

Catalysis by shape selective zeolites – science and technology

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Abstract. Pores of uniform dimensions characterize zeolite catalysts. If the pores are small, the fate of reactants and the probability of forming products are determined by molecular dimensions and configurations as well as by the types of catalytically active sites present. Reactant shape selectivity occurs when some of the molecules in a reactant mixture are too large to diffuse into the zeolite pores. Product selectivity occurs when, among all the product molecules formed within the pores, only those with the proper dimensions can diffuse out and appear as products. In restricted transition state type selectivity, certain reactions are prevented because the corresponding transition state requires more space than is available. Most commercial applications of shape selectivity involve either (1) cracking of undesirable molecules to smaller, easily removable fragments, or (2) avoiding undesirable competing reactions such as coking and transalkylation. Applications discussed are distillate and lube oil dewaxing, the production of *para*-xylene, ethylbenzene, and *para*-ethyltoluene, and the methanol-to-gasoline, methanol-to-olefins, and olefins-to-gasoline-and-distillates processes. Most of these processes use the pentasil type ZSM-5 zeolite.

INTRODUCTION

Shape selective catalysis differentiates between reactants, products, or reaction intermediates according to their shape and size. If almost all of the catalytic sites are confined within the pore structure of a zeolite and if the pores are small, the fate of reactant molecules and the probability of forming product molecules are determined by molecular dimensions and configurations as well as by the types of catalytically active sites present. 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 appear in the final product.

Shape selective catalysis can be used to increase yields of preferred products or to hinder undesirable reactions.

It has been 25 years since Weisz and Frilette first described the concept of shape selectivity (ref. 1). The significance of this phenomenon was recognized immediately. Scientific experimentation went hand-in-hand with the exploration of commercial possibilities. Desktop laboratory experiments were soon followed by development work, and pilot plant demonstrations soon led to the construction and start-up of commercial units.

P.B. Weisz, C.D. Chang, N.Y. Chen, F.G. Dwyer, V.J. Frilette, W.E. Garwood, R.L. Gorring, W.O. Haag, H. Heinemann, W.W. Kaeding, R.M. Lago, J.N. Miale and A.J. Silvestri were not only the pioneers of shape selective catalysis but in their many publications described its many possible applications. Furthermore, they and other workers at Mobil Research and Development eventually contributed to most of the commercial applications of shape selectivity we will discuss today.

Shape selective catalysis has been reviewed by S.M. Csicsery (ref. 2,3,4), H. Heinemann (ref. 5), T.E. Whyte and R.A. Dalla Betta (ref. 6), and J. Dwyer and A. Dyer (ref. 7).

In the first half of this discussion we will describe the phenomenon of shape selectivity and the catalysts which make it possible. Applications will be covered in the second half.

TYPES OF SHAPE SELECTIVITIES

We can distinguish three types of shape selectivities depending on whether pore size limits the entrance of the reacting molecule, the departure of the product molecule, or the formation of certain transition states:

(1) Reactant selectivity occurs when some of the molecules in a reactant mixture are too large to diffuse through the catalyst pores (Fig. 1).

(2) Product selectivity occurs when some of the product formed within the pores are too bulky to diffuse out as observed products. They are either converted to less bulky molecules (e.g., by equilibration or cracking) or eventually deactivate the catalyst by blocking the pores (Fig. 1).

(3) Restricted transition-state selectivity occurs when certain reactions are prevented because the corresponding transition state would require more space than available in the cavities or pores. Neither reactant nor product molecules are prevented from diffusing through the pores. Reactions requiring smaller transition states proceed unhindered.

Zeolites

Most shape selective catalysts today are molecular sieve zeolites. Zeolites are porous crystalline aluminosilicates possessing intracrystalline channels with reproducible morphology. They are built up from SiO_4 and AlO_4 tetrahedral elements, cross-linked to each other through the oxygens.⁴ In natural zeolites, aluminum or silicon occupy all the tetrahedra but in some synthetic zeolites gallium, germanium, boron, and phosphorus have been also incorporated into the framework.

Natural zeolites are frequently found in rocks of volcanic origin (e.g., glassy tuffs near alkaline lakes).

Synthetic zeolites are made by precipitation from supersaturated alkaline solutions of various inorganic or organic bases. The organic cations (often various tetraalkylammonium hydroxyls) serve as templates to direct crystallization toward the desired structure.

Zeolites have four properties which make them interesting and valuable for heterogeneous catalysis: (1) they have exchangeable cations, allowing the introduction of different cations with various catalytic properties; (2) if these cationic sites are exchanged to H^+ , they can have a very high number of very strong acid sites; (3) they have pore diameters with one or more discrete sizes; and (4) they have pore diameters that are in the order of molecular dimensions, i.e., less than 1 nm. Properties 1 and 2 account for catalytic activity and properties 3 and 4 are responsible for the molecular sieving action.

Pore diameters in molecular sieves depend on the number of tetrahedra in a ring (Table 1). Zeolites with 8 tetrahedra are commonly called small-pore zeolites, those with 10 tetrahedra are medium-pore, and those with 12 tetrahedra are large-pore zeolites. Most industrial applications of shape selectivity today employ medium-pore zeolites. If the plane of the ring is not perpendicular to the axis of the pore, or if the elements forming the ring are not in the same plane (i.e., puckered) than the pore diameter is less than the possible maxima shown in Table 1.

Table 1. Pore diameters in zeolites.

