

## 《解 說》

# THE SCIENCE AND TECHNOLOGY OF SHAPE SELECTIVE CATALYSIS IN ZEOLITES

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Shape selectivity differentiates between reactants, products, or reaction intermediates according to their shape and size. Only molecules whose dimensions are less than a critical size can enter the pores, have access to internal catalytic sites, and react there. Furthermore, only molecules that can leave will appear in the final product.

The first half of this presentation discusses the phenomenon of shape selectivity, its origin and its types. The second half will cover new types of shape selectivities, new developments in selectivity improvements, new reactions, new zeolites and other shape selective materials, and some recently proposed or implemented commercial applications.

Most cations in zeolites are exchangeable. This allows the introduction of different cations with various catalytic properties. If these sites are exchanged to H<sup>+</sup>, the zeolite can have many very strong acid sites. In addition, high surface area (> 600 m<sup>2</sup>/g), good thermal and hydrothermal stability, and the ability to sorb and concentrate hydrocarbons account for the high catalytic activity of zeolites. They have well defined crystal structure with pore diameters of discrete sizes. These pores are similar to molecular dimensions (< 1 nm). These properties are responsible for the shape selectivity.

Shape selective catalysis depends on the pore dimensions of the zeolite and the types of catalytically active sites presents, as well as on the configurations and dimensions of reactants, intermediates, and products. The concept of shape selectivity has been first described thirty years ago by Paul Weisz and coworkers.<sup>1)</sup>

Pore diameters in zeolites depend on the number of MO<sub>4</sub> tetrahedra (where M = Si, Al, or a heteroatom) in the ring encircling the pore. Thus, we can distinguish small-, medium-, large-, and extra-large-pore zeolites, depending on whether 8, 10, 12, or 18 tetrahedra comprise the ring. Maximum possible free diameters are 0.43, 0.63, 0.8, and about 1.5 nm, respectively (Table 1). In many zeolites, however, the actual diameters are frequently less than these maximum values because the plane of the ring may not be perpendicular to the axis of the pore, or the ring may be puckered (i.e., the tetrahedra comprising the ring are not in the same plane), or the ring is not circular, etc. Thus, factors determining shape selectivity depend not only on the number of tetrahedra of the ring, but also on the shape of the pore (circular, elliptical, pear-shape, etc.), the presence of intersections, cavities, or side-pockets within the pore system, and whether the pore system is one-, two-, or three-dimensional.

Table 1. Pore diameters in zeolites

Number of Tetrahedra in Ring	Maximum Free Diameter, nm	Examples
6	0.28	
8	0.43	Erionite, A
10	0.63	ZSM-5, Ferrierite
12	0.80	L, Y, Mordenite
18	1.3 ~ 1.5	VPI-5

Some Hydrocarbon Dimensions:

Benzene = 0.57 nm x 0.22 nm

n-Hexane = 0.35 nm x 0.42 nm

We can distinguish three types of shape selectivities (Fig. 1):

**In Reactant Selectivity** some of the mole-

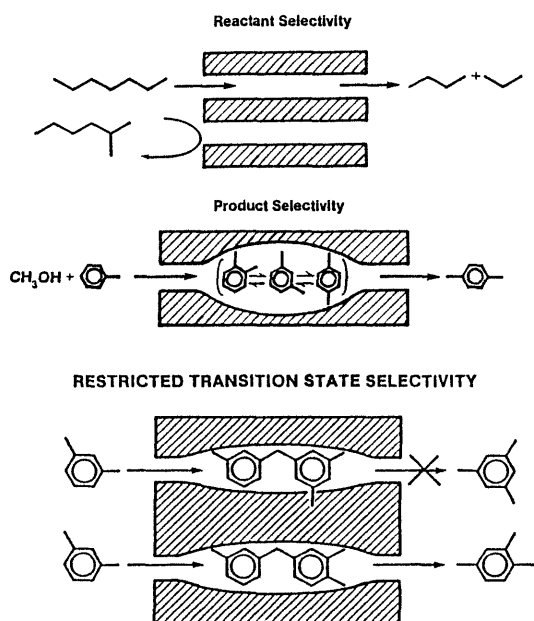


Fig. 1 Three types of shape selectivities

cules in a reactant mixture are too large to diffuse into the catalyst pores.

**In Product Selectivity** only product molecules with sufficiently small dimensions can diffuse out and appear as products. Bulky molecules formed within the interior of the zeolite may not be able to diffuse through and appear as observed products. They are either converted to less bulky molecules by isomerization or cracking, or eventually deactivate the catalyst by blocking the pores.

**In Restricted Transition State Selectivity,** certain reactions are prevented because the corresponding transition state requires more space than is available in the cavities or pores. Neither reactant nor product molecules are prevented from diffusing through the pores. Reactions proceeding through smaller transition states may proceed unhindered.

Reactant and product selectivities are mass transfer limited and therefore affected by crystallite size, whereas restricted transition state selectivity is not. This is a very useful way to distinguish between these shape selectivities.

The cracking of  $C_6$  paraffins is an example of both reactant and product selectivities.<sup>2)</sup> Both 3-methylpentane and n-hexane react over silica-alumina but only n-hexane can react in the shape selective, small-pore zeolite CaA. The iso/normal ratios of butanes and pentanes produced show product shape selectivity: whereas more isobutane and isopentane than n-butane and n-pentane are produced over silica-alumina, the iso-products are practically absent from the product made in CaA (Table 2).

Other examples of reactant type selectivity are the competitive hydrogenations of hexene and 4,4-dimethylhexene-1 and styrene and 2-methylstyrene over Pt-ZSM-5,<sup>3)</sup> and of cyclopentene and methylcyclohexene over Rh-zeolites.<sup>4)</sup> In the last example, non-shape-selective Rh sites located on the outside surface of the zeolite crystals were poisoned with  $P(Bu)_3$ . [Note that  $P(Bu)_3$  is larger than the pores of ZSM-5 and therefore affects only the Rh on the outside of the crystals. The much smaller  $P(Me)_3$  would enter the pores and poison all Rh.] Another interesting aspect of this work is that shape selectivity was increased about ten-fold by hydrating the zeolite to about one-third of its water adsorption capacity prior to the reaction. Surface site poisoning and altering pore dimensions (by hydration in this case) are examples of enhancing shape selectivity (Fig. 2). Other examples will follow below.

An example of restricted transition state selectivity is the acid catalyzed transalkylation

Table 2. Reactant and product selectivity in the case of 3-methylpentane cracking at  $500^\circ C$ <sup>2)</sup>

Catalyst	3-Methylpentane Cracking %	Normal Hexane		
		Cracking %	$\frac{iC_4}{nC_4}$	$\frac{iC_5}{nC_5}$
Silica-alumina	28	12	1.4	10
Linde Ca-A	< 1	9.2	< 0.05	< 0.05

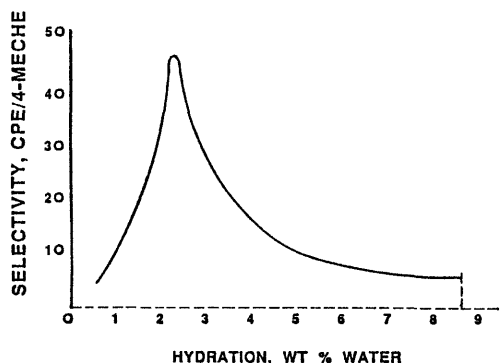


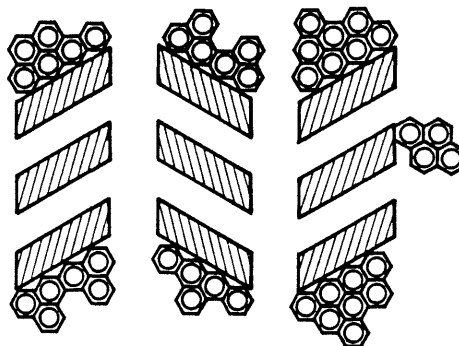
Fig. 2. Enhancement of shape selectivity by adsorbed water in the case of hydrogenation of cyclopentene and 4-methylcyclohexene over Rh-ZSM-11 at 60°C<sup>4)</sup>

of dialkylbenzenes. This reaction involves a bimolecular diphenylmethane-type transition state. Products are a monoalkylbenzene and various trialkylbenzene isomers. At equilibrium, symmetrical 1,3,5-trialkylbenzenes are the main components of the isomer mixtures. Over H-mordenite, however, the symmetrical trialkylbenzenes are almost absent from the reaction product because there is not enough space for their bulky transition states. The other trialkylbenzenes can form because their transition states are smaller.<sup>5, 6)</sup>

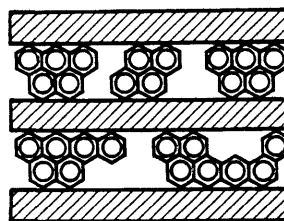
The presence or absence of restricted transition state type selectivity in dialkylbenzene reactions may be used to measure void space around acid sites in unknown zeolites.<sup>7)</sup>

In ZSM-5 and other pentasil zeolites, restricted transition state selectivity affects isomerization and cracking of low MW paraffins, transalkylation of xylenes, and coking. Coke deactivates large pore zeolites and amorphous materials by forming inside the pores. However, in pentasils and some other medium and small pore zeolites, it forms a layer on the outside of the crystals, almost like an eggshell around an egg (Fig. 3). Electron microscopy provided the evidence. It shows filament-like coke in HY zeolite and external eggshell type coke over H-ZSM-5 and H-offretite after n-heptane cracking at 450°C.<sup>8)</sup> The structure of the filament-like coke resembles pentacene

#### A. Pentasil Zeolites



#### B. Mordenite (and Other Large Pore Zeolites)



Dejaifve, et al., J. Catal., 70, 123 (1981).

Fig. 3 Different types of coke formation

whereas the eggshell-type coke is more like coronene.

Low coking rate, and therefore longer life is perhaps the most important advantage of pentasil zeolites over other crystalline and amorphous catalysts. This longer life made the commercialization of a number of pentasil zeolite-based processes possible.

#### New Type of Shape Selectivity

**Restricted Growth Shape Selectivity** may be either restricted transition state selectivity or product shape selectivity. It limits the number of consecutive reactions in oligomerizations, polycondensations, and other reactions in which a reactants may react a second or third time with the product of the first reaction. Typical examples are base-catalyzed aldol condensation and the production of mono- and dimethylamines from methanol and ammonia. In base-catalyzed aldol condensation the end-product from acetone over X and Y zeolites is isophorone (a trimer). Over NaKL the reaction stops at mesityl oxide (a dimer).<sup>9)</sup> Whereas over amorphous catalysts the CH<sub>3</sub>OH

+ NH<sub>3</sub> reaction gives mostly trimethylamine, over SiCl<sub>4</sub> treated Na-mordenite the yield of the more valuable mono- and dimethylamines surpasses 99% (Table 3).<sup>10, 11, 12, 13, 14)</sup>

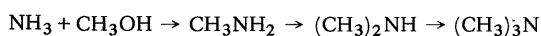
### New Developments in Enhancing Shape Selectivity

Shape selectivity may be increased by eliminating the non-shape-selective catalytic sites on the outside surface of the zeolite crystals. We have already discussed the use of P(Bu)<sub>3</sub> to poison "external" Rh sites.<sup>4)</sup> Another recent example is the deactivation of external acid sites of ferrierite with 2,4-dimethylquinoline.

2,4-dimethylquinoline is larger than the pores of ferrierite and therefore cannot penetrate the crystals and neutralize internal acid sites (Table 4).<sup>15)</sup> Restricted transition state type selectivity allows only the formation of para-diethylbenzene inside the pores. Non-shape-selective external acid sites isomerize the para isomer to the other two isomers in untreated catalysts. Thus, ethylation of ethylbenzene over the untreated catalyst produces all diethylbenzene isomers. Once the external sites are poisoned with 2,4-dimethylquinoline, only the para isomer is formed.

Shape selectivity may be enhanced by nar-

Table 3. Restricted growth type shape selectivity



The catalytic activity and selectivity for methylamine synthesis on various synthetic zeolites.<sup>14)</sup>

Catalyst	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Initial Rate <sup>a</sup> /10 <sup>-5</sup> mol g <sup>-1</sup> s <sup>-1</sup>	Selectivity/mole % <sup>b</sup>		
			MMA	DMA	TMA
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	6.3	4.01	6.3	14.2	79.5
Al <sub>2</sub> O <sub>3</sub>	—	6.86	8.6	17.0	74.4
5A	1.2	1.55	5.5	13.0	81.6
Na-Y	4.8	0.08	2.6	11.8	85.6
H-Y	5.2	5.61	0.0	3.9	96.1
K-FE	12.3	0.31	6.1	24.6	69.3
H-FE	12.3	4.18	18.8	32.3	49.0
Na-M	9.8	0.53	17.9	59.5	22.6
H-M	9.9	3.82	14.7	25.5	59.8
SC-Na-M <sup>c</sup>	10.7	0.98	26.1	72.7	1.2
H-SC-M <sup>d</sup>	10.9	4.04	26.5	57.4	16.2
Na-ZSM-5	25.0	0.17	1.7	11.3	87.0
H-ZSM-5	25.0	5.37	6.4	19.9	73.7

<sup>a</sup> Reaction temperature: 673 K.

<sup>b</sup> Selectivities were obtained at 100 % conversion of CH<sub>3</sub>OH.

<sup>c</sup> SC-Na-M: Na-M was treated with SiCl<sub>4</sub> vapor at 973 K for 3 h.

<sup>d</sup> H-SC-M: SC-Na-M was ion-exchanged by NH<sub>4</sub><sup>+</sup>, and calcined at 773 K.

Table 4. Selective poisoning of acid sites on external surfaces<sup>15)</sup>

Catalyst	Diethylbenzene Yield <sup>a</sup> /%	Fraction <sup>b</sup> /%			1,3,5-TIPB Conversion <sup>d</sup> /%
		o-	m-	p-	
HZSM-5	26.3	1.7	59.1	39.2	51.1
HZSM-5 <sup>c</sup>	16.9	0	42.8	57.2	0
H-ferrierite	1.5	19.8	32.7	47.5	11.8
H-ferrierite <sup>c</sup>	0.4	0	0	100.0	0

<sup>a</sup> Reaction temperature, 673 K; W/F, 7.14 g·h·mol<sup>-1</sup>.

<sup>b</sup> Fraction of each isomer in diethylbenzene produced.

<sup>c</sup> Poisoned with 2,4-dimethylquinoline.

<sup>d</sup> Cracking of 1,3,5-triisopropylbenzene.

rowing the pores or partially blocking pore entrances. This may be done by hydration<sup>4)</sup> (see above), or by treating the zeolite with Si<sub>2</sub>H<sub>6</sub>.<sup>16)</sup> Xenon adsorption data show that when used at 25°C, Si<sub>2</sub>H<sub>6</sub> penetrates the pores and makes them narrower. If, however, Si<sub>2</sub>H<sub>6</sub> is applied at 100°C, most of it reacts with surface hydroxyles near pore entrances.

### The Nest Effect

The "Nest Effect" is a new concept in shape selective catalysis. According to this concept, the reacting molecules and its environment tend to reciprocally optimize their van der Waals interactions.<sup>17)</sup> Molecules which can easily adapt their geometry (i.e., "nest" within channels or cavities) will adsorb easier than those which cannot. These structure dependent surface curvature effects can act separately or add to acid strength. Examples include the disproportionation of n-pentane to butane and hexane over H-ZSM-4<sup>18)</sup> (Table 5), and the selective conversion of butyric acid to 4-heptanon over erionite.<sup>19)</sup>

Table 5. The nest effect in the pentane disproportionation over H-ZSM-4<sup>18)</sup>

2C <sub>5</sub> H <sub>12</sub> → C <sub>4</sub> H <sub>10</sub> + C <sub>6</sub> H <sub>14</sub>	
Catalyst	Relative Rate at 240°C
H-ZSM-4	100
H-Mordenite	4.6
REX	0.5

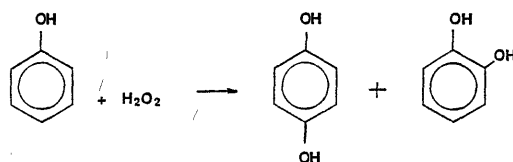
#### H-ZSM-4

Probably involves two carbenium ions in adjacent sites.  
Has one-dimensional pores, and therefore limited coking.

### New Materials

Over a hundred new molecular sieves have been synthesized in the last decade. Some contain heteroatoms on their framework, others have entirely new crystal lattice or new chemical composition (AlPO's, SAPO's, etc.). Shape selectivity has been demonstrated over many of these new materials. An interesting example is Ti-silicalite, used commercially to produce dihydroxyphenols from phenol (Table 6). The reaction is done in the liquid phase

Table 6. Shape selective oxidation of phenol with H<sub>2</sub>O<sub>2</sub> over Ti-silicalite (Si/Ti > 40) at 60 ~ 100°C<sup>20)</sup>



Solvent	para, %	ortho, %
Methanol	65	35
Acetone	43	57

with H<sub>2</sub>O<sub>2</sub> as the oxidant. The plant in Ravenna, Italy, produces about 10,000 t/yr hydroquinone, or about one-fifth of the World's demand. Product para/ortho ratios are significantly higher than those in competing processes.<sup>20)</sup>

A few non-zeolitic new materials also exhibit shape selective catalysis. Most notable are pillared clays.<sup>21, 22)</sup> "Pillars" may be built into certain hydrated clays by intercalating (usually positively charged) inorganic or organic substances between the layers. Subsequent dehydration may leave evenly spaced pillars. These separate the clay layers from each other. Advantages are that the pore size may be tailored between 0.6 and 4 nm. Disadvantages are fast deactivation by coking and poor thermal or hydrothermal stability. Examples of shape selective reactions are the disproportionation of trimethylbenzenes into 1,2,4,5-tetramethylbenzene, and the dimerization of oleic acid. A clay containing 0.8 nm alumina pillars catalyzes the first reaction. The latter reaction has been demonstrated in montmorillonite crosslinked with (CH<sub>4</sub>)N<sup>+</sup> pillars. Dimerization selectivity peaks at a pillar density of 0.28 electron charge/(Si, Al)<sub>4</sub>O<sub>10</sub>. If the pillar density is much lower than this value, oligomerization proceeds to trimers. If, however, the pillar density is above this critical value, the reaction cannot proceed because there is not enough space for the reaction intermediate. (This is an example of both restricted transition state and restricted growth type selectivities.) A potential com-

mercial application is the alkylation of benzene with 1-dodecene to produce intermediates for biodegradable detergents. HF-alkylation produces all isomers but over Al-pillared montmorillonite the product contains mostly the most desirable 2-phenyldodecene.<sup>23)</sup>

### New Commercial Applications

Most applications of shape selectivity involve either cracking of undesirable molecules to smaller, easily removable fragments, or avoiding undesirable competing reactions such as coking and transalkylation as shown in Table 7.

In most cases isoparaffins crack and isomerize much faster than normal paraffins. This order is reversed in shape selective acid catalysis. That is, normal paraffins react faster than branched ones, which sometimes do not react at all. This reversal of the usual order of reaction rates is the essence of most applications in the first group. Examples are distillate and lube oil dewaxing, Selectoforming, and M-forming. The production of para-xylene, ethylbenzene, para-ethyltoluene, and hydroquinone, the methanol-to-gasoline, methanol-to-olefins, and olefins-to-gasoline-and-distillates

processes and dehydrocyclodimerization are some of the applications in the second category.

Research to exploit shape selective catalysis is active. Selected examples of new shape selective reactions and commercial processes are the already mentioned production of hydroquinone over Ti-silicalite, yield improvement in adiponitrile production over Na-P-B-pentasil,<sup>24)</sup> yield improvement in n-paraffin aromatization over Pt-BaKL,<sup>25)</sup> and the forthcoming dehydrocyclodimerization ("Cyclar") plant in Scotland.

### Conclusions

Some of the benefits of shape selective catalysis:

Higher yields due to better selectivities.

More efficient use of available resources because less low-value byproducts.

Environmentally more acceptable processes.

Elimination of costly separation steps because the reactions are more selective.

The field of shape selective zeolite catalysis is very active. The number of patent applications covering zeolite processes has been

Table 7. Process applications of shape selectivity

Process	Type of Selectivity			Number of Plants
	Reactant	Product	Transition State	
I. Undesirable Molecules are Cracked to Removable Fragments.				
Distillate Dewaxing	+	+		9
Lube Dewaxing	+	+		4
Selectoforming	+			
M-Forming	+		?	
FCC	+			Many
II. Coking, High MW Products, and Undesirable Isomers are Avoided or Minimized.				
Ethylbenzene			+	6
p-Ethyltoluene		+	+	
Xylene Isomerization		+	+	13
Toluene Alkylation			+	
Toluene Disproportionation			+	2
Methanol-to-Gasoline			+	1
Methanol to Olefins			+	
Olefins to Gasoline and Distillates			+	
Dehydrocyclodimerization			+	1
Phenol Oxidation			+	1

increasing every year of the last twenty-five years.<sup>26</sup> We may expect this trend to continue.

Zeolite catalysts have been first used commercially in the nineteen-sixties. Most of those applications were in petroleum processing. The seventies saw the use of zeolite catalysts for large volume petrochemicals. Intermediate volume, "specialty" chemicals have been first processed commercially in the eighties. We may predict that in the nineties zeolite catalysts will be used for fine chemicals and maybe for the processing and upgrading of heavy petroleum fractions. Biochemical materials, perhaps even some chiral compounds may be produced with shape selective zeolite catalysts in the following decade.

Most likely areas of future developments are new chemical compositions, new crystalline structures, heteroatom substitution in framework, better control of morphology (i.e., crystal size and shape, crystal aggregates, macropores, etc.), better control of spatial distribution of active sites, and polyfunctional and composite catalysts.

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