MOLECULAR SHAPE SELECTIVE CATALYSIS

Paul B. Weisz

Central Research Division, Mobil Research and Development
Corporation, P.O. Box 1025, Princeton, New Jersey 08540, USA

Abstract - Molecular shape selective catalysis in intracrys-
talline space of siliceous zeolites has opened up a spectrum
of new opportunities in catalytic science and in industry.
The mechanisms involved include: (a) selective, diffusional
mass transport dynamics, and (b) steric modification of the
intrinsic reaction rates.

THE CHALLENGE

Almost any thermodynamically possible chemical reactions may occur to some
extent at a sufficiently high temperature. It follows that the most unique
role and purpose of a catalyst is to provide selectivity to direct the trans-
formation along a very specific, desired path.

Manmade catalysts are usually only "class selective". For example, a hydro-
genation catalyst will hydrogenate double bonds in any reactant molecule, and
regardless of position in a molecule, with very few exceptions.

In contrast, nature's catalysts possess detailed structural selectivity, in-
cluding position of the reactive group, structural shape, size, and symmetry.
This presents a challenge to man's science and design of catalysts.

"ACCURATE" CATALYTIC SOLIDS, AND MOLECULAR SHAPE SELECTIVITY

Kinetic principles require existence of at least some 10^{18} reactive centers
per cm^3 of catalyst volume to obtain typically useful catalytic conversion
rates (1) in a process requiring an activation energy of 30 kcal/mole, at
500°C. For solid contact, this requires large specific surface areas, corre-
sponding to subdivision in the range of hundreds of Angstroms or less. It was
traditionally assumed that only amorphous solids were candidates for such
catalysis. In the 1950's, it was demonstrated (2) that a unique class of
crystalline solids could provide catalytic activity at exceptionally high rates
within intracrystalline space. These materials are certain siliceous zeolites,
members of the tectosilicate family.

In these solids, the location of catalysis is the intracrystalline environment.
As such, it is accurately describable by available physical chemical tech-
niques. Controllable physical and chemical manipulations can be undertaken.

Intracrystalline molecular shape selectivity

In some of the available zeolites, the intracrystalline space accessible to
molecules has dimensions near those of the molecules themselves. Thus arose
the concept of providing suitable catalytic centers within such a crystalline
structure so that only certain molecular structures could move or could exist
within the structural environment of the intracrystalline catalytic apparatus.

Reactant selective catalysis was demonstrated (3) using the internal acidic
sites of a Linde 5A zeolite. As shown in Fig. 1, it was possible to catalyze
the dehydration of n-butanol without reacting isobutanol on this catalyst. On
the large pore CaX zeolite catalyst, such size discrimination was shown not to
occur. There, in fact, the isomeric alcohol is actually more actively decom-
posed. Other demonstrations followed: the near complete discrimination in
catalyzed combustion of linear aliphatic molecules without any noticeable
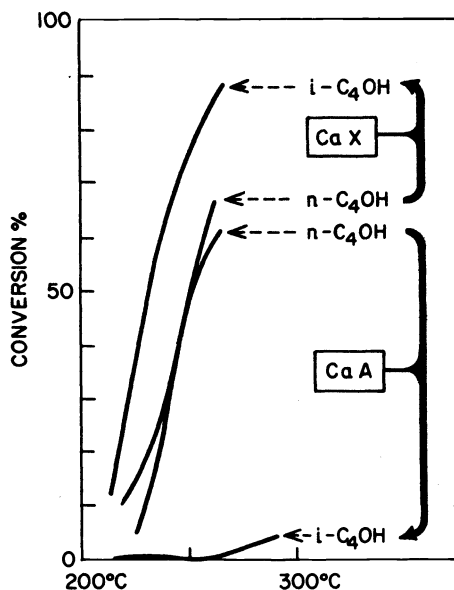
Fig. 1. Conversion of isobutanol vs. n-butanol on non-
shape selective CaX and on shape selective CaA catalyst
(data from Ref. 2).

reaction of their branched species (3b) as shown in Table 1; selective hydro-
genation of the linear diolefin piperylene without conversion of isoprene
(3b); and selective hydrogenation of linear olefins (3a,b).