Number of tetrahedra in a ring	Maximum free diameter, nm	Example
6	0.28	
8	0.43	Erionite, A
10	0.63	ZSM-5, Ferrierite
12	0.80	L, Y, Mordenite
18	1.5	Not yet observed

Typical hydrocarbon dimensions: Benzene = 0.57 x 0.22 nm
n-Hexane = 0.35 x 0.42 nm

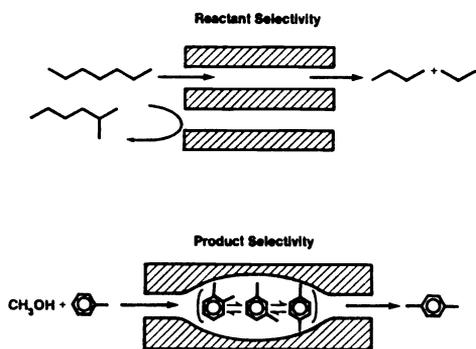


Fig. 1 Reactant and product selectivities (Ref. 3)

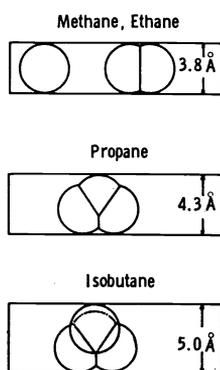
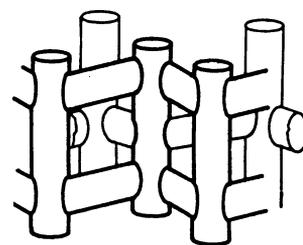


Fig. 2 Molecular diameters (Ref. 3)



Zig-Zag Channels = 5.4 Å x 5.6 Å
Straight Channels = 5.2 Å x 5.8 Å

Fig. 3 The pore structure of ZSM-5

The actual pore size also depends on the type of cation present. Type A sieves have cubic structure with pores just about big enough to allow normal paraffins through. Cations, however, occupy positions which block part of the pores. Monovalent cations (e.g., sodium, potassium) reduce the actual pore size to below ~ 0.4 nm. With the exception of methane, no organic molecule can penetrate Li-A or Na-A zeolites. Divalent cations, however, occupy only every other cationic site and leave enough space for normal paraffins to diffuse through. Isobutane is slightly larger than normal butane and therefore cannot enter Ca-A (Fig. 2).

At higher temperatures the pores enlarge slightly and the diffusing molecules have higher kinetic energy to overcome repulsion forces at pore entrances. These, and molecular vibration allow molecules to wiggle through somewhat narrower pores than expected. Thus, dimensions presented within two decimal points are not meaningful; molecules about 0.05 nm too large can sometimes make their way through pores because they (and the atoms forming the pores) vibrate. In addition, bond cleavage, followed by reconstruction of the broken bond could facilitate the diffusion of larger molecules through narrow pores (ref. 8).

One medium-pore size zeolite family is called 'pentasil' because their framework is composed of five-member oxygen rings, and because they can contain more silicon than most other zeolites. ZSM-5 is by far the most important member of the pentasil family because of its catalytic activity, stability, acid strength, many commercial applications, and other remarkable properties. It wouldn't be an exaggeration to say that today commercial shape selective catalysis is the catalysis of ZSM-5.

The structure of ZSM-5 is described by Kokotailo, Lawton, and Olson (ref. 9) and Olson, Haag, and Lago (ref. 10). Thomas et al. and Dominguez, Acosta, and Schifter have published high resolution electron microscope images of ZSM-5 together with selected area diffraction studies which show that ZSM-5 has a high degree of crystallinity and a uniform pore distribution (ref. 11-14).

ZSM-5 and silicalite (a related pentasil zeolite with a very high silica/alumina ratio) have two types of pores. Both are composed of ten-membered rings. One is sinusoidal with a nearly circular cross section (0.54 nm x 0.56 nm). The other system has elliptical pores (0.52 nm x 0.58 nm). These are straight and perpendicular to the first system (Fig. 3) (ref. 15,16).

The silica/alumina ratio in ZSM-5 varies from the teens to the thousands. High silica/alumina ratios have several important consequences: hydrophobicity, very strong acid strength, and thermal, hydrothermal, and acid stability. Hydrophobicity depends on the aluminum concentration and it is independent of the structure. Very low alumina ZSM-5 and silicalite are therefore more hydrophobic than most other crystalline and amorphous oxide catalysts. Acid sites are associated with framework aluminum atoms. In most zeolites, including

in ZSM-5, the strength of the acid sites is inversely proportional to the concentration of framework aluminum up to about a silica/alumina ratio of 10. Above this ratio the aluminum level does not affect acid strength. The number of the acid sites is directly proportional to the concentration of framework aluminum. In ZSM-5 the acid sites are probably located at pore intersections.

Diffusion

In general, one type of molecule will react preferentially and selectively in a shape-selective catalyst if its diffusivity is at least one or two orders of magnitude higher than that of the competing types. If the dimensions of the reacting or diffusing molecules approach the dimensions of the pores even subtle changes in the dimensions or configurations of the reacting or product molecules can cause large changes in diffusivity (ref. 17). For example, the diffusivity of *trans*-2-butene in Ca-A zeolite is about 200 times larger than that of *cis*-2-butene (ref. 18,19).

Reactant and product type shape selectivities depend on diffusion rate differences. However, even those molecules which react preferentially have much smaller diffusivities in shape selective catalysts than in large-pore catalysts. For example, normal paraffins have diffusivities at least five orders of magnitude lower in the zeolite KT than in the large-pore Y-type zeolite.

Decreased diffusivities, of course, affect reaction rates (ref. 20).

Shape selectivity in acid catalysis

Many manifestations and applications of shape selective catalysis involve acid catalyzed reactions such as isomerization, cracking, dehydration, etc. In these reactions shape selectivity reverses the usual order of relative carbocation reaction rates. Acid catalyzed reactivities of primary, secondary, and tertiary carbons differ. Tertiary carbon atoms form carbocations easily; therefore, they react much easier than secondary carbon atoms. Primary carbon atoms do not form carbocations under ordinary conditions and therefore do not react. Only secondary carbocations can form on normal paraffins; whereas tertiary carbocations can be generated on singly branched isoparaffins. Therefore, in most cases isoparaffins crack and isomerize much faster than normal paraffins. This order is reversed in most shape selective acid catalysis; that is, normal paraffins react faster than branched ones, which sometimes do not react at all. This is the essence of many applications of shape selective acid catalysis.

Reactant and product-type selectivities

Examples of reactant selectivity are alcohol dehydration (Table 2), cracking (Table 3), and hydrogenation (Table 4).

Over non-shape-selective catalysts, such as Ca-X, secondary alcohols dehydrate much easier, and therefore they require much lower temperature than primary alcohols. Over the shape selective Ca-A catalyst secondary alcohols do not react at all. Note that the dehydration rate of the branched primary alcohol, isobutanol is also very low (ref. 1,24).

