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MOLECULAR SIEVE ZEOLITE TECHNOLOGY – THE FIRST TWENTY-FIVE YEARS

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ABSTRACT

In twenty-five years molecular sieve zeolites have substantially impacted adsorption and catalytic process technology throughout the chemical process industries; provided timely solutions to energy and environmental problems; and grown to over a hundred million dollar industry worldwide. The evolution in zeolite materials with improved or novel properties has strongly influenced the expansion of their applications, and provided new flexibility in the design of products and processes.

INTRODUCTION

The year 1979 marked the twenty-fifth anniversary of the commercial birth of molecular sieve zeolites as a new class of industrial materials. They were introduced in late 1954 as adsorbents for industrial separations and purifications. Since that time the fascination with and the elegance of, this unique class of materials has generated a mass of scientific literature describing their synthesis, properties, structure and applications, which probably now numbers well over 15,000 scientific contributions and over 10,000 issued patents. The molecular sieve industry has been projected to have grown into an estimated quarter of a billion dollar market [1] serving all of the major segments of the chemical process industries including major applications in the petroleum refining and petrochemical industries, and has generated a myriad of other adsorption, catalytic, and most recently ion exchange applications.

Milton reviewed the beginnings and development of molecular sieve zeolites in 1967 [2]. He traced the early discoveries and synthesis of the new zeolites A, X, and Y, which led to their commercial applications as selective adsorbents and catalysts. It will be the purpose of this paper to review the evolution of molecular sieve materials, their synthesis, properties and applications, over the span of 1954 to 1979, with emphasis on the major milestones and trends in these areas. There will be no attempt here to repeat the in depth coverage of zeolite molecular sieves given by Breck [3] or Barrer [4], or recent up-to-date review articles on the applications of molecular sieve zeolites [5] as adsorbents [6], catalysts [7,8], and ion exchangers [9], and on natural zeolites and their applications [10,11,1,5].

Success of molecular sieve zeolites has been due primarily to the discovery of new materials whose properties have been engineered into improvements in known processes and into the development of new ones. This discussion will therefore emphasize the materials and properties aspects of molecular sieve zeolites as they evolved and developed into various application areas.

THE EVOLUTION IN MATERIALS

The theme in research on molecular sieve zeolite materials over the twenty-five year period has been a quest for new structures and compositions. Because zeolites are unique as crystalline porous materials, with structure as well as composition controlling properties, there arose the strong conviction that novel and useful properties would result from the discovery of new compositions and structures. Let us now trace the web of change in those discoveries over twenty-five years.

"Low-Silica" Zeolites or Aluminum-Rich Zeolites. The discovery of zeolites A and X by Milton [12] at the Union Carbide Corporation Laboratories represented a fortunate optimum in composition, pore volume, and channel structure, guaranteeing these two zeolites their lasting commercial prominence out of more than 150 synthetic species known and discovered over the last twenty-five years. Both zeolites are nearly "saturated" in aluminum in the framework composition with a molar ratio of Si/Al near one, the maximum aluminum content possible in tetrahedral aluminosilicate frameworks if one accepts Loewenstein's rule. As a consequence they contain the maximum number of cation exchange sites balancing the framework aluminum, and thus the highest cation contents and exchange capacities. These compositional characteristics combined give them the most highly heterogeneous surface known among porous materials, due to exposed cationic charges nested in an aluminosilicate framework which results in high field gradients. Their surface is highly selective for water, polar and polarizable molecules which serves as the basis for many of their applications particularly in drying and purification. Their pore volumes of nearly 0.5 cm^3/cm^3 are the highest known for zeolites and give them a distinct economic advantage in bulk separation and purifications where high capacity is essential to an economic design. Their 3-dimensional channel structures allow the maximum in diffusion characteristics. By a judicious selection of cation composition achieved by facile ion exchange reactions, nearly the entire spectrum of known pore sizes in zeolites can be obtained. The pore sizes achievable by cation exchange of types A and X span the entire range from the smallest pore-sized zeolite known, Cs-A at 0.2nm in size [13] through the 0.3nm potassium A, the 0.4nm sodium A, the 0.5nm calcium A, to the largest known which is about 0.8nm in sodium X. This large pore size of zeolite X was a key to its introduction as a catalytic cracking catalyst.

"Intermediate Silica" Zeolites. The next evolution in zeolite materials was the impetus to synthesize more siliceous zeolites, primarily to improve stability characteristics, both thermal and acid.

