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Transport and Reaction of *t*-Butyl Alcohol in H-Mordenite Pores

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Initial rates of *t*-butyl alcohol dehydration catalyzed by crystallites of H-mordenite suspended in liquid reactant were measured at temperatures between 45 and 75°C. Rate was not affected by addition of *n*-heptane diluent to the reactant, but when *n*-heptane or methylcyclohexane initially filled the mordenite pores, rate at 75°C was reduced to 81 or 44% of the former value, respectively. Reaction took place within the intracrystalline pores and was hindered by the difficulty of passage of entering reactant and exiting diluent and product molecules. Molecules with critical diameters summing to about 13 Å are capable of passing one another within a pore, although the narrowest apertures measure only 6.7 × 7.0 Å.

INTRODUCTION

The uniqueness of zeolites as catalysts derives from their networks of uniform, molecular-scale voids with apertures which restrict the entry of reactant molecules and confine some reactions to exterior crystallite surfaces or pore mouths. Though the shape-selective transport restriction is exploited industrially in isomerization of straight-chain paraffins from mixtures containing branched-chain paraffins, quantitative characterizations of coupled mass transport-reaction phenomena in zeolites are still lacking. Even the extent to which internal catalyst surface is utilized in catalytic cracking is unclear (*1*, *2*), and dimensions of molecules which can just pass one another in zeolite pores remain undetermined.

Experiments reported here provide a preliminary characterization of mass transport influence on the rate of dehydration of *t*-butyl alcohol to isobutene catalyzed within the straight, tubular pores of H-mordenite crystallites.

EXPERIMENTAL METHODS

In a typical experiment 125 g of reactant *t*-butyl alcohol was stirred in a thermostated 500 cm^3 reactor, to which was added 0.3 g of H-mordenite crystallites, previously activated for 2 hr in air at 350°C. Product samples (0.5 cm^3) were withdrawn periodically from the closed reactor with a syringe, filtered through a 0.22 μm Millipore filter to remove suspended catalyst, then analyzed by gas chromatography.

Experimental details are summarized in Table 1. Most experiments were performed at 75.0 ± 0.1°C with fractions of mordenite crystallites obtained by air-elutriation of Zeolon H powder (Norton Co., Worcester, MA). Most samples had a mean pore length of 5.9 μm; crystallites used in a single experiment had a mean pore length of 11.3 μ. Unfractionated crystallites were used at 45.0, 55.0, and 75.0°C. Some reactant solutions initially contained *n*-heptane or water, and occasional mordenite samples were initially saturated with *n*-heptane or methylcyclohexane at 75.0°C. Separate references provide details of re-

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TABLE 1

RATE OF *t*-BUTYL ALCOHOL DEHYDRATION CATALYZED BY H-MORDENITE

Composition of reactant solution (mole %)	Temp (°C)	Mean catalyst pore length (μm)	$10^7 \times$ Initial reaction rate (mole/sec g of catalyst)
100% *t*-butyl alcohol	45.0	—[a]	0.32
	55.0	—[a]	1.08
	75.0	—[a]	9.3 ± 1.2[b]
	75.0	11.3 ± 4.3[c]	6.1
	75.0	5.9 ± 3.2[c]	7.4 ± 0.5[b]
90% *t*-Butyl alcohol, 10% *n*-heptane	75.0	5.9 ± 3.2[c]	8.0
90% *t*-butyl alcohol, 10% *n*-heptane[d]	75.0	5.9 ± 3.2[c]	6.0
90% *t*-butyl alcohol 10% methylcyclohexane[d]	75.0	5.9 ± 3.2[c]	3.2
99.0% *t*-butyl alcohol 1.0% water	75.0	5.9 ± 3.2[c]	1.7

[a] Unfractionated crystallites, mean value undetermined.

[b] Mean value ± standard deviation, calculated from three experimental values.

[c] Mean value ± standard deviation. For detailed data see Ref. (*5*).

[d] Paraffin contacted with catalyst at 75°C to fill pores before addition of *t*-butyl alcohol.

actor operation and product analysis (*3*) as well as of catalyst handling, size fractionation, and size determination (*4*, *5*).

