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Modifications of *n*-Hexane Hydroisomerization over Pt/Mordenite as Induced by Aromatic Cofeeds

In this note, we present evidence of competitive reaction in intrazeolitic media, showing that coreactants in the feed can induce rate and selectivity modifications of a primary reactant. The specific reaction considered is the hydroisomerization/hydrocracking of *n*-hexane over Pt/H–mordenite in the presence of an aromatic cofeed. In earlier work (*1*) we have found that the presence of benzene in the feed significantly inhibits the reaction of the paraffin. In this work, we further examine such competitive reaction over Pt/mordenite by considering the effect of a series of aromatics on *n*-hexane reaction rate and isomer selectivities. The aromatics used include benzene, toluene, *p*-xylene, and mesitylene. The objective was to determine if correlations could be found among the aromatic size relative to zeolite pore size, the inhibition of the hexane reaction, and modifications to isomer selectivities.

Synthetic H–mordenite was obtained from the Norton Chemical Co. (Zeolon 900-H), washed extensively with NH_4OH, and heated to remove NH_3 to ensure that the H^+ form was used in experiments. Pt^{2+} exchange to a level of 0.6 wt% was done by the method of Chick *et al.* (*2*); the final Pt dispersion as measured by pulse chemisorption was 85%. All experiments were carried out in an automated microreactor system (Chemical Data Systems 8100) incorporating a $\frac{5}{8}$-in.-i.d. tubular reactor into which was packed 6 g of catalyst (14–30 mesh). The experiments were conducted under operating conditions of 548 K, 0.76 MPa, with a liquid hydrocarbon flow rate (LHSV) of 1 ml liquid/h/g · cat. and a H_2 flow rate (GHSV) of 1870 cc (STP)/h/g · cat.; this results in a H_2/hydrocarbon molar ratio of approximately 10/1.

In data analysis, it was assumed that all isohexanes formed are through the reaction of *n*-hexane, since experimental runs with pure aromatic feeds showed essentially no isohexane formation under such mild hydroisomerization conditions. The ability to distinguish the individual reactions is an important reason for choosing paraffin + aromatic hydroisomerization as the model reaction. All experiments were also carried out at the same temperature (548 K) so that intrinsic site activities could be assumed constant in comparing reaction rates without and with cofeed addition.

Figure 1 lists results for the rate of *n*-hexane conversion to isohexanes in mixed binary feeds containing *n*-hexane together with 20 wt% aromatic. With a pure *n*-hexane hydrocarbon feed, the observed isomer formation rate was 89.9×10^{-8} mol/s/g · cat (42% *n*-hexane conversion to isomers) with an isomerization/cracking ratio greater than 10/1. On observation, we immediately note the inhibition of hydroisomerization activity with aromatic addition to the feed. With 20% benzene addition, for example, the rate of isomer formation decreases to less than 15×10^{-8} mol/s/g · cat (7.1% hexane conversion to isomers). It is also noted that as aromatic kinetic diameter is increased, the isomer formation rate appears to pass through a minimum. We attribute this result to the size and shape selectivity of the zeolite. H–mordenite has a reported effective size of 8–9 Å (*3*). The kinetic diameters of

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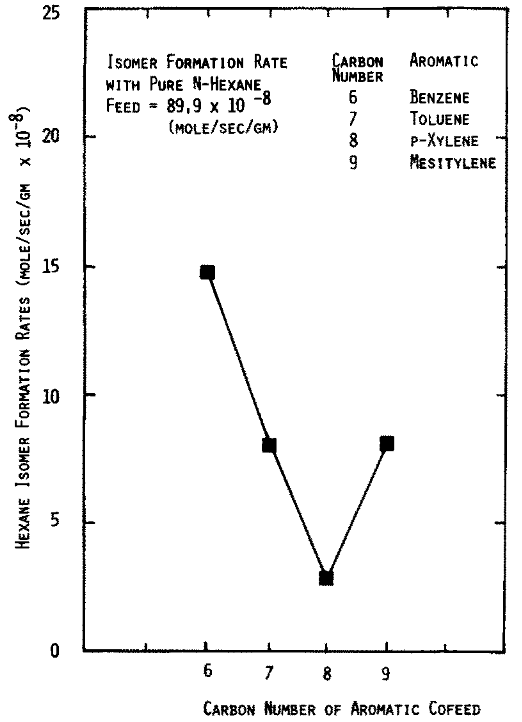


FIG. 1. Influence of aromatic molecular weight on *n*-hexane reaction rate. T = 548 K, P = 0.76 MPa, LHSV = 1 ml liquid/h/g · cat., GHSV = 1870 cc(STP)/h/g · cat.

benzene, toluene, and *p*-xylene are 6.75 Å each (*4*), reflecting the ability of toluene and *p*-xylene to diffuse into the zeolite with the molecular longitudinal axis parallel to the pore. Mesitylene has an effective size of 8.4 Å (*4*) and would therefore have difficulty entering the pore structure. Competition by aromatics for access to interior sites is thereby reduced, allowing the paraffin reaction to proceed to a greater extent.