It was recognized in the early 1950's by scientists at Union Carbide Laboratories that the tetrahedral framework aluminum provided a site of instability for attack by acid and water vapor or steam. Also, the siliceous mineral zeolite mordenite was known with a Si/Al molar ratio of 5 and possessing superior stability characteristics. Breck provided the first success in this quest with the discovery of the third commercially important molecular sieve zeolite type Y [14], with an Si/Al ratio of from 1.5 to 3.0, and a framework topology like that of zeolite X and the rare zeolite mineral faujasite. Not only was the desired improvement in stability over the more aluminous X achieved, but also the differences in composition and structure had a striking, unpredicted effect on properties that has led to the preeminence of zeolite Y based catalysts in nearly all of the important catalytic applications involving hydrocarbon conversion, (i.e., cracking, hydrocracking and isomerization) since its initial commercial introduction in 1959.

The next commercially important synthetic zeolite introduced in the early 1960's was a large pore mordenite made by the method of Sand [15] and marketed as "Zeolon" by the Norton Co. [16], which continued the progression toward higher Si/Al ratio, in this case a value near 5. Again, thermal, hydrothermal, and acid stability improvement was evident. This improved stability coupled with its specific structural and compositional characteristics found it a small but significant commercial market as both an adsorbent and hydrocarbon conversion catalyst. Type L zeolite, discovered in the early 50's by Breck and Acara [17] with an Si/Al ratio of 3.0 and a unique framework topology, has only recently received attention as a commercial catalyst in selective hydrocarbon conversion reactions [18].

Other zeolites with "intermediate" Si/Al compositions of from 2 to 5 and their own unique framework topologies which have achieved commercial status are the zeolite minerals mordenite, erionite, chabazite, and clinoptilolite, and the synthetic zeolite omega [19] with a typical Si/Al of 3 to 4. Their properties exhibit a common characteristic in terms of improved stability over the "low" silica zeolites. However, unique properties as adsorbents, catalysts and ion exchange materials are also exhibited which reflect their unique structural features. The surface of these intermediate silica zeolites is still heterogeneous and exhibits high selectivity for water and other polar molecules.

"High Silica" Zeolites. The most recent stage in the quest for more siliceous molecular sieve compositions was achieved in the late 1960's and the early 1970's with the synthesis at the Mobil Research and Development Laboratories of the "high silica zeolites", compositions exemplified first by zeolite beta discovered by Wadlinger, Kerr and Rosinski [20], and later ZSM-5 discovered by Argauer and Landolt [21]. Subsequently, ZSM-11 [22], ZSM-12 [23], ZSM-21 [24], and ZSM-34 [25] were described. These compositions are molecular sieve zeolites with Si/Al ratios from 10 to 100 or higher, and with unexpected, strikingly different surface characteristics. In contrast to the "low" and "intermediate" silica zeolites, representing heterogeneous hydrophilic surfaces within a porous crystal, the surface of the high silica zeolites approaches a more homogeneous characteristic with an organophilic-hydrophobic selectivity. They more strongly adsorb the less polar organic molecules and only weakly interact with water and other strongly polar molecules. In addition to this novel surface selectivity, the high silica zeolite compositions still contain a small concentration of aluminum in the framework and the accompanying stoichiometric cation exchange sites. Thus, their cation exchange properties allow the introduction of acidic OH groups via the well known zeolite ion exchange reactions, essential to the development of acid hydrocarbon catalysis properties.

Silica Molecular Sieves. The ultimate in siliceous molecular sieve compositions, and a much discussed aspiration of early workers in zeolite synthesis in the 1950's, was also achieved in the 1970's with the synthesis of the first pure silica molecular sieve, silicalite [26], containing essentially no aluminum or cation sites. In the complete absence of strong field gradients due to framework aluminum and exchangeable metal cations which serve as hydrophilic sites, silicalite exhibits a high degree of organophilic-hydrophobic character, capable of separating organic molecules out of water-bearing streams [26]. Silicalite does however contain extraneous or defect hydroxyl groups which contribute a small concentration of hydrophilic sites capable of interacting with water and polar molecules. A related new composition, fluoride-silicalite [27], completely free of hydroxyl groups, exhibits the ultimate in near perfect hydrophobicity, adsorbing less than 1 wt. % water at 20 torr and 25°C, and even exhibits bulk hydrophobicity: the crystals ($d = 1.7\ g/cm^3$) actually float on water. Silicalite reportedly [26a] has the same framework topology as zeolite ZSM-5 [28]. Other silica molecular sieve compositions have been reported, including silicalite-2 [29], and TEA-silicate [30].

