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The Nature of Active Sites on Zeolites

VII. Relative Activities of Crystalline and Amorphous Alumino-Silicates

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The rate constants for *o*-xylene isomerization over silica-alumina, several faujasite type zeolites and synthetic mordenite have been measured at various temperatures and compared at 260°C to silica-alumina. The rate constants vary over a range of 40,000. Of the catalysts examined, H-mordenite was the most active and MnX zeolite the least active. Many of the faujasite type catalysts were less active than silica-alumina. The activities of the most active faujasite catalysts were only about forty times the activity of silica-alumina and the differences in activities of the various catalysts can be reasonably interpreted in terms of the Bronsted acid site concentrations. No evidence of superactivity is observed in this reaction.

INTRODUCTION

Synthetic zeolite catalysts have been the subject of many recent investigations and are used in a number of important commercial applications. They have been shown to be catalysts for a wide spectrum of reactions. The catalytic uses have been reviewed recently (*1*, *2*). For many reactions, zeolites have been shown to be more selective and more active than amorphous silica-alumina catalysts. Thus, Rabo, Pickert, Stamires, and Boyle (*3*) showed the advantages of zeolites for hexane isomerization. Frilette, Weisz, and Golden (*4*) showed that NaX and CaX zeolites were similar or greater in activity than amorphous silica-alumina cracking catalysts. Plank, Rosinski, and Hawthorne (*5*) demonstrated the high activity of synthetic zeolites for gas oil conversion. Many others have studied hydrocarbon cracking over zeolites (*1*). Pickert, Rabo, Dempsey, and Schomaker (*6*) have shown the high isomerization activity of zeolites containing noble metals, while zeolites have been shown to promote alkylation reactions (*7*, *8*). Venuto and co-workers (*2*) have shown that zeolites can catalyze a wide range of organic reactions.

Miale, Chen, and Weisz (*9*) have compared the relative rates for *n*-hexane cracking by a wide variety of zeolite catalysts with those of amorphous silica-alumina catalysts. With few exceptions, they found that the zeolite catalysts (synthetic faujasites and mordenites and several natural minerals) were many times more active than amorphous silica-alumina. A number of the catalysts were found to be "superactive": that is, the relative rate, compared to silica-alumina taken as 1, is $\geqslant 10{,}000$. The high reactivity of zeolites has led to suggestions that the active sites on crystalline alumino-silicates are considerably different from those on amorphous alumino-silicates. Electrostatic fields (*6*, *7*), Lewis acid sites (*1*, *10*, *11*) and Bronsted acid sites (*12–16*) have been suggested as possible active centers. Dual sites, such as a Bronsted and a Lewis acid site acting together, have also been suggested (*17*).

Several observations of zeolite structures and catalytic activities suggest that, in hydrocarbon reactions, Lewis acid sites alone are not responsible for the catalytic activity (*2*, *14*, *15*). Similarly, under reaction conditions, it is doubtful that strong electrostatic fields can exist in the zeolites since the magnitude of any field is likely to be markedly decreased by its interaction with adsorbed water (*2*, *12*, *16*). A number of workers (*2*, *12*, *14*, *16*) have suggested that Bronsted acid centers are responsible for the catalytic activity. If this is so, it is difficult to see how a 10- to 15-fold difference in Bronsted acidity between the most acidic zeolite (hydrogen Y) and silica-alumina can explain the huge difference in catalytic activity for hexane cracking observed by Miale, Chen, and Weisz (*9*). It is not to be expected that diffusion factors would favor the zeolites by such a large margin.

In order to shed more light on this problem, a variety of different zeolites have been investigated with respect to the *o*-xylene isomerization reaction. *O*-xylene isomerization has long been considered to be a proton acid catalyzed reaction.

EXPERIMENTAL

Apparatus

Catalytic activity measurements were made in a flow micro-reactor at atmospheric pressure. A helium carrier gas was used at a flow rate of 50 ml min^{-1}. The helium passed through a saturator containing ortho-xylene thermostated at 20°C. The reactor consisted of a stainless steel tube and contained one gram of catalyst in the form of 20–40 mesh granules supported on quartz wool. The feed passed through a preheat section before entering the reactor. Analysis of feed and product streams was made by gas chromatography using a five foot column filled with a 20 percent mixture of 60 percent Silicone Fluid 96 and 40 percent Carbowax 20M supported on 60–80 mesh Chromosorb W. The column was maintained at 150°C. The catalyst was dried by heating in the reactor in flowing helium for three hours at 480°C. The catalyst was then cooled to about 200°C and the helium diverted through the *o*-xylene saturator. The catalyst activity was measured by observing the isomerization of the *o*-xylene to *m*- and *p*-xylene. After steady-state had been obtained, the conversion was measured by determining the concentration of *o*-xylene and *m*- plus *p*-xylene in the product. The conversion was measured at several temperatures. Temperatures were adjusted so that conversions were sufficiently low (<40 percent) that diffusion effects were minimized. Temperatures were in the range 250 to 480°C. Only small amounts of products other than the isomeric xylenes were detected. The contact time calculated from the catalyst volume and the flow rate was about 2 seconds. Surface area and x-ray diffraction measurements after reactor tests showed negligible or no loss of structure. The coke level on the used catalysts was 2–4% by weight. Some runs were made on 60–80 mesh granules so that the influence of diffusion could be investigated.

