Shuttlecock–Shuttlebox Model for Shape Selectivity of Medium-Pore Zeolites in Sorption and Diffusion

VASANT R. CHOUDHARY[1] AND DEEPAK B. AKOLEKAR

Chemical Engineering Division, National Chemical Laboratory, Pune 411 008, India

A shuttlecock–shuttlebox model for a sorbate–zeolite channel system is proposed to explain for sorbate molecules the importance of configuration and flexibility over size in sorption/diffusion in zeolites, the pore dimensions of which are comparable to the size of sorbate molecules. The model helps in predicting at least qualitatively the relative penetrability and diffusivity of bulkier (i.e., larger size) sorbate molecules. © 1989 Academic Press, Inc.

INTRODUCTION

Shape selectivity is a unique property of zeolites, the pore dimensions of which are close to the size of molecules such as simple branched paraffins and aromatics. A number of interesting results showing a strong influence of molecular configuration on the penetration and sorption dynamics (or diffusion) in the channels of ZSM-5-type zeolites (Table 1) have been observed. For example, (i) 2,3-dimethylbutane (DMB; critical molecular diameter, $d_c = 0.56$ nm) is not sorbed at room temperature (it is sorbed slowly at elevated temperatures), but 3-methylpentane ($d_c = 0.56$ nm) is sorbed readily (*1*) and benzene ($d_c = 0.67$ nm) is sorbed at an appreciable rate (*2–4*). (ii) Isopropylbenzene ($d_c = 0.67$ nm) diffuses in H–ZSM-5 at a much slower rate than *n*-propylbenzene ($d_c = 0.67$ nm) (*4, 5*). (iii) Isooctane ($d_c = 0.7$ nm) does not penetrate the channels of H–ZSM-5 at room temperature (*4, 6*) and its conversion on H–ZSM-5 at 673 K is not significant (*7*), whereas 2,2-dimethylbutane ($d_c = 0.7$ nm) (*8*), *o*- and *m*-xylenes ($d_c = 0.74$ nm) (*4, 6, 9, 10*), 1,2,4-trimethylbenzene ($d_c = 0.8$ nm) (*7, 10*), and 1,2,3-trimethylbenzene (*7*) and 1,3,5-trimethylbenzene ($d_c = 0.86$ nm) (*6, 7*) can diffuse in the zeolite channels, although

slowly, even at about room temperature. (iv) Diffusion of ethylbenzene ($d_c = 0.67$ nm) is slower than that of *p*-xylene ($d_c = 0.67$ nm) (*4*).

The GC retention data for various sorbates on silicalite (*7, 11*) presented in Table 2 are also consistent with the above observations which indicate for sorbate molecules the importance of configuration over critical size in sorption/diffusion in medium-pore zeolites. We propose here a shuttlecock–shuttlebox model for a sorbate–zeolite channel system to explain the above observations and to predict qualitatively the relative penetrability and diffusion of bulkier sorbates in medium-pore zeolites. The critical molecular diameter is defined (*12*) as the diameter of the smallest cylinder which can circumscribe the molecule in its most favorable equilibrium conformation.

SHUTTLECOCK–SHUTTLEBOX MODEL

The shuttlecock–shuttlebox model for a sorbate molecule–zeolite channel system is shown in Fig. 1. Insertion of the shuttlecock into the shuttlebox and/or movement of the shuttlecock within the shuttlebox can be accomplished with ease only in the direction of the rounded cork of the shuttlecock as a result of the compression of its feathers inside. Insertion and/or movement in the direction of the feathers is prohibited

---

[1] To whom all correspondence should be addressed.