TABLE 1.   Highly selective combustion of hydrocarbon mixtures
           over Pt-containing CaA zeolite (see: Ref. 3b)

Reactant Mixture (about equal parts)	Conversion, % (combustion)
n-Butane	97.0
i-Butane	<0.1
Propylene	98.6
n-Butene-2	98.6
i-Butene	<1.0

Molecular engineering became possible in the sense of deliberately "designing"
a catalyst to accomplish a desired activity. A selective hydrogenation cata-
lyst was devised (5) that hydrogenated only ethylene in admixture (1:1) with
propylene, by removing sodium from mordenite, then adsorbing platinum-contain-
ing ions (that are otherwise too large to penetrate the sodium-mordenite) and
thereafter replacing the sodium. The intracrystalline structure of a sodium-
mordenite provides adequate mobility for ethylene, propylene, and ethane, but
not for propane (4). Therefore, linear olefins and hydrogen could reach Pt
sites, but after hydrogenation, only ethane could escape.

Product selectivity was operative in this case: the platinum-sodium-mordenite
acted selectively by virtue of the difference in transport capabilities of the
product alternatives, rather than by differentiation between reactant mole-
cules.

Similarly, in the cracking of hydrocarbons on protonic sites contained in
gmelinite (3b), isoparaffin products are virtually absent. Chen, Lucki and
Mower (6) demonstrated this extensively for cracking in erionite of n-paraffins
as large as from C_{10} to C_{36}.

EARLY CHOICES AND NEW ZEOLITES

These early developments were greatly limited by two circumstances: first, a limited choice of zeolites--the only narrow pore structure readily available was the Linde A zeolite structure; second, high concentration of Al sites in a silica zeolite structure prevents the ready conversion to and maintenance of protonic sites.

In a search for zeolites with lower Al site density (e.g., with high Si/Al ratio), we had to resort to the use of mineral collectors' samples, such as chabazite or gmelinite (3b). Awareness of large scale deposits of sedimentary zeolites developed later. But most of these are either dense (e.g., phillipsite), or penetrable by only linear molecules (e.g., chabazite and erionite). However, access to erionite in sizeable quantity led to the first industrial shape selective process (Selectoforming (7)).

There was a need for synthetic zeolites with high Si/Al ratio, and for structures with intracrystalline apertures larger than the 8 oxygen ring structures in zeolite A, chabazite, erionite, etc. For example, shape selective cracking of linear paraffins was potentially useful for removing waxes from petroleum oils, but these waxes turned out to contain appreciable numbers of long chain paraffins with single methyl groups. They would not penetrate these zeolites.

Mordenite was available, with some potential for shape selectivity, by insertion of suitably bulky ions (for a review, see (8)). Mordenite has a linear channel structure with no intersecting pathways. This presented special problems: single file diffusion (9) tends to create a tendency for rapid deactivation due to channel obstruction by relatively few adsorbed molecular entities, or decomposition products.

The discovery of methods for zeolite synthesis that used large organic cations (10, 11) as templates, in place of the traditional all-inorganic ionic species, opened the way to the synthesis of many new zeolites (11).

One of the new zeolites was ZSM-5 (12). Chen and Garwood observed that it was able to accept and crack mono-methyl in addition to normal paraffins. It was therefore a candidate for "dewaxing" heavy oils. It also allowed selective reaction involving some mono-cyclic hydrocarbons (see: Ref. 14). Its crystal structure (13) has a two dimensional network of intersecting channels, with dimensions of about 5.4 x 5.6 Angstroms (see Note a) created by a 10 oxygen atom ring. This allows a large variety of molecular discriminations to occur (14).

In a relatively short time, a number of novel commercial processes were developed which made use of ZSM-5-type catalysts.

CONVERSION PROCESSES

Table 2 summarizes the major shape selective conversion processes that have been developed.

"Selectoforming" was developed and used to crack n-paraffins from a gasoline, to mostly propane (7). This simultaneously removes from the gasoline the components having the lowest octane number (ON) contribution (thus raising the ON), and produces LPG as a valuable product.

In *M-forming* (15), the unique and graduated selectivities of ZSM-5 for cracking various paraffin structures are utilized. These are illustrated by the data of Chen and Garwood (14) in Fig. 2. The cracking ability of the catalyst for these paraffin structures correlates inversely with their blending octane numbers, Fig. 3, making the ZSM-5 conversion catalyst an "intelligent" octane number improver. In the same process, alkylation of aromatics with cracked fragments also occurs, thereby increasing the liquid yield. Contrary to conventional relative alkylation activities of benzene and toluene, benzene is reacted preferentially (14). This results in lowering benzene/toluene ratios in the product.

Note a. Based on X-ray structure determination using an oxygen radius of 1.35 Angstroms. Zeolite A, on this basis, has a circular aperture diameter of 4.1 Angstroms.