Chemically Modified Zeolites. An alternate method for producing highly siliceous zeolite compositions had its beginnings in the mid-1960's when thermochemical modification reactions that lead to framework dealumination were first reported [31,32]. These reactions include those described as "stabilization," or "ultrastabilization" involving high temperature steaming of ammonium exchanged or acid forms of the zeolite [31], and framework aluminum extraction with mineral acids or chelates. Repetitive treatments in effect produce zeolites with framework Si/Al compositions and stability characteristics comparable to those observed in the synthesized high silica zeolite compositions. Such highly siliceous variants have been described by Scherzer for zeolite Y [33], by Chen [34] and others for mordenite, and by Eberly et al. [35] and Patton et al. [36] for erionite. The stabilized Y zeolite of McDaniel and Maher [31] and the highly siliceous mordenite products of Chen [34], were reported to be hydrophobic. Although the "ultrastabilized" and other dealuminated forms of zeolites emerged at the same time as the synthesized high silica zeolite beta, focus in the former case in the late 60's was on their improved stability characteristics and catalytic applications, rather than on their surface selectivity.

Other highly siliceous analogs or "pseudomorphs" of clinoptilolite and mordenite prepared during the same period by acid extraction [37] have Si/Al compositions like the high silica zeolites and silica molecular sieves. However, their crystallinity, stability, and hydrophobicity are substantially less than the thermochemically derived ultrastabilized and dealuminated compositions, presumably due to the presence of high concentrations of hydroxyl defects [37b], and the absence of substantial silicon reinsertion into framework tetrahedral sites.

Natural Zeolites. In contrast to the development of the synthetic zeolites which required their discovery and successful synthesis in the laboratory, the evolution of the natural or mineral zeolites depended on their availability in mineable deposits. The discovery in 1957 of mineable deposits of relatively high purity zeolite minerals in volcanic tuffs in the western United States and in a number of other countries represents the beginning of the commercial natural zeolite era [10]. Prior to that time there was no recognized indication that zeolite minerals with properties useful as molecular sieve materials occurred in large deposits. Commercialization of the natural zeolites chabazite, erionite, and mordenite as molecular sieve zeolites commenced in 1962 with their introduction as new adsorbent materials with improved stability characteristics in various "acid" natural gas drying applications. Their improved stability over the then prevalent synthetic zeolite adsorbents, types A and X, again reflects their higher "intermediate" Si/Al ratio of 3-5. The applications of clinoptilolite in radioactive waste recovery and in waste water treatment during the same period of the 60's was based not only on superior stability characteristics but also a high cation exchange selectivity for cesium and strontium, or for the ammonium ion.

A summary of the evolution of molecular sieve materials as developed above is given in Table 1, with emphasis on the framework Si/Al variation.

Table 1
THE EVOLUTION OF MOLECULAR SIEVE MATERIALS

"Low" Si/Al Zeolites (1 to 1.5):
    A, X
"Intermediate" Si/Al Zeolites (~2 to 5):
    A) Natural Zeolites:
        erionite, chabazite, clinoptilolite, mordenite
    B) Synthetic Zeolites:
        Y, L, large pore mordenite, omega
"High" Si/Al Zeolites (~10 to 100):
    A) By thermochemical framework modification:
        highly siliceous variants of Y, mordenite, erionite
    B) By direct synthesis:
        ZSM-5
Silica Molecular Sieves:
    silicalite

During this period of twenty-five years of research and development over 150 species of synthetic zeolites have been synthesized and some 7 mineral zeolites have been found in substantial quantity and purity [38]. Yet commercially only twelve basic types are utilized. Table 2 lists these twelve types from Ref. 5. The major large volume commercial molecular sieve zeolites used in adsorption and catalysis remain after twenty-five years, the zeolites A, X and Y.

Table 2
ZEOLITE TYPES IN COMMERCIAL APPLICATIONS [5]

Zeolite Minerals	Synthetic Zeolites	
Mordenite	A	Na, K, Ca forms
Chabazite	X	Na, Ca, Ba forms
Erionite	Y	Na, Ca, NH_4, rare earth forms
Clinoptilolite	L	K, NH_4 forms
	Omega	Na, H forms
	"Zeolon", Mordenite	H, Na forms
	ZSM—5	Various forms
	F	K form
	W	K form

TRANSITION IN PROPERTIES

The transition in properties of molecular sieve materials is summarized in Table 3. The emphasis chosen is on the framework Si/Al increasing from aluminum saturated "Si/Al = 1" to infinity, as represented by the aluminum-free, pure silica molecular sieve, silicalite. The property transitions shown are somewhat generalized and should be considered only as trends.

