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Catalysis by Crystalline Aluminosilicates
II. Molecular-Shape Selective Reactions

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Molecular-shape discriminating catalytic reactions have been demonstrated with crystalline aluminosilicate salts of the "molecular sieve" family, using catalytic activities intrinsically possessed by these solids as well as by catalytic centers introduced into their intracrystalline cavities.

INTRODUCTION

The crystalline aluminosilicates (*1*) known as "molecular sieves" are solids consisting of microcrystals. When dehydrated, they contain an appreciable intracrystalline volume formed by uniform chambers interconnected by ports of uniform size. These make the intracrystalline volume accessible to only those molecules that have a shape which permits ready passage. Larger molecules are restricted to contact with only the relatively small external surface of the crystals. Because of their unique physical structures, these materials have been used as selective absorbents (*2*), e.g. for the batch separation of straight chain from branched chain paraffins.

Catalytic activity located within the intracrystalline volume of host crystals would make possible continuous chemical transformations of invading molecules as with other porous catalysts. With crystalline aluminosilicates, however, transport restrictions could involve selectively molecules of only such shapes which can pass through the host structure. In pursuing this investigation, certain intrinsic catalytic activities were found to be present in the intracrystalline volume, as reported in an accompanying paper (*3*). In addition, we have found that other activities may be imparted by suitable modifications. This paper will describe various molecular-shape selective catalytic reactions which have been obtained.

PRINCIPLES

We will be concerned with essentially two types of molecular shape selective catalysis. The first leads to charge molecule selectivity, the second to product molecule selectivity.

1. A class of molecules a_i which passes the "ports" of a molecular sieve host is catalyzed to a conversion product (or products) b_i, while another class of molecules, A_i, usually catalyzed by the same catalytic sites is excluded from contact with them and thus from being converted:

$$a_i \rightarrow [a_i] \rightarrow [b_i] \rightarrow b_i$$
$$A_i \xrightarrow[\wedge]{\vee} \ldots$$

We shall adopt the convention of using lower case letters for the small molecular species which will pass, and capital letters for the large ones which cannot pass into the host crystal containing the effective catalytic sites; the bracketted species represent those within the catalytic cavities.

2. One or more molecular species which can pass to catalytic sites are converted to products some of which can and some of

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which cannot pass out of the crystalline cavities.

$$\begin{tikzcd}
 & & {[b_i]} \arrow[r] \arrow[dl, shift left] & b_i \\
a_i \arrow[r] & {[a_i]} \arrow[ur, shift left] \arrow[dr, shift left] & & \\
 & & {[B_i]} \arrow[ul, shift left] \arrow[r, "\vee", "\wedge"'] & \cdot\ \cdot\ \cdot\,\cdot\cdot
\end{tikzcd}$$

There can be a sustained net rate of production only of b_i species but not of B_i. The latter species may be produced in a transient manner internally, either until its concentration is high enough to interfere with the rate process, e.g. by "fouling"; or, if a reasonable back-reaction rate is feasible, $[b_i] \rightleftharpoons [B_i]$, until an internal steady state concentration of B_i has established itself.

SHAPE SELECTIVE CATALYSIS USING INTRINSIC ACTIVITIES

Cracking of Paraffin Hydrocarbon

Experimental. The catalytic cracking of *n*-hexane, of 3-methylpentane, and of a mixture of C_6 hydrocarbons containing the three methylpentane isomers was studied. The normal hexane was obtained as pure hydrocarbon from Humphrey Wilkinson Corp., the 3-methylpentane was a Phillips research grade hydrocarbon. The mixed hydrocarbons were a C_6 naphtha fraction analyzing 27.1 wt % *n*-hexane, 26.7% 2-me-pentane, 18.9% 3-me-pentane, the remaining materials being various minor isomeric and cyclic C_6 components. The catalysts compared were the sodium and calcium salts of the "A" lattice aluminosilicate (4A and 5A) "molecular sieves," and the calcium salt of the "X" lattice (10X). These were obtained from the Linde Co. as clay-free powders and each was formed into $\frac{1}{8} \times \frac{1}{8}$-inch cylindrical pellets. Also, standard silica-alumina cracking catalyst (Socony Mobil Oil Co., 46 AI bead catalyst, 420 m^2/g surface area, 10 wt % Al_2O_3, crushed and sized to 14/20 mesh). All experiments were made in a 50 ml Pyrex reactor tube packed with catalyst, at either 500°C or 540°C, with a residence time $\tau = 7$ sec (based on empty reactor) and for 2 hr duration. The purity and composition of each reactant was determined by chromatographic analysis. Total product analyses were obtained from combined analyses of the gaseous and the liquid products. We estimate the accuracy of each analyzed component to be within $\pm 1\%$, i.e. each component analysis may be interpreted as reading $(x \pm 1)$ mole % of total charge.

