversion of branched isomers is the same as that of the silica–alumina catalyst (*6*). These reasons plus the fact that the zeolite has negligible sorption capacity for branched hexanes at these temperatures led us to attribute the conversion of branched isomers to the catalytic activity of the external surface of the zeolites.

The results over ZSM-5 are noteworthy in two respects: (1) For the first time it was shown that a zeolite can have a pore system which differentiates catalytically molecules having a straight chain, a methyl substitution, and a dimethyl substitution, and (2) the relative rate constants for the hexane isomers vary significantly with temperature. For example, Fig. 1 shows that at 375°C, *n*-hexane was converted 8.8 times faster than 3-methylpentane; raising the temperature to 510°C, both molecules were converted at the same rate. It would be expected that further increase in temperature would remove completely the steric hinderance to the 3-methylpentane molecule, and the intrinsic ratio of 0.5 would be observed. Both *n*-hexane and 3-methylpentane are readily sorbed by ZSM-5. However, the zeolite has a markedly lower sorption capacity for 3-methylpentane. It appears that 3-methylpentane, being a bulkier molecule than *n*-hexane, has a much lower packing density inside the zeolite possibly due to steric factors. It follows that the observed catalytic shape selectivity between *n*-hexane and 3-methylpentane could also be the result of steric hinderance within the pores rather than molecular screening as in the case of erionite.

The doubly branched 2,3-dimethylbutane molecule is not sorbed by ZSM-5 at room temperature but is slowly sorbed at elevated temperatures. This temperature-dependent differential process is reflected in the catalytic shape selective exclusion of the 2,3-dimethylbutane molecule. As shown in Fig. 2, at below 370°C the conversion of 2,3-dimethylbutane is negligibly small (<1/10 that of 3-methylpentane and <1/100 that of *n*-hexane). The selectivity ratio of 3-methylpentane to 2,3-dimethylbutane did not appear to approach the intrinsic value of 0.6 at higher temperatures

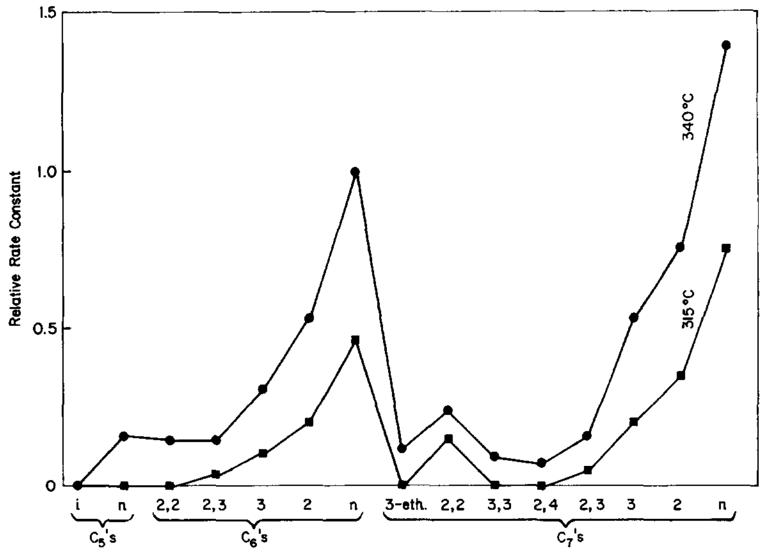

FIG. 3. Shape selectivity among C_5-C_7 paraffins.

but leveled off at about 1.5 We conclude from these results that the rate of diffusion of doubly branched hexane isomers in ZSM-5 is sterically hindered and highly activated. While it is generally believed that the pore openings in zeolites are not rigid, earlier studies on sorption (*7*) and catalysis (*8*) have found a sharp molecular sieving effect between molecules differing in their critical dimensions by as little as 0.2 Å. It is thus unusual to find that ZSM-5 has such a dynamic molecular sieving effect among molecules differing more than 1 Å in their critical dimensions.

