

# ZEOLITES IN INDUSTRIAL CATALYSIS

By

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## A) Unifying Principles in Zeolite Catalysis

### 1. Introduction

The "zeolitic surface" within zeolite crystals is different from ordinary crystal surfaces. It is a real surface in a physical sense because adsorbed molecules are in direct contact with it. However, it is also part of a crystal fully surrounded by the crystal lattice. Consequently, both the "surface" atoms and the molecules adsorbed within the zeolite crystal are subject to the zeolite crystal field. Indeed, the zeolitic surface has properties of both the ordinary crystal surface and the crystal lattice. Accordingly, a substantial part of zeolite chemistry resembles phenomena found in the solid state. To emphasize the influence of the zeolite crystal lattice upon the "zeolitic surface" it has been suggested that zeolites are strong solid electrolytes.

In this discussion we shall attempt to relate the unusual chemistry of zeolites with their unusual catalytic behavior based on some unifying physical principles which control both phenomena. It is proposed that the strong polar environment of the zeolitic surface caused by both the zeolite cations and the crystal field of the surrounding anionic crystal lattice results in a strong polarizing interaction between the zeolite crystal and adsorbed molecules. The results of this electrolytic behavior are: 1. the stabilization of ionic species with the resulting ionizing influence upon adsorbed molecules and reaction intermediates, and 2. an unusually high concentration of the reactants in the zeolite crystal with a resulting enhancement of the rates of bimolecular reaction steps over unimolecular reaction steps.

### 2. Fundamentals

The principle features of zeolite catalysts are their molecular sieve property and their outstanding activity as acidic catalysts. The molecular sieve selectivity for size and shape of the reactant molecule results from the size and shape of the pores and cavities within the zeolite crystal. However, some question about the selectivity of the molecular sieve effect still remains in the cracking of large molecules such as occurs in the cracking of heavy feedstocks: the zeolite catalyst efficiently cracks mole-

cules both smaller and larger than the crystal aperture. Here the precise nature of the zeolite crystal surface as well as a more detailed knowledge about the kinetics of the cracking process for both small and large molecules will be necessary to define the limitations of shape selectivity.

The acidic character of zeolites containing OH groups attached to framework cations (Si, Al) has been characterized by numerous investigators. There is good agreement that these OH groups are very polar and possess strong proton donating ability. There are indications suggesting that the nature of the zeolite (Si/Al ratio and structure) has strong influence upon OH groups acidity. It has been suggested that the influence of the zeolite framework and overall structure is related to the crystal field of the crystal lattice [1, 2].

What physical principle is responsible for the unusually high acidity, exceeding that of all other known oxides? The search for such a principle is greatly facilitated by the large body of surface chemistry and catalytic properties reported for zeolites. With this information in hand, it is of interest to look for unifying principles which are consistent with catalytic as well as chemical behavior.

Since the intracrystalline zeolitic surface is surrounded by the crystal lattice, it seems reasonable to infer that the special behavior of zeolites is inherent in the zeolite structure itself. Among the various potential causes for the special behavior, it seems reasonable to examine whether the chemical and catalytic behavior of zeolites is mainly influenced by thermodynamics, namely by the tendency to minimize crystal lattice energy. Of course, here one must consider not only the crystal lattice but the occluded molecules, the reactants, as well.

Unfortunately, the lattice energies of zeolite crystals are not known. Their calculation with any degree of reliability is impossible without knowing the covalent and ionic character of the linkages between lattice atoms. Several observations, especially the preference of zeolite cations for water over framework oxygen indicate that the bond between framework cations and oxygen is strongly covalent. Nevertheless, a certain amount of ionic character must exist, and a corresponding crystal field must pervade the whole porous crystal. Adsorbed molecules, especially the polar or strongly polarizable ones, will be polarized by the zeolite and they will exert a similar effect on the zeolite crystal as well. The overall interaction between zeolite and adsorbate must tend to minimize the free energy of the zeolite-adsorbate system, and therefore, the simplest way to forecast thermodynamically favored reactions in zeolites is just to evaluate their effect on the energy of the zeolite lattice.

Inspection of the ionic lattice energy equation shows that with regular ionic crystals the lattice energy is enhanced by placing more ion pairs and ions of higher valence within the same crystal volume. According to this simple principle the *occlusion of added ionic matter* into the porous zeolite lattice *should generally lower the lattice energy and increase the thermodynamic stability of the overall system*. Of course, the occluded ionic matter may affect the zeolite structure and symmetry, ultimately affecting the Madelung constant or other parameters and thus rendering the interaction between zeolite and occluded ionic matter complicated and difficult to analyze. In spite of these limitations, the study of interactions between zeolites and occluded ionic matter is a convenient technique to assess the role of the zeolite lattice upon zeolite chemistry and catalysis, and generally as a solid electrolyte.