RESULTS

Representative conversion data at 75.0°C are shown in Fig. 1. Conversion of undiluted alcohol increased linearly with time to a value of about 0.002 moles/g of catalyst; the slope of the line provides a precise determination of initial reaction rate. Rate decreased markedly, becoming nearly zero at conversions not greatly exceeding those shown. A similar pattern was observed in all experiments, exemplified by the results of Fig. 1. The initial rate data are summarized in Table 1.

These data show the effects of paraffin

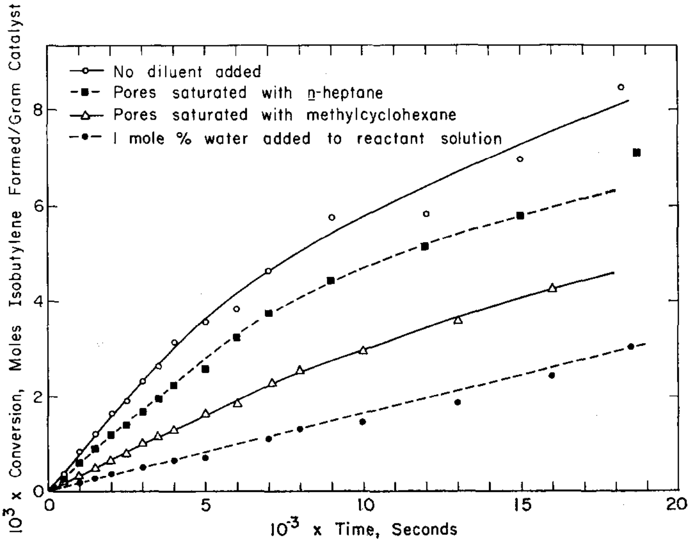

FIG. 1. Conversion of *t*-butyl alcohol catalyzed by H-mordenite crystallites at 75.0°C.

diluents: On addition of 10 mole % *n*-heptane, the initial rate was essentially unchanged from that for pure alcohol. But when catalyst pretreatment included filling of the pores with the *n*-heptane diluent, the initial rate was reduced to 81% of the value for pure alcohol. Further, when the catalyst pores were saturated instead with methylcyclohexane, the initial rate was only 44% of the value for undiluted alcohol.

Reaction was strongly inhibited by water, as shown by the data of Fig. 1. When reactant solution initially contained 1.0 mole % water, rate was reduced to 22% of the value for pure alcohol.

An effect of mean crystallite pore length is shown by results for the two size fractions: Relative initial rates of 1.0 and 0.82 were observed for mean pore lengths of 5.9 and 11.3 μm, respectively. Unexpectedly, initial rate was higher for the unfractionated catalyst than for either size fraction (Table 1), although the average pore length of the unfractionated sample was intermediate to the values for the two fractions (*4*, *5*). It is possible that amorphous impurity in the unfractionated sample contributed significantly to its activity.

Rates for the unfractionated catalyst are shown in the linear Arrhenius plot of Fig. 2. The apparent activation energy is 25 kcal/mole, a value high enough to demonstrate that mass transport in the stirred liquid phase was not rate determining.

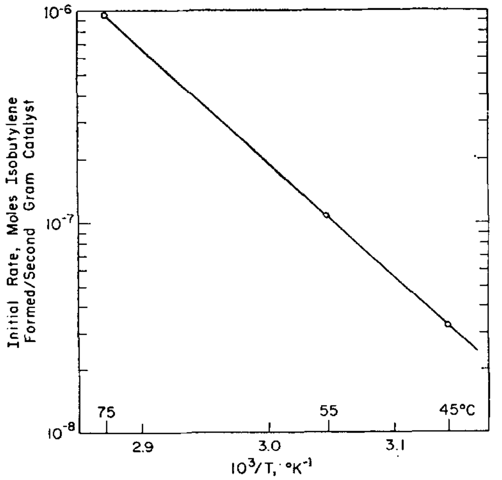

FIG. 2. Arrhenius plot: initial rate of *t*-butyl alcohol dehydration catalyzed by unfractionated H-mordenite crystallites.