Table 2. Reactant selectivity; dehydration of alcohols (ref. 24).

Reactant alcohol	Reaction temp. °C	Conversion, wt%	
		Ca-A	Ca-X
normal Butanol	260	60	64
secondary Butanol	130	0	82
Isobutanol	260	< 2	85

Table 4. Reactant selectivity; olefin hydrogenation (ref. 25).

Catalyst	Temp. °C	Pt-Al ₂ O ₃	Pt-ZSM-5
Conversions, %			
normal Hexene	275	27	90
4,4-Dimethylhexene-1	275	35	< 1
Styrene	400	57	50
2-Methylstyrene	400	58	< 2

Table 3. Reactant and product selectivity; cracking of C₆ at 500°C (ref. 24).

Catalyst	3-Methylpentane		n-Hexane	
	cracking	conversion, %	cracking conv. %	
Silica- alumina		28	12	iC ₄ /nC ₄ 1.4 iC ₅ /nC ₅ 10
Linde Ca-A		< 1	9.2	<0.05 <0.05

Table 3 compares cracking conversions of 3-methylpentane and normal hexane. Both hydrocarbons react over silica-alumina but only normal hexane can react over the shape selective Ca-A. The iso/normal product ratios of the product butanes and pentanes show product selectivity here. These ratios are high over silica-alumina: 1.4 for the butanes and over 10 for the pentanes. Isobutane and isopentane are practically absent from the product made over Ca-A because even if formed internally, they would not be able to diffuse out (ref. 24).

Linear olefins are hydrogenated about two orders of magnitude faster than branched ones over Pt-ZSM-5 (Table 4). Dessau has prepared this catalyst by first ion-exchanging ZSM-5 with $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$, then reducing the platinum with hydrogen, and finally neutralizing all acid sites with ammonia (ref. 25).

Restricted transition state-type selectivity

In restricted transition state-type selectivity certain reactions are prevented because the transition state is too large for the space available inside the molecular sieve. However, neither reactants nor potential products are hindered from diffusing through the pores; only the formation of the transition state is inhibited.

Acid catalyzed transalkylation of dialkylbenzenes provides an example (ref. 26). In this reaction one of the alkyl groups is transferred from one molecule to another. The reaction is bimolecular and it involves a 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. For example, at 315°C the equilibrium mixture of methyl-diethylbenzenes contains 46.8% 1-methyl-3,5-diethylbenzene (ref. 27). Over HY zeolite and amorphous silica-alumina symmetrical trialkylbenzenes are formed together with the other isomers. Relative concentrations are close to equilibrium. Over H-mordenite, however, the symmetrical trialkylbenzene is almost absent from the reaction product (Table 5) (ref. 28,29).

Table 5. Restricted transition state selectivity; the transalkylation of methylethylbenzenes (ref. 29).

Catalyst	H-Mordenite	H-Y	Silica-alumina	Thermodynamic equilibrium
Temperature, °C	204	204	315	315
1,3-dimethyl-5-ethylbenzene, % of total C ₁₀	0.4	31.3	30.6	46.8
1-methyl-3,5-diethylbenzene, % of total C ₁₁	0.2	16.1	19.6	33.7

Product type selectivity is excluded here by demonstrating that isomerization rates of the symmetrical mesitylene and the smaller hemimellitene over H-mordenite and H-Y are almost identical. This shows that the diffusion of symmetrical trialkylbenzenes is not hindered within the pores of H-mordenite. The transition state of isomerization involves only one molecule whereas the transition state of transalkylation is bimolecular.

Symmetrical trialkylbenzenes cannot form directly in H-mordenite because there is not enough space for their bulky transition states. The other trialkylbenzenes can form because their transition states are smaller (Fig.4).

Restricted transition state selectivity in ZSM-5 affects reactions with bimolecular transition states. Examples are isomerization and cracking of low MW paraffins, transalkylation of xylenes, and coking.

Isobutane isomerization proceeds by a bimolecular mechanism over large-pore zeolites. Over these materials the product also contains propane and pentanes

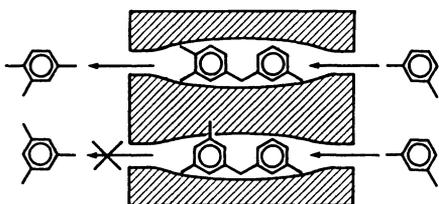


Fig. 4 Restricted transition state selectivity (Ref. 3)

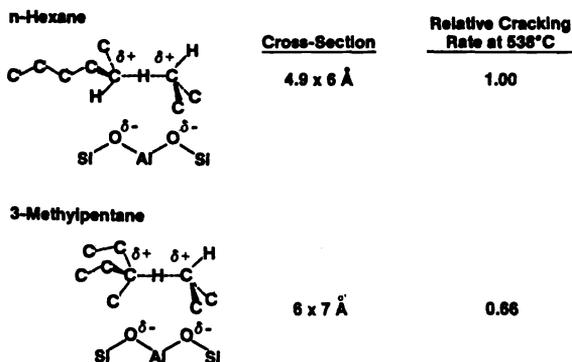


Fig. 5 Dimensions of transition states of C₆ paraffins (Ref. 33)

in addition to normal butane. In H-ZSM-5, however, there is not enough space for a bimolecular transition state. As a consequence isobutane isomerization is almost two orders of magnitude slower in H-ZSM-5 than in H-mordenite (ref. 30), although the acid sites of the former are stronger than those of the latter (ref. 31). Furthermore, pentanes are absent from the reaction product. This, too, suggests a monomolecular mechanism (Table 6).

Cracking of small (i.e., less than C₇) paraffins over amorphous acid catalysts and large-pore zeolites also involves a bimolecular transition state. The rate determining step involves hydride transfer between a carbocation and a neutral molecule; the transition state would be composed of these two entities. There is not enough space in ZSM-5 for this bulky transition state. According to Haag, above ~500°C, in H-ZSM-5 cracking proceeds by an unimolecular mechanism (ref. 32). This monomolecular transition state involves a pentavalent carbonium ion intermediate. Products of the two reactions differ. The predominant low molecular weight products of the unimolecular reaction are hydrogen, methane, and ethane. The main end-products of the bimolecular reaction are propane, propylene, isobutane, and isobutylene.