TABLE 1

Data on Diffusion of Various Sorbates in ZSM-5-Type Zeolites

Sorbate	Molecular critical size d_c (nm)	Zeolite	Temperature (K)	Diffusion coefficient (cm^2 sec^{-1})	Ref.
n-Hexane	0.49	H–ZSM-5 (Si/Al = 39.7)	298	$>10^{-9}$	(4)
Benzene	0.67	H–ZSM-5 (Si/Al = 39.7)	308	3.09×10^{-11}	(4)
Ethylbenzene	0.67	H–ZSM-5 (Si/Al = 39.7)	308	6.82×10^{-13}	(4)
p-Xylene	0.67	H–ZSM-5 (Si/Al = 39.7)	308	5.13×10^{-12}	(4)
n-Propylbenzene	0.67	H–ZSM-5 (Si/Al = 39.7)	308	1.6×10^{-13}	(4)
Isopropylbenzene	0.67	H–ZSM-5 (Si/Al = 39.7)	308	1.0×10^{-13}	(4)
n-Butanol	0.49	H–ZSM-5 (Si/Al = 39.7)	308	6.5×10^{-10}	(4)
sec-Butanol	0.56	H–ZSM-5 (Si/Al = 39.7)	308	7.5×10^{-12}	(4)
tert-Butanol	0.65	H–ZSM-5 (Si/Al = 39.7)	308	1.0×10^{-12}	(4)
Isooctane	0.70	H–ZSM-5 (Si/Al = 39.7)	308	No sorption	(4)
o-Xylene	0.74	H–ZSM-5 (Si/Al = 38)	303	2.4×10^{-14}	(6)
m-Xylene	0.74	H–ZSM-5 (Si/Al = 38)	303	1.6×10^{-14}	(6)
1,3,5-TMB	0.86	H–ZSM-5 (Si/Al = 38)	303	9.0×10^{-16}	(6)
2,2-DMB	0.70	H–ZSM-5	373	8.0×10^{-15}	(8)

Note. DMB, dimethylbutane; TMB, trimethylbenzene.

because of the larger diameter of the shuttlecock and also because of expansion of its feathers if the shuttlecock is forcefully inserted into or moved within the shuttlebox. Similarly to insertion of the shuttlecock into the shuttlebox, penetration of a larger or bulkier sorbate molecule into the zeolite channel is expected to take place only when
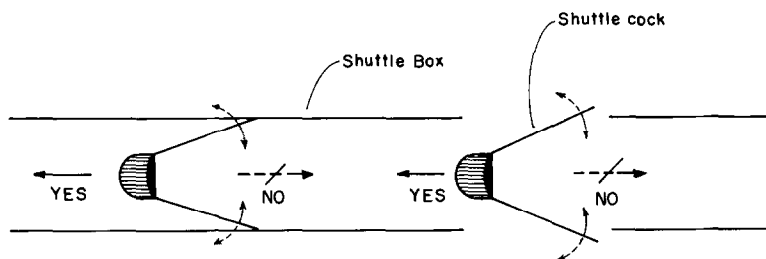

FIG. 1. Shuttlecock–shuttlebox model for sorbate–zeolite channel system.

Sorbate	Molecular critical size d_c (nm)	t_R (min)
Zeolite : silicalite		
n-Hexane	0.49	2.16
2,2-DMB	0.70	1.33
2,3-DMB	0.56	0.94
p-Xylene	0.67	1.86
o-Xylene	0.74	0.68
n-Propylbenzene	0.67	6.56
Isopropylbenzene	0.67	0.51
n-Butylbenzene	0.67	9.82
sec-Butylbenzene	0.67	0.42
tert-Butylbenzene	0.70	0.18
n-Octane	0.49	8.85
Isooctane	0.70	0.09
Zeolite : Na-mordenite (Zeolon 900 Na)		
n-Octane	0.49	9.5
Isooctane	0.70	0.4
m-Xylene	0.74	50.6
1,2,4-TMB	0.80	41.5
1,2,3-TMB	0.80	15.4

Note. Experimental conditions: Zeolite (2.1 g) packed in a column 2 mm (i.d.) × 63 cm (length); He flow rate, 10 cm^3 min^{-1}; pulse size, 0.1 μl. t_R is the corrected retention time at 673 K.

the molecule enters the channel opening in an orientation(s) in which its compression to the size of the channel is accomplished with relative ease. Otherwise, its sorption is either totally rejected or expected to occur with only a very low probability, because of a much larger steric hindrance experienced by the molecule in the sorption process. Also, similarly to the restriction on the direction of movement of the shuttlecock within the shuttlebox, the diffusion of a sorbate molecule in the zeolite channel is favored in the direction in which resistance of the compressed group(s) of the diffusing molecule to movement is a minimum.

Application of the model to explain the observations concerning sorption and diffusion in the zeolite is illustrated in Figs. 2, 3, and 4 (← and ↚ indicate that entry or diffusion of the molecule in the direction shown by the arrow is favored or not favored, respectively).

According to the model, sorption/diffusion of a larger (bulkier) sorbate molecule in

the medium-pore zeolites can occur only when the molecule is oriented in its most favorable conformation (i.e., the conformation in which the molecule can be easily compressed to the size of the channel), as illustrated in Figs. 2, 3, and 4, and also possesses sufficient energy to overcome the penetration barrier by compressing and forcing the molecule through the channel opening and/or to diffuse inside the zeolite channels. If the above requirements are not satisfied, either the entry of the sorbate molecule into the channel is not permitted or the probability of entry is very low. Hence, the penetration and diffusion of bulkier sorbates in medium-pore zeolites depend strongly on the configuration and flexibility (or compressibility) of the sorbate molecules and also on the temperature of sorption. The molecular diameters (d) for the different sorbates (Figs. 2–4) in their different orientations (with different conformations) have been estimated from knowledge of their structures, configurations, bond angles, and bond lengths (13), using data given elsewhere (13, 14). The 2,3-DMB molecule [which possesses isopropyl groups ($d_c = 0.56$ nm) at both ends] penetrates into the ZSM-5 channels at higher temperatures ($\geq$643 K) (1). Therefore, it is expected that the isooctane molecule, oriented with its isopropyl group in the direction of the zeolite channel, enter the channel but this is not observed. This is expected because even though the isooctane molecule may somehow manage to penetrate partially with difficulty (due to high steric hindrance) in the direction of its isopropyl group ($d_c = 0.56$ nm), the higher resistance imparted by its tert-butyl group ($d_c = 0.7$ nm) for further penetration may be responsible for the rejection of its penetration (Fig. 3). The 2,2-DMB ($d_c = 0.7$ nm) is also found to be sorbed faster than the 2,3-DMB ($d_c = 0.56$ nm). These observations indicate that when the sorbate molecule possesses two larger groups (viz. isopropyl and tert-butyl groups), as in the case of 2,3-DMB (which possesses two iso-pro-
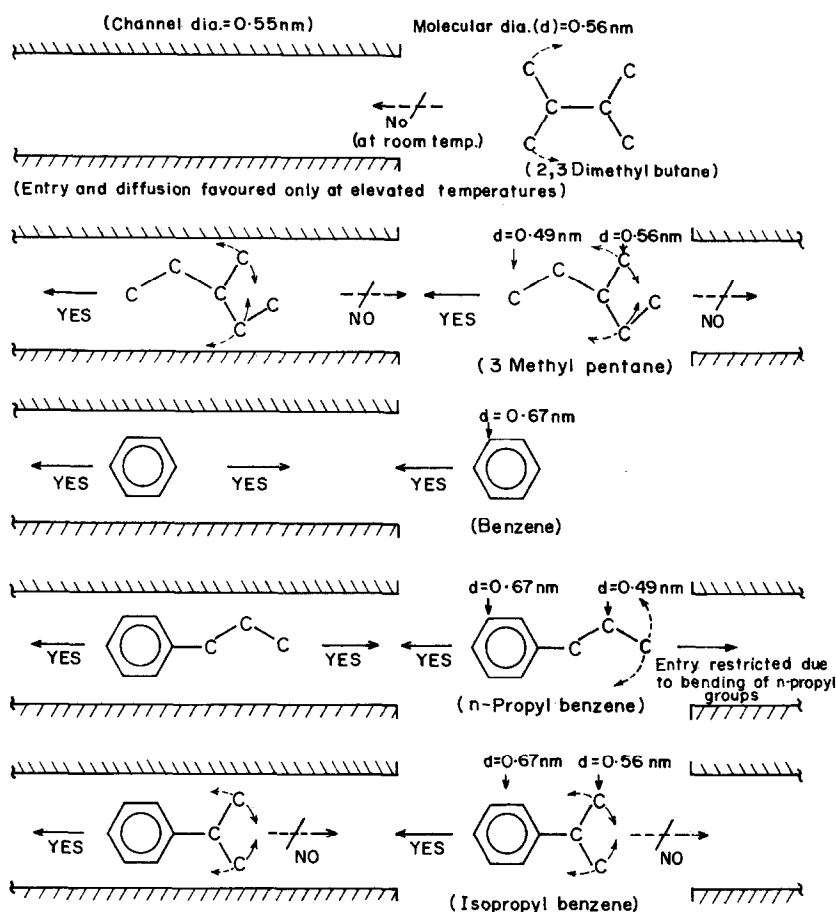
FIG. 2. Sorption of larger size hydrocarbons oriented/aligned in the conformation most suitable for their entry and diffusion in medium-pore zeolites (channel diameter 0.55 nm).

pyl groups) and isooctane (which possesses one isopropyl and one *tert*-butyl group), the effective steric hindrance produced is so large that either the sorption or the penetration of sorbate molecule cannot occur at all or occurs only at higher temperatures.

In the process of sorption in medium-pore zeolites such as ZSM-5 the sorbate molecules are subjected to the following two intracrystalline mass transfer resistances, which are operating in series:

(i) resistance to entry of the sorbates into channel openings at the external surface of zeolite crystallites,

(ii) the resistance to movement of the sorbate molecules inside the channels because of their configurational diffusion.

Therefore, the rate of sorption or sorption kinetics is expected to be limited or controlled by one of the two mass transfer resistances or by a combination of both, depending on the sorbate (mainly its size relative to zeolite channel size and also its configuration)–zeolite (mostly its pore size, channel structure, and all other factors affecting the configurational diffusion inside the zeolite channels) system.

The first mass transfer resistance, which controls the entry of sorbate molecules into the zeolite channels, is expected to play a
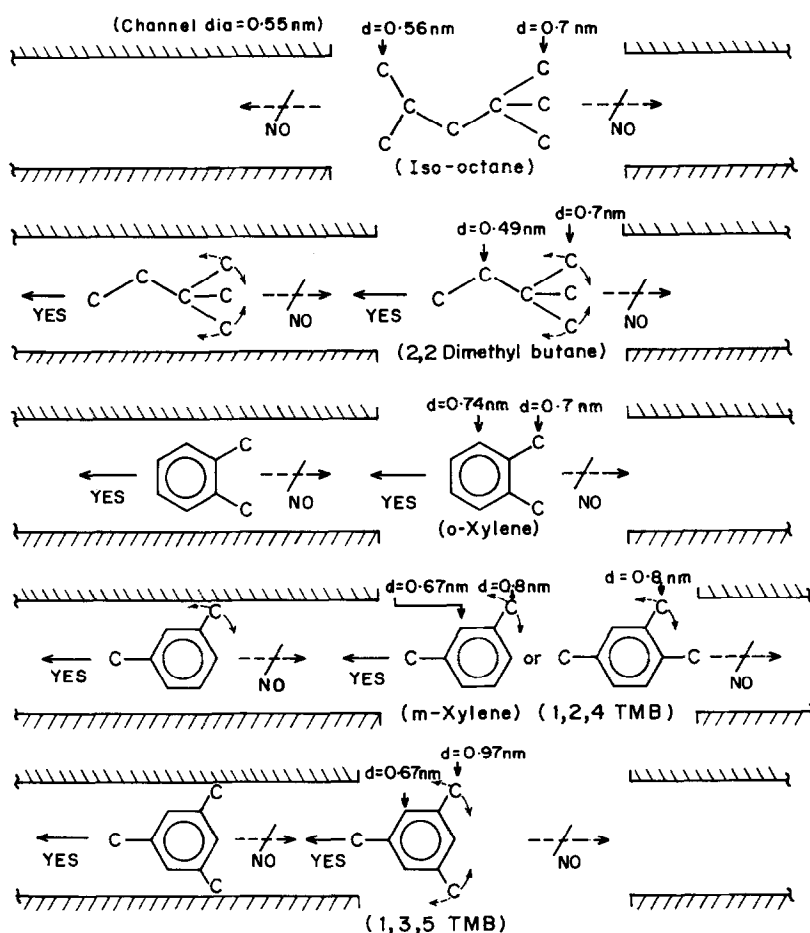
FIG. 3. Sorption of larger size hydrocarbons oriented/aligned in the conformation most suitable for their entry and diffusion in medium-pore zeolites (channel diameter 0.55 nm; TMB, trimethylbenzene).

very significant role in the sorption process, particularly when the size and configuration of the sorbate molecule in its different possible orientations, as shown in Figs. 2–4, are such that either its entry in the channel is not permitted or the probability of its entry is very small. The penetration of sorbate molecules is expected to take place only when the molecules, oriented with their most favorable conformation and possessing the minimum energy required for penetration in that conformation, collide with the channel openings. All the other collisions, which do not satisfy the above conditions, do not result in penetration of the sorbate molecules. The probability of penetration (α_p) of a particular sorbate is, therefore, expected to be dependent on the fraction of molecules (f_m) possessing the minimum energy required for the complete penetration of the molecule in the channel and also on the probability of the orientation of sorbate molecules in the most favorable conformation (α_0). Hence

$$\alpha_p = f_m \cdot \alpha_0.$$

f_m will depend on the size (relative to that of the channel opening), configuration, and compressibility (or molecular dynamics) of the sorbate molecules and on temperature,

Channel dia. = 0·55nm)   Molecular dia.(d) = 0·67 nm

YES   YES   NO   p-Xylene   C   or   C or   C   (d=0·74nm)   (d=0·99nm)   (d=0·93nm)

YES   Entry restricted   (d=0·67nm)   (d=0·49nm)   YES   Entry restricted   Ethyl Benzene

YES   NO   NO   C   or   or   or   (d=0·92 nm) (d=0·99nm) (d=0·92nm) (d=0·92nm)   (d=0·8 nm)   1,2,4-Trimethyl benzene

YES   NO   NO   or   or   or C   or   (d=0·80nm)   (d=0·87nm)   (d=0·8nm)   1,2,3-Trimethyl benzene
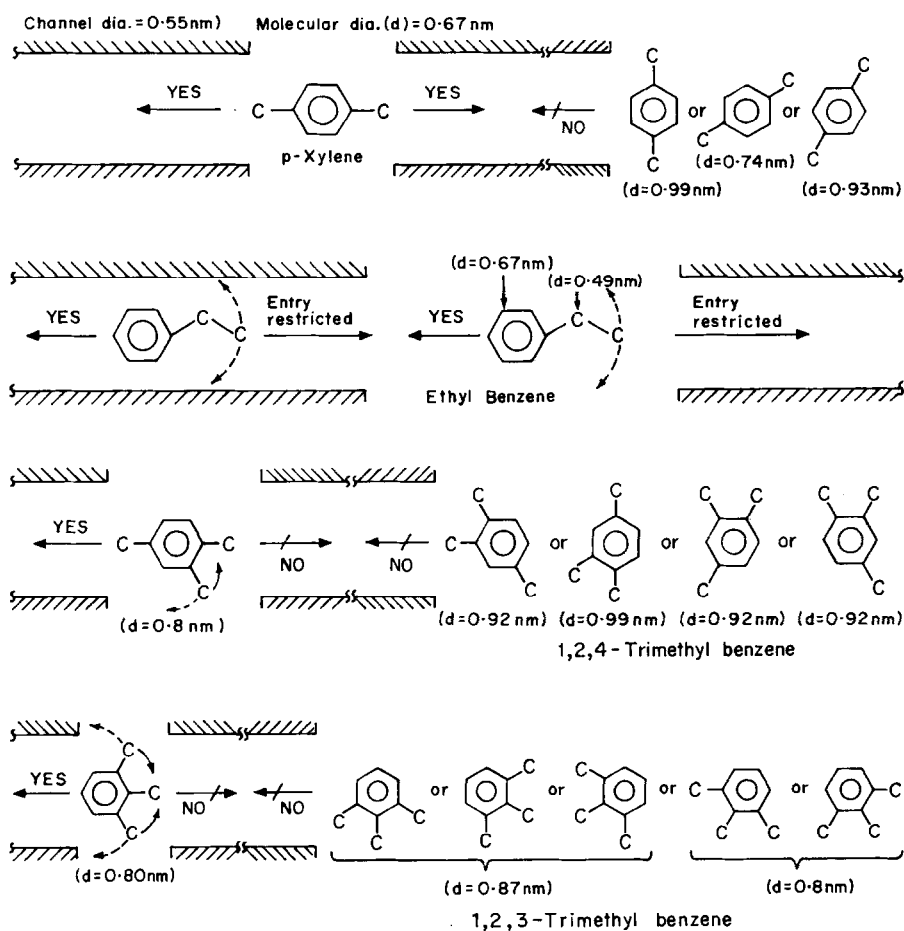
FIG. 4. Sorption of larger size hydrocarbons oriented/aligned in the conformation most suitable for their entry and diffusion in medium-pore zeolites (channel diameter 0.55 nm).

whereas α_0 depends on the number of possible orientations of the molecules. For the penetration of small, simple molecules such as methanol molecules ($d^* = 0.4$ nm) in ZSM-5, the value of f_m or α_0 is nearly unity, therefore, $\alpha_p = 1$, whereas for bulkier molecules such as 1,3,5-TMB, the values of both f_m and α_0 are expected to be much less than one, hence $\alpha_p \ll 1$.

However, the second mass transfer resistance (concerning the mass transfer inside zeolite channels) is expected to show its greater significance in the sorption of molecules whose entry into zeolite channels occurs with ease. Moreover, for sorption oc-

curring with chemical reactions, the situation can be very interesting. For example, for the sorption of methanol with reaction on ZSM-5, the entry of methanol, because of its smaller size, is expected to occur very easily, its diffusion inside the channel is also expected to be faster, but the products of its reaction (i.e., higher hydrocarbons, including aromatics) are expected to diffuse at much slower rates. The overall process is, therefore, expected to be controlled by the diffusion of product hydrocarbons in the zeolite. In contrast, the sorption of 2,3-dimethylbutane in ZSM-5 with chemical reaction is expected to be

controlled by its entry into the zeolite channels. Because of its very high apparent reactivity (which is due to its very slow diffusion inside the channel), 2,3-dimethylbutane is expected to be cracked at the first intersection it meets while diffusing inside the channels. The products of its cracking, which are simpler and smaller in size, can, however, easily diffuse out from the zeolite channels.

REFERENCES

1. Chen, N. Y., and Garwood, W. E., *J. Catal.* **52**, 453 (1978).
2. Heering, J., Kotter, M., and Riekert, L., *Chem. Eng. Sci.* **37**, 581 (1982).
3. Nayak, V. S., and Riekert, L., *Acta Phys. Chem.* **31**, 157 (1985).
4. Choudhary, V. R., and Nayak, V. S., unpublished.
5. Choudhary, V. R., Akolekar, D. B., and Singh, A. P., *Chem. Eng. Sci.,* in press.
6. Choudhary, V. R., and Singh, A. P., *Zeolites* **6**, 206 (1986).
7. Akolekar, D. B., Ph.D. thesis, Univ. of Poona, Pune, 1987.
8. Post, M. F. M., van Amstel, J., and Kouwenhoven, H. W., *in* "Proceedings, 6th Int. Zeolite Conf., Reno, July 10–15, 1983" (D. Olson and A. Bisio, Eds.), p. 517. Butterworth, Surrey.
9. Mao Van Le, R., Ragaini, V., Leofanti, G., and Foìs, R., *J. Catal.* **81**, 418 (1983).
10. Ma, Y. H., Tang, T. D., Sand, L. B., and Hou, L. Y., *in* "Proceedings, 7th Intl. Zeolite Conf., Tokyo" (Y. Murakami, A. Iijima, and I. W. Ward, Eds.), p. 531, 1986.
11. Choudhary, V. R., and Akolekar, D. B., *J. Mol. Catal.,* in press.
12. Ruthven, D. M., "Molecular Sieves II 4th Inter. Conf. Zeolites, Chicago" (J. P. Katzer, Ed.), Vol. 40, p. 320. ACS Symp. Ser., Washington, DC, 1977.
13. Pauling, L., "The Nature of Chemical Bonds," 3rd ed. Cornell Univ. Press, New York, 1960.
14. "Tables of Interatomic Distances and Configuration in Molecules and Atoms" (L. E. Sutton, Ed.). Chem. Soc. London, England, 1958.