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Acidity and Sorbate Shape Selectivity of H-ZSM-22, H-ZSM-48, and H-ZSM-50 Zeolites

ZSM-22 (*1*), ZSM-48 (*2*), and ZSM-50 (*3*) zeolites have unidimensional channels, formed by 10-membered rings, having pore dimensions 0.45 × 0.55 nm, 0.53 × 0.56 nm, and 0.41 × 0.58 nm, respectively. These zeolites belong to the class of medium-pore zeolites. The pores of ZSM-48 are near circular, whereas those of the other two zeolites are elliptical. The channels of ZSM-22 and -48 zeolites are linear and have uniform cross sections. However, the zeolite ZSM-50 has side pockets (0.58 × 0.68 nm in cross section and 0.81 nm deep) to the channels (*4*).

Since these zeolites differ from each other in their channel structure, it is interesting to know the shape selectivity of these zeolites in sorption for sorbates/reactants of different critical sizes and configurations and also their acid-strength distribution. The present investigation was undertaken for obtaining information on the above.

The properties of H-ZSM-22, H-ZSM-48, and H-ZSM-50 zeolites used in this study are presented in Table 1. The H-ZSM-22, H-ZSM-48, and H-ZSM-50 zeolites were obtained by deammoniating the respective NH_4-zeolite at 813 K in air for 16 h. The preparation and characterization of the zeolites have been given earlier (*5–8*). All the zeolites were pressed binder free and crushed to particles of 0.2–0.3 size. Before carrying out the pulse experiment for the acidity distribution or shape selectivity, the zeolite was heated *in situ* at 673 K for 1 h in the flow of helium (10 $cm^3 \cdot min^{-1}$).

For studying the shape selectivity of zeolites in sorption, GC pulse experiments for sorbates with different critical sizes and configurations were carried out by injecting about 0.1-μl sorbate in the zeolite column (stainless-steel column: i.d. 4 mm) packed with zeolite particles (50 mg) under isothermal conditions. Helium (10 $cm^3 \cdot min^{-1}$) was used as a carrier gas. The retention time (t_R) data were corrected for the voids present in the zeolite column and connecting tubes between the injector and the detector. The detailed procedure for the pulse experiment is described elsewhere (*9*).

The number of strong acid sites on the zeolites were measured in terms of the chemisorption of pyridine at 673 K by the GC pulse technique (*10*) based on the TPD of pyridine under chromatographic conditions. The acid-strength distribution of the weaker acid sites on which pyridine is chemisorbed at <673 K has been obtained by the stepwise thermal desorption (STD) (*11*) of the pyridine (chemisorbed initially at 353 K) from 353 to 673 K in a number of temperature steps. The chemisorption of pyridine on the zeolites at 353 K was obtained from the STD data and the chemisorption at 673 K. Detailed procedures for measuring the chemisorption and acid-strength distribution by gas chromatographic TPD and STD techniques have been described earlier (*10, 11*).

The total acid sites (measured in terms of pyridine chemisorbed at 353 K and of the sites on the zeolites) are given in Fig. 1. The fifth column gives the number of strong acid sites obtained by the chemisorption of pyridine at 673 K. Whereas, the first four columns give the acid strength distribution of the weaker sites. Here, the site energy (or acid strength) is expressed in terms of a tem-

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TABLE 1

Properties of H-ZSM-22, H-ZSM-48, and H-ZSM-50 Zeolites

Zeolite	Channel systems		Si/Al ratio	Degree of H^+-exchange (%)	Crystal size (shape) (μm)	Sorption capacity $Cm^3 \cdot g^{-1}$	
	Pore dimensions (nm)	Characteristics				Liquid N_2[a] at 77 K ($p/p_s = 0.3$)	Benzene[b] at 300 K ($p/p_s = 0.4$)
H-ZSM-22	0.45 × 0.55	Undimensional elliptical (Ref. (*1*))	57	>98	3 × 0.2 (needle)	0.09	0.08
H-ZSM-48	0.53 × 0.56	Undimensional, circular (Ref. (*2*))	80	>98	3 × 0.2 (needle)	0.08	0.07
H-ZSM-50	0.41 × 0.58	Undimensional, elliptical, (side pockets: 0.68 × 0.58 × 0.81) (Refs. (*3, 4*))	58	>98	2.0 (cuboid)	0.15	0.13

[a] Measured by dynamic adsorption/desorption technique using Quantasorb adsorption meter.

