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Shape Selectivity in Catalysis by Zeolites: The Nest Effect

Acid activity and molecular shape selectivity are common factors used to characterize the behavior of zeolite catalysts. Their carboniogenic activity depends to a large extent on their framework Si/Al ratio. Indeed, proportionality between structural Al content and catalytic activity for several organic conversions is observed for highly siliceous materials such as zeolite ZSM-5 (*1–3*). The essence of their molecular shape selectivity, on the other hand, resides in the intracrystalline nature of the processes which they catalyze. Diffusional limitations imposed on the products and/or the reactants, structural constraints acting on reaction intermediates or transition state(s), and channel differentiation (size and shape) are determining in this case (*4–6*).

It was recently proposed by Andersson *et al.* (*7*) that the geometrical description of chemical bonding in solids should be possible using the concept of surface curvature. Periodic minimal Gaussian surfaces were used to describe several materials, among which were faujasite and Linde Type A zeolites. van der Waals bonding was suggested to be proportional to the Gaussian curvature of such surfaces. This principle was applied to discuss water sorption and to allude to possible effects in hydrocarbon cracking by zeolites.

We suggest that this concept may serve as a basis to propose that molecular shape selective effects are not necessarily restricted to the intracrystalline volume of zeolites. In addition, this idea could also help to rationalize the difference in catalytic activity (turnover frequency) of zeolites characterized by distinct structures and/or framework Al contents.

In both cases, we will refer to and use the "nest effect" image wherein a molecule and its direct environment tend reciprocally to optimize their van der Waals interaction. This scheme should involve a perturbation of the sorbed species shape and electronic structure. It could also be at the origin of sorbate-induced framework structural changes, for example those observed by NMR and X-ray diffraction spectroscopies upon sorption of various organic molecules by zeolite ZSM-5 (*8*).

We deal in this case with a stereochemical, rather than diffusional, issue which enables molecules to achieve and reach minimum energy points on the sorbate-zeolite van der Waals potential surface. Arriving at such a situation should increase the sorption equilibrium constant and thereby, possibly, the local concentration of the chemical species (reactants, intermediates, transition state complexes) involved. This could affect reaction kinetics; both activity and selectivity.

External Surface Molecular Shape Selectivity

The external surface of zeolite crystallites possesses catalytic activity depending on the concentration of acidic sites associated with the presence of superficial framework aluminum. For example, the percentage of acidic surface sites (T(%)) in ZSM-5 crystallites of average size D (nm) containing an atomic fraction, F, of structural Al is given by $T(\%) = 181 \cdot (F/D)$, assuming the absence of Al-zoning and crystallites larger than 10 nm (*9*). External catalytic activity is commonly believed to be non-shape-selective. It has been reported to have detrimental effects in several processes, for example, in durene formation in the

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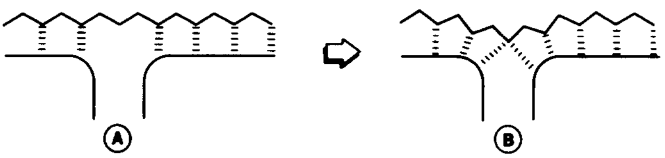

FIG. 1. Conformations of a linear paraffin on the "hilly" surface of a zeolite crystallite. Adsorption (and conversion) is favored for molecules which match best the surface geometry and reach a van der Waals energy minimum. Situations A and B correspond to the molecule without and with the optimization of its interactions with the surface (schematized by the symbols /////), respectively.

methanol-to-gasoline conversion (*10*) and undesired secondary isomerization in *para*-aromatics-directed reactions (*11*).

Molecular shape selective effects, however, should not necessarily be restricted to the intracrystalline volume of zeolites, although the latter clearly favors their occurrence (*4–6*). Indeed, molecular shape selectivity should occur whenever a catalyst selects or prefers specific reactants (or products) on the basis of their size and shape (conformation) in order to match its own active sites steric requirements.

Nature achieves it with enzymes that carry on a given reaction at one reactive site with a defined stereochemical outcome, when there is harmony between the substrate molecule and the active site. Examples of man-made related systems are enantioselective catalysts possessing asymmetric centers (*12*) or supported metal catalysts with varying degree of "congestion" at their active sites (*13*). Note also that both geometric and electronic factors may have complementary roles in defining optimal associations and reaction kinetics (activity and selectivity).

The external surface of zeolites offers pore openings, cut channels, and/or cavities due to their open framework structure. We propose that such hilly environments will elect (and shape) adsorbed molecules depending on their stereochemistry and their ability to optimize their van der Waals interaction with the framework, i.e., their capacity to "nest." Adsorption will be favored for molecules (or intermediates) which can easily adapt their geometry. Thus, it is readily conceived that this effect may influence the overall or relative catalytic (activity and) selectivity. Figure 1 illustrates this principle for a paraffinic molecule interacting with a pore mouth or half-cavity (channel).