In order to evaluate this concept we shall review in the next two sections some relevant data in zeolite chemistry and catalysis.

### 3. Chemical Properties of Zeolites

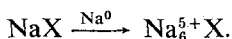
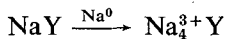
It was suggested in the previous section that the porous zeolite lattice must have high affinity for occluded ionic matter. This ionic matter may consist of regular ionic compounds such as salts, or it may consist of atoms or molecules which are not ionic outside the zeolite but which become ionized only upon occlusion into the zeolite crystal. There are many examples of both types of occlusion.

a) *The occlusion of salts* has been described in several publications [1]. The experimental evidence on zeolites A, X and Y clearly shows that ionic compounds such as salts readily penetrate the zeolite crystal, filling up the available space in the large cavities. Salts, especially salts of univalent anions, can even penetrate the sodalite cages in zeolites A and Y. This is surprising because the  $O_6$ -ring port of the sodalite cage is only about  $\sim 2.4 \text{ \AA}$  wide, much smaller than any anion. It was found that the occlusion of salts into sodalite cages requires high temperatures, presumably to provide the high activation energy needed for enlarging the  $O_6$ -ring port, probably by the temporary cleavage of O—Al or O—Si bonds. Interestingly, halide salts as well as salts of large complex anions such as  $\text{ClO}_3^-$  and  $\text{NO}_3^-$  can be occluded in the sodalite cage.

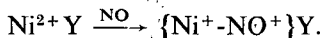
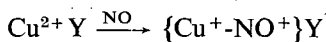
From the point of view of our discussion on fundamentals the most important aspect of salt occlusion is the stability of the zeolite-salt occlusion compound. It was reported that in every salt occlusion experiment both Y zeolite and the occluded salt were greatly stabilized, well beyond the decomposition temperatures of the zeolite and of guest salts. It was also found that the guest salt can not be removed from the host Y crystal even by steaming at  $700^\circ\text{C}$  [2]. Thus, the zeolite lattice is stabilized by the occluded salt and vice versa. Consequently, the salt occlusion phenomena are consistent with the principal discussed earlier.

b) *Ionization of occluded atoms and molecules.* The most frequently observed ionization phenomenon in zeolites is the ionization of water through cation hydrolysis. This is a particularly important reaction for zeolite catalysts because it generates acidic OH groups attached to framework cations which are directly responsible for the acid behavior of multivalent cation zeolites. While the hydrolysis has been well demonstrated by X-ray and IR spectroscopy as well as other techniques, no specific data are available which can be used for quantitative evaluation of the contribution of the zeolite lattice to cation hydrolysis.

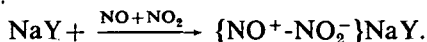
The most revealing information on ionization effects in the zeolite lattice comes from the occlusion of alkali metals and certain gas molecules. It was reported that alkali metals readily reduce both alkali X and alkali Y zeolites [1] and the sodium ions of the host crystal capture the electron from the occluded alkali atoms forming symmetrical  $\text{Na}_4^{3+}$  or  $\text{Na}_6^{5+}$  centers



It was also reported that certain transition metal zeolites readily ionize adsorbed NO radicals forming electron transfer complexes with the zeolite cation [1].



Another interesting ionization phenomenon is observed on the simultaneous interaction of both NO and NO<sub>2</sub> radicals in zeolites. Here, both radicals become ionized, presumably forming a salt-like complex in the zeolite [1].



From the point of view of our discussion *the most* important aspect of these redox reactions is that they are all highly endothermic in the gas phase without the stabilizing effect of the zeolite. For example, the formation of the NO<sup>+</sup> and NO<sub>2</sub><sup>-</sup> species from NO and NO<sub>2</sub> radicals is endothermic by about 5.5 eV (~126 kcal/mol), not considering coulombic interaction between the products. In spite of this, this reaction readily occurs on NaY at moderate temperatures. In the case of interaction between sodium metal and NaY zeolite the highly endothermic ionization of sodium metal (I. P. = 5.14 eV ~ 118 kcal/mol) is readily accomplished at 300 °C, with a Na<sub>4</sub><sup>3+</sup> center formed in each large cage.

These examples demonstrate the high affinity of zeolites for ionic matter, and they also provide semi-quantitative information on the size of the contribution of zeolites to the ionization of occluded species. It should be noted that in the cases described above the ionization processes readily occurred on Na-zeolite or cation exchanged zeolites, and thus, the ionization phenomena did not require the presence of acidic OH groups.

