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NOTES

Catalysis by Crystalline Aluminosilicates: Characterization of Intermediate Pore-Size Zeolites by the "Constraint Index"

INTRODUCTION

Crystalline aluminosilicate zeolites have become materials of considerable scientific and commercial importance (*1*). For example, the synthetic Zeolite A (*2*) is used as a sorbent and ion exchanger. Zeolite X and the closely related Y (*3*), both synthetic zeolites of the faujasite structure, became the basis of an important new type of cracking catalyst in the petroleum industry (*4*). Numerous scientific papers have appeared discussing the catalytic behavior of zeolites (*5*).

Of special significance is the ability of zeolites for shape-selective catalysis: they may catalyze the conversion of only those molecules which can enter the free intracrystalline space, or generate only those molecules than can emerge therefrom (*6, 7*). The intracrystalline pore volume of zeolites such as Linde 5A crystal, chabazite, and erionite is accessible through apertures formed of rings of eight oxygen atoms which are selectively permeable to normal paraffins, but exclude isoparaffins and cyclic structures. These 8-ring zeolites are usually referred to as small-pore structures. The faujasite-like zeolites (X and Y), mordenite, and several other zeolites (*8*) are characterized by 12-membered rings. These zeolites sorb fairly large molecules and do not distinguish among large classes of materials such as normal and isoparaffins. In contrast with the 8-ring structures, these 12-ring structures are sometimes referred to as "large-pore."

New zeolites have been discovered with shape-selective properties intermediate between those exhibited by the small-pore and the large-pore zeolites. Examples of these are ZSM-5, -11, -12, -35, and -38. Of these, ZSM-5 has been investigated in greatest detail. At room temperature, it permits sorption of normal paraffins and singly methylbranched paraffins, such as 3-methylpentane, but excludes the bulkier doubly branched hydrocarbons such as 2,2-dimethylbutane (*9*). As catalysts, these zeolites showed a variety of unusual properties: they convert methanol selectively to high-octane gasoline (*10a, 10b*); they remove wax molecules from petroleum fractions (*11*); and they will synthesize ethylbenzene, isomerize xylene, and disproportionate toluene (*10a*). The exceptional selectivity and low aging characteristics in these processes are a result of the intermediate pore size of this class of catalysts. Because of the importance of these zeolites, it is of interest to have a test method which can readily identify a zeolite as a member of this class. This paper describes such a test based on the observation of the relative rate of cracking of 3-methylpentane and *n*-hexane. Since this method measures the degree of constraint of the internal zeolite structure upon the reacting molecules, the term "Constraint Index" is used to identify the numerical value obtained from this measurement.

DETERMINATION OF THE CONSTRAINT INDEX

The determination of the "Constraint Index" is made by continuously passing a mixture of equal weight of normal hexane and 3-methylpentane over a small sample, approximately 1 g or less, of zeolite at atmospheric pressure according to the following procedure: a sample of the zeolite

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is crushed to a particle size about that of coarse sand and placed in a vertically positioned glass tube. Prior to testing, the zeolite is treated with a stream of air at 1000°F for at least 15 min, and preferably for 1 hr. The zeolite is then flushed with helium and the temperature adjusted between 550 and 950°F to give an overall conversion between 10 and 60% as determined from a preliminary experiment. The mixture of hydrocarbons is passed over the zeolite with a syringe pump at one liquid hourly space velocity (i.e., one volume of hydrocarbon per volume of zeolite per hour) together with a helium dilution to give a mole ratio of helium to total hydrocarbon of 4:1 (700 ml of helium (STP) per hour per milliliter of liquid hydrocarbon mixture pumped per hour). After 20 min on stream, a sample of the effluent is taken and analyzed, most conveniently by gas chromatography, to determine the fraction remaining unchanged for each of the two hydrocarbons.

The above experimental procedure usually makes it possible to achieve the desired overall conversion of 10 to 60%. It is occasionally necessary to use more severe conditions for samples of very low activity. This can occur, for example, with zeolite samples having a very high silica-to-alumina ratio. In those instances, a liquid hourly space velocity of less than one, such as 0.1 or less, can be employed in order to achieve a minimum total conversion of about 10%.