Materials

O-xylene was Eastman Research Grade. It was used without further purification.

The catalysts investigated are listed in Tables 1 and 2. The X and Y zeolites were prepared by ion exchange of single parent batches of sodium X and Y zeolites. The X zeolite had a SiO_2/Al_2O_3 ratio of 2.6 and the Y zeolite had a ratio of 4.9. The Y zeolites were obtained from the Linde Division of Union Carbide Corporation. The Zeolon (synthetic mordenite) was obtained from the Norton Company. The ultrastable zeolite (Sample 11) was made from NaY according to the Procedure "A" of Davison Chemical (*18*). The amorphous silica-alumina was Davison 13% alumina cracking catalyst. The rare earth forms were prepared by ion exchange with a solution of mixed rare earth chlorides (American Potash and Chemical Company, Rare Earth Division). A typical analysis of the mixture for major components was CeO_2, 47.8; La_2O_3, 24.2; Nd_2O_3, 18.2; Sm_2O_3, 2.8; Gd_2O_3, 0.9.

Sample 13 was prepared by ion exchange of sodium Y zeolite having a SiO_2/Al_2O_3 ratio of 3.4. Sample 12 was made by steam calcination of ammonium Y zeolite at 650°C (*19*). Samples 9 and 14 were prepared by ion exchange of the ammonium form with the appropriate cation until the cations accounted for 40 percent of the ion exchange capacity.

Sample 15 was hydrogen mordenite as received (Lot BP-123). Sample 16 was obtained by treatment of sodium zeolon (Lot HB-23) with N hydrochloric acid and

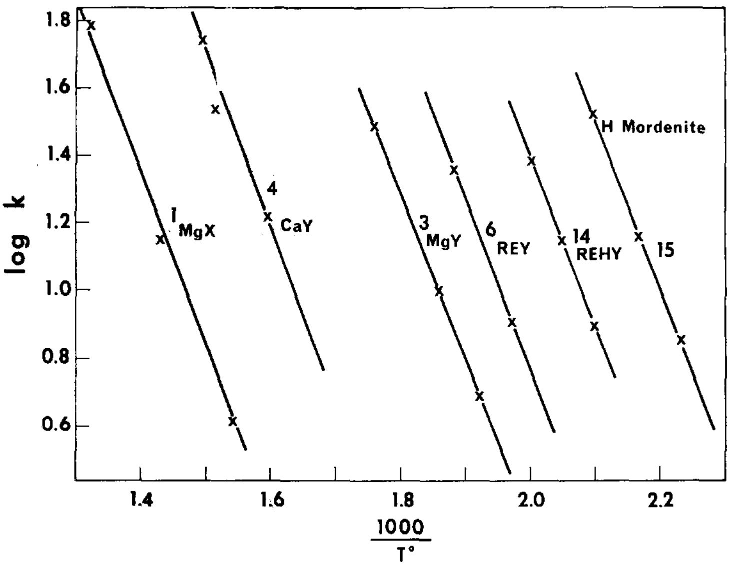

FIG. 1. Arrhenius plots for various representative catalysts. (Numbers correspond to catalysts listed in Tables 1 and 2).

Sample 17 by exhaustive exchange of sodium zeolon with ammonium nitrate solution.

The parent source, major cation, degree of exchange and surface area are given in Tables 1 and 2. Table 1 lists catalysts less active than the reference silica-alumina and Table 2 catalysts more active than silica-alumina.

RESULTS

The isomerization of xylene has been shown to be a first order reaction over several catalysts (*20*). Hence, the reaction rate is given by

$$k = \left(\frac{\mu}{\nu}\right) \ln \frac{C_0}{C}$$

where k is the first order rate constant, μ is the flow rate in ml per minute, ν is the volume of catalyst in ml, C_0 is the initial concentration of *o*-xylene, and C is the steady state concentration of *o*-xylene.

C_0/C is obtained from the chromatogram and is the ratio of the *o*-xylene peak area in the feed to the *o*-xylene peak area in the products. It can be expressed in terms of the conversion as 100/(100-percent conversion). Hence, the rate constant can be expressed as:

$$k = \left(\frac{\mu}{\nu}\right) 2.303 \log\,[100/(100-\%\,\text{conversion})]$$

From the reactor data, the rate constants were calculated and Arrhenius plots of log

TABLE 1

Sample	Zeolite	Major cation	% Ion exchange 100% − % residual Na	Surface area, $m^2\,g^{-1}$	Rate constant at 260°C
8	X	Mn	92	758	0.02
2	X	Ca	99	774	0.03
13	Y (3.4)[a]	Ca	95	927	0.08
5	Y	Sr	90	810	0.09
1	X	Mg	83	797	0.39
7	X	Zn	94	679	0.42
4	Y	Ca	94	872	0.61
18	Silica Alumina	—	—	350	3.1

[a] SiO_2/Al_2O_3 mole ratio.