#### 4. Catalytic behavior

In the context of the large chemical effects of zeolites upon occluded molecules as shown in the previous section, it is relevant to examine to what extent these effects are operative in catalysis. Since most of the chemistry discussed here was carried out on alkali-cation zeolites we shall first review the reactions of hydrocarbons over such zeolites.

a) *The influence of alkali zeolites (K-Y)* on the cracking of hydrocarbons was investigated [3] with hexanes as reactants. For all the hexanes the zeolite gave conversion levels 2 to 5 times as high as in the empty tube. The product composition obtained from *n*-hexane and its isomers over K-Y was markedly different both from that typical of acidic zeolites and that obtained at the same reaction conditions in an empty reactor (Table I).

An analysis of the reaction mechanism based on product distributions obtained from all the hexane isomers showed that the thermal, free radical mechanism still occurred but with specific changes in the relative rates of the chain steps. The K-Y does not change the selectivity of alkyl radicals either in the choice between competitive β-scission steps or among competitive H atom abstraction steps when positionally different choices are available. In contrast, the K-Y has a very large effect upon the ratio of rates of H atom abstraction to β-scission. Mechanistic analysis of the cracked products obtained from the hexane isomers shows that over K-Y the ratio  $\frac{\text{rate of H-abstraction}}{\text{rate of } \beta\text{-scission}}$  is increased for alkyl free radicals by a factor of 6 to 9. This effect accounts for the large difference in product distribution between the non-catalysed and the K-Y "catalysed" reactions [3].

Table I

Products from pyrolysis and KY-catalyzed<sup>a</sup> cracking at 500°  
(mol/100 mol converted)

	n-hexane		2-methylpentane		3-methylpentane	
	thermal	KY	thermal	KY	thermal	KY
Hydrogen	2.8	3.1	24.4	4.3	5.6	3.9
Methane	50.3	23.5	27.9	21.7	63.5	57.3
Ethylene	56.5	26.0	11.5	6.5	23.7	23.0
Ethane	37.7	37.4	42.2	43.5	44.2	44.3
Propylene	55.7	58.5	57.8	44.2	20.5	15.7
Propane	10.7	38.2	19.2	36.4	—	0.5
1-butene	31.3	12.0	—	—	7.6	11.2
2-butene	—	19.6	—	—	34.2	34.8
Isobutene	—	—	40.5	40.1	—	—
Isobutane	—	—	0.2	1.6	—	—
1-pentene	7.3	1.9	1.0	2.3	—	<i>b</i>
2-pentene	—	4.7	8.5	8.4	13.3	6.4
2-methyl-1-butene	—	—	—	—	20.9	<i>b</i>
3-methyl-1-butene	—	—	4.5	1.6	—	1.0
2-methyl-2-butene	—	—	—	1.7	—	19.5

*a* = rate enhancements ~ 5-fold

Speculating over the reason why zeolites enhanced the rate of H-abstraction over  $\beta$ -scission, it was considered that H-abstraction is a bimolecular process step whose rate is strongly influenced by the concentration of the reacting substrate whereas  $\beta$ -scission, being a unimolecular process, is unaffected by changes in reactant concentration. Accordingly, the effect of K-Y could be largely a matter of increasing the reactant concentration within the zeolite cavities relative to the surrounding gas phase [4].

The concentration, or adsorption, of hydrocarbons within the zeolite crystals is, of course, well documented in adsorption studies carried out at low temperatures. For the temperature range used in the hexane cracking study the hexane loading on K-Y at 500°C was estimated from the reported Arrhenius plot of loading on NaX at temperatures up to 300°C. The estimated hexane loading at 500°C is substantial and is consistent with the reactant concentration suggested by the mechanistic analysis [4]. Thus, it is concluded that zeolites concentrate hydrocarbon reactants to a large extent within the zeolite crystal, and that this concentration effect is responsible for a substantial shift in product formation, specifically by enhancing the rate of bimolecular reaction steps.

From the total absence of hexane skeletal isomerization during these cracking experiments over K-Y, the absence of ionic (carbenium ion) cracking intermediates can be inferred. Hence, OH group free K-Y is not capable of ionizing either hexane or the radicals formed upon its fragmentation. One has to recognize, however, that these ionization processes in the gas phase require very high energy. Thus, ionization of a *tert.*-C—H bond to form a *tert.* carbenium ion and hydride ion is endothermic by 240—250 kcal/mol while the ionization potential of a *tert.* radical is ~ 170 kcal/mol.

b) *Hydrocarbon cracking over H-zeolites* shows markedly different behavior from that obtained over alkali cation zeolites. Activity is further increased, skeletal

isomerization becomes dominant, and the product distribution is generally consistent with what occurring with other strong Brønsted acid catalysts, (Table II) for which a carbenium ion rather than free radical mechanism is generally accepted.