The Constraint Index is calculated as follows:

$$\text{Constraint Index} = \frac{\log\text{ (fraction of }n\text{-hexane remaining)}}{\log\text{ (fraction of 3-methylpentane remaining)}}.$$

The Constraint Index, therefore, approximates the ratio of the cracking rate constants for the two hydrocarbons.

THE CONSTRAINT INDEX FOR DIFFERENT ZEOLITES

The Constraint Index was determined for a variety of zeolites at 600°F and for amorphous silica–alumina at 950°F. The results are summarized in Table 1.

Erionite, which is representative of shape-selective catalysts with an 8-ring window, has a Constraint Index of 38 which indicates no substantial cracking activity for 3-methylpentane, as reported previously. At the other extreme, the large-pore zeolites, with 12-ring windows, such as ZSM-4, H-Zeolon, REY (rare-earth exchanged zeolite Y) whose structure is known, as well as zeolite beta and amorphous silica–alumina, have constraint indexes between 0.4 and 0.6. These latter values reflect the intrinsic cracking reactivity of the two hydrocarbons; the structural dimensions of the pores are large enough to exert little if any discriminatory influence of these zeolites. Zeolites exhibiting a Constraint Index of 1 to about 12 can be regarded as indicative of a structure effectively intermediate in pore size.

The crystal structures of the zeolites ZSM-5 (*12a*) and ZSM-11 (*12b*) have been published recently. Consistent with the expectations from sorption data and the Constraint Index, which rank them as intermediate between 8-ring and 12-ring zeolites, ZSM-5 and ZSM-11 have been found to have a channel system with windows of 10-membered rings. TMA offretite (*13*), an experimental material produced in these laboratories, also exhibits constrained cracking of 3-methylpentane. The structure of this material appears to be similar to that proposed for natural offretite and the latter is characterized by 12-ring windows (*14*). The explanation in this case for the constrained cracking

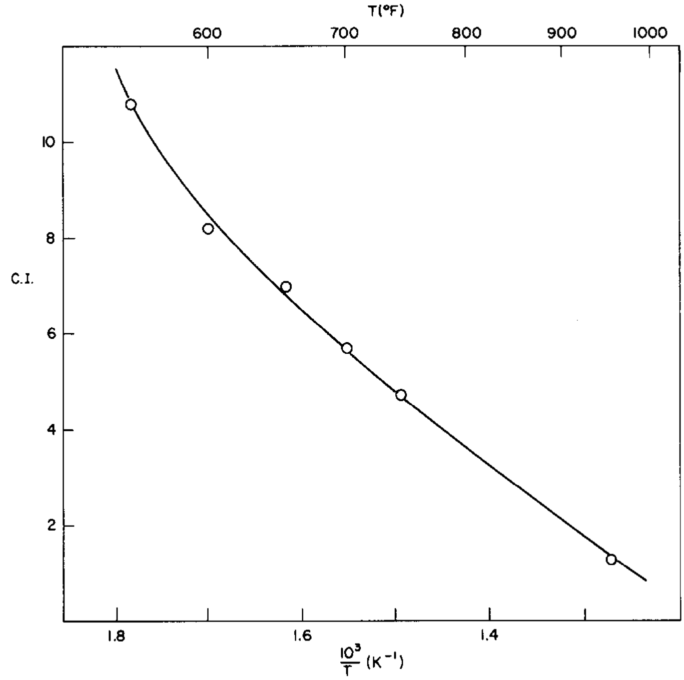

FIG. 1. Temperature dependence of constraint index of HZSM-5.

could be that the effective size of the 12-ring window is reduced because of marked departure from planarity, or puckering.

If the Constraint Index of ZSM-5 is measured at different temperatures, but within the bounds of the foregoing limits for conversion, it is found to vary but remains within the range of 1 to 12. This variation is shown in Fig 1. Other zeolites have been observed to vary less than

TABLE 1

Zeolite	Constraint Index
ZSM-5	8.3
ZSM-11	8.7
ZSM-12	2
ZSM-35	4.5
ZSM-38	2
TMA offretite	3.7
Beta	0.6
ZSM-4	0.5
H-Zeolon (Mordenite)	0.4
REY	0.4
Amorphous silica–alumina	0.6
Erionite	38

ZSM-5, and in some cases with a reversal of the temperature dependence.