One can distinguish experimentally between restricted transition state selectivity and reactant (and product) type selectivities by studying particle-size effects. In general, observed rates depend on intrinsic (uninhibited) rate constants and, if mass transfer is limiting, on the diffusivities of the reactant (or product) molecules, and on catalyst particle size. Reactant and product selectivities are mass transfer limited and therefore affected by crystallite size, whereas restricted transition state selectivity is not (ref. 33). Intrinsic cracking rates of monomethyl paraffins over ZSM-5 are affected by steric constraints on their transition states (Fig. 5).

Haag, Lago, and Weisz calculated effective diffusivities from crystal-size effects. This was the first known case for determination of molecular diffusivities in a zeolite at steady-state and actual reaction conditions (Table 7) (ref. 33). Branching has a large effect: diffusivities decrease by four orders of magnitude from normal to gem-dimethyl paraffins. The effect of molecular length is small. Olefins have similar diffusivities to the corresponding paraffins.

Table 6. Isobutane isomerization at 350°C with a hydrogen/hydrocarbon molar ratio of 4 (ref. 30).

Zeolite	Rates of Formation, 10 ⁻⁴ mol/hr/g		
	Propane	n-butane	Pentanes
H-Mordenite	41	24	11
H-ZSM-5	0.6	0.35	0

Table 7. Diffusivities in ZSM-5 at 538°C (ref. 33).

Hydrocarbon	D, at 538°C, cm ² /s
1-Hexene	3 x 10 ⁻⁴
3-Methyl-2-pentene	4 x 10 ⁻⁵
2,2-Dimethylbutane (neohexane)	2 x 10 ⁻⁸
3,3-Dimethyl-1-butene	7 x 10 ⁻⁸
2,2-Dimethylhexane	3 x 10 ⁻⁸

The diffusivity of *para*-xylene in ZSM-5 is about ten thousand times faster than that of the other two isomers (ref.34). As it selectively diffuses out from the catalytic sites the primary product distributions are changed by isomerization, and more *para*-xylene is made. Therefore, in toluene alkylation with methanol and in toluene disproportionation the preferred isomer over ZSM-5 is *para*-xylene. For example, Chen, Kaeding, and Dwyer obtained up to 97 % selectivities over ZSM-5 zeolites impregnated with phosphoric acid, boron compounds, etc. (ref. 17,34). Restricted transition state selectivity may also contribute here to high *para*-xylene selectivity.

Advantages of restricted transition state selectivity

One of the most important advantages of ZSM-5 over other crystalline and amorphous catalysts is low coking rate. Because coking is low in ZSM-5, it deactivates much more slowly than other catalysts. This longer life made the commercialization of a number of processes possible (ref. 35-40).

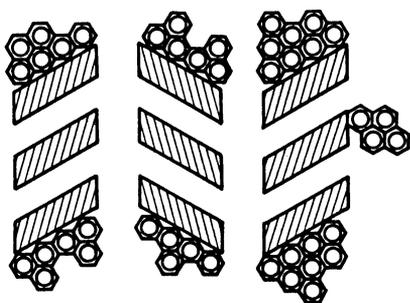
Coking is less severe in ZSM-5 than in most other catalysts because the pores lack enough space for the polymerization of coke precursors. In ZSM-5 coke is deposited on the outer surface of crystals; whereas in large-pore zeolites, such as mordenite or offretite, most of the coke forms within the pores (ref. 35). Activity is barely affected in the first case but decreases rapidly in the second. Fig. 6 shows an oversimplified picture of these phenomena.

Control of shape selectivity

Shape selectivity may be improved by reducing the number of active sites on the external surface of the zeolite crystallites. This may be achieved by poisoning 'outside' sites with large molecules which cannot enter the pores (ref. 41), or by reducing the aluminum content in the last stage of crystallization of the zeolite.

Diffusivities within zeolites can be reduced by reacting the outside surface of the zeolite crystallites with reactive silicon or other reactive materials (ref. 23,42-46). The silane reagent should be larger than the pore entrance so that it does not affect internal pore diameters or acid sites. A frequently used silane reagent is tetraethyl orthosilicate (ref. 45,46). As the silane reacts with surface silanol hydroxyls it forms a surface layer which extends over part of each pore entrance. The surface silane group is converted to the oxide or hydroxide after hydration or oxidation. As access to the interior of the catalyst is inhibited, reactant- and product-type selectivities increase but internal diffusion is unaffected (Fig. 7). Complete plugging of some pores (as opposed to partial plugging of all pores) is a better explanation. The effect is similar to that observed in larger crystals: longer diffusion paths, favoring products with higher diffusivities (ref. 23).

A. Pentasil Zeolites



B. Mordenite (and Other Large Pore Zeolites)

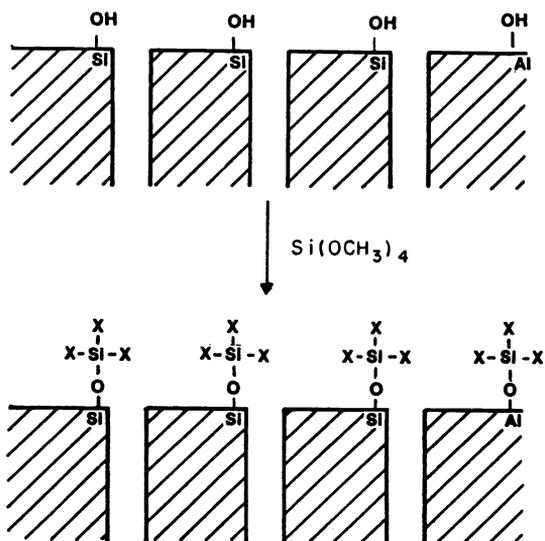
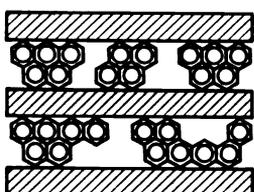


Fig. 6 Coke formation in zeolites (Ref. 35)

Fig. 7 Pore entrance modification
(Ref. 45, 46)

APPLICATIONS

Most commercial applications of shape selectivity either (1) crack undesirable molecules to smaller fragments which are easily removed by distillation, or (2) avoid undesirable competing reactions.