Catalysis with H zeolites does, however, show certain special, new features not found with other acid catalysts. Zeolites show greater selectivity to gasoline than

Table II

*Products from cracking n-hexane*

Catalyst — 93% exchanged NH<sub>4</sub>Y activated at 550°

Cracking temperature — 350°

Conversion — 11% isomerization  
7% cracking

*Isomerized products, mole %*

2-methylpentane	49.5
3-methylpentane	34.9
2,3-dimethylbutane	12.3
2,2-dimethylbutane	3.3

*Cracked products, mole %*

Methane	<0.1
Ethane	} 0.8
Ethylene	
Propane	28.7
Propylene	0.7
iso-butane	31.8
n-butane	11.4
Butenes	<0.2
iso-pentane	25.1
n-pentane	5.5
Pentenes	<0.2
Benzene	0.4
Toluene	2.0
Xylenes	1.6
C <sub>6</sub> H <sub>5</sub> C <sub>3</sub> H <sub>7</sub>	1.1

Tung and McInich (Continental oil)

does silica-alumina when cracking gas oil. Different gasoline compositions are also obtained on cracking gas oil over H-Y and amorphous silica-alumina (Table III). Mechanistic suggestions by WEISZ [6] regarding these inter-related differences in gasoline yield and composition have been made to the effect that there is a more efficient hydrogen redistribution between hydrocarbon molecules over the zeolite

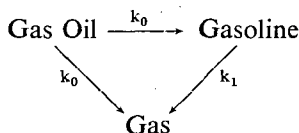
Table III

*Gasoline Composition as a Function of Catalyst\**

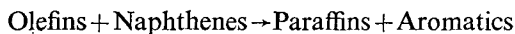
Catalyst	Composition (%)			
	P(araffin)	O(lefin)	N(aphthene)	A(romatic)
Silica-alumina	13	17	41	29
Zeolite	23	5	23	49
Difference	+10	-12	-18	+20

\* Data from Ref. [6]

catalyst as shown below. According to the gasoline selectivity model of WEEKMAN and NACE [5] the primary cracking ( $k_0$ ) produces gasoline and gas whereas while the secondary cracking ( $k_1$ ) produces only gas and thus lowers gasoline yield. The differences in product



distribution between zeolite and silica-alumina (Table III) can be quantitatively explained by the greater occurrence of the following overall hydrogen redistribution reaction in the zeolite:



WEISZ, therefore, suggested [6] that this reaction effectively reduces  $k_1$  in the gas oil cracking model by converting the initially produced olefins and naphthenes to more refractory paraffins and aromatics before they crack further to gas. The high efficiency of the conversion of olefins + naphthenes to paraffins and aromatics may be explained by the superior hydrogen redistribution *via* hydride ion shift between carbenium ions and neutral hydrocarbons over the zeolite catalyst.

Although distinctly different mechanisms are thus involved over K-Y and H-Y, the following parallelism can be drawn. During the free-radical mechanism, enhanced hydrogen atom abstraction compared with  $\beta$ -scission alters the product distribution over K-Y from that observed thermally. During the carbenium ion mechanism, enhanced hydride ion abstraction compared with  $\beta$ -scission alters the product distribution over H-Y from that observed over silica-alumina. *The common feature of both H-Y and K-Y is then that they favor bimolecular reaction (hydrogen transfer) steps over the unimolecular reaction (fragmentation) steps. This tendency in both cases may be interpreted on the same basis: zeolites concentrate hydrocarbon reactants to a larger extent than other catalysts.* This mechanistic conclusion is confirmed by adsorption measurements showing that toluene is desorbed at a significantly higher temperature from H-Y than from amorphous silica-alumina [7].

### 5. Conclusion

The unusual chemical environment of the zeolitic surface and especially the crystal field of the surrounding crystal lattice render it a strong solid electrolyte. Zeolites interact strongly with polar and polarizable atoms and molecules resulting in unusually strong adsorption, or even ionization of adsorbed species.

