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A Novel Effect of Shape Selectivity: Molecular Traffic Control in Zeolite ZSM-5

Zeolite ZSM-5 (*1, 2*) shows unique shape-selective properties which are best described by referring to its published structure (*2, 3*) and that of silicalite (*4*), which is isostructural.

The ZSM-5 framework contains *two types of intersecting channels* which have *ten-membered ring openings* and are therefore intermediate between those of classical shape-selective zeolites (erionite, offretite, . . .) and of large pore zeolites (faujasite, X, Y, . . .). One channel system runs parallel to the *a* axis of the orthorhombic unit cell; it is sinusoidal and has near-circular (0.54 to 0.56-nm (*3, 4*) openings. The other channels are straight, parallel to the *b* axis, and have elliptical openings (0.52–0.58 nm (*3, 4*). The published structures of ZSM-5 (*2, 3*) and of silicalite (*4*) show that the total length of the pore system per unit cell (sinusoidal, near-circular channels plus linear, elliptical channels) is 8.8 nm, whilst that of the linear, elliptical channels alone is 5.9 nm. Rather than the molecular screening which is observed for classical shape-selective zeolites, the slightly higher pore size of ZSM-5 imposes configurational diffusion restrictions (*5*), i.e., a continuous matching of size and shape for the diffusing molecule(s) and the host channels. "Charge selectivity" effects are then observed in hydrocracking of paraffinic hydrocarbons while "product selectivity" effects clearly show up in various *para*-aromatics directed reactions (*5–7*).

The *channel intersections* or *intersecting elements* have a critical dimension of nearly 0.9 nm. They were shown to play a distinct role in the ordering of simple molecules (*8*) and are probably the locus of the catalytic activity of ZSM-5, mainly with respect to the conjunct polymerization of light-molecular-weight olefins (*9, 10*). The size and shape of the channel intersections are essential to explain "transition state selectivity" effects: a high resistance to coking is observed because polyaromatics cannot be formed (*11*), xylenes isomerization to *para*-xylene is extremely selective and efficient because of the lack of *trans*-alkylation (*12*), and a rather sharp cutoff at C_{10} is observed in the conversion of various feedstocks on ZSM-5 catalysts (*10, 13*).

The *tortuosity* of the channels must also be suspected to play a role in the transient behavior of molecules inside the zeolite framework as recently suggested for long-chain aliphatics (*14*), in a way related to the so-called "window" effect observed in zeolite T (*15*).

The former shape-selectivity effects have been known and reported for a variety of other zeolitic catalysts since they were first observed (*16*). The present note aims to report some preliminary but quantitative data that lead us to propose a new shape-selectivity effect, i.e., *molecular traffic control* (MTC) in the intracrystalline volume (or the channel network) of the zeolite. In the particular case of ZSM-5, it refers to a situation in which reactant molecules preferentially enter the catalyst through a given channel system while the products diffuse out by the other, thereby preventing the occurrence of important counterdiffusion limitations in the catalytic conversions.

Table 1 summarizes some relevant data for the adsorption of model hydrocarbon molecules by zeolite ZSM-5. From the knowledge of the adsorbed amounts, using molecular dimensions and assuming an

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TABLE 1

Adsorption of Hydrocarbons by Zeolite ZSM-5

Hydrocarbon	Adsorbate length (nm) (1)	Total adsorbed amount (molecules/unit cell) (2)	Total length of adsorbate in pores (nm)[a] (3) = (1) × (2)	Reference
n-Pentane	0.90	9.94	8.95	(*8*)
		9.72	8.79	This work[b]
n-Hexane	1.03	7.91	8.15	(*8*)
		7.56	7.79	(*17*)[c]
		8.14	8.38	This work[b]
3-Methyl-pentane	0.90	6.02	5.42	(*17*)[c]
		6.74	6.09	This work[b]
p-Xylene	0.98	5.84	5.72	(*17*)[c]
		5.94	5.82	This work[b]
Toluene	0.86	6.58	5.65	(*17*)[c]
Isopentane	0.78	9.62	7.50	(*8*)

[a] Total channel length (estimated from published structures (*3*, *4*): 8.8 nm; length of linear and elliptical channels: 5.9 nm.

[b] Adsorbed amounts determined using a Stanton Redcroft TG-780 thermobalance, values measured at 298 K.

[c] Values from Ref. (*17*) appear systematically lower than those of Ref. (*8*) or this work, probably indicating the presence of phases other than ZSM-5 as impurities or intergrowth and occlusion compounds.

end-to-end configuration of the adsorbed molecules (*8*), one can evaluate the channel length occupied per unit cell by the adsorbates. This analysis clearly shows that linear paraffins (up to C_6) fill the whole pore volume while 3-methyl-pentane and *p*-xylene adsorb exclusively in the linear and elliptical channels. The latter is also true for toluene as evaluated from published data (*17*). Isoparaffins show intermediate values (7.3–7.5 nm) (*8*) probably indicating that their diffusion and adsorption in the sinusoidal channels is hindered to some extent.