Table 3
THE TRANSITION IN PROPERTIES

Transition in:

- Si/Al, from 1 to ∞
- Stability, from ≤ 700°C to ~1300°C
- Surface selectivity, from hydrophilic to hydrophobic
- "Acidity", increasing strength
- Cation concentration, decreasing
- Structure, from 4, 6, and 8-rings to 5-rings

The *stability* characteristics vary substantially from a crystalline decomposition temperature near 700°C for the "low" silica zeolites, to above 1300°C for silicalite. The low silica zeolites are at best "fragile" in the presence of acid, whereas the high silica zeolites are completely stable even in boiling, concentrated mineral acids. In contrast, the high silica zeolites show decreased base stability.

The *surface selectivity* changes from the highly polar or hydrophilic surface exhibited by the aluminum-rich zeolites to a more homogeneous or nonpolar organophilic or hydrophobic surface for the high silica zeolites. The onset of hydrophobic properties appears to occur at an Si/Al near 10.

Characterization of the surface selectivity of the high silica zeolites as compared to the low silica zeolites has been studied extensively in this laboratory [39]. In the adsorption of H_2O, O_2, and n-hexane, the hydrophilic NaX zeolite exhibits the near rectilinear type I isotherm shape typical of zeolite adsorption where the mechanism of volume filling of micropores controls isotherm shape. The hydrophobic silicalite similarly pore fills with oxygen and n-hexane at low relative pressure, but "fills" only about 25% of its pore volume with water near saturation [26a]. The hydrophilic NaX zeolite removes the water, and the hydrophobic silicalite removes the organic, from organic-water mixtures. As a consequence, separations and catalysis which usually require the absence of water with hydrophilic zeolites, can now be carried out in the presence of water with the hydrophobic zeolites.

The transition in hydrophobic properties within one zeolite structure type is illustrated in the case of the zeolite mordenite ["Zeolon"] by Chen [34] who shows a quantitative linear relationship of water capacity with increasing framework Si/Al ratio for a series of variously stabilized and dealuminated mordenite materials. There is only a small loss in crystal pore volume for cyclohexane over the Si/Al range of 5 to 50. The onset of change in surface selectivity from polar to nonpolar appears to occur here near an Si/Al ratio of 7.5.

The change in *cation concentration* accompanying the change in Si/Al affects cation specific interactions in adsorption, catalysis and ion exchange, where the effect of crystal structure and resulting cation siting are also important. Cation exchange selectivity is perhaps most strongly affected. Its importance is observed in many adsorbent applications involving cation specific interactions such as air separation involving specific interaction of the nitrogen quadrupole with cations [40], in ion exchange applications such as ammonium removal, and perhaps equally strikingly in acid catalysis, where the catalytic advantages of zeolite Y versus zeolite X are well established.

The concept of increasing acidity as well as stability in hydrogen and "decationized" forms of zeolites with increasing framework Si/Al has persisted since the early work in catalysis by Rabo et al. [41]. Recently several attempts to quantify and predict that change have been published. Barthomeuf [42] showed a linear decrease in infrared frequency of the acid hydroxyl group with increasing framework Si/Al for a large number of zeolite structural types, and related this to increase in acid strength of the proton with the change in framework charge density. Subsequently [43] invoking the concept of acid activity coefficients in zeolites, she noted that both acid strength and proton activity coefficients increased with decreasing aluminum content in the zeolite framework, whereas acid site concentration decreases. This suggested that there should be a maximum in acid site activity and in catalytic reaction rate at a specific aluminum content. Vedrine et al. [44] report that the acid sites present in H-ZSM-5 (Si/Al = 19.2) are similar to, but slightly stronger than, those present in hydrogen mordenite ("Zeolon", Si/Al = 5). The concentration of acid sites is substantially higher in the lower Si/Al mordenite.