Distillate and lube dewaxing processes

Distillate and lube oil dewaxing processes are based on the first principle. High MW normal paraffins have poor solubility in other hydrocarbons. This leads to cloud point problems at low storage temperatures which decreases the quality of most stocks. Selective removal of the normal (and some slightly branched) paraffins improves low-temperature characteristics such as cloud point, pour point, and cold flow plugging point of gas oils and lube oil stocks.

Traditionally normal paraffins were removed by solvent dewaxing. Solvent dewaxing is an expensive process. Catalytic processes are usually more economical. However, cracking catalysts available before the advent of shape selective catalysis cracked branched hydrocarbons faster than normal ones, and therefore could not improve quality. Shape selective catalysts can remove the normal paraffins without appreciable loss of other components.

Dewaxing processes remove waxy paraffins from intermediate and heavy gas oils (diesel fuel and heating oils) and lube oil base stocks by converting them to gasoline and LPG fractions. Mobil Oil Corporation's distillate and lube oil dewaxing processes use H-ZSM-5 catalyst. Some of the catalysts may contain a hydrogenation component such as nickel, zinc, and/or palladium (ref. 47-53). The catalyst in the similar British Petroleum Process is mordenite, and it probably contains platinum (ref. 54,55).

Fig. 8 shows the flowsheet of the Mobil Distillate Dewaxing process (MDDW). There are nine MDDW plants in operation today. The first plant, a 6500 barrel per day reactor went onstream in Bertinico, Italy in August 1978 (ref. 51). MDDW is a fixed bed process. Operating conditions are 260-430°C and 20-55 atm. The reaction may be performed in the presence of hydrogen. The severity of the reaction is controlled by temperature. The process decreases the pour point of the product by ~ 30-40°C. The byproduct gasoline has a relatively high octane number and therefore it may be added to the gasoline pool without further reforming.

Lube oil stocks range from C₁₈ to C₃₈ hydrocarbons. Catalytic lube dewaxing can process practically all lubricating stocks ranging from light neutral oils to bright stocks. Practically all the normal paraffins and some of the slightly branched ones have to be removed to reach pour point specifications.

In lube oil dewaxing a hydrofinishing reactor follows the dewaxing unit (Fig. 9).

Advantages of catalytic lube dewaxing over solvent dewaxing are lower capital and operating costs and better yield. A possible disadvantage is the loss of wax (mostly to C₃-C₄ paraffins). Catalytic dewaxing yields a higher viscosity, lower viscosity-index product than solvent dewaxing. If there is a sufficient demand for wax, solvent dewaxing may be combined with catalytic dewaxing.

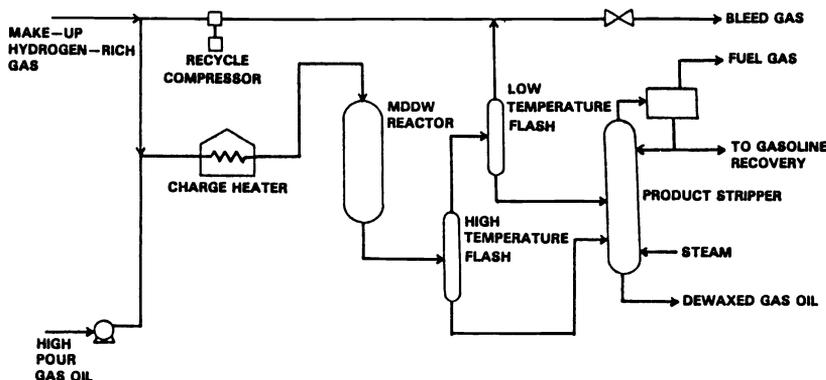


Fig. 8 Distillate dewaxing (Ref. 59)

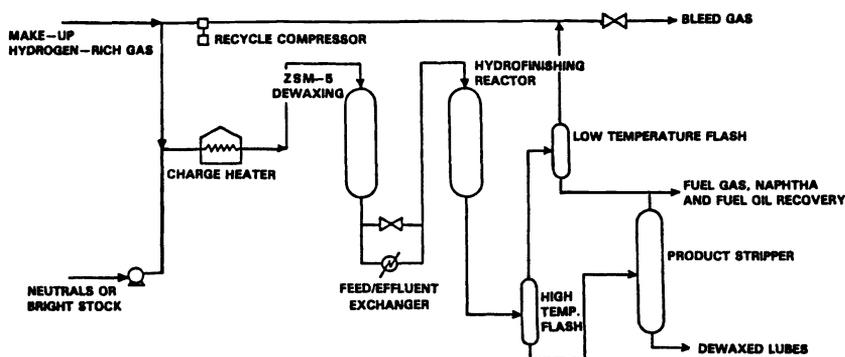


Fig. 9 Lube oil dewaxing (Ref. 59)

Partial solvent dewaxing may be followed here by a catalytic dewaxing unit. The partial solvent dewaxing is significantly less expensive than complete dewaxing because it can operate above 0°C, and because filtering conditions are less severe.

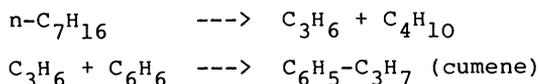
There are four lube dewaxing plants, all installed by Mobil Oil Corporation.

Selectoforming and M-forming

Other processes which convert undesirable low-octane normal paraffins to gaseous products are Mobil Oil Corporation's Selectoforming (ref. 56,57) and M-Forming (ref. 58). Selectoforming was introduced in the mid-sixties. The catalyst is erionite. It cracks only n-paraffins. The product is mostly propane. A hydrogenation component prevents catalyst deactivation by inhibiting coking.

Selectoforming is operated in combination with reforming. The catalyst could be placed in the bottom of the last reforming reactor or in a separate reactor.