2. Shape Selectivity with Respect to Chain Length

Over erionite, *n*-hexane is preferentially cracked in a mixture of C_5 to C_8 paraffins (*9*). This unique selectivity with respect to molecular chain length known as "cage effect" has been attributed to the channel structure of erionite which inhibits the diffusion of *n*-paraffin molecules in the range of C_7 to C_9 (*10, 11*). Such a "cage effect" was not found with ZSM-5. Shown in Fig. 3 are the relative rate constants obtained at 35 atm and at 315 and 340°C, respectively, for the paraffinic components in the feed (Table 1). The relative rate of disappearance of the paraffins are:

1. With respect to chain length:

$$n\text{-}C_7 > n\text{-}C_6 > n\text{-}C_5$$

2. Among the isomers:

$$n\text{-}C_7 > 2\text{-methyl-}C_6 > 3\text{-methyl-}C_6 > \text{dimethyl-}C_5\text{s and ethyl-}C_5$$

$$n\text{-}C_6 > 2\text{-methyl-}C_5 > 3\text{-methyl-}C_5 > \text{dimethyl-}C_4\text{s.}$$

Thus the rate of conversion for each group of molecules having about the same critical dimension increased with increasing molecular chain length as would be expected from chemical reactivity considerations. The critical dimension of the molecule appears to be more important than the length of the molecule in determining its rate of diffusion through ZSM-5. In other words, the diffusion rate is probably controlled by the matching of the size and shape of the molecule with that of the pore opening rather than by the tortuosity of the channel as in the case of erionite.

TABLE 2

Rate of Aromatics Alkylation[a]

Conversion (Wt%)	Temperature (°C)	
	315	340
Benzene	25	41
Toluene	18	31
k(toluene)/k(benzene)	0.69	0.70

[a] 35 atm. No hydrogen was used.

3. Shape Selectivity in Aromatics Alkylation

Since ZSM-5 sorbs monocyclic aromatics, it was not surprising to find a significant amount of alkylation reaction between benzene/toluene and the cracked fragments. The noteworthy observation was the relative rate of conversion between benzene and toluene at 35 atm. Toluene is intrinsically more reactive for alkylation than benzene. According to the selectivity relationship developed by Stock and Brown (*12*), the relative rate constants, k(toluene)/k(benzene), for alkylation should be about 1.4. This relationship was found to hold for both homogenous and heterogeneous catalyst systems (*13, 14*). However, over ZSM-5, as shown by the data in Table 2, the reverse relationship was found. Although sorption data indicate that ZSM-5 is accessible to both benzene and toluene, the methyl group in the toluene molecule apparently decreased the diffusivity of the alkylated molecule to such an extent that the rate of benzene alkylation surpassed the rate of toluene alkylation.

4. Catalyst Deactivation

The primary products of alkylation are isopropylbenzene, sec-butylbenzene, isopropyltoluene, and sec-butyltoluene, which rapidly isomerize and transalkylate to a mixture of C_8–C_{13} aromatics. The reaction was remarkably free of catalyst deactivation problems in the absence of hydrogen or hydrogenation component on the catalyst. Earlier studies by Venuto and Hamilton (*15*) on the alkylation of benzene with ethylene over rare-earth exchanged zeolite X showed that the main cause of catalyst deactivation was due to condensed polyalkyl aromatics formed within the supercage and unable to escape through the channels. Thus the lack of catalyst deactivation suggests that the effective shape and size of the pore opening and the tortuosity of the channels must be such to inhibit the formation and accumulation of bulky condensed polyalkyl aromatics.

CONCLUSION

Diagnostic catalytic reactions used in this study showed that ZSM-5 exhibits molecular sieving effect among large molecules, such as alkylbenzenes and alkyltoluenes, as well as among smaller molecules, such as *n*-hexane, 3-methylpentane, and 2,3-dimethylbutane. Unlike the eight-membered oxygen ring zeolites, which generally have a sharp molecular sieving effect, often within ±0.2 Å of a molecule, ZSM-5 has a wide dynamic range in its shape selective properties which are strongly temperature dependent. It does not exhibit a "cage effect" with respect to the chain length of the molecule and does not deactivate rapidly in the absence of hydrogen.

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