In a somewhat different approach, Mortier [45] applied the Sanderson electronegativity model to zeolites, and concluded that the acid strength of zeolitic protons increases along with the calculated residual hydrogen charge, with decreasing aluminum content. Mortier, Jacobs and Uytterhoeven [46] confirmed that the overall catalytic efficiency in the dehydration of isopropanol increased linearly with the residual charge on the proton for several zeolite structure types.

EVOLUTION IN SYNTHESIS

The early era of the discovery of zeolites in the late 1940's and the early 1950's, which led to about 20 novel synthetic zeolites [47] in a short period of time, flowed from the discovery of a new regime of chemistry [2] involving highly reactive alkaline aluminosilicate gels, metastable crystallization, and low temperature, low pressure crystallization. It was later emphasized that the cation played a dominant role in directing the formation of specific structures [48]. These early zeolites resulted from nearly the same chemistry and the use of only two alkali cations, sodium and potassium, or mixtures thereof. A second important variable in synthesis as well as in properties was the Si/Al ratio. Increase in the Si/Al in the reaction mixture resulted in synthesis of intermediate or transition Si/Al zeolites, such as T [49] and L, still using the same two alkali cations.

The next major advance in synthesis of new zeolite materials was the introduction of a new chemistry into zeolite synthesis, that of the addition of alkylammonium cations to synthesis gels. Barrer et al. [50] first reported the synthesis of N-A, a siliceous analog of zeolite A, by adding tetramethylammonium cations to sodium aluminosilicate gels, and noted the effect of the alkylammonium ion on increasing framework Si/Al composition. Nitrogenous analogs of zeolites B, X, and Y were also synthesized [50b]. Thus the first effect of the addition of the alkylammonium cations was to generate more siliceous framework compositions of previously known structure types. Subsequently the addition of alkylammonium cations to sodium aluminosilicate gels led to the crystallization of new zeolite structure types, exemplified by zeolite ZK-5 [51], omega [19,52], and zeolite N [53]. In the recent work by Mobil Research and Development Corporation scientists [7] the addition of some numbers of alkylammonium and other nitrogenous organic molecules [54], such as TEA, TPA, TBA, and pyrrolidine, to highly siliceous gels (Si/Al = 10 to 100) resulted in the high silica zeolite materials. These compositions represent siliceous analogs of previously known structure types, ZSM-21 [24], a ferrierite-type, and ZSM-34 [25], an erionite-offretite type, as well as new structure types in the case of ZSM-5 [21], ZSM-11 [22], and probably ZSM-12 [23] and zeolite beta [20]. The addition of alkylammonium cations to pure silica systems ultimately resulted in the silica molecular sieves: silicalite [26] and fluoride-silicalite [27] with TPA; silicalite-2, structurally related to the zeolite ZSM-11 [55], with TBA [29]; and TEA-silicate [30], an apparent structural analog of zeolite ZSM-12, with TEA.

Thus, variation in two important parameters in synthesis, cation and Si/Al ratio, has resulted in the spectrum of synthetic zeolites now known. Their synthesis still uses the basis reactive gel crystallization method developed by Milton [2] in the late 40's.

The synthesis mechanisms of the low silica and high silica zeolites appear to differ. It is suggested here [56] that the nucleation mechanism in the low silica zeolites involves the formation of stabilized alkali metal cation aluminosilicate complexes and is primarily controlled by the aluminate and aluminosilicate solution chemistry. Four and six-membered rings and "cages" of aluminosilicate tetrahedra, stabilized by alkali metal cations, dominate the synthesis chemistry and appear in the structures. In the case of the highly siliceous molecular sieves, a true "templating" or clathration mechanism pervades wherein the alkylammonium cation forms complexes with silica via hydrogen bonding interactions [26a]. These complexes template or cause replication of the structure via a stereo specific hydrogen-bonding interaction of the quaternary ammonium cation with the framework oxygens. Synthesis chemistry and structure is now dominated by silica, five-rings of tetrahedra, and the stereospecific interactions with alkylammonium ion. The concept of cation templating in zeolite synthesis has been discussed by Flanigen [48] and more recently developed and summarized by Rollman [57].

It is interesting to note that recent theoretical work on molecular electrostatic potential by Mortier et al. [58] shows stabilization of a 6-ring containing aluminum due to the presence of metal cations near its center, in support of the mechanistic concept of a stabilized metal aluminosilicate species in alumina-rich synthesis. Also of note is the observation that the cross-over in zeolite surface selectivity from hydrophilic to hydrophobic at an Si/Al near 7.5 to 10, corresponds to the change in zeolite structural features from 4, 6, and 8-ring structures to those containing an increasing fraction of 5-rings (for example, Y→Ω→mordenite→ZSM-5). This suggests that as the fraction of Al decreases below one per 6-ring corresponding to an Si/Al of 5, 5-ring formation is favored.