M-Forming is more sophisticated and complex than Selectoforming. The olefins produced from the cracking of the low octane normal paraffinic gasoline components are made to alkylate the benzene and toluene present in the gasoline in situ to alkylbenzenes.



M-Forming offers three advantages: (1) a higher octane gasoline, (2) a low-benzene, and therefore environmentally more acceptable product, and (3) high gasoline yield.

M-Forming, developed by Mobil Oil Corporation, uses a ZSM-5 based catalyst (ref. 58). The process may be operated with or without hydrogen. However, it is probably best to integrate it with reforming. When high-octane product is required M-Forming is more advantageous than high severity reforming because it gives higher yields. A large M-Forming plant has been used for two years in Germany.

Reactions which would give undesirable isomers and/or high molecular weight byproducts and coke are avoided or diminished by shape selective catalysis in the following processes.

Ethylbenzene production

Ethylbenzene is the source material for styrene which in turn is polymerized to polystyrene and styrene copolymers. It is produced by alkylating benzene with ethylene. Earlier processes used Friedel-Crafts catalysts such as $AlCl_3$ in a vapor-liquid phase operation. The Badger-Mobil ethylbenzene process uses ZSM-5 catalyst in a vapor phase operation (ref. 53).

Advantages of the Badger-Mobil process are that (1) it can use either dilute or concentrated ethylene streams, (2) it is non-polluting while the earlier, $AlCl_3$ based processes were hampered by spent catalyst disposal problems, (3) its catalyst is non-corrosive (4) and regenerable, (5) it recovers most of the exothermic reaction heat, and (6) its capital and operating costs are much less (ref. 59-61). Reaction conditions are a benzene/ethylene mole ratio between 6 and 7, ~20 atm, 400°C, and a benzene WHSV between 300 and 400. Below 400°C appreciable di- and triethylbenzenes are made. Toluene and xylenes are formed above 400°C. These byproducts reduce yields and increase costs because their removal increases distillation requirements.

About six plants use the Badger-Mobil process today, producing about one-fourth of the World's ethylbenzene requirement.

***p*-ethyltoluene**

para-Methylstyrene, another useful monomer may be produced from 1-methyl-4-ethylbenzene ("*para*-ethyltoluene") by dehydrogenation. The 1-methyl-4-ethylbenzene process is similar to the ethylbenzene process discussed above. The catalyst is phosphorous-doped ZSM-5. 1-Methyl-4-ethylbenzene may be made from toluene and ethylene (ref. 59,62,63). Note that whereas the benzene produces only one isomer (i.e., ethylbenzene), three isomers may be made from toluene (i.e., *ortho*-, *meta*-, and *para*-ethyltoluenes). Shape selectivity helps here. The desired *para*-ethyltoluene is formed preferentially because it has higher diffusivity than the other two isomers.

Xylene isomerization

The xylene isomerization process converts *meta*- and *ortho*-xylenes to *para*-xylene. *para*-Xylene is more valuable than the other two isomers because it is the intermediate for terephthalic acid, the monomer of many polyesters. In some cases the *ortho*-xylene is also recovered and sold.

Two types of catalysts have been used in the past: dual-functioning catalysts which operated under mild hydrogenating conditions (e.g., the platinum-containing Octafining catalyst), and various monofunctional acid catalysts (e.g., silica-alumina). ZSM-5, or modified ZSM-5 catalysts are better than these because (1) they produce much less trialkylbenzenes (Table 8) (ref. 63), and therefore xylene yields are better, (2) they make less coke and therefore the catalyst can operate much longer between regenerations, and (3) they can convert ethylbenzene to easily removable products (ref. 23).

Table 8. Xylene isomerization versus transalkylation at 316°C (ref. 63).

Zeolite	HY	Mordenite	ZSM-5
Isomerization/Transalkylation rate ratio	20	71	1000

Trialkylbenzene formation and coking are inhibited in ZSM-5 because there is not enough space for the large, bimolecular transition states of these reactions ("restricted transition state selectivity").

Xylene isomerization feedstocks usually contain more than 10 % ethylbenzene. If not removed, ethylbenzene will accumulate to undesirable high levels. ZSM-5 helps to remove ethylbenzene. In one version of the xylene isomerization process ethylbenzene is converted to dialkylbenzenes and benzene which may be easily removed by distillation. In another version ethylbenzene dealkylates to benzene and ethylene. This dealkylation is reversible. The backward reaction is inhibited by hydrogenating the ethylene to ethane. The catalyst therefore contains a hydrogenation component (probably platinum) and the reaction is conducted under moderate hydrogen pressure. The hydrogenation of ethylene makes dealkylation irreversible.

Reaction conditions are 300-400°C, and near atmospheric pressure. Process steps are (1) isomerization, (2) *para*-xylene separation, usually by crystallization, and (3) recycle of the unconverted xylenes.

Four versions of the process are licensed by Mobil Oil Corporation: the vapor phase, liquid phase, high temperature, and high severity processes. Combined, in 13 operating plants they account for more than 50 % of the Free World's *para*-xylene production.

Toluene disproportionation

Toluene disproportionation (i.e., transalkylation) is the conversion of two moles of toluene to one mole each of xylene and benzene (ref. 19,20,59,64). The economic incentive is obvious: xylenes and benzene are more expensive than toluene. The catalyst is ZSM-5. Shape selectivity here helps to minimize coking and the formation of higher molecular weight hydrocarbons.

There are two operating plants today. The first went onstream in 1975 in Naples, Italy (ref. 52).

Toluene alkylation

In this process toluene is alkylated with methanol. Whereas over ordinary acid catalysts the three xylene isomers are produced at or near equilibrium concentration, over ZSM-5, or especially over ZSM-5 doped with magnesium, phosphorous, or other compounds, para-xylene is made preferentially (ref. 17,65). Although the three isomers may be made at equilibrium concentrations inside the pores, para-xylene can diffuse out about 10,000 times faster than the other two xylene isomers (Fig. 10) (ref. 17,23,65).

