

Diffusion of Cumene in H-ZSM-8 and Modified H-ZSM-8 Zeolites

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ZSM-8 zeolite is a medium-pore (pore size = 0.6 nm) high-silica zeolite, belonging to a pentasil family of zeolites, introduced by Mobil Oil Corporation in 1971. The X-ray diffraction spectrum of ZSM-8 is somewhat similar to that of ZSM-5, which is a very widely investigated zeolite, except for a splitting in the highest peak in the region $2\theta = 22-25^\circ$ observed for ZSM-8 (Lechert, 1984). Earlier studies (Akolekar and Choudhary, 1987) have indicated that the influence of degree of H^+ -exchange and calcination temperature on strong acid sites and catalytic activity and paraselectivity (in hydrocarbon conversion and alcohol-to-aromatics conversion reactions) of ZSM-8 are quite similar to those observed for ZSM-5. For ZSM-8, however, the number of strong sites per framework Al (Choudhary and Akolekar, 1989) and the rate of catalyst deactivation due to deposition of large hydrocarbon molecules in zeolite channels (Akolekar and Choudhary, 1987; Akolekar, 1987) are found to be higher. Also the diffusion of cyclohexane (Chon et al., 1985) in H-ZSM-8 is found to be faster.

Extensive studies have been reported on ZSM-5-type zeolites for the sorption/diffusion properties (Ruthven, 1984; Choudhary and Srinivasan, 1986a, b) and also on the zeolite modified with MgO , P_2O_5 , and B_2O_3 (Kaeding and Butter, 1980; Kaeding et al., 1984; Mamman, 1988). For ZSM-5, intracrystalline species like MgO can produce a two order of magnitude change in diffusivity and also significant changes in catalytic properties (Olson and Haag, 1984).

No detailed investigation on the diffusion in ZSM-8 and modified ZSM-8 zeolites has been reported so far. The present investigation was undertaken with the objective of studying the influence of cations (H^+ or Na^+) and modification by MgO , P_2O_5 , and B_2O_3 on the diffusion in ZSM-8-type zeolite, using a model sorbate (*viz.*, Cumene).

Experimental Studies

The preparation and characterization of H-ZSM-8 and $H \cdot Na$ -ZSM-8 zeolites ($Si/Al = 29.6$ and crystal size = $3.5\mu m$) have been described earlier (Akolekar and Choudhary, 1987). The degrees of H^+ -exchange of the H-ZSM-8 and $H \cdot Na$ -ZSM-8 zeolites were 0.96 and 0.08, respectively. The magnesium, phosphorous and boron modified H-ZSM-8 zeolites have been prepared by contacting the H-ZSM-8 zeolite with aqueous solutions of magnesium acetate, ortho-phosphoric acid, and boric acid (all BDH AnalaR), respectively, at room temperature for two weeks while shaking the flask containing the zeolite and the solution occasionally. The zeolite was then filtered using a Gooch crucible and washed quickly to remove the material impregnated on the external surface of the zeolite crystals. The zeolite was then dried in a vacuum oven at 373 K for 12 h, calcined in air at 773 K for 12 h and analyzed for its magnesium, phosphorous or boron content by atomic absorption spectroscopy or spectrophotometry.

All the zeolites were pressed (without any binder) and crushed into particles of about 0.2 mm size. This has not caused significant change in the crystal size and morphology examined by scanning electron microscopy.

The number of strong acid sites on the zeolites were determined in terms of the amount of pyridine chemisorbed irreversibly at 673 K, using GC pulse method (Choudhary and Nayak, 1982) based on temperature-programmed desorption under chromatographic conditions.

Diffusion of liquid cumene in the zeolites has been investigated at 298 and 313 K by measuring volumetrically the sorption of cumene in the empty channels of the zeolite as a function of time. The volumetric measurements were carried out by contacting an evacuated zeolite with liquid cumene and following the change in the liquid level in a calibrated capillary, using a novel volumetric sorption apparatus described earlier (Choudhary et al., 1989). The details of the apparatus and

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Table 1. Data on the Diffusion of Liquid Cumene in ZSM-8 and Modified ZSM-8 Zeolites

Zeolite	Conc. of MgO, P ₂ O ₅ , B ₂ O ₃ , wt. %	No. of Strong Acid Sites, mmol · g ⁻¹	Diffusion Data			Activation Energy, <i>E</i> (kJ · mol ⁻¹)
			Temp. K	(<i>D/r</i> ²) × 10 ⁴ s ⁻¹	<i>D</i> × 10 ¹² (cm ² · s ⁻¹)	
H-ZSM-8	—	0.29	298	1.19	3.6	113
	—	—	313	10.1	30.1	—
H · Na-ZSM-8	—	0.07	313	0.38	1.2	—
MgO · H-ZSM-8	0.10	0.23	298	0.69	1.4	124
			313	4.81	14.7	
P ₂ O ₅ · H-ZSM-8	0.41	0.11	298	0.98	3.0	117
			313	9.08	27.8	
B ₂ O ₃ · H-ZSM-8	5.4	0.20	298	0.27	0.8	163
			313	5.60	17.1	

procedure of carrying out volumetric measurements have been given earlier (Choudhary et al., 1989).