Although the level of understanding of the synthesis chemistry and its relationship to the resulting structural features of zeolites has advanced substantially over the period of twenty-five years, the ability to execute chemical architecture in the laboratory has unfortunately eluded zeolite synthesis scientists for the same period. The synthesis of new zeolites has flowed from the innovative alteration of the chemistry of the synthesis system, rather than from the ability to design the chemistry to form a desired structure.

The manufacture of basic zeolite materials still remains similar to that developed in the initial work in the late 1940's by Milton [2]. The temperature range for crystallization has tended to increase with increasing Si/Al ratio in the zeolite, from 25 to 125°C for the aluminum-rich zeolites, to 100 to 150°C for the intermediate Si/Al zeolites, L, omega, and mordenite, and to near 125 to 200°C for the high silica zeolites as exemplified by ZSM-5. This is consistent with the suggested relationship of pore volume and synthesis temperature [2], that the lower temperatures favor the highest pore volume materials (near 0.4 cm^3/g) such as A, X and Y, and the higher temperatures favor lower pore volumes (0.15-0.20 cm^3/g) for mordenite, L, omega and ZSM-5.

THE EVOLUTION IN APPLICATIONS

The molecular sieve behavior of crystalline zeolites and their large potential in performing molecular sieving separations was first demonstrated in the pioneering work of Barrer [4] and colleagues in England. With the commercialization of molecular sieve zeolites in late 1954 a new class of materials became available, capable of being tailor-made in terms of structure, composition and properties. Yet many of their early adsorbent and catalytic applications involved simple replacement of the then used adsorbent and catalyst materials in known adsorption and catalytic processes, based on the improved properties and performance of the molecular sieve zeolites. This is exemplified by the replacement of silica gel and activated alumina in drying and purification applications by zeolites A and X, due to the improved capacity and greater selectivity of the zeolites. Their introduction into catalytic cracking in 1962 was as a replacement for amorphous silica-alumina catalysts in existing moving bed and fluid bed catalytic cracking processing. Replacement followed the discovery of the higher activity of zeolite X in the cracking reaction and the higher selectivity to gasoline compared to silica-alumina.

Applications engineered specifically for zeolites were developed and continue to evolve over the twenty-five year span, especially in the adsorbent area, in such processes as isoparaffin/paraffin separation, xylene separation and olefin separation, and pressure swing adsorption air separation [6]. All of these adsorbent applications combine the unique adsorptive properties of a specific tailor-made molecular sieve adsorbent, and an adsorption process designed and engineered to optimize the product-process characteristics.

Interestingly, the original incentive of Milton to use molecular sieve zeolites was to separate oxygen from nitrogen as a new method for air separation. The commercialization of that application in oxygen and nitrogen production from air via the now used pressure swing adsorption processes [6,59], occurred nearly twenty years later when a market in waste water purification and other applications requiring relatively low tonnage production of oxygen allowed it to finally compete successfully with the established cryogenic separation technology.

Adsorbent Applications. The use of molecular sieve zeolite adsorbents to perform a host of separations and purifications has become firmly established in the chemical process industries. A summary list of major adsorbent applications adapted from Anderson's review at the last Molecular Sieve Zeolite Conference in Chicago [6] is given in Table 4.

Table 4
COMMERCIAL ADSORBENT APPLICATIONS OF MOLECULAR SIEVE ZEOLITES

A. Purification

- I. Drying
  - natural gas (including LNG)
  - cracked gas (ethylene plants)
  - insulated windows
  - refrigerant
- II. CO_2 Removal
  - natural gas
  - cryogenic air separation plants
- III. Sulfur Compound Removal
  - sweetening of natural gas and liquified petroleum gas
- IV. Pollution Abatement
  - removal of Hg, NO_x, SO_x

B. Bulk Separations

- I. Normal/iso-paraffin separation
- II. Xylene separation
- III. Olefin separation
- IV. O_2 from air
- V. Sugar separation [60]

It can be seen that present day applications fall into two categories, purification applications which in general depend on surface selectivity for polar or polarizable molecules such as water, CO_2 or sulfur compounds; and bulk separations many of which are based on molecular sieving principles. Pressure swing adsorption in air separation, originally envisaged by Milton as a molecular sieving separation based on the slight difference in size of the oxygen and nitrogen molecule, is rather based on the strong specific interaction of the nitrogen molecular quadrupole with the cation [40]. Many of the purification applications also involve molecular sieving in that the selection of the zeolite adsorbent involves a pore size designed to exclude potentially co-adsorbed molecules, for example the use of type 3A molecular sieve in cracked gas drying to prevent the co-adsorption of ethylene and heavier unsaturated hydrocarbons. Refrigerant drying and purification (of halogenated hydrocarbons), the first broadly applicable commercial use of molecular sieves [2], still remains a major nonregenerative application.