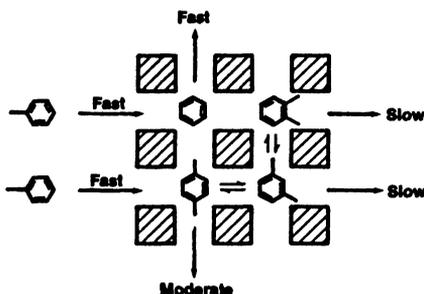


Fig. 10 Selective para-xylene formation in toluene disproportionation (Ref. 17, 19)

TABLE 9. Catalyst deactivation in the Methanol to Gasoline process (ref. 63).

Catalyst	ZSM-5	Montmorillonite	
Time on Stream, Hours	5000	0.1	1.5
Conversion to C ₄ ⁺ Hydrocarbons, %	80	<70	< 8
Coke, % of CH ₂	<0.02	?	>30

Methanol to gasoline

This process makes gasoline from methanol. Since methanol can be made from practically any organic material, the process can make synthetic gasoline from coal, natural gas, petroleum residues, agricultural wastes, municipal garbage, wood, etc. Thus, the Methanol to Gasoline (MTG) process is an alternative to the earlier Fischer-Tropsch and Bergius processes.

Chang reviewed the MTG reaction in depth (ref. 66).

Methanol may be converted to liquid hydrocarbons over most acid catalysts. However, with the exception of ZSM-5 and some other medium- or small-pore zeolites (e.g., Zeolite T, ref. 67) most catalysts deactivate rapidly (Table 9).

Advantages of ZSM-5 catalyst are that it forms much less coke than the other catalysts, and that it does not make pentamethylbenzene and hexamethylbenzene whereas most other catalysts do.

The MTG process converts methanol to 44% hydrocarbons and 56% water. Product hydrocarbons over ZSM-5 include paraffins (60-67%), olefins (6-8%), and aromatics (27-32%). An additional advantage of ZSM-5 over most other catalysts is that the product hydrocarbons are in the gasoline range (i.e., up to C₁₀). Non-shape-selective catalysts produce considerable amounts of hexamethylbenzene and other high molecular weight hydrocarbons.

Over ZSM-5 the predominant C₉ and C₁₀ isomers are 1,2,4-trimethylbenzene and 1,2,4,5-tetramethylbenzene (durene), respectively. Note that these isomers have smaller cross sections than the other tri- or tetramethylbenzene isomers.

The reaction involves many consecutive steps. Methanol is converted first to dimethylether. This step is very much faster than the following ones. The exact nature of the next step, i.e., the creation of a covalent bond between two C₁ units to a C₂ species is still unresolved (ref. 66). The species involved in this step is probably a cationic C₁ fragment, and the product is most likely ethylene (ref. 68-71), or possibly propylene. This initial olefin

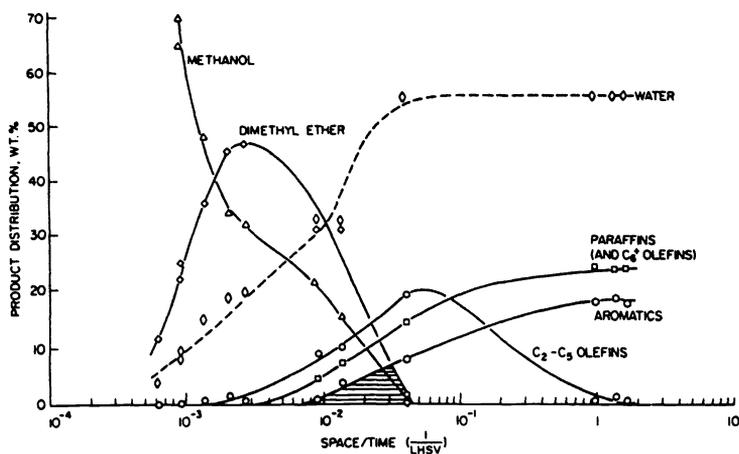


Fig. 11 Reaction path for methanol conversion to hydrocarbons over HZSM-5 at 371°C (Ref. 66, 72) (courtesy Marcel Dekker, Inc.)

is further transformed to longer aliphatics which later cyclize, dehydrogenate to aromatics, get alkylated by methanol or shorter olefinic intermediates, etc. (Fig. 11). In ZSM-5 these reactions stop at durene because there is no space to form larger polyalkylaromatics.

The composition of the MTG gasoline is very similar to that of other high octane reformat gasolines. It has 93-96.8 (unleaded) research octane rating, and it does not contain any nitrogen and sulfur. The only quality-related problem with MTG gasoline is the formation of durene. Although durene has a high octane number, it solidifies at 80°C and blocks the carburetor. Durene formation can be minimized by controlling process conditions.

The Maui field of New Zealand has an estimated capacity of 5500 petajoules of gas and 780 petajoules of condensate. The New Zealand government has a 30 year contract for natural gas from the Maui field to be used in power plants. New Zealand's power demand is less than that. According to the contract, however, the gas had to be paid for by the New Zealand Government whether used or not.

A thorough economic analysis suggested the conversion of the excess natural gas to gasoline by Mobil Oil Corporation's MTG process (ref. 73,74). Alternative options explored were the production and sale or export of compressed natural gas or LNG, the manufacture of methanol to be used as a fuel additive or base fuel, or the manufacture of synthetic gasoline by the Fischer-Tropsch process.

A fixed-bed plant has been constructed jointly by the government of New Zealand and Mobil Oil Corporation to convert 50-60 petajoules of natural gas per year to gasoline by the MTG process. The plant went on stream in November 1985. It produces about 14,000 barrels of gasoline per day. This satisfies about one-third of New Zealand's gasoline demand (ref. 53). In February, 1986 the plant was running at 105% design capacity.

The MTG reaction is highly exothermic and therefore the reaction is best carried out in two stages. The first reactor converts most of the methanol over an alumina catalyst to dimethylether and water. About 15% of the total reaction heat is evolved in the first stage. This mixture is converted in the second reactor over ZSM-5 to gasoline. Table 10 shows MTG operating conditions (ref. 66).

Table 10. MTG operating conditions (ref. 66).

Reactor	First	Second
Temperature, inlet, °C	316	343
outlet, °C	~399	~454
Inlet pressure, atm	14-24	14-23
Space velocity, h ⁻¹	20	1.5-5

(courtesy Marcel Dekker, Inc.)