[b] Measured by gravimetric technique.

perature range in which the base chemisorbed at lowest temperature of the temperature range is desorbed (T_d is the desorption temperature of the base).

The results reveal that the acid-strength distribution on the zeolite is quite broad. It is interesting to know that the H-ZSM-50 and H-ZSM-22 zeolites have nearly the same Si/Al ratio and degree of H^+-exchange (Table 1) but these zeolites differ widely in their acidity. Both the total and strong acid sites on the H-ZSM-50 zeolite are much higher. The higher acidity of H-ZSM-50 is consistent with its higher activity observed in the methylation of toluene (*6*). The higher acidity and catalytic, activity of the H-ZSM-50 is probably attributed to its peculiar channel structure. Because of the side pockets, H-ZSM-50 has higher sorption capacity and surface area and is also expected to contain larger number of accessible tetrahedral Al^-, which are responsible for the acidity and catalytic activity. Its higher activity may also be due to its lower diffusional resistance for flat molecules (aromatics), as indicated by its lower shape selectivity in xylene isomerisation.

The shape selectivity of the zeolites in sorption has been investigated by the GC pulse technique (*9*) at temperatures close to that used in catalytic processes. The GC retention time (t_R) data for the sorbates, differing widely in their molecular critical size and configurations, on the H-ZSM-22, H-ZSM-48, and H-ZSM-50 zeolites at differ-

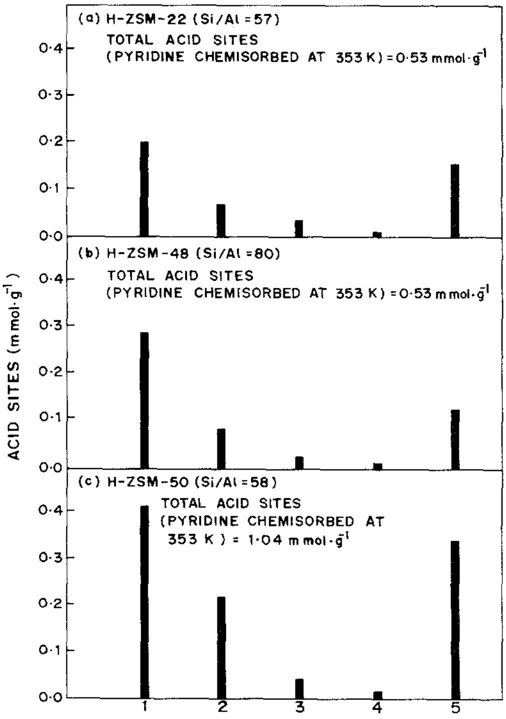

FIG. 1. Acid strength distribution on H-ZSM-22, H-ZSM-48, and H-ZSM-50 zeolites. (1) 353 < Td ≤ 433 K; (2) 433 < Td ≤ 513 K; (3) 513 < Td ≤ 593 K; (4) 593 < Td ≤ 673 K; (5) Chemisorption at 673 K (Strong acid sites).

TABLE 2

GC Retention Data on H-ZSM-22, H-ZSM-48, and H-ZSM-50 for the Sorbates of Different Critical Molecular Sizes and Configurations