In contrast with the effect of temperature, the Constraint Index is relatively little effected by other parameters: for example, by the presence of alumina binder; or by changing the crystallite size of the ZSM-5 sample over two orders of magnitude, from about 0.05 to 15 μm. Figure 2 shows an Arrhenius plot for the cracking of the individual hexane isomers over two HZSM-5 samples of different crystal size. The higher cracking rate of the 2- to 4-μm–sized zeolite crystal for *n*-hexane is an indication of a somewhat higher intrinsic acid activity of this particular sample. That this is not shown in the cracking of 3-methylpentane points to a minor diffusional retardation of the branched hexane in the larger zeolite crystallite. This fact, however, has only a small effect on the ratio of the rate constants, i.e., the Constraint Index. Thus, the method appears to provide a very useful tool for identifying zeolites of intermediate pore size.

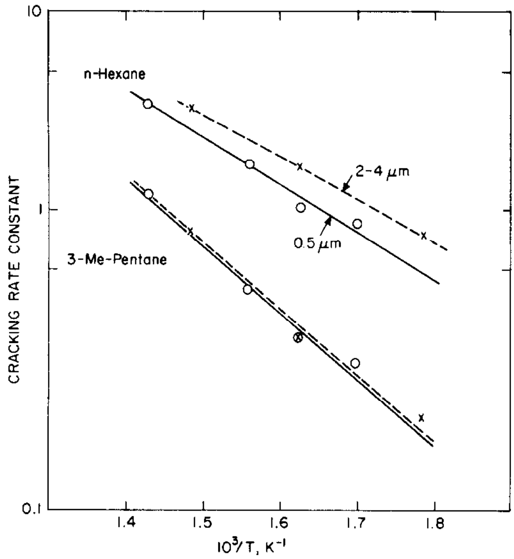

FIG. 2. Arrhenius plot for the cracking of hexane isomers by HZSM-5 of different crystal size.

CORRELATION WITH CATALYTIC SELECTIVITY FOR PRODUCTS

It is of some interest to examine how the Constraint Index correlates with the product distribution in a reaction ordinarily capable of forming fairly large molecules. Such a reaction is the direct catalytic conversion of methanol to a mixture of hydrocarbons, a reaction discovered in the Mobil laboratories (*10, 15*) and since studied elsewhere (*16*). This reaction was conducted with a variety of zeolite catalysts for the purpose of comparing the distribution of molecular weight of the aromatic hydrocarbons produced (*17*). The results of this comparison are shown in Table 2.

TABLE 2

Aromatics Distribution from Methanol Conversion[a]

Zeolite	CI	Distribution of aromatics (%)	
		C_6–C_{10}	C_{11}–C_{12}
Erionite	38	—	—
ZSM-5	8.3	99	1
ZSM-11	8.7	100	0
ZSM-35	4.5	100	0
ZSM-12	2	75	25
Beta	0.6	17	83
ZSM-4 (omega)	0.5	22	78
H-Zeolon (mordenite)	0.4	25	75

[a] 700°F, 1 LHSV, Atmospheric Pressure.

Clearly, small-pore zeolites (CI > 12) make no aromatics and large-pore zeolites (CI < 1) give heavy aromatics, mainly penta and hexamethylbenzene, whereas zeolites with a CI of 1–12 produce predominantly light aromatics (C_6–C_{10}). ZSM-12, with a CI on the lower end of the range, produces a small but significant fraction of heavy aromatics. Thus, the product selectivity from methanol, too, is consistent with the concept that zeolites which have a Constraint Index of about 1 to 12 exhibit intermediate pore size behavior.

CONCLUSION

A new class of zeolites, of which ZSM-5 is a member, has been found to be characterized by its relative activity for cracking *n*-hexane and 3-methylpentane, which is numerically defined as a Constraint Index of 1–12. The value of the latter for any zeolite correlates well with its catalytical properties in many reactions. As shown here, in methanol conversion the Constraint Index value is indicative of the aromatic product selectivity.

Other correlations of pore size and, hence, of the Constraint Index are found in the selectivity of xylene isomerization (*18*), transalkylation of C_8-aromatics (*18*), shape selective dewaxing (*11*), and in the selectivity and low aging properties of ZSM-5 during ethylbenzene synthesis (*18*).

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