TABLE 2

Sample	Zeolite	Major cation	% Ion exchange 100% − % residual Na	Surface area, $m^2 g^{-1}$	Rate constant at 260°C
18	Silica-Alumina	—	—	350	3.1
3	Y	Mg	83	889	7.8
6	Y	RE	92	776	22.9
10	Y	NH_4	98	931	44.7
11	Y	H	99	749	48.8
9	Y	MgH	90	932	49.2
12	Y	H	90	802	49.9
14	Y	REH	98	825	122
15	Mordenite	H	33	450	417
16	Mordenite	H	99	518	816
17	Mordenite	NH_4	99	455	826

k against 1/T were made. A similar expression has been derived recently by Miale, Chen, and Weisz (*9*) for *n*-hexane conversion.

From the Arrhenius plots, the rate constant was calculated at a suitable temperature for all the catalysts studied. A temperature of 260°C was chosen as the standard temperature since this involved minimum extrapolation outside the range of temperature at which activities were actually measured. In general, the extrapolations were over less than a 50°C range.

The calculated values of k for a wide range of catalysts are listed in Tables 1 and 2.

Discussion

The results of this study of *o*-xylene isomerization show a wide range of rate constants for the various catalysts depending on their compositions. The rate constants vary by a factor of 4×10^4 between the most active and the least active catalysts investigated (H-Zeolon and MnX zeolites). This range of activities is distributed on both sides of the silica-alumina activity. For faujasites only, the range of rate constants is 6×10^3.

A number of general trends are observed in the data. As observed previously, the activity of the alkaline earth zeolites increases with decreasing cation radius of the exchanged cation. The order of reactivity corresponds to the order of increasing acidity (*16*). For both magnesium and calcium zeolites, the activity with increasing silica-to-alumina ratio again is the same order as the acidity. Of the faujasite type zeolites, the hydrogen form is more active than the rare earth form which in turn is more active than the magnesium and calcium forms, again conforming to the order of Bronsted acidities. The calcium X and Y forms are both less active than the silica-alumina catalyst in agreement with the results of Frilette, Weisz, and Golden (*4*) for cumene conversion. Topchieva and Romanovski (*21*) obtained similar results.

The rate constants obtained for xylene isomerization are in marked contrast to those reported by Miale, Chen, and Weisz (*9*) for hexane conversion. Whereas Miale *et al.* (*9*) report superactivities for a number of zeolites of $\alpha > 10{,}000$ when compared to a silica-alumina catalyst, the results of this study show that the most active catalyst has a rate constant only 150 times that of silica-alumina while a large number of the catalysts are considerably less active than silica-alumina. The most active faujasite is only forty times more active than silica-alumina. However, for comparable samples, the activity ranking of the catalysts is similar for the two reactants.

Since the reactions were carried out under conditions such as to minimize diffusion effects, it is to be expected that diffusion phenomena are making no important contribution to the magnitude of the observed rate constants. Similar considerations must be given to the results of Miale *et al.* (*9*). The absence of a particle size effect on the activity confirmed that the influence of diffusion effects was absent or very small.

It has been shown previously (*16*, *17*, *22*, *23*) that hydrogen Y, magnesium hydrogen Y, and rare earth hydrogen Y zeolites possess about 14–18 times as many Bronsted acid sites as silica-alumina. Hence, it may be feasible to explain the 15–40 fold greater activity of these zeolites in terms of the greater acid site concentration. Samples of intermediate acidity, such as rare earth and magnesium Y zeolites exhibit intermediate activities.

It is difficult to explain the "superactivities" of the catalysts reported by Miale *et al.* in terms of the acidity increase. The results suggest that the hexane conversion and *o*-xylene isomerization reactions must proceed via very different mechanisms at least in the rate determining step. By comparison of the data for the two reactions, it is seen that the rate constant for the xylene isomerization is one to three orders of magnitude greater than for the hexane conversion. Calculations of the activation energy for the reaction from the slopes of the Arrhenius plots give value of 20 ± 3 kcals mole^{-1} (the activation energy for MnX and ZnX was 33 ± 3 kcals mole^{-1}) compared to values of 30 kcals mole^{-1} obtained for hexane conversion (*9*). From the work of Miale *et al.* (*9*), and Tung and McInnish (*24*), it would appear that some property of certain ion-exchanged forms of zeolites promotes hexane cracking much more effectively than silica-alumina. This could be the electrostatic field or other properties associated with the structure of the zeolites. However, since many of the zeolite forms are shown to be less active, at least for *o*-xylene isomerization, than silica-alumina, the property responsible for "superactivity" is not a universal catalytic property of zeolites.

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