DISCUSSION

The lack of change in rate on dilution of reactant with 10 mole % *n*-heptane suggests that the accessible catalyst surface was almost saturated with reactant. The lower rate observed when the same total amount of *n*-heptane was present, initially filling the catalyst pores, shows that the diluent in the pores prevented utilization of catalyst surface that had been accessible previously. The still lower rate observed when methylcyclohexane filled the pores shows that this paraffin prevented utilization of still more catalyst surface. We infer that the cycloparaffin initially occupied more pore volume than the straight-chain paraffin and/or that the bulkier cycloparaffin molecules experienced more hindrance in their transport out of the pores past incoming alcohol.

This interpretation of mass transport influence implies that reaction occurred within the intracrystalline voids of H-mordenite, not just on exterior crystallite surfaces. The interpretation demands there be a range of crystallite sizes for which the influence of mass transport is evidenced by a decreased reaction rate for an increased pore length; the data for the two crystallite size fractions therefore confirm the interpretation.

In summary, we infer the following physical picture of the catalytic process in a crystallite pore. The *t*-butyl alcohol reacts on intracrystalline surfaces to give water and isobutene, which are transported out of the pore to be replaced by alcohol. The critical molecular diameters (Table 2) are small enough that each of the molecules can separately pass through the narrowest [6.7 × 7.0 Å (*9*)] apertures in a pore, while either of the two product molecules can just pass a reactant molecule at a wide point near a side pocket. When *n*-heptane initially fills the pores, it (as well as isobutene) can leave with relatively little hindrance from the entering alcohol

TABLE 2
Critical Molecular Diameters[a]

Molecule	Estimated critical diam (Å)
Water	2.8
Isobutene	5.4
n-Heptane	4.9
Methylcyclohexane	6.6
t-Butyl alcohol	6.4

[a] Critical diameter is the diameter of the smallest circle through which the undeformed molecule can pass. The van der Waals diameter of water is given by Barrer (*6*). The van der Waals radii of methyl groups and methylene groups were taken to be 2.0 Å (*7*). Bond lengths and angles were estimated from handbook values (*8*).

which replaces it. However the methylcyclohexane, which has a critical molecular diameter about 1.2 Å greater than that of isobutene, offers sufficient additional bulkiness that its transport counter to incoming *t*-butyl alcohol is relatively strongly hindered by the difficulty of passage of the two molecules even at the side pockets (Fig. 3). Therefore, a significant part of the interior surface is inaccessible to reactant when the cycloparaffin initially fills the pores. These conclusions suggest that the largest molecules which can pass one another in an H-mordenite pore have critical diameters summing to about 13 Å.

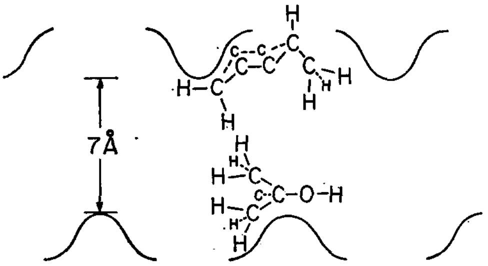

Fig. 3. Schematic representation of *t*-butyl alcohol and methylcyclohexane molecules passing in an H-mordenite pore. Some hydrogen atoms are omitted for clarity.

The inhibition of reaction by water added to the reactant solution is qualitatively consistent with the general decrease in rate as reaction proceeds (Fig. 1). But the inhibition by water formed within the pores is enough to suggest that strongly adsorbed product water ultimately occupies sufficient pore volume to prevent access of reactant. Support for this suggestion of pore blocking is found in the maximum conversion values of about 0.01 mole/g of catalyst, which is roughly equal to the amount of water required to fill the available pore volume (*10*). We may speculate that a significant fraction of the water molecules formed within a pore remained, and that pores initially filled with paraffin finally still contained some paraffin molecules trapped within them; correspondingly, maximum conversions were reduced in these experiments (Fig. 1).

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