In the case of the "thermal" control runs, the reactor was packed with Vycor chips in place of catalyst solid.

Results. Table 1 summarizes and compares the amount of conversion obtained for *n*-hexane and for 3-methylpentane as reactants when contacted with the different solids.

TABLE 1
CHARGE SELECTIVITY IN THE CRACKING OF HEXANES[a]

Hydrocarbon charge	Conversion (%)			
	Thermal	4A	5A	Silica-alumina
n-hexane	1.1	1.4	9.2	12.2
3-methylpentane	<1.0	<1.0	<1.0	28.0

[a] $\tau = 7$ secs, 500°C.

Table 2 shows an analysis of the hexanes mixture after size-selective catalytic cracking over 5A aluminosilicate, and, for comparison, after cracking over conventional silica-alumina, and after thermal contact without catalyst.

Table 3 gives the ratios of isobutane to *n*-butane and isopentane to *n*-pentane in the products for *n*-hexane cracking experiments over 5A and, for comparison, results with silica-alumina and also with 10X calcium aluminosilicate.

Discussion. The selective cracking by 5A calcium aluminosilicate of the normal paraffin structure is shown by the data of Table 1. When various structures are simultaneously admitted to this material as a cracking catalyst, the *n*-paraffin again is selectively catalytically converted (Table 2). The usual behavior of conventional catalysts to preferentially crack branched chain paraffins is shown for silica alumina in both sets of experiments. The inactivity of the 4A molecular sieve (Table 1) sug-

TABLE 2

COMPOSITION OF HEXANES AFTER CRACKING OF MIXED C_6 HYDROCARBON CHARGE STOCK[a]

Hexane component	Thermal (wt %)[b]	$SiO_2-Al_2O_3$		5A	
		(wt %)[b]	(Δ)[c]	(wt %)[b]	(Δ)[c]
n-hexane	26.7	24.0	2.7	15.4	11.3
2-methylpentane	28.0	19.7	8.3	26.6	1.4
3-methylpentane	22.7	16.1	6.6	21.3	1.4

[a] 1 atm, 540°C, $\tau = 7$ sec.

[b] Grams in product/100 grams of total charge.

[c] Δ = difference between catalytic and thermal conversion.

gests that, even at cracking temperatures, this structure does not admit normal paraffins at an appreciable rate.

Product selectivity is observed in that for the calcium aluminosilicate of the "A" structure, having about 5 Å port dimensions, isoparaffin products are essentially absent, while they are prevalent with conventional catalysts as well as with the calcium aluminosilicate of the "X" structure, which has unrestrictive port dimensions of about 10 Å.

TABLE 3

ISOPARAFFIN/*n*-PARAFFIN PRODUCT RATIOS FROM *n*-HEXANE CRACKING

	5A	$SiO_2 \cdot Al_2O_3$	10X
iso-C_4/*n*-C_4	<.05	1.4	0.7
iso-C_5/*n*-C_5	<.05	10.0	1.0

Dehydration of Alcohols

The calcium salts of the A and X lattice were reported previously to be active catalysts for the dehydration of alcohols (*4*). The reaction of the primary alcohols proceeds appreciably at temperatures of about 225°C, and sec-butyl alcohol dehydration could be catalyzed at temperatures as low as 100°C. The virtual absence of hydrogen formation permits a good estimation of catalytic activity directly from determination of gas evolution rates. We have used this method as well as direct chromatographic analysis of the product stream. These reactions can be made to obey the shape-selective principles outlined above.

Experimental. Dehydration studies on alcohols having linear and branched structures were made by techniques and catalyst materials similar to those used for paraffin cracking. The catalyst was dried for several hours at 320°C in a stream of inert gas. The temperature was then lowered and the alcohol charged at a rate adjusted to give a contact time of $\tau = 3$ or 6 sec based on the empty reactor volume. After approximately 1 hr to establish steady state conditions, conversion velocity was determined by determining the rate of olefin production.

Reagent grade *n*-butyl alcohol (J. T. Baker Chemical Co.) and *sec*-butyl alcohol were used as received. Reagent grade isobutyl alcohol was stored over 5A molecular sieve to remove traces of *n*-butanol before use.