The adsorption properties of zeolites well demonstrate the strong electrostatic interaction between zeolites and occluded molecules. The redox chemistry of zeolites testifies that the interaction often goes beyond physical interaction and even to the extent of ionization of the adsorbed molecules. Reactions resulting in the ionization of adsorbed molecules which would otherwise be endothermic by as much as

$\sim 126$  kcal/mol in the gas phase readily proceed at moderate temperatures because of the "solvation" effect of the zeolite on the ionic products.

Mechanistic studies show that ionization of hexanes or their reaction intermediates does not occur on *alkali zeolites*, and that the cracking of hydrocarbons proceeds by a radical mechanism. It is worth noting that the ionization energy of hexanes and their radical fragments is  $\cong 170$  kcal/mol, significantly higher than the free energy change of redox reactions readily occurring in zeolites. The radical mechanism over alkali zeolites shows distinct differences in product distribution from the non-catalyzed thermal process. These differences are explained on the basis that zeolites concentrate the reactants in the zeolite, resulting in a strong enhancement of bimolecular reaction steps over unimolecular reaction steps. Thus, zeolites generate a substantially higher reactant concentration relative to the gas phase outside the zeolite crystal.

In the cracking of hydrocarbons over H-Y zeolite, an unusually strong Brønsted acid activity is observed. The product distribution indicates great enhancement of H redistribution, presumably through hydride ion shifts. Here again, as with K-Y, bimolecular reaction steps (H redistribution) are favored over unimolecular reaction steps (fragmentation). The cause of this phenomenon is that zeolites concentrate the reactants in the zeolite pore-and-cavity system. Enhanced concentration of reactants on catalyst surfaces is, of course, characteristic of any heterogeneous catalyst. However, from the mechanistic evidence reviewed here it appears that this concentration effect is greater with zeolites than with other, amorphous acidic catalysts. In respect to the strong acidity of H-zeolites the acidic nature of structural OH groups has been well established by IR spectroscopy and other techniques. In addition to their OH acidity we expect that zeolites exert a strong stabilizing influence on ionic hydrocarbon reaction intermediates (carbenium ions), similar to that shown in their redox reactions with other adsorbed atoms and molecules.

## B) Applications in industrial catalysis

### 1. Established processes employing zeolite catalysts

At present, the large-scale, well-established industrial processes that utilize zeolite-based catalysts are catalytic cracking, certain hydrocracking processes, and paraffin isomerization. It is the purpose of this section to highlight the important aspects of these processes and to provide references to more detailed discussions of them.

a) *Catalytic cracking.* The addition of relatively small amounts of hydrothermally stable acidic zeolites to conventional cracking catalyst formulations has been found to result in significant increases in both the yield and quality of the products from fluidized bed and moving bed cracking reactors [8]. Since catalytic cracking is so extensively practiced in petroleum refining, it is at present the largest-scale industrial process employing zeolite catalysts [9]. A recent estimate indicated that about 22,000 tons of synthetic zeolite, principally zeolite Y but also some zeolite X, is produced annually to satisfy world-wide requirements of 150,000 tons per year of cracking catalysts [9]. In general, the rare-earth exchanged form of the zeolites are used, but some catalysts based on  $\text{NH}_4\text{-Y}$  have been also marketed. At present, all commercial catalysts comprise 5–40% zeolite dispersed in a matrix of synthetic silica-alumina,



semi-synthetic clay-derived gel, or natural clay [10]. It should be noted that such composites can be prepared either by blending a synthetic zeolite with a binder, or by chemical treatments of suitable clays so as to produce the zeolite component *in situ*. There exists no consensus among U. S. refinery operators as to whether one of the types of catalysts is of inherent superiority.

The advantages associated with zeolite-promoted cracking catalysts accrue from high-rates of intermolecular hydrogen transfer coupled with extremely high intrinsic cracking activity [11, 12], (see previous chapter). Data presented by WEISZ *et al.* (Table III) exemplify the effects of hydrogen transfer activity and account for the observations that zeolite catalysts increase yields of light cycle oil, increase the yield and octane of the gasoline product fraction, and decrease the production of coke. The high cracking rates found with zeolite catalysts result in greatly reduced catalyst-oil contact times for given conversion levels, thus leading to further increases in liquid product yields, plus additional advantages such as increased tolerance to poisons, and greater operating flexibility. The relationships between catalyst properties, feedstock composition, and reactor operating conditions are very complex, and have been reviewed recently in several articles that also describe additional benefits of the use of zeolite-promoted cracking catalysts [9, 10].

b) *Hydrocracking for fuels production.* Hydrocracking, catalytic cracking in the presence of hydrogen and a dual function catalyst possessing both cracking and hydrogenation-dehydrogenation activity, is at present the second largest use for zeolite-containing catalysts [13]. In general, such catalysts consist of an acidic, hydrothermally stable, large pore zeolite loaded with a small amount of a noble metal, or admixed with a relatively large amount of an active hydrogenation system such as  $\text{NiO} + \text{MoO}_3$  [14, 15].