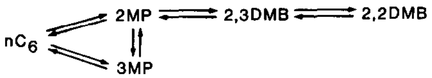
Inhibition of the paraffin reaction by aromatics is thus a result of competitive reaction between paraffin and aromatic. The strongly adsorbed aromatic causes inhibition through one or both of two mechanisms, (a) a site suppression mechanism wherein the number or the effectiveness of catalytic sites available for the paraffin reaction is reduced and (b) an induced pore blockage mechanism whereby the adsorbed cyclic creates diffusional barriers to pore penetration by the paraffin. At this point, it is not clear which of the two mechanisms of inhibition predominates. The fact that the pore structure of mordenite is essentially unidimensional implies that strongly adsorbed cyclics could significantly affect diffusion and counter-diffusion which take place along the same channels of the zeolite. Similar experiments with other zeolites will indicate if structure is an important determinant of the inhibition effect.

Table 1 lists isomer product distributions from *n*-hexane hydroisomerization with both pure hexane and mixed hexane + aromatic feeds. Also listed is the equilibrium distribution from the data by Condon (*5*). To understand the effect of the aromatic cofeed on isomer selectivity, we write the *n*-hexane reaction network as in Scheme 1, where branching/debranching essentially occurs through protonated cyclopropane mechanisms, and isomerizations without a change in the degree of branching occur through alkylhydride shifts (*6*). Isomer transformations that are not indicated explicitly are considered much less favorable since they involve transitions through less stable carbenium ions. Details of the bifunctional catalysis of paraffin isomerization, and of the carbenium ion transformation mechanisms involved, are well reviewed elsewhere (*7, 8*); here we simply examine the isomer selectivities in light of the above network.

TABLE 1

Effect of Aromatic Addition on Isohexane Selectivities

Feed	Normalized isomer product distribution (mole fraction)			
	2MP	3MP	2,2DMB	2,3DMB
Equilibrium (548 K) (*5*)	0.464	0.281	0.149	0.106
Pure NC_6	0.484	0.317	0.073	0.126
20% benzene + NC_6	0.501	0.273	0.116	0.110
20% toluene + NC_6	0.494	0.277	0.114	0.115
20% *p*-xylene + NC_6	0.467	0.273	0.145	0.115
20% mesitylene + NC_6	0.455	0.259	0.162	0.123



SCHEME 1

The data of Table 1 indicate that the isomer selectivities do not differ substantially from the equilibrium distribution. One observation of note is the ratio of 2,2-dimethylbutane to 2,3-dimethylbutane. With a pure *n*-hexane feed the observed ratio (0.58) differs from the equilibrium ratio (1.4) due to the fact that the transformation from the tertiary 2,3-dimethylbutyl carbocation to the less stable secondary 2,2-dimethylbutyl carbocation is the slowest step in the network shown above. On cofeed addition, the ratio increases and approaches the equilibrium ratio; we note the ratio of 1.32 with a mesitylene cofeed. We again attribute this change in isomer selectivity with cofeed addition to a modification in transport characteristics. It is possible that isomer products once formed in the pores have difficulty exiting the pores due to cofeed-induced diffusional barriers. The resulting increase in intrazeolitic residence times may thus allow reaction to proceed to relative equilibrium.

Information on the aromatic reaction can be obtained from Table 2. In contrast to hexane isomerization, the hydroisomerization/hydrocracking products of the reaction of the heavier aromatics are not easy to characterize. Hence the conversions listed in the table are not very accurate and were obtained from approximate carbon balances over the feed and reactor effluent. The complete disappearance of the benzene peak implies a 100% conversion level of benzene during cofeed experiments, which is much higher than the 24% conversion observed with a pure benzene feed. The observation could again be interpreted in terms of reaction and diffusion. Site suppression and self-induced pore blockage could self-inhibit the reaction of pure benzene; such effects could be mitigated if the benzene feed is significantly diluted with paraffin. Similar observations are noted for the reactions of toluene and *p*-xylene. For mesitylene, the smaller conversion levels of the aromatic are yet another indication of the difficulty in pore entrance.

TABLE 2

Approximate Aromatic Conversion Levels for Pure Aromatics and Mixed Paraffin + Aromatic Feeds

	Conversion (%)	
	Pure aromatic feed	20% aromatic + 80% paraffin
Benzene	24.0	100.0
Toluene	12.2	96.9
p-xylene	4.23	85.7
Mesitylene	4.00	42.6

Thus such binary model compound experiments indicate aspects of reaction and diffusion in zeolite pores that cannot be deduced from pure component experiments. In addition to increased understanding of the behavior of complex feeds, the ability to modify reaction rates and selectivities transiently through controlled amounts of appropriate cofeed may have applications to catalyst design and reactor operations. As a specific example, the selective reaction of aromatics in mixed paraffin + aromatic feeds, as discussed in this note, has applications to jet fuel production where aromatic concentrations must be reduced to minimize the smoke point.

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