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Shape-Selective Reactions of Zeolites. Selective Metal-Catalyzed Hydrogenation and Oxidation Using ZSM-5

The ZSM-5 zeolite was shown to act as a shape-selective support for the platinum-catalyzed hydrogenation of olefins and for the copper-catalyzed oxidation of hydrocarbons.

The small uniform pores and large intracrystalline volumes characteristic of zeolites make them ideally suited as shape-selective catalysts or catalyst supports (*1*). Since the first demonstration of molecular shape-selective zeolite catalysis by Weisz and Frilette in 1960 (*2*), numerous articles and patents have appeared in the literature. The vast majority of these involved the use of small-pore zeolites in which the pore openings consisted of 8-membered oxygen rings, such as zeolite A and erionite. The molecular sieving action of these zeolites was due to the fact that the intracrystalline space of these zeolites was inaccessible to molecules having a critical diameter larger than about 5 Å, thereby permitting the selective reaction of linear compounds in the presence of their branched isomers. Significantly less use has been made of the large-pore zeolites with pore openings consisting of 12-membered oxygen rings, typical of faujasites, since these zeolites are incapable of discriminating effectively between molecules having critical diameters less than 8 Å.

With the recent discovery of ZSM-5, a zeolite of novel structure (*3*), possessing pore openings composed of ten-membered oxygen rings and intermediate in size between the small-pore and large-pore zeolites, it became feasible to perform shape-selective separations hitherto unobtainable. ZSM-5 at room temperature totally excludes such highly branched molecules as 1,2,5-trimethylbenzene, 2,2,4-trimethylpentane, and 3,3-diethylpentane, while, unlike the small-pore zeolites, permitting entry of many simple aromatic and branched hydrocarbons. The use of ZSM-5 for the shape-selective, acid-catalyzed cracking of linear and singly branched paraffins, as well as the selective alkylation of aromatics, has recently been reported (*4*). Separation of *para*-xylene from its isomers (*5*), as well as the selective alkylation of toluene to produce *para*-xylene (*6*), has also been accomplished by means of ZSM-5, due to differences in diffusional rates of the xylene isomers in the zeolite. On this basis, ZSM-5 appeared ideally suited as a potential catalyst or catalyst support for a variety of shape-selective chemical conversions of organic substrates.

The ability of zeolites to function as a shape-selective support for platinum-catalyzed hydrogenations has been reported for a platinum co-crystallized A zeolite (*7*) and for an externally poisoned platinum mordenite (*8*). We now wish to report the first example of a shape-selective hydrogenation using ZSM-5 as a shape-selective catalyst support.

The relative diffusivities of various olefins in ZSM-5 were assessed by studying the relative rates of isomerization of these terminal olefins to their internal isomers, over an acid form of ZSM-5, a reaction shown to be diffusion controlled. The relative conversions obtained under competi-

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TABLE 1

Competitive Isomerizations of Olefins

T (°C)	A	B	Percentage conv. A	Percentage conv. B	Selectivity k_A/k_B
150	Hexene-1	6-Methyl-1-heptene	41	24	1.8
175	Hexene-1	3-Ethyl-1-pentene	64	2.8	35
175	Hexene-1	4,4-Dimethyl-1-hexene	54	0.65	120

tive conditions (see Table 1) indicated relatively little difference between a linear and a methyl-branched olefin, whereas the presence of ethyl branching or a geminal dimethyl group greatly reduced the rates of diffusion of these molecules in ZSM-5 (*9*).

In view of the large difference in the diffusivities of hexene-1 and 4,4-dimethyl-1-hexene in ZSM-5, the competitive hydrogenation of an equimolar mixture of these two olefins over platinum-containing ZSM-5 catalysts was investigated. Platinum incorporation in the zeolite was accomplished by direct ion exchange with aqueous solutions of $Pt(NH_3)_4Cl_2$. Platinum contents in the catalysts ranged from 0.6 to 3 wt%.

Reduction of these catalysts, followed by ammonia injection to suppress acid activity, resulted in highly shape selective hydrogenation catalysts. With these shape-selective catalysts, greater than 90% hydrogenation of the linear olefins was observed, whereas conversion of the branched olefin was limited to less than 1% (see Table 2). In a similar manner, styrene was selectively hydrogenated relative to 2-methylstyrene.

Shape-selective oxidation, or rather combustion, has been reported for a platinum-entrained A zeolite (*10*), where linear paraffins were selectively oxidized to carbon dioxide. We now wish to report the shape-selective air oxidation of *para*-xylene in the presence of an equimolar amount of its *ortho* isomer at 400–450°C over a cupric ion-exchanged ZSM-5 (see Table 3). The predominant oxidation products detected under these conditions were CO_2 and water. The combustion of the *para* isomer was approximately 15 times faster than that of the *ortho* isomer, due to the greater diffusivity of *p*-xylene in ZSM-5.

These results clearly demonstrate the ability of ZSM-5 to act as a shape-selective catalyst and catalyst support for a variety of chemical conversions, the full potential of which has yet to be established.

TABLE 2

Shape-Selective Hydrogenation over Pt/ZSM-5

Catalyst	Temperature (°C)	Percentage hydrogenation	
		Hexene-1	4,4-Dimethyl-1-hexene
0.5% Pt/Al_2O_3	275	27	35
Pt/ZSM-5	275	90	<1
		Styrene	2-Methylstyrene
0.5% Pt/Al_2O_3	400	57	58
Pt/ZSM-5	400	50	<2

TABLE 3

Selective Oxidation of Xylene Isomers over Cu-ZSM-5 (1% Cu)

T (°C)	Percentage conversion[a]		Percentage *ortho* isomer in product
	ortho	*para*	
390	<3	21	54
410	10	79	83
450	18	97	97

[a] Relative to 3,3-dimethylpentane used as inert internal standard.

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