While several proprietary hydrocracking technologies are in use, the Unicracking-JHC process, in which zeolite catalysts are used exclusively, exemplifies the value of such catalysts in broadening the range of feedstocks that can be handled and in simplifying hydrocracker design and operation [13, 16, 17].

The most elaborate and versatile Unicracking process scheme is the two-stage configuration shown in Figure 1. Feedstock is mixed with hydrogen and admitted to reactor  $R-1$ , a conventional hydrotreater in which it is substantially freed of nitrogen and sulfur. The product then enters the first stage Unicracker,  $R-2$ , in which it is hydrocracked, typically at a per-pass conversion of 40–70%. It is especially significant that the zeolite catalysts that have been developed for the Unicracking process can operate stably and efficiently in the presence of hydrogen sulfide and ammonia, thus separation of these substances from the  $R-2$  feed is unnecessary.

In single-stage Unicracking, the product of  $R-2$  is treated in liquid-gas separators and fractionated. Additional flexibility in terms of processing refractory feed-

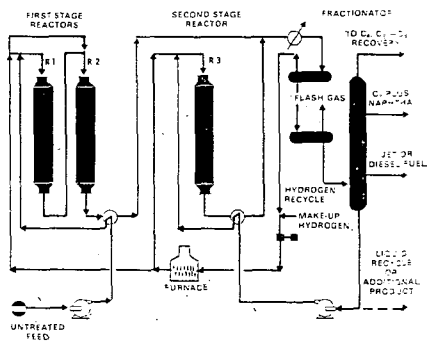


Figure 1  
A Two-Stage Unicracking — JHC Plant

stocks is obtained through the use of the two-stage process that is illustrated, in which the fractionator bottoms are recycled through second-stage reactor  $R-3$ . The recycled gas which is mixed with the  $R-3$  feed is essentially ammonia-free, thus the reactor can be operated efficiently at comparatively low temperatures and pressures while maintaining conversion at 50–80% per pass.

In hydrocracking, as with all multi-purpose refinery processes, the relationships between feedstock properties, catalyst type, operating conditions, and product yield and character, are very complex. A number of detailed reviews of these matters have appeared recently [16–19] but it should be noted in general that zeolite catalyzed hydrocracking can efficiently convert a very wide variety of feedstocks, some of which cannot be processed by other techniques, into a range of fuels including LPG, medium octane unloaded motor gasoline, and jet, diesel, and heating oils, or into feedstocks suitable for catalytic cracking, catalytic reforming, or petrochemical manufacture. It should also be noted that zeolite hydrocracking catalysts are now noted for permitting long (2–6 year) periods of highly efficient reactor operation at moderate conditions, and that following such service, many of the catalysts are susceptible to treatments that completely restore their original levels of activity [20].

In considering new applications for hydrocracking, it has been suggested that the process may be used in the future as a means of preparing catalytic cracker feedstocks from special types of crude oils and residua [18].

c) *Special purpose hydrocracking using shape-selective catalysts.* Two special types of hydrocracking processes in which the shape-selectivity of certain zeolite molecular sieves is exploited are in current use.

The Selectoforming process of the Mobil Corporation employs a metal-loaded zeolite of the offretite-erionite variety to selectively hydrocrack the normal-paraffin components of catalytic reformate [13, 21]. The process thus allows either an increase in reformate octane at a particular operating severity, or an increase in reformate yield at a specified octane. The former is the usual mode of operation, with plant experience indicating a typical gain of 2–5 octane numbers.

A second type of shape-selective hydrocracking process is catalytic dewaxing, which has been commercialized by several companies, and which typically employs as a catalysts a metal-loaded tubular pore zeolite such as mordenite [21]. Using such catalyst, long chain normal paraffins, waxes, can be more-or-less selectively hydrocracked to propane, isobutane, and isopentane. Uses for the processes include upgrading of diesel and heating oils, conversion of low-sulfur, waxy crudes directly to fuel oils, and general improvement of lubricating oils.

d) *Paraffin isomerization.* Other than catalytic cracking and hydrocracking, the only well-established commercial process which employs zeolite catalysts at present is the isomerization of normal paraffins into higher octane, branched isomers. The catalyst for the well known "Hysomer" process of the Shell Oil Company is dual functional, and consists of a highly acidic, large pore zeolite loaded with a small amount of a noble metal hydrogenation component [13, 22].