Results on primary alcohols and discussion. The intrinsically similar behavior of *n*-butyl alcohol and isobutyl alcohol when catalyzed by the *non–shape-selective* 10X catalyst is shown in Table 4. Both alcohols are dehydrated rapidly in the temperature range of about 230–260°C, with the isobutyl alcohol showing somewhat greater reactivity. This behavior is compatible with the fact that both are primary alcohols and should resemble each other.

Both calcium salts, the *shape-selective* 5A and the *non–shape-selective* 10X, show little difference in activity with *n*-butyl alcohol which can penetrate both crystals. However, the isobutyl alcohol, which is excluded from the crystal interior of the 5A crystal shows a dramatic lack of conversion unless one goes to excessively high temperatures. This conversion of excluded molecule at high temperatures is reason-

TABLE 4

DEHYDRATION OF PRIMARY BUTYL ALCOHOLS[a]

Temp. (°C)	Wt % dehydration			
	10X Catalyst		5A Catalyst	
	n-Butyl	Isobutyl	n-Butyl	Isobutyl
220	—	22	10	<2
230	9	46	18	<2
240	22	63	28	<2
260	64	85	60	<2
290	—	—	—	5

[a] $\tau = 6$ sec, 1 atm.

able, since we may expect a small number of catalytic sites to be located at the *exterior* surfaces of the crystals. Catalysis by such sites is also demonstrated by the behavior of secondary butanol.

Results on secondary butanol and discussion. Table 5 shows the results of dehydration of *sec*-butanol over the 10X and 5A calcium aluminosilicates. The rates observed on 10X catalyst demonstrate the very much greater reactivity of the secondary relative to the primary alcohol (cf. Table 4): appreciable conversion of secondary alcohol is achieved in the temperature range of 100 to 130°C. The shape-selective 5A material, however, shows no appreciable conversion at these temperatures. At sufficiently higher temperature, i.e. above about 180°C, conversion can be achieved. From the data at low conversion, x, we have estimated an Arrhenius plot, by assuming a first order approximation of the rate to be valid, i.e., $x = 1 - e^{-k\tau}$, as shown in Fig. 1. It will be seen that the rate constant per unit catalyst volume of the 5A material is between two and three orders of magnitude smaller than is that of 10X catalyst. These relative magnitudes are consistent with the ratio of available surface areas: the B.E.T. data give total surface areas of the order of 500–700 m^2/g (*1*) when the internal surface is accessible to the sorbate; the magnitude of external area of 1 to 5 micron-sized crystals (*1*) calculates to about .6 to 3.5 m^2/g. Thus the surface areas in the two cases also differ by two to three orders of magnitude which is consistent with the observed difference in reactivity at comparable temperatures.

TABLE 5

DEHYDRATION OF *sec*-BUTANOL ON 10X AND 5A CRYSTALS

Temperature (°C)	Conversion (%)	
	10X	5A
109	15	~0
116	25	~0
130	82	~0
190	>90	11
205	>90	26
210	>90	45

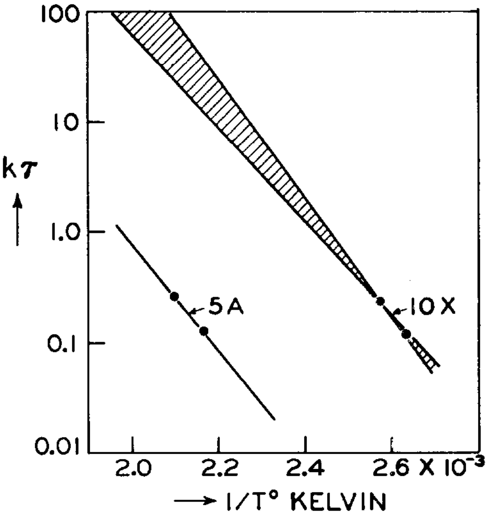

FIG. 1. Arrhenius representation of relative activities of 10X and 5A crystals for *sec*-butanol dehydration.

SHAPE-SELECTIVE CATALYSIS USING INDUCED ACTIVITY

Selective Olefin Hydrogenation Activity

A shape-selective catalyst containing the activity of platinum effective only for hydrocarbons of linear structure has been prepared by incorporation of the platinum in the calcium salt of the "A" crystal.

The commonly available ionic species which contain Pt are too large to penetrate the 5 Å port dimensions of these crystals. A model of the anhydrous $[PtCl_6]^{2-}$ ion has an effective minimum dimension of at least 5.2 Å. Also, no ion exchange was found experimentally when tetrammine platinic chloride was contacted with the "A" structure for several days. The introduction of platinum in this lattice by ion exchange or impregnation from solution is therefore difficult, if not impossible. The method used for successful platinum incorporation was to form the "A" structure sodium aluminosilicate crystals in solution containing cationic platinum complex, with the objective of trapping platinum within the crystalline cavities during their formation. The sodium form was then base-exchanged to form the calcium sieve by the usual techniques. A very selective catalyst was obtained by this procedure when tetrammine platinous chloride was used as the platinum carrier.