Sorbate	Critical molecular size, *d*(nm) (Refs. (*9*, *12*))	GC Retention time, t_R (sec)								
		H-ZSM-22			H-ZSM-48			H-ZSM-50		
		523 K	573 K	623 K	523 K	573 K	623 K	573 K	623 K	673 K
n-Hexane	0.49	6.7	3.6	2.3	20.2	6.6	2.3	10.6	4.3	3.0
2,2-DMB	0.70	0.7	0.6	0.3	1.8	1.6	1.3	1.6	1.3	1.0
2,3-DMB	0.56	0.7	0.6	0.3	0.7	0.7	0.6	3.6	3.4	2.0
n-Octane	0.49	29.7	7.5	2.3	245	35.1	8.3	—	—	—
3-Methyloctane	0.56	10.2	3.0	1.3	9.7	3.6	1.3	14.6	9.8	4.0
Isooctane	0.70	0.7	0.6	0.3	0.7	0.6	0.5	1.6	1.3	1.0
p-xylene	0.67	50.2	8.6	3.3	31.7	11.1	2.8	14.1	15.8	8.0
m-xylene	0.74	1.2	0.8	0.5	2.1	1.7	1.3	39.1	14.8	8.0
o-xylene	0.74(0.80)[a]	1.2	0.8	0.5	1.7	1.6	1.3	30.5	12.3	6.5
n-Propyl benzene	0.67	35.7	9.6	3.3	60.7	14.1	3.3	74.6	19.3	—
Isopropyl benzene	0.67	2.7	2.6	2.3	4.9	4.3	2.4	12.1	5.3	—
n-Butylbenzene	0.67	46.7	6.6	3.3	131	—	—	—	—	—
Sec.-Butylbenzene	0.67	3.7	3.1	2.0	5.7	—	—	—	—	—
tert-Butylbenzene	0.70	0.7	0.6	0.3	1.7	—	—	—	—	—
1,2,4 TMB	0.80	—	—	—	—	—	—	61.6	23.8	13.0
1,2,3 TMB	0.80(0.97)[a]	—	—	—	—	—	—	2.0	—	9.0
1,3,5 TMB	0.86(0.97)[a]	—	—	—	—	—	—	1.6	—	3.0

Note. DMB—dimethylbutane, TMB—trimethylbenzene.

[a] In most favorable conformation for sorption (*9*).

ent temperatures (523–673 K) are given in Table 2.

The data in Table 2 indicate a very strong influence of chain branching in aliphatic hydrocarbons and also in alkyl group of monoalkyl benzenes (viz. *n*- and isopropyl benzenes and *n*-, *sec.*-, and *tert.*-butyl benzenes) on the GC retention time. The above observations indicate a sharp decrease in the retention time (or sorption) of sorbate (during the passage of the sorbate pulse) on the zeolite with the increase in the steric hindrance due to the chain branching.

A comparison of the retention time data (Table 2) for the different sorbates on the H-ZSM-22, H-ZSM-48, and H-ZSM-50 zeolites shows that the zeolites could be arranged for the sorption of the sorbates in the following order:

H-ZSM-50 > H-ZSM-48 > H-ZSM-22. (1)

The relative retention data [$t_{R(\text{sorbate})}/t_{R(p\text{-xylene})}$] for the different sorbates on the zeolites at 573 and 623 K are compared in Table 3. The results lead to the following conclusions on the relative shape selectivity of the zeolites in the sorption of the different sorbates.

1. In all the zeolites, isooctane molecules cannot penetrate the zeolite channels. This is consistent with observations of the other medium-pore zeolites like ZSM-5 (*12*, *13*) and silicalite (*9*).

2. 2,3-DMB is not sorbed in the H-ZSM-22 and H-ZSM-48 zeolites even at 623 K but it is sorbed, although slowly, in the H-ZSM-50. 2,2-DMB is not sorbed at 623 K in the H-ZSM-22 and H-ZSM-50, which have elliptical channels, but it is sorbed in H-ZSM-48, which has near circular channels.