Such external surface molecular shape selective effects are more likely to be observed for large (or bulky) molecules (small intracrystalline diffusion coefficients) conversions, small zeolite crystallites, or (X-ray invisible) submicrocrystalline zeolite-type materials, and (coked, modified) zeolites with restricted access to their intracrystalline volume.

Experimental observations possibly pertaining to this type of nest effect have already been reported by Fraenkel *et al.* (*14*) and Ducarme and Védrine (*15*) for the alkylation of aromatics over ZSM-5 type catalysts. In particular, it was proposed that active sites located in the "half" cavities found at the external surface of H-ZSM-5 crystallites were responsible for the highly β-selective methylation of naphthalene (*14*). We also expect that a similar effect could play a nontrivial role in the catalytic conversion of heavy or refractory feeds by zeolites.

Pore Size Effect on Intrinsic Catalytic Activity

Changes in the acidic catalytic activity of zeolites differing by their Al content and structure are customarily attributed to differences in acidic site strength, as a result of collective effects which consider zeolites as ionic solvents (*16*) or use intermediate electronegativity concepts (*17, 18*). In view of the framework negative charge delocalization, as evaluated from quantum chemical calculations (*19*), it appears however that such approaches may become inappropriate when the Si/Al ratio exceeds about 3–4. In addition, such models usually neglect the possible effect of geometrical factors. Thus, the need arises to consider structure-dependent contributions which can act separately or in addition to acid strength.

The effect of molecular conformation on the adsorption equilibrium constant of isomer molecules in zeolites has been observed and quantified. For example, in the case of the adsorption of *n*-butenes (and their subsequent isomerization) on a synthetic near-faujasite germanium zeolite, *cis*-2-butene which matches better the geometry of the supercage was found to adsorb preferentially to *trans*-2-butene (*20*). Post et al. (*21*) pointed out recently the necessity to include adsorption equilibrium constants in the expression for the Thiele modulus used to quantify diffusion-kinetic interactions in zeolite catalysis. It thus becomes apparent that reaction rate constants for intracrystalline zeolite catalysis should be affected by the sorption equilibria which, in turn, influence the local (internal) concentrations of the chemical species (reactants, intermediates, transition state complexes) which are involved.

As discussed above, sorption will be favored for the species which have the best ability to "nest" within the zeolite channels. It is easily conceived that this will depend on the relative match between the molecules and the pore (cavity) sizes, shapes, and lengths. Thus, it implies that, for a given type of molecular species, there should be an optimum sorption pore size (and shape) which will favor its catalytic conversion.

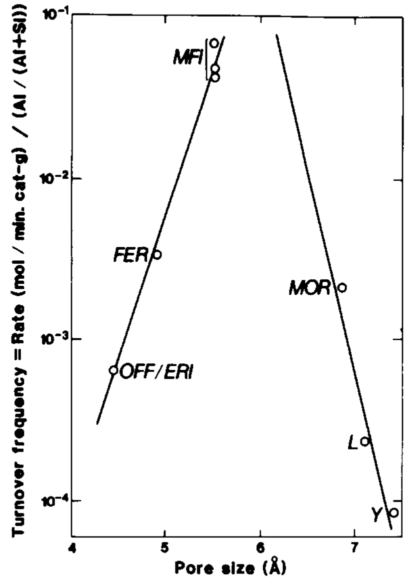

FIG. 2. Dependence of turnover frequency for *n*-pentane cracking as a function of zeolite pore size (Å) (data adapted from Ref. (*22*)). OFF/ERI = offretite-erionite; FER = ferrierite; MFI = ZSM-5; MOR = mordenite; L = Linde Type L; Y = Linde Type Y (faujasite).

The above considerations can be illustrated by examining the cracking of paraffins. Turnover frequencies for *n*-pentane cracking on several zeolites were recently measured by Kikuchi *et al.* (*22*). Plotting these values as a function of pore size (see Fig. 2) results in a "volcano-type" plot indicating the existence of an optimal diameter equal to 5.8–6.0 Å. A quite analogous plot is obtained when considering relative activities for the cracking of *n*-butane (*23*). This optimal pore opening exceeds only slightly the diffusional cross section of linear paraffins and agrees well with the critical dimension of the transition reaction complex postulated for paraffin cracking (*24*). This observation suggests to us that activity differences may not be due to changes in acidic strength, as concluded by these authors in accordance with generally accepted principles, but may well arise from the nest effect which is the object of the present note. A similar hesitancy about the relative importance of the roles played by acidity differences vs physical dimensions was the conclusion of Burch (*25*) in a recent paper dealing with the conversion of methanol on Zr-containing pillared interlayer clays.

We wish to emphasize that although pore size could affect reaction kinetics (activity and selectivity) via molecular "nesting" as described above, this does not exclude the simultaneous occurrence of other molecular shape selective contributions. Note, in addition, that the nest effect of essentially enthalpic nature should not be regarded as similar to the window effect (*26, 27*), which is mainly entropic.

The above interpretations thus lead to a concept which deserves consideration and needs to be further substantiated. Theoretical and experimental work is in progress to assess the occurrence, role, and potential of the nest effect in zeolite catalysis.

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