Hydrogenation of several aliphatic olefins was used to demonstrate the shape-selective properties of the described platinum catalyst. The activity of this catalyst was compared for propylene, 1-butene, and isobutene individually. Also, the selective conversion of propylene in a mixture was demonstrated.

Catalyst preparation. Seventy-eight grams of $NaAlO_2$ (actual assay 75% $NaAlO_2$, 10–15% NaOH, 10–15% H_2O) was dissolved in 275 ml water; Solution A. Sodium metasilicate, 113 g, was dissolved in 275 ml water; Solution B. Tetrammine platinous chloride monohydrate was obtained by the procedure described by Keller (*5*), with the exception that K_2PtCl_4 with slight excess of HCl was used in place of H_2PtCl_4. Of this solid, .55 g was dissolved in 70 ml water; Solution C. Solutions A and C were combined. Solution B was added at room temperature, stirred under reflux for 7 hr, and filtered. Without prior drying the solid was washed in copious excess of $CaCl_2$ solution to convert it from the Na- to the Ca- form and dried. Its X-ray diffraction pattern was that of 5A calcium aluminosilicate. The Na content was 0.23% showing nearly complete (98.6%) conversion to the calcium form had been accomplished. The material contained 0.31 wt % of platinum.

Experimental. A small amount of finely powdered catalyst distributed over a pad of glass wool was placed in a 7 mm Pyrex tube in a furnace. The catalyst was pretreated at 450°C in a stream of dry helium for 1 hr. Previous to each of the experiments to be described, air was passed over the catalyst for 30 min at this temperature, and the catalyst cooled to reaction temperature in a stream of helium. With this technique, the initial 0.15 g of catalyst was used for all the experiments.

In each experiment, a mixture of hydrogen and olefin (or an equimolar olefin mixture) in a molar ratio 3:1 was passed over the catalyst at a total flow rate of 30 ml/min to give an approximate residence time of 0.3 sec at atmospheric pressure. Samples of the effluent stream were diverted periodically to a vapor chromatography column for analysis.

Results. The results on the conversion of the three olefins, 1-butene, isobutene, and propylene, to the corresponding paraffins, after 10 min of on-stream time, and in the sequence in which the experiments were done, were as follows:

1-butene; 70%
isobutene; <2
propylene; 52

In each of the above experiments, the individual hydrocarbon was used at 25°C. The relatively smaller conversion of propylene as compared to 1-butene does not represent a true comparison of rates, due to catalyst aging during the sequence.

The results with an equimolar mixture

of isobutene and propylene are shown in Fig. 2 for a 3-hr period. This experiment was done at 343°C. As can be seen from the graph, no detectable hydrogenation of isobutene occurred. Propane was the only reaction product detected.

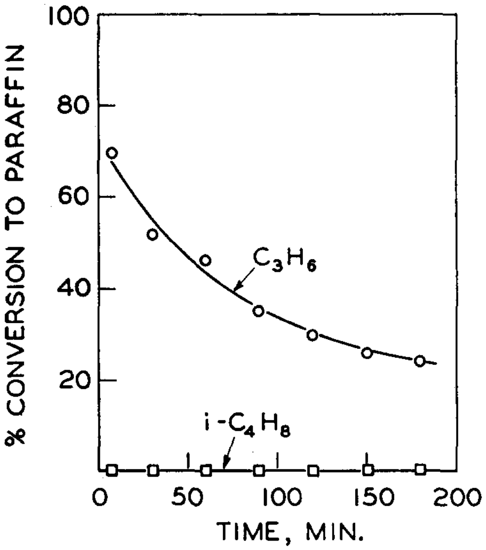

FIG. 2. Selective hydrogenation of propylene in propylene/isobutene mixture.

Discussion. For all practical purposes, the three olefins studied can be considered to have similar reactivities for hydrogenation. The results found with the individual olefins thus reflect that the active platinum sites are successfully shielded from isoolefins. It may be of interest that isobutene hydrogenation activity has been observed when the crystallized catalyst is *not* subjected to thorough removal of extracrystalline platinum complex by repeated exposure to cation-exchanging solutions. This observation serves to demonstrate that, as with alcohol dehydration, extracrystalline as well as intracrystalline catalysis can be caused to occur.

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