TABLE 2. Industrial processes based on shape selective zeolites

PROCESS	OBJECTIVE	MAJOR CHEMICAL/PROCESS CHARACTERISTICS
Selectoforming	Octane number increase in gasoline; LPG production	Selective n-paraffin cracking
M-Forming	High yield; octane number increase in gasoline	Cracking depending on degree of branching; aromatics alkylation by cracked fragments
Dewaxing	Light fuel from heavy fuel oil; lube oils with low temperature pour point	Cracking of high molecular weight n- and mono-methyl paraffins
Xylene Isomerization	High yield para-xylene production	High throughput, long cycle life; suppression of side reactions
Ethyl Benzene	High yield ethyl benzene production; eliminate AlCl$_3$ handling	
Toluene Dis-proportionation	Benzene and xylenes from toluene	
Methanol-to-Gasoline	Methanol (from coal or natural gas) conversion to high grade gasoline	Synthesis of hydrocarbons only, restricted to gasoline range (C$_4$ to C$_{10}$) including aromatics

Fig. 2. Relative cracking rate constants at 340°C in HZSM-5 catalyst (after Ref. 14).
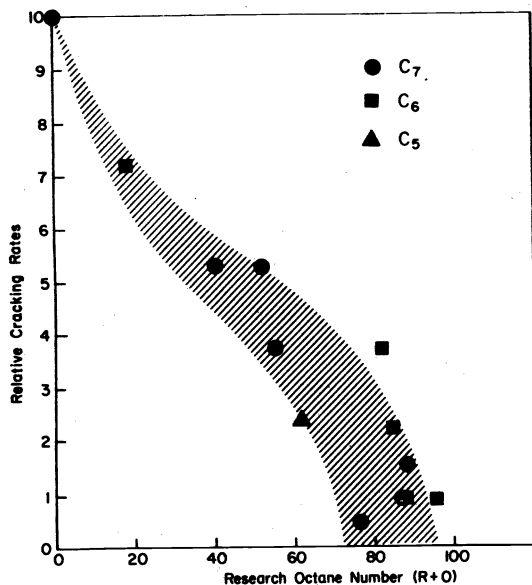
Fig. 3. Selective cracking vs. octane number of paraffins
(after Ref. 18)

The *dewaxing processes* (16-19) have made it possible to make use of a larger
fraction of heavy portions of petroleum raw material as diesel and heating
oils, and to provide high grade lubricating oils with low energy expendi-
ture. The catalyst removes selectively those paraffinic portions of a heavy
oil responsible for its deficient flow properties at low ambient temperature
(high "pour point"). The catalyst also has the potential of converting waxy
crude oils into upgraded, transportable fluids.

The new *xylene isomerization* and *ethyl benzene* processes (16, 21, 35), based
on ZSM-5 type catalysts, create the desired products at unprecedented yields
by reducing all important side reactions. The xylene processes are now used
in some 90% of U.S. and 60% of existing western world capacity. Some of the
mechanistic aspects are noted below.

Toluene disproportionation catalysis (16, 18, 35) provides high product selec-
tivity in the manufacture of xylenes and benzene from toluene. Again, side
product suppression is achieved by the catalyst. Potential improvements that
would selectively create high concentrations of para-xylene produced directly
have been demonstrated, as noted below.

Development of a *methanol-to-gasoline (MTG) process* (16, 22, 23) followed the
finding that the ZSM-5 catalyst is capable of converting oxygen compounds such
as alcohols, aldehydes, ketones, carboxylic acids, and esters to hydrocarbons
in a limited range of structural sizes, as demonstrated by Chang and Silvestri
(20), and Kaeding and Butter (24).

The MTG process, developed to the stage for commercialization, converts the
one carbon compound methanol into a mixture of hydrocarbons, in the gasoline
range, with high antiknock quality. The process is the final link in systems
to convert coal or natural gas into motor fuel. Fixed bed and fluidized bed
reactors have been demonstrated in pilot units. Construction of a pilot plant
for scale-up of the fluidized bed reaction is planned with cooperation of the
United States and the Federal Republic of Germany. The New Zealand government
plans to produce gasoline from natural gas in a commercial plant based on the
fixed bed scheme.

PRINCIPLES

It is convenient to consider a pair of molecular species, P and A. P shall be
the "proselective" species, and A the "antiselective" species in the sense that
shape selective discrimination will favor the reaction (or creation) of P.
The degree of shape selectivity S is the ratio of the appropriate observed

effective rates or rate constants, as compared to their usual ratio in the
absence of structural constraints on molecular motion:

$$S = (k'_p/k'_a)/(k_p/k_a).$$

Or, if the intrinsic rates in the absence of spatial constraints are equal,
then:

$$S = k'_p/k'_a.$$

Shape selectivity via mass transport discrimination

Shape selectivity (S > 1) will occur, not only when A is entirely unable to
move through intracrystalline space, but also when $D_a << D_p$, i.e., when the
diffusivity of the antiselective species A is <u>sufficiently</u> smaller than that
of the proselective species P. Shape selectivity will result from the well
known diffusion/reaction dynamics.