In considering the "Hysomer" process, it is essential to note that the catalysts possesses the hydrogenation-dehydrogenation and acid functions which characterize hydrocracking catalysts. However, since hydrocracking of the "Hysomer" feedstock, which is usually a light, straight run naphtha containing principally pentanes and hexanes, is not desired because it represents a direct reduction of gasoline yield, the process operating conditions are more stringently defined than those for hydro-

cracking. In general, reaction conditions are adjusted to allow the lowest possible reactor temperature consistent with economical production rates, and the lowest hydrogen pressure consistent with economical run lengths. By doing this, yields of the highest octane highly branched isomers are maximized, and hydrocracking is minimized.

In commercial practice, use of the Hysomer process has been found to produce an increase of about 12 octane numbers (RON clear) in suitable naphtha feedstocks. It is interesting to note, however, that the process can be operated in conjunction with the Union Carbide Corporation's "Isosiv" molecular sieve adsorbent procedure for the separation of normal and iso-paraffins in such a manner that complete isomerization of a  $C_5/C_6$  stream can be achieved. The combined process is tradenamed TIP (Total Isomerization Process), and results in octane number increases of about 20 rather than the 12 found with a once-through "Hysomer" treatment [22].

## 2. Recent developments in zeolite catalysis

In the 1960's, zeolite synthesis systems which included organic cations such as quaternary ammonium species in addition to the traditional alkali metal ions began to receive much attention. Such work continues, and has resulted in the discovery of a number of new families of molecular sieves. One of the groups that was developed at Mobil Corporation laboratories includes the zeolites ZSM-5, -12, and -21, and is characterized by an unusual pore structure, the openings of which are 10-member rings, and highly siliceous frameworks,  $SiO_2/Al_2O_3$  of 20–100 [23–25]. Another group of unusual molecular sieves was recently developed at Union Carbide Corporation laboratories, and includes the large pore silicalite, the first example of a pure silica molecular sieve [26].

The members of the ZSM-5 family of zeolites have been used to prepare some unique catalysts for a variety of processes. In this section, the unusual features of a number of the catalysts will be described.

a) *Xylene Isomerization*. Among the processes for which ZSM-5 based catalysts offer unique advantages, those for the treatment of  $C_8$  aromatics streams for petrochemical use are the closest to becoming firmly established commercially.

The objective of  $C_8$  aromatics processing is the conversion of the usual four component (ethylbenzene and the three xylenes) feedstream into an isomerically pure xylene. Although the bulk of current demand is for the *para* material for polyester fiber manufacture, significant markets for the other isomers also exist [26]. In the execution of such processing, the primary problem is disposing of the 8–40% ethylbenzene that is present in the usually available feedstocks, a task that is complicated by the closeness of the boiling points of ethylbenzene and *p*-xylene. A major secondary facet of the processing is reestablishment of equilibrium concentrations of the xylenes present in the isomer separation train raffinate so as to maximize the yield of the desired isomer [12]. Some schemes which have been devised to achieve these goals include quantitative separation of the ethylbenzene in the feedstock *via* "superfractionation" followed by isomerization and separation of the resulting mixture of xylenes, and use of the Octafining or Isomar processes, vapor-phase hydroisomerization procedures which not only isomerize xylenes, but also convert a portion



of any ethylbenzene present into xylenes, and thus require that only a partial separation of the ethylbenzene in the initial feed be effected.

In what is apparently the most readily adopted  $C_8$  aromatics process based on ZSM-5 and related zeolites, the catalyst is an acid form of the sieve to which is added a group VIII metal hydrogenation-dehydrogenation component [28]. Such catalysts can be used in existing Octafining plants in place of the Pt/silica-alumina ones that were originally developed for the process. Their advantages of higher throughput due to the ability to operate at low  $H_2$ /hydrocarbon ratios, and longer run life between regenerations, can thus be obtained without capital expenditure.

Acidic ZSM-5 type derivatives can be used in other ways to process  $C_8$  aromatics streams, although neither of the techniques can be easily retrofitted to "Octafining" plants. It has been stated, for example, that H-ZSM-5 can, under carefully selected operating conditions, equilibrate the concentrations of xylenes in a four-component  $C_8$  mixture, while causing ethylbenzene to disproportionate about 125 times faster than xylene [29]. Because both benzene and diethylbenzene can be readily separated from the  $C_8$  fraction, with suitable engineering, this liquid-phase selective disproportionation method could be used in processing a mixed  $C_8$  stream, although very little flexibility in operating conditions would be possible.

It has also been stated that under high temperature, vapor-phase conditions using an acid ZSM-5 catalyst in the absence of hydrogen, the xylenes present are merely isomerized to equilibrium whereas the ethylbenzene is partially converted into benzene in such a manner that there is an increase in the number of moles of aromatics present [30]. This unusual reaction could, as in the previous case, form the basis of a  $C_8$  aromatics processing technology.

The mechanism of the conversion of ethylbenzene into benzene as described above is now unknown, but the discoverers speculate that ethylene cracked from the ethylbenzene is "reassembled" into benzene. Another totally unrelated process in which this type of reaction is exploited will be discussed later.

b) *Ethylbenzene Synthesis*. The synthesis of ethylbenzene for styrene production is another process in which ZSM-5 type catalysts are beginning to attract significant amounts of attention. While some ethylbenzene is obtained directly from petroleum, the majority, about 90%, is synthesized. The alkylation of benzene with high purity ethylene is generally accomplished in liquid phase slurry reactors employing promoted  $AlCl_3$  catalysts [31]. The chemical can also be prepared by the vapor phase reaction of benzene with a dilute ethylene-containing feedstock obtained by partial purification of catalytic cracker off gases [32]. The catalyst for this process, which is tradenamed Alkar, is  $BF_3$  supported on alumina.

In slurry-type ethylbenzene processes, catalyst handling including disposal of spent aluminum chloride is troublesome, and in both the slurry and solid-catalyzed processes, the catalysts are quite corrosive and necessitate special feed pretreatments and the use of expensive materials of construction. It is these problems that are alleviated through use of the new zeolite catalyst.

It has been reported that a reactor loaded with an acidic ZSM-5 catalyst has been employed successfully to produce ethylbenzene on a semiworks scale, about  $4 \times 10^7$  lbs./year, using both pure and dilute ethylene sources [33—35]. In both cases, the alkylation was accomplished, somewhat surprisingly, under vapor-phase conditions: about 800°F, 200—300 psig, 300—400 lbs. benzene/lb. cat-hr., and a benzene: ethylene feed ratio of about 30. With both types of ethylene sources, raw material

efficiency in ethylbenzene production exceeded 99%, and heat recovery efficiency was high due to the high temperature at which the reactor was operated. It was noted, however, that the catalyst deactivated moderately rapidly, and required, biweekly oxidative regeneration [34, 35].

c) *The methanol-to-gasoline process.* In a recent paper, [36] workers at Mobil Corporation laboratories described the conversion of methanol and some other oxygenated organic compounds to hydrocarbons using an acidic ZSM-5 catalyst. In the case of methanol, the highly exothermic reaction sequence included the formation of dimethyl ether, and was quite selective in producing an aromatics-rich, gasoline-range mixture of hydrocarbons which was free of oxygenates. It was proposed that the highly charged zeolite framework induced carbene formation, and that these species reacted with each other, methanol or dimethyl ether to form  $C_2-C_5$  olefins, which were subsequently converted to the final product. The hydrocarbon product contained no compounds with more than 10 carbon atoms, and this, in conjunction with the lower than predicted concentrations of certain multiply alkylated benzenes, was construed as evidence of some shape selectivity due to the moderate pore size of the catalyst.

The interesting transformation described above forms the basis of a pilot-scale methanol-to-gasoline plant that has been developed by Mobil Corporation under a contract with the U. S. Department of Energy [37—39]. Because of the highly exothermic nature of the conversion, the reaction sequence is split into two stages to simplify management of the evolved heat. In the first step, the methanol feed is partially dehydrated to a mixture of methanol, water, and dimethyl ether in a catalyst bed of gamma-alumina. The energy evolved is used to heat the feed to the zeolite catalyst bed in which the gasoline formation occurs; this reactor is operated under vapor-phase conditions at a pressure of about 300 psig and a temperature that increases from about 650 °F to 850 °F along its length. The reactor effluent is cooled, the product recovered and light paraffin gases, which are added as a heat sink, recycled. An auxiliary process is the continuous oxidative regeneration of deactivated zeolite catalyst.

The methanol-to-gasoline process, which is an interesting route from coal to motor fuel, is not yet of commercial interest because, although the processing cost is only about 10 ¢/gallon of gasoline produced, the price of coal-derived methanol leads to a gasoline price 40—50 ¢/gallon more than that of the petroleum product. This situation could, of course, and likely will change [40]. In addition, the gasoline produced using the current catalysts contains enough of the high melting compound, durene (1,2,4,5-tetramethylbenzene) to make it unsuitable for use in some climates. It is stated, however, that this problem can be overcome.

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