Results and Discussion

The data on the strong acid sites (measured in terms of pyridine chemisorbed irreversibly at 673 K) on the zeolites are given in Table 1. It is interesting to note that the acidity of H-ZSM-8 is reduced due to its modification with MgO, P₂O₅, and B₂O₃. These results are consistent with that observed for the ZSM-5 zeolite modified by boron (Auroux et al., 1985; Sayed et al., 1986) and phosphorous (Lercher et al., 1985; Lercher and Rumpelmayr, 1986).

The Q_t/Q_∞ vs. \sqrt{t} plots for the sorption of pure cumene from the liquid phase in H-ZSM-8 and H · Na-ZSM-8 zeolites are shown in Figure 1, whereas the sorption kinetics plots for the MgO · H-ZSM-8, P₂O₅ · H-ZSM-8 and B₂O₃ · H-ZSM-8 zeolites are presented in Figures 2, 3 and 4, respectively. The lines drawn in the figures are only as an aid to the eye. Coefficient values of diffusion of cumene in the ZSM-8 zeolites have been obtained using the \sqrt{t} law (Barrer, 1971) from the slopes of the initial linear section of the Q_t/Q_∞ vs. \sqrt{t} plots. The values of diffusion coefficient (*D*) and energy of activation for the diffusion are given in Table 1. Values of Q_∞ for the sorption of liquid cumene in H-ZSM-8, H · Na-ZSM-8, MgO · H-ZSM-8, P₂O₅ · H-ZSM-8 and B₂O₃ · H-ZSM-8 zeolites were 0.12, 0.11, 0.11, 0.12 and 0.11 cm³ (liquid cumene) · g⁻¹.

In the present case, the sorption is expected to be controlled mostly by the intracrystalline mass transfer because the reduction in the zeolite particle size from 0.2 mm to 0.1 mm (Figure 1a) showed no significant effect on the sorption kinetics at 313 K. Thus, there was no influence of intercrystalline (i.e., macropore) diffusional mass transfer on the sorption process.

The results (Table 1) reveal that the diffusion of cumene in H-ZSM-8 and modified H-ZSM-8 zeolites is highly activated and it is strongly influenced by the replacement of H⁺ by Na⁺ in the zeolite and also by the modification of H-ZSM-8 zeolite with MgO, P₂O₅, and B₂O₃. The diffusion of cumene in H-ZSM-8 is faster and highly activated as compared to that in H-ZSM-5 (Choudhary et al., 1989). This reveals a significant difference in the channel structure or effective channel diameter of the two zeolites.

Influence of cations

A comparison of the diffusion data (Table 1) for H-ZSM-8 and H · Na-ZSM-8 shows that the diffusion in the latter zeolite

is much slower. The large decrease in the diffusivity due to increase in the Na⁺ content of the zeolite is expected to be mostly due to the stronger interaction of π electrons of the benzene nucleus of cumene molecule with the Na⁺ cations than with H⁺ cations in the zeolite. Earlier studies have indicated that aromatics are sorbed more strongly on Na-ZSM-5 (Choudhary and Srinivasan, 1986b; Choudhary et al., 1988) and Na-ZSM-8 (Akolekar, 1987) than on the zeolites in their H form. The larger size of Na⁺ cation (size of H⁺ is negligible) may also cause a small but significant reduction in the channel size and consequently reduce the diffusivity to some extent. The influence of cation on the diffusion in ZSM-8 zeolite is similar to

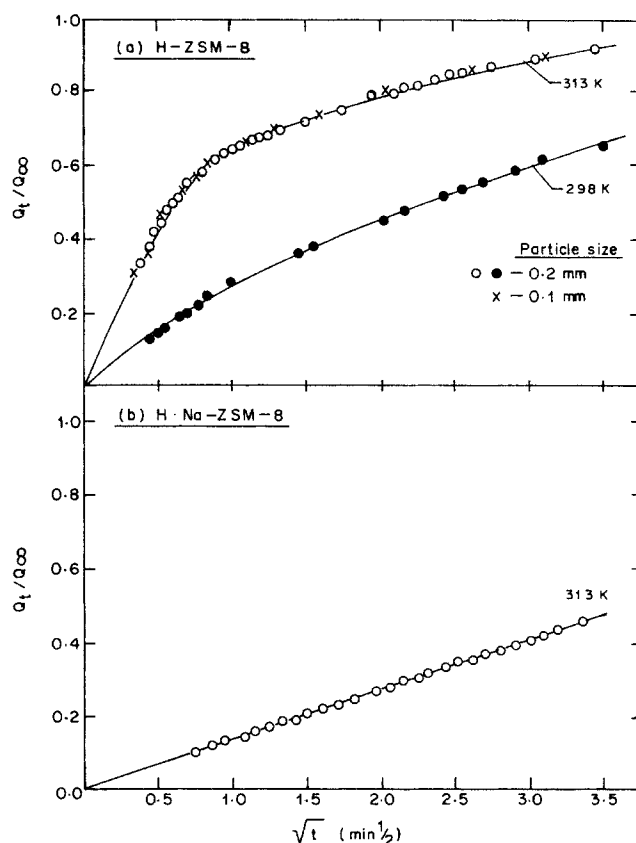


Figure 1. Q_t/Q_∞ vs. \sqrt{t} plots for the sorption of cumene: a. in H-ZSM-8; b. in H · Na-ZSM-8.

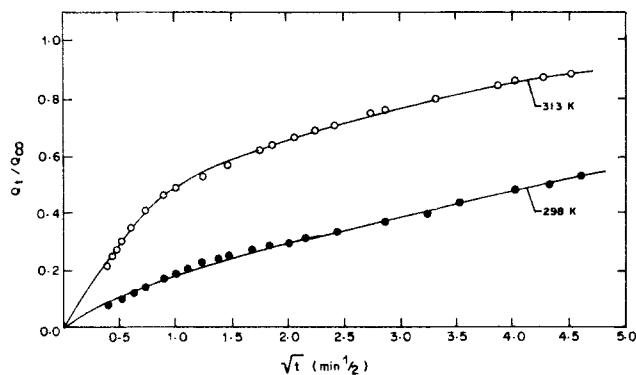


Figure 2. Q_t/Q_∞ vs. \sqrt{t} plots for the sorption of cumene in $\text{MgO} \cdot \text{H-ZSM-8}$.

that observed for ZSM-5 zeolite (Choudhary and Srinivasan, 1986b; Choudhary et al., 1989).

Influence of modification by MgO , P_2O_5 and B_2O_3

The results (Table 1) clearly show that the modification of H-ZSM-8 by MgO , P_2O_5 or B_2O_3 causes reduction in the diffusivity of cumene and increase in the activation energy of the diffusion.

In the process of the modification of zeolite, the deposition of extra zeolitic material (*viz.*, MgO , P_2O_5 , and B_2O_3) is expected to occur on both the external and internal surface of the zeolite crystals. The deposition on the external surface may cause a complete and/or partial blockage of some of the channel openings. On the other hand, the deposition on the internal surface may result in a complete and/or partial blockage of some of the zeolite channels and also causes a reduction in channel size, particularly at channel intersections. These changes in the zeolite resulting from its modification are responsible for the observed decrease in the diffusivity and the increase in the activation energy of the diffusion. The extent to which the diffusion in the zeolite is influenced by its modification may depend on a number of factors such as:

- Concentration of modifying agent and the procedure of its deposition

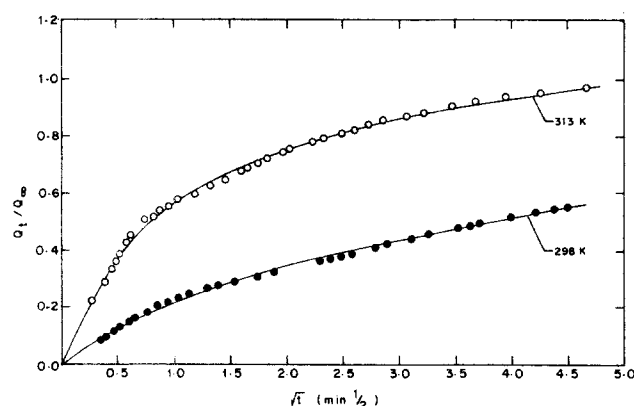


Figure 3. Q_t/Q_∞ vs. \sqrt{t} plots for the sorption of cumene in $\text{P}_2\text{O}_5 \cdot \text{H-ZSM-8}$.

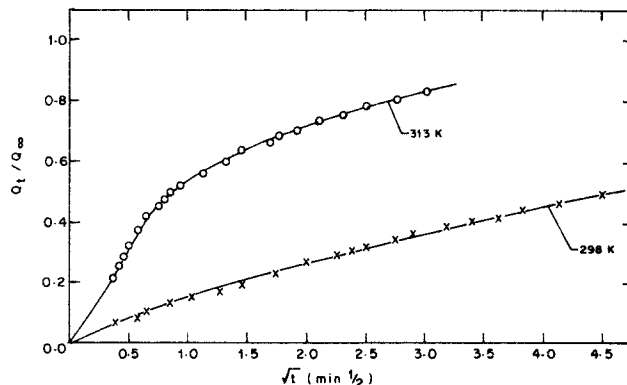


Figure 4. Q_t/Q_∞ vs. \sqrt{t} plot for the sorption of cumene in $\text{B}_2\text{O}_3 \cdot \text{H-ZSM-8}$.

- Location of the deposition (*viz.*, external surface, channel walls, and channel intersections),

- Distribution of modifying agent in the zeolite crystals (*i.e.*, uniform distribution and concentration changing from external surface to the center of zeolite crystals)

- Dispersion of modifying agent (or its average crystal size) and other unknown factors.

For the diffusion of cumene in the zeolite, the isopropyl group of the sorbate is expected to impart larger steric hindrance when the channel diameter and/or the size of channel opening are decreased even to a small extent due to the modification. Hence, the modification causes an increase in the activation energy for the diffusion.

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