The effective diffusivity. In shape selective catalysis, the motion of mole-
cules is restricted when the structural dimensions of the catalyst approach
those of the molecules. We have termed this the regime of "configurational"
diffusion (1). Even subtle changes in the dimensions of molecules can result
in large changes in diffusivity.

For example, a greater than 200-fold reduction in the diffusion rate of butene
in CaA zeolite results for the change from the *trans* to the *cis* form (5).
Similarly, the measurements by Riekert (26) in T zeolite demonstrate a pro-
found (three orders of magnitude) increase in mobility on "stiffening" one
bond in the 4 carbon chain, as we compare n-butane with n-butene-2, Fig. 4.
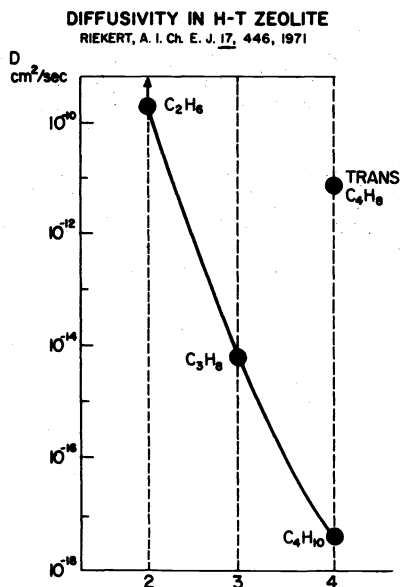

Fig. 4. Diffusivity in HT zeolite. Effect of "stiffening"
one bond in the 4 carbon hydrocarbon.

In molecular shape selectivity, not only the size, but also the dynamics of
the structure of the molecules, need to be considered. For example, we have
demonstrated (27) that a triglyceride as large as $C_{57}H_{104}O_6$ will successfully
react in ZSM-5 to substantially the same product spectrum of hydrocarbons as
does methanol, CH_3OH; see Fig. 5A. While the conventional "writing" of the
structural formula, Fig. 5B, suggests a structure too large to penetrate the
crystalline channel, molecular dynamics is such as to easily attain configur-
ations that have an effective cross section no greater than that of trimethyl
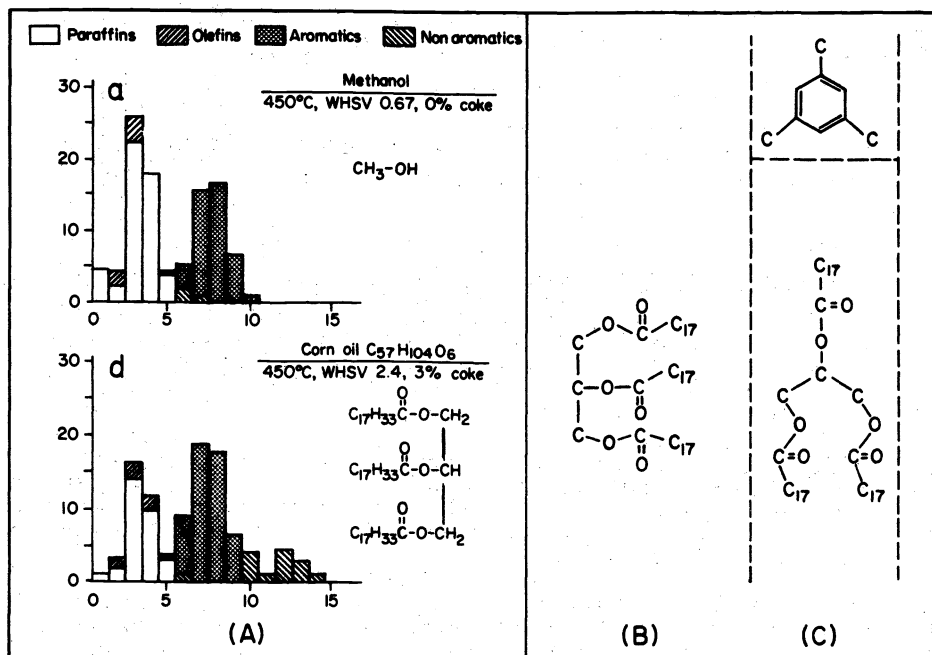benzene, Fig. 5C.

Fig. 5. (A) Conversion of corn oil triglyceride $C_{57}H_{104}O_6$ compared to that of methanol, on ZSM-5; (B) "written"; (C) possible configuration of C_{57} molecule.

In the configurational regime, motion occurs in a force field with replusive potential rising rapidly with closer approach between molecular and structural atoms. The effective cross section for successful motion will depend on translational energy, resulting in a temperature dependency, i.e., an "activation energy" for the diffusivity (28).

Just as has been demonstrated for monotonic gases in denser zeolites (see: e.g., Barrer (29)), this applies to organic molecules in shape selective zeolites. For example, Gorring (30) has measured (see Fig. 6) rising activation energies for diffusion range up to about 16 kcal/mole of ethane, n-butane, and n-octane in a T zeolite. These, and measurements by Gorring for some
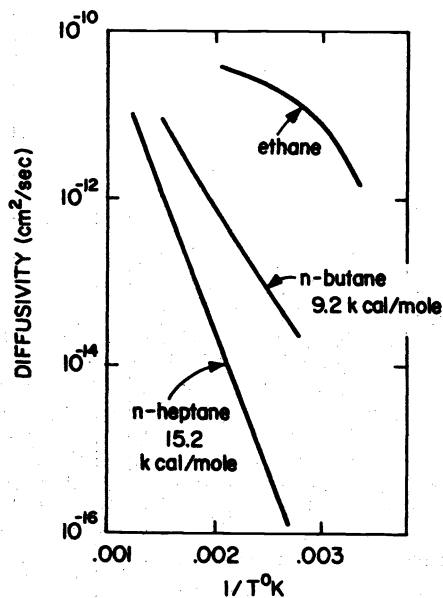

Fig. 6. Diffusion coefficients of hydrocarbons in potassium T zeolite.

alkyl benzenes in Na-ZSM-5, Table 3, reflect the experience, common with other fields (gases in dense zeolites and glasses or carbons, dyes in fibers and polymers), that the activation energy rises with closer approach between the void dimensions and those of the molecular configurations.

TABLE 3. Activation energies for diffusion in Na-ZSM-5, from sorption studies at 250°C to 350°C

	kcal/mole
o-Xylene	9
m-Xylene	14
t-Butyl benzene	12
1,2,4-trimethyl benzene	14
1,3,5-trimethyl benzene	19

Diffusion/reaction interaction. The behavior that can be expected for shape selective kinetics between the antiselective species A and the proselective P, due to mass transport inhibition, can be illustrated by using the usual diffusion/reaction models for first order reactions (see Note b).

For each species, the reaction rate inhibition due to diffusion effects will be determined by the effectiveness factor η and its well known relationship (Fig. 7, top) to the characteristic parameter $\phi = k(R^2/D)$. R is the particle radius of the zeolite crystallite, k the intrinsic reaction rate constant, and D the diffusivity. To test the discrimination between two species due to a large diffusivity difference, we assume k to be the same. Then, the shape selectivity S can be read from the ratio of the η values in Fig. 7 (top).

Figure 7 (bottom) shows how the shape selectivity S depends on the ratio of the diffusivities D_p/D_a, and on the location of the parameter $k(R^2/D)$ for the antiselective species.
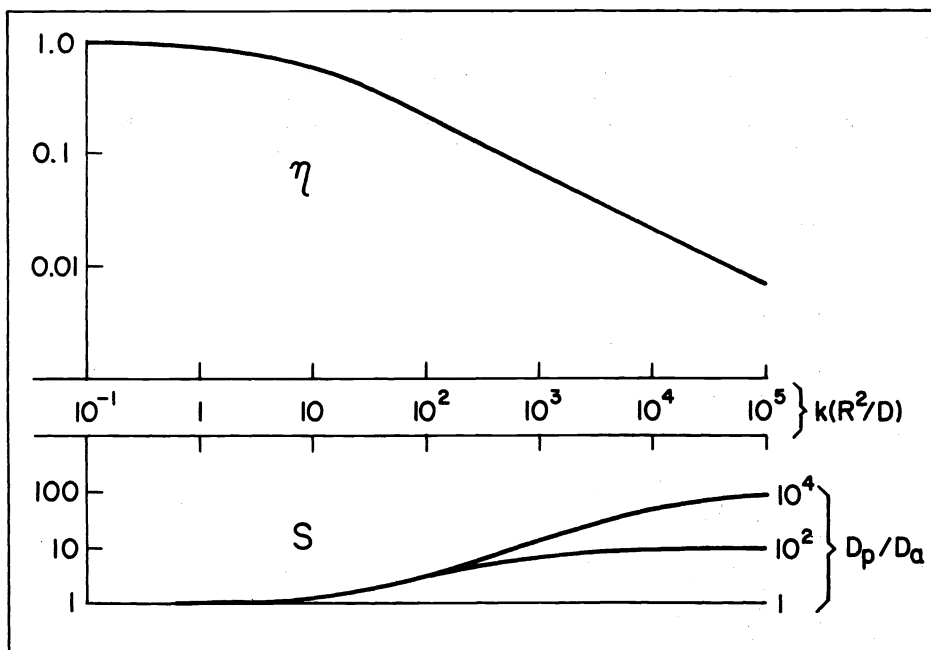

Fig. 7. Top: the conventional dependence of utilization factor η. Bottom: selectivity S vs. $k(R^2/D)$ of the antiselective species.

Note b. Because of symmetry of the equations, the same considerations apply to reactant as well as to product selectivity, when these products are generated internally in a first order reversible reaction.

The selectivity ratio can always vary from S = 1.0 (no shape selectivity) to S = $(D_p/D_a)^{1/2}$ for the highest shape induced selectivity. For any given intrinsic activity level, we note that shape selectivity requires not only the favorable D_p/D_a ratio but, in addition, demands operation with a minimum factor of R^2/D_a. This factor is proportional to the characteristic diffusion time τ_a of the antiselective species in the crystallite, since $\tau_a \sim R^2/D_a$.

Thus, a potential shape selective effect by virtue of a large D_p/D_a, when not observed, can be developed or increased by increasing the crystallite size. A similar shift in diffusive residence time would be achieved by inducing pore blockage in a fraction of the pore passages, thus increasing the random walk tortuosity. This would keep constant D_p/D_a, but would decrease the effective D_a.

Both of these methods have been used successfully to obtain selectivity for highly selective generation of only the para-xylene isomer in methanol-toluene addition and in disproportionation of toluene, Fig. 8.
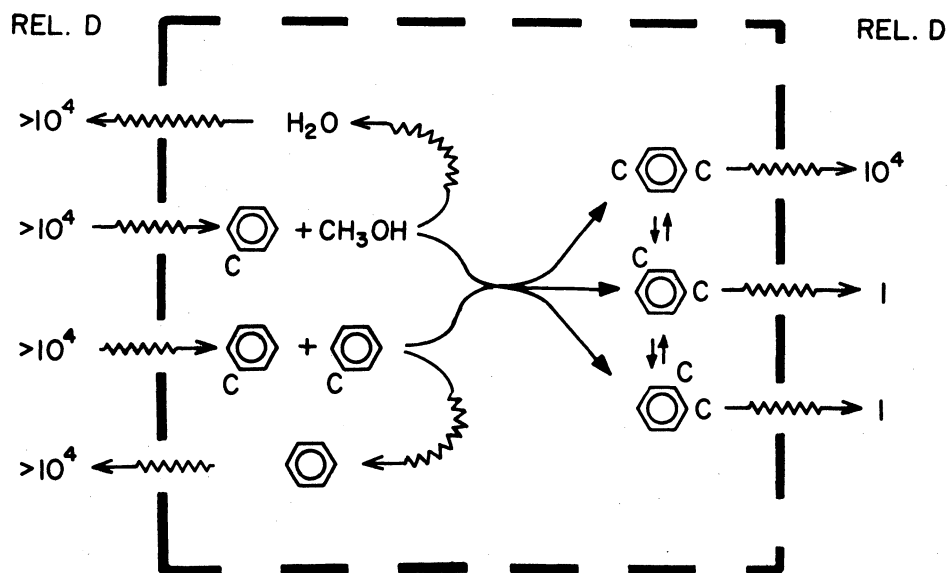

Fig. 8. Diffusion/reaction kinetics in para-xylene generation from disproportionation or methanol alkylation of toluene.

Chen, Kaeding and Dwyer (31) have achieved para-xylene selectivities of 90% or more of total xylenes by introducing inorganic matter into the pore structure of ZSM-5 catalyst. Also, increasing the crystallite size alone from <0.5μm to 3μm increased para-xylene concentration from 23% (equilibrium) to 46%. Haag and Olson (33) have obtained this also by closure of a fraction of the external pore mouths, again effecting a tortuosity increase.

Haag and Olson (32) demonstrated data for para-xylene concentrations achieved in toluene disproportionation at standard conditions for twelve ZSM-5 catalysts modified in various ways--by crystal size variation, coke deposition, or inorganic fillers--all of which correlate uniquely with R^2/D, a diffusion residence time for ortho-xylene (an antiselective species) determined independently by sorption measurements. Their data, shown in Fig. 9, are fully consistent with the shape selectivity resulting from a classical diffusion/reaction mechanism as illustrated in Fig. 7.

Para-selectivity has also been achieved in modified mordenites (34). For example, CeNa mordenite showed high selectivity for mono-alkylation, and for para-positional generation of cymene.

Shape selectivity via local configurational constraint
In the configurational regime, molecular motion is subject to the energetics of molecule/framework force fields. This constraint at the local level finds
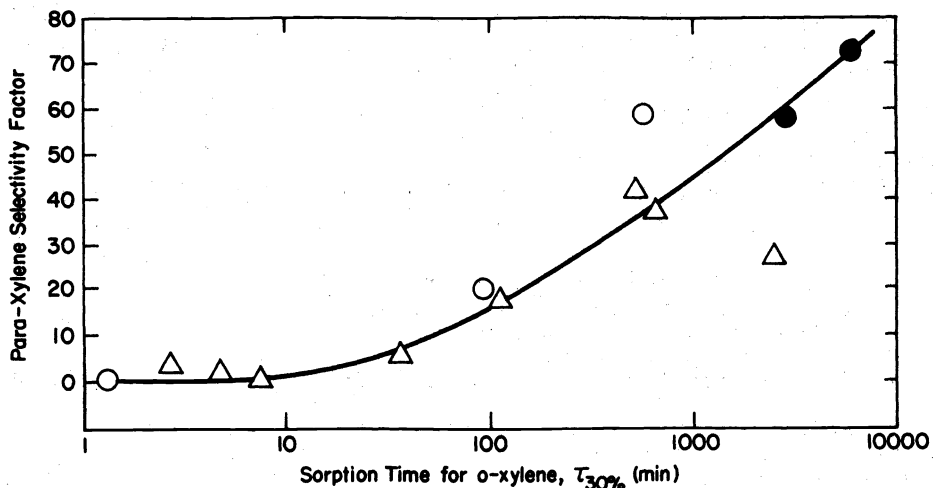
Fig. 9. Para-xylene selectivity vs. o-xylene sorption time in
various ZSM-5 catalysts. O = various crystallite sizes; Δ =
increased tortuosity by inorganic salts; ● = increased tortu-
osity by coke plugging. (After Ref. 32)

expression in the sizable "activation energy" of diffusivity. If the cataly-
tic sites are located within the same constraining structure, then the fre-
quency of successful encounters in local kinetic events can be expected to
also be sensitively dependent on size, spatial molecular configuration and
dynamics, and on temperature; this could include successful molecule/site
contact, or successful creation or transition of a specific reaction complex.

Discrimination in reactions with bimolecular complexes. The accommodation of
successful bimolecular encounters and reaction complexes on a catalytic site
in constrained space will be more difficult than a monomolecular event.

This is believed to be a major phenomenon in creating the high selectivity in
the ZSM-5 xylene isomerization process. Fig. 10 shows this in terms of the
ratio of the rate constants for the unwanted bimolecular disproportionation
reaction to that of the desired monomolecular xylene isomerization, observed
by Haag and Dwyer (35) for four zeolite catalysts of varying intracrystalline
channel dimensions. A similar discrimination exists in the ethyl benzene dis-
proportionation.

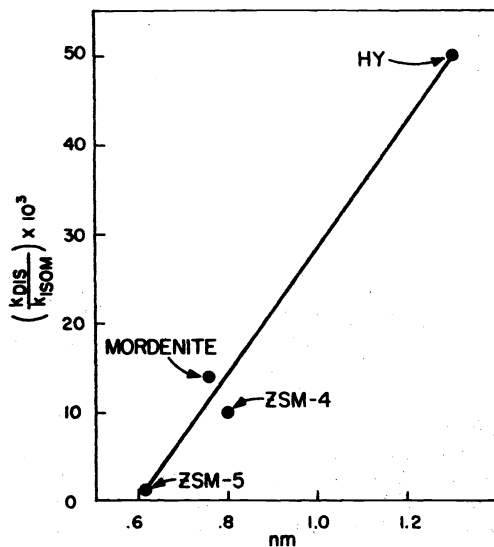EFFECTIVE DIAMETER OF INTRACRYSTALLINE CAVITY
Fig. 10. Selectivity in xylene isomerization vs. zeolite pore diameter.

Csicsery (8) has observed the suppression of bulky 1,3,5-trialkyl benzene formation in the disproportionation of dialkyl benzenes in mordenites, and has pointed out the mechanisms of constraint or prohibition of the transition state (8).

The characteristic of these reactions is the fact that the reaction complex is larger than either the reactants or the products. The question of a transport mechanism does not apply for the spatial inhibition mechanism operating on the complex.

Shape selective inhibition of reactant reactivity. It is natural to assume that reactant selectivity in shape selective catalysts is due to mass transport inhibition of the antiselective species in line with diffusion/reaction interaction discussed previously. However, there is evidence that shape selective constraints on the local site kinetics can be operative.

The classical diffusion/reaction mode requires the selectivity between species to increase with increasing temperature unless the activation energy of diffusion exceeds that of the intrinsic reactivity. The first observations made on alcohol dehydration (3) showed selectivity decreasing with temperature. Then Chen and Garwood (14) established a strong decrease of n-hexane/3-methyl pentane selectivity in cracking over HZSM-5 catalyst. Judging from the diffusivity measurements (Table 3) with much bulkier aromatics molecules, we cannot expect the paraffin diffusivities to have appreciable activation energies, let alone exceed that of catalytic reactivity. Definitive proof for shape selectivity constraints on intrinsic kinetics, rather than via diffusive transport inhibition, developed from work by Frilette, Haag and Lago (36). Measurements of the cracking rates were made in a differential reactor for catalyst with crystallite sizes differing by two orders of magnitude (or by four orders of magnitude for R^2/D). Figure 11 shows virtual independence of behavior on size R.
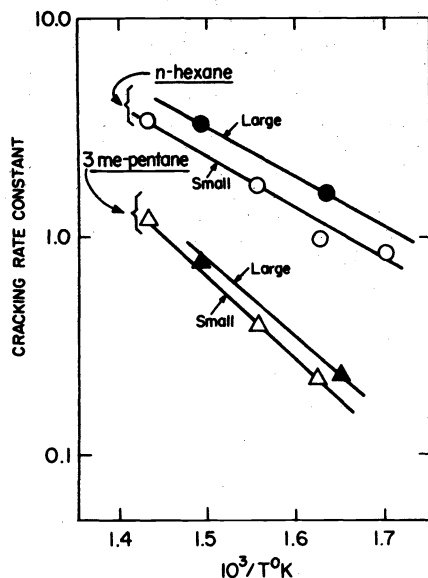

Fig. 11. Cracking rates of ZSM-5 catalysts of two crystallite sizes, 0.02 to 0.5 nm (open symbols) and 2 to 4 nm (solid symbols).

It may be too early to speculate concerning the detailed mechanism of steric inhibition, whether it occurs due to the need for forming a large reaction complex between a molecule and a sizable site-anchored carbonium ion, or whether the formation of the site complex ("sticking factor") requires such special geometric approach as to be hindered by the surrounding crystal structure.

It is notable that Derouane, et al (37), in extensive recent work on ZSM-5 selectivity, have been led to suggest behavior influenced by intermediate complex structures being able to form only in special locations in ZSM-5; for example, the formation of aromatics from cycloaddition of a carbonium ion and an olefin is a complex that may form only at a channel intersection, while the aromatic product is small enough to diffuse through the channels. The system would be analogous to the cases described previously. The complex cannot move, but the reactant and product molecules, being smaller, can diffuse adequately.

Shape selective inhibition in product formation. Since the early demonstrations of product selectivity, many more different cases have been observed, many reviewed and reported by Csicsery (8) and Derouane (37), including anti-Markownikoff additions of HBr to α-olefins by Fetterly and Koenitz (38), a case of base catalyzed shape selectivity in crossed aldol condensations by Shabtai (34), and others. Shabtai also has demonstrated new potentials for shape selective catalysis with inorganic materials that are not siliceous zeolites (34).

It is not clear yet when product selectivities are produced by mass transport (diffusion) inhibition of the antiselective species, and where steric inhibition in the formation of the relevant reaction complex or product is operative. Most likely, there are cases where both mechanisms are operative. The study of kinetic behavior of various crystallite sizes is likely to be the most important method in discriminating between the two effects in future work.

CONCLUSIONS

Shape selective catalysis has created opportunities for new chemistry and new industrial processes. We appear to be in the typical early stage of entering new territory: discoveries and utilization of new features have been outpacing our ability to grasp all quantitative detail of the mechanism. It now appears that selective diffusion inhibition, as well as selective steric inhibition in site kinetics, or a combination of both phenomena, are operative in shape selective catalysis. The selectivities achievable move our abilities a step further toward the precise structure specific selectivities of the biochemical processes.

ACKNOWLEDGMENT

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