The complete plant includes units for gas compression, separation, scrubbing, conversion to methanol via the ICI process, and finally for the conversion of methanol to gasoline in a fixed-bed reactor.

Design data for an improved fluidized bed process have been gathered in a 100 barrels per day pilot plant in Germany between 1982 and 1984. In fixed-bed operation the composition of the product changes as the catalyst is deactivated. Fluid-bed operation is better than fixed-bed operation because the product composition does not change.

Methanol to olefins

The methanol reaction discussed above may be stopped before the C_2-C_4 olefinic intermediates are converted to higher molecular weight paraffins and aromatics. The modified process could make light olefins. The Mobil workers used low acidity ZSM-5 (ref. 75,76). Hölderich and coworkers at BASF used pentasil borosilicate zeolites and pentasil aluminosilicates treated with hydrogen fluoride (ref. 77,78). The borosilicate catalysts are less active than the aluminosilicate ones and convert methanol to propylene. The fluoridated aluminosilicate pentasils convert methanol to ethylene.

The Methanol to Olefins (MTO) process is still in its development stage.

Olefins to gasoline and distillates

Mobil Oil and Development Corporation's Olefins to Gasoline and Distillates (MOGD) process converts light olefins to a whole range of liquid products. The process is flexible: products are either gasoline or jet and diesel fuels or even No. 2 fuel oil. While many processes, such as alkylation or polymerization, can convert C_2-C_4 olefins to gasoline, few will convert them to acceptable jet and diesel fuels. The catalyst is ZSM-5 which selectively oligomerizes the feed olefins to high molecular weight isoolefins. Coking would rapidly deactivate amorphous oxides and non-shape-selective other zeolites. In ZSM-5 shape selectivity assures the absence of coking.

MOGD yields approximately 100% high quality (~92 research octane) gasoline in its "gasoline mode", and between 80 and 90% jet and diesel fuels plus 10-20% gasoline in the "distillate mode" (ref. 79). The "distillate mode" is achieved by recycling the gasoline.

The process can use olefins from practically any source from ethylene up to about 200°C end point olefinic streams. Ethylene, however, is less reactive than the higher olefins (ref. 79,80).

Chen and Yen have reviewed the chemistry of converting olefins and other compounds (including some very high molecular weight vegetable oils!) to aromatics and paraffins over ZSM-5 (ref.81).

An interesting possible MTO application is its combination with MOGD. The combined process can be an alternative to the MTG process (Fig. 12.) Both routes could use methanol from coal, natural gas, agricultural or municipal waste, or other sources. Neither route produces undesirable byproducts. Both routes make high quality, sulfur- and nitrogen-free products. The MTO+MOGD combination is flexible: it can make either gasoline or jet and diesel fuels. MTG makes only gasoline. A 14,000 barrel per day MTG plant is in operation; the MTO+MOGD combination is still in the development stage.

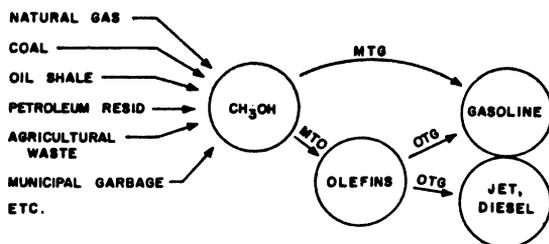


Fig. 12 Gasoline and distillate production options through methanol from various sources

Dehydrocyclodimerization

Dehydrocyclodimerization is the conversion of light (C_3 - C_5) paraffins or olefins to aromatics (ref. 82). The reaction may proceed over many different catalysts. ZSM-5, however, is much more stable than the other catalysts because it forms much less coke. Another advantage of ZSM-5 is that it does not form polycyclic aromatics while most other catalysts do. The Cyclar process of British Petroleum uses ZSM-5 (ref. 83), or ZSM-5 modified with gallium (ref. 84-86). In the Cyclar process propane, butanes, pentanes, and even ethane are converted to aromatics continuously in a series of stacked reactors. Deactivated catalyst is transferred to the regeneration section where its activity is restored.

A feed containing only butane yields an aromatic product containing about 28 weight per cent benzene, 43 % toluene, 20 % xylenes and ethylbenzene, and about 9 % higher aromatics. Byproducts are hydrogen, methane, ethane, and C_3 - C_5 aliphatics. Olefin-containing feeds yield more aromatics.

CONCLUSIONS

The benefits of shape selective catalysis are:

- * More efficient use of available resources because less low-value byproducts are made,
- * Environmentally more acceptable processes,
- * Elimination of costly separation steps because the reactions are more selective,
- * Increased conversion of alternative feedstocks to liquid fuels.

The principles involved in the various shape selective catalytic processes are:

- Dewaxing : Reactant type shape selectivity, and also product type shape selectivity, because the cracked products contain more normal than iso hydrocarbons.
- Ethylbenzene: Restricted transition state type shape selectivity prevents the formation of polyalkylated products and coke.
- p-Ethyltoluene: Restricted transition state type shape selectivity prevents the formation of polyalkylated products and coke. Product type selectivity prevents the formation of the ortho and meta-isomers.
- Xylene Isom.: Product type selectivity prevents the formation of the ortho and meta-isomers.
- Selectoforming: Reactant type selectivity.
- M-Forming: Reactant type selectivity.
- MTG, MTO, MOGD: Restricted transition state type shape selectivity prevents the formation of coke and high boiling aromatics.

Countless other potential shape selective processes have been described in the patent literature. Many of these are under development. Some of these will be commercialized in the near future. The use of crystalline aluminophosphates and silicoaluminophosphates, pillared clays, and other materials not discussed above will increase. The possibilities are only limited by our imagination.

Shape selectivity will be applied in the syntheses of fine chemicals, pharmaceuticals, monomers for polymers, etc. Low-aluminum, hydrophobic materials will have a special role here. The preparation of biologically active materials is another area in which shape selective catalysis could play an important role in the future. This should not surprise us: life on Earth may have originated in shape selective clay catalysts!

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