Recently molecular sieve zeolite adsorbent separations have been extended to liquid phase aqueous systems in the separation of fructose from fructose-dextrose-polysaccharide mixtures [60].

Catalyst Applications. Fundamental discoveries in the use of zeolites in hydrocarbon catalysis were made in the 50's primarily at the laboratories of Union Carbide and Mobil Oil Corporations, and Esso Research and Engineering Company [61], with the recognition of the acidic properties of hydrogen, multivalent metal cation, and decationized forms of zeolites X and Y [41,62], and the novel shape selective properties of zeolite A [63]. A commercial zeolite Y isomerization catalyst, introduced by Union Carbide in 1959 [2], was the first of a series of molecular sieve based catalysts for the petroleum industry.

The first major commercial catalytic application resulted from the introduction of the use of zeolite X in catalytic cracking of crude to produce liquid fuels in 1962, based on the early work of Plank and Rosinski [64]. The introduction of zeolite containing catalysts caused a revolution in catalytic cracking [65], because of their increased catalytic activity and improved yields to gasoline compared to amorphous silica-alumina catalysts. Mechanistically this has been related by Weisz [66] and others to the more efficient hydrogen redistribution between hydrocarbon molecules over zeolite catalysts, resulting in high rates of intermolecular hydrogen transfer, coupled with extremely high intrinsic cracking activity. Because of the very strong adsorption forces within zeolites they also concentrate hydrocarbon substrates to a much larger extent than other catalysts and favor bimolecular reactions [7] such as hydrogen transfer.

Developments since 1962 in zeolite catalytic cracking have occurred both in materials and process [67,65]. Zeolite X has been essentially replaced by the more stable and active zeolite Y. Metals resistant, and controlled combustion zeolite catalysts have been developed, the former to allow handling of heavier feedstocks, and the latter for pollution control to convert CO emissions to CO_2. Zeolite content has been increased from 5-10% in 1964, to as high as 40% in 1979 [68]. Process innovations to utilize the unique properties of zeolites include concepts based on short contact riser cracking and have led to some number of proprietary zeolite engineered designs now in commercial use [67]. Recent developments have been strongly influenced by environmental requirements in pollution control and the need for higher octane unleaded gasoline (especially in the United States).

Other established industrial processes that utilize zeolite based catalysts in addition to catalytic cracking, are hydrocracking, and paraffin isomerization [7]. All are based on the unique properties of zeolite catalysts which have in common, extremely high strength acid sites, and selectivities related to strong adsorptive forces within the zeolite. All use hydrothermally stable acid forms of large pore zeolites. Two examples of shape selective catalysis [63,69] utilizing, in additon to the above properties, a specific pore size and shape of zeolite, are in commercial use. The "Selectoforming" process of Mobil Oil Corp. selectively hydrocracks the normal paraffin components of catalytic reformate using an offretite-erionite type catalyst which excludes non-normal paraffin molecules from adsorption and reaction. A second commercial shape selective hydrocracking process is catalytic dewaxing which typically employs a large pore mordenite containing single channels approximately 0.7nm in diameter which contribute to selectivity [7].

The catalytic properties of the high silica zeolite ZSM-5 have received much attention [70,7]. The initial commercial or near commercial applications reported [7] for ZSM-5 include: a) the isomerization of C_8 aromatics to produce isomerically pure xylenes, especially paraxylene for polyester manufacture; b) ethylbenzene synthesis for styrene production; and c) catalytic dewaxing [71]. The conversion of methanol to gasoline [72] as a new route from coal or synthetic or natural gas to motor fuel is under development [73], with the first plant based on coal scheduled for construction in New Zealand [74]. More recently Mobil workers have also reported [75] a similar conversion of oxygenated hydrocarbon compounds in biomass to gasoline.