The zeolites could be arranged in the order of their shape selectivity in the sorption as follows:

For the sorption of 2,3-DMB:

H-ZSM-22 ≃ H-ZSM-48 > H-ZSM-50. (2)

For the sorption of 2,2-DMB and isopropyl benzene:

H-ZSM-50 ≥ H-ZSM-22 > H-ZSM-48. (3)

3. In the sorption of xylene isomers and

TABLE 3

Comparison of Relative Retention Data $[(t_{R(\mathrm{sorbate})}/t_{R(p\text{-xylene})}]$ on the H-ZSM-22, H-ZSM-48, and H-ZSM-50 Zeolites

Sorbate	Critical molecular size, d(nm)	$t_{R(\mathrm{sorbate})}/t_{R(p\text{-xylene})}$ Ratio					
		573 K			623 K		
		H-ZSM-22	H-ZSM-48	H-ZSM-50	H-ZSM-22	H-ZSM-48	H-ZSM-50
m-Xylene	0.74	0.09	0.15	0.95	0.15	0.46	0.94
o-Xylene	0.74	0.09	0.14	0.74	0.15	0.46	0.78
1,2,4-TMB	0.80	—	—	1.49	—	—	1.51
Isopropylbenzene	0.67	0.30	0.40	0.29	0.70	0.86	0.34
2,2-DMB	0.70	Not sorbed	0.14	Not sorbed	Not sorbed	0.46	Not sorbed
2,3-DMB	0.56	Not sorbed	Not sorbed	0.09	Not sorbed	Not sorbed	0.22
Isooctane	0.70	Not sorbed	-do-	Not sorbed	Not sorbed	Not sorbed	Not sorbed

1,2,4-TMB, the zeolites could be arranged in the following order for their shape selectivity:

$$\text{H-ZSM-22} > \text{H-ZSM-48} \geqslant \text{H-ZSM-50}. \quad (4)$$

This order is very much consistent with that observed for the product and restricted transition state shape selectivities of these zeolites observed earlier in the isomerization of *m*-xylene and methylation of toluene (*5*, *6*).

It may be noted that the observed changes in the order of the zeolites for their shape selectivity in the sorption of the different sorbates are attributed to the difference in the shape (i.e., circular or elliptical) and size of the channels in the zeolites. The zeolites having elliptical channels (viz. ZSM-22 and ZSM-50) are highly shape selective in the sorption of sorbates having bulkier group(s) of spherical symmetry but their shape selectivity reduced in the sorption of planar (or flat) sorbate molecules. The shape and/or configuration of sorbate molecules plays a vital role in deciding the shape-selective sorption/diffusion in these medium-pore zeolites. The observations are consistent with what is expected according to the shuttle cock-shuttle box model (*12*) for the shape selectivity of medium-pore zeolites in sorption and diffusion.

For all the zeolites, their shape selectivity is reduced with the increase in the temperature. This is expected mostly due to the fact that the diffusion of sorbates, whose sorption/diffusion in the zeolite is hindered, is highly activated as compared to the diffusion of freely diffusing sorbate molecules.

REFERENCES

1. Valyocsik, E. W., US Patent 4,481,177 (1984).
2. Chu, P., US Patent 4,397,827 (1981).
3. Rubin, M. K., US Patent 4,640,829 (1987).
4. Briscoe, N. A., Johnson, D. W., Shannon, M. D., Kokotailo, G. T., and McCusker, L. B. *Zeolites* **8,** 74 (1988).
5. Kumar, R., and Ratnasamy, P., *J. Catal.* **118,** 68 (1989).
6. Kumar, R., Rao, G. N., and Ratnasamy, P., *Stud. Surf. Sci. Catal.* **49,** 1141 (1989).
7. Rao, G. N., Kumar, R., and Ratnasamy, P., *Appl. Catal.* **49,** 307 (1989).
8. Kumar, R., and Ratnasamy, P., *J. Catal.* **116,** 440 (1989).
9. Choudhary, V. R., and Akolekar, D. B., *J. Mol. Catal.* **60,** 173 (1990).
10. Choudhary, V. R., and Nayak, V. S., P., *Appl. Catal.* **4,** 31 (1982).
11. Choudhary, V. R., *J. Chromatogr.* **268,** 207 (1983).
12. Choudhary, V. R. and Akolekar, D. B., *J. Catal.* **117,** 542 (1989).
13. Choudhary, V. R., and Singh, A. P., *Zeolites* **6,** 206 (1986).

VASANT R. CHOUDHARY[1]
ANAND P. SINGH
RAJIV KUMAR

National Chemical Laboratory
Pune 411 008
India

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[1] To whom correspondence should be addressed.