These observations may be generalized as follows:

(i) linear aliphatics diffuse rather freely in the ZSM-5 framework and can be adsorbed in both channel systems;

(ii) isoaliphatic compounds experience steric hindrance effects which may restrict their diffusion in the sinusoidal channel system;

(iii) aromatic compounds and methyl-substituted aliphatics have a strong preference for diffusion and/or adsorption in the linear and elliptical channels.

They of course agree with the logical assumption that flat and large molecules will prefer to diffuse in wider and elliptical channels.

The methanol-to-hydrocarbons (and light olefins) conversion reaction has been shown to occur sequentially: methanol is first converted to dimethylether and light-molecular-weight olefins, the latter are oligomerized or alkylated by methanol, and ultimately dehydrocyclized to aromatics and hydrogenated to aliphatics (*18–20*). Counterdiffusion effects do not appear to limit the conversion rate, which needs to be explained in terms of the diffusion pathways available in zeolite ZSM-5.

Figure 1 illustrates the proposal of a shape-selective molecular traffic control. Let P_1^o and P_1^i be the partial pressures of the reactants outside and inside of the zeolite, respectively, P_2^o and P_2^i being the corresponding values for the products. It is

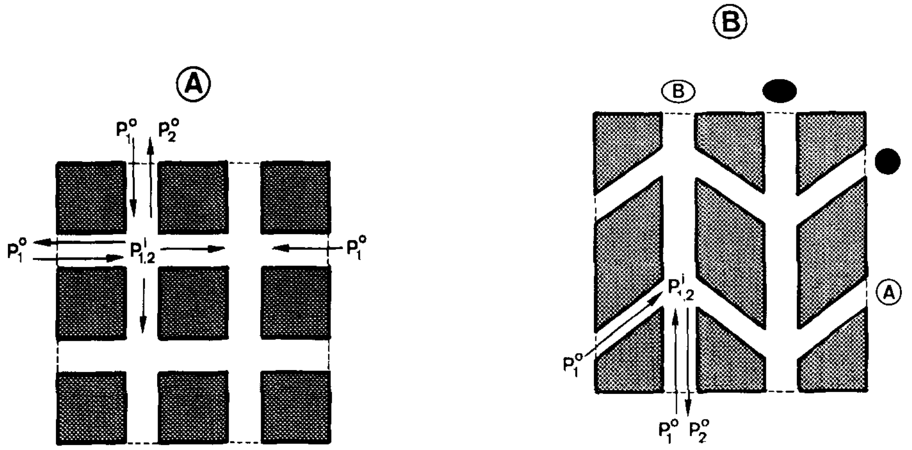

FIG. 1. Illustration of the molecular traffic control effect. A. Zeolite with single type of channel. B. Schematic representation of zeolite ZSM-5: a. near-circular and sinusoidal channels, b. elliptical straight channels.

of course implied that P_1^o is larger than P_1^i, the reverse holding for $P_2^{o,i}$. In a system where only one type of channel network is present (whether or not channels are intersecting), counterdiffusion effects will occur as P_1^o is larger than P_2^i (the conversion reaction indeed leads to a decrease in the total number of molecules) and the diffusion of the product molecules outside the crystallites will be impeded by the faster (because of their smaller size) diffusion of the reactants toward the inside of the catalyst in pores of near-molecular dimensions. This situation is depicted in Fig. 1a while Fig. 1b schematizes the same for ZSM-5.

For ZSM-5 catalysts, reactant molecules may enter the structure through either the linear or the sinusoidal channels provided that they comply to the known shape-selective requirements (*5*). By contrast, the present investigation shows that isoaliphatics, methyl-aliphatics, and monocyclic aromatics diffuse preferentially in the linear and elliptical channels. As seen from Fig. 1b, it implies an out-of-equilibrium situation in which the product (isoaliphatics and aromatics) molecules diffuse out through the linear and elliptical channels while the reactant molecules are essentially entering the catalyst by its sinusoidal channels at the stationary state. Molecular traffic control is then imposed on the molecules which are diffusing in the intracrystalline volume of the zeolite: reactant molecules are entering by the near-circular sinusoidal channels while the bulkier products are desorbing through the linear and elliptical channels. Reactants continuously diffuse toward the inside of the zeolite, *without counterdiffusion;* they are converted at channel intersections (where active sites are probably located (*10*)) to bulkier molecules; the latter diffuse out of the zeolite lattice through a specific type of channel.

Shape-selective molecular traffic control accounts for the absence of major counterdiffusion effects in the conversion of simple molecules by zeolite ZSM-5. It also adds a new dimension to shape-selectivity. Work is in progress to ascertain its importance by comparing data for catalysts with nearly identical structures [such as zeolite ZSM-5 (linear and sinusoidal channels) and zeolite ZSM-11 (linear elliptical channels (*21*))] but having different channel networks.

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