These initial commercial applications for ZSM-5 appear to be elegant examples of shape selective catalysis [63,69] reflecting its unique crystal structure with 0.6nm pores outlined by 10-membered rings of oxygen. In addition they depend upon the other zeolite-specific properties of highly acidic sites as in the H-ZSM-5 catalyst, and the substrate or reactant concentration effect. The novel organophilic-hydrophobic selectivity also appears to contribute to the apparently unique selectivity of ZSM-5 for the conversion of oxygenated hydrocarbons to paraffins and aromatics.

The entrance into several of these commercial applications by ZSM-5 reportedly [7] may involve retrofit of existing processes with a new catalyst. In the case of C_8 aromatic isomerization ZSM-5 replaces the platinum/silica-alumina catalysts developed for the "Octafining" process. In ethylbenzene synthesis ZSM-5 could replace the current technologies based on $AlCl_3$ and BF_3 supported on alumina. In the case of catalytic dewaxing ZSM-5 may replace the use of metal loaded tubular zeolite catalysts such as mordenite. Early reports of performance advantages of ZSM-5 in the process suggest that the H-ZSM-5 catalyst carries out the needed hydrogenation function without the addition of noble metal to the catalyst [71].

A summary of present and projected applications of zeolites in catalysis from Ref. 5 is shown in Table 5.

Table 5
PRESENT AND PROJECTED APPLICATIONS OF ZEOLITES IN CATALYSIS [5]

- Hydrocarbon conversion
  - Alkylation
  - Cracking
  - Hydrocracking
  - Isomerization

- Hydrogenation and dehydrogenation
- Hydrodealkylation
- Methanation
- Shape-selective reforming
- Dehydration
- Methanol to gasoline
- Organic catalysis
- Inorganic reactions
  - H_2S Oxidation
  - NO Reduction of NH_3
  - CO Oxidation
  - $H_2O \rightarrow O_2 + H_2$

The first interesting application of a combined catalytic-adsorptive integrated process, named TIP (total isomerization process) for gasoline octane improvement weds the Union Carbide "IsoSiv" molecular sieve adsorption process for separating normal and isoparaffins employing 5A zeolite, with the "Hysomer" catalytic process of the Shell Oil Co. to isomerize normal paraffins to higher octane branched isomers using a highly acid, large pore zeolite catalyst based on a large pore mordenite [7].

Thus, molecular sieve zeolites have found wide use in both catalytic conversion and adsorption separation processes over the last twenty-five years. In both adsorbent and catalytic applications the initial commercial introduction tended to involve replacement of existing non-zeolite adsorbents or catalysts because of improved zeolite performance. Zeolite engineered processes evolved subsequently and more facilely in adsorption applications where the capital costs are generally lower than those in major hydrocarbon conversion processes such as cracking and hydrocracking. In the latter case the introduction of zeolites resulted in improved performance and production without expenditures of capital. After twenty-five years both kinds of processes are still in use. The retrofit processes have been extensively modified or redesigned to utilize unique properties of zeolites, and the sophistication or tailor-making of the zeolite designed or engineered processes have become more innovative and systematized to take maximum advantage of zeolite properties.

Ion Exchange Applications. The third unique property of zeolite molecular sieves, that of selective cation exchange, went through a quite different history of development. Among the earliest application areas explored in the Union Carbide laboratories by Thomas [76] in the early 50's was the use of zeolites A, B and X in cation exchange applications, including industrial and domestic water softening. The synthetic polymeric ion exchange resins, which themselves were replacements for the amorphous metal aluminosilicate permutite-type products, had only recently been introduced to the marketplace. At that time it appeared that the organic resins had technical performance advantages in the regeneration cycle over the synthetic zeolites A and X. Thus the performance advantages of zeolites realized in adsorption and catalysis did not apparently exist in ion exchange.

Cation exchange of zeolites is used routinely in modifying the properties of zeolite products used in adsorption and catalysis, and a large body of literature on cation exchange selectivities, structural characteristics, and thermodynamics by Barrer, Sherry, and others [77], evolved very shortly after the commercial introduction of zeolites A and X in 1954. Yet, significant use of the zeolites as ion exchangers has occurred only recently. Their development as commercial ion exchangers strongly followed the enactment of new environmental pollution standards in the late 60's.

Sherman [9] recently reviewed the subject of ion exchange separations with molecular sieve zeolites. The summary of present and potential ion exchange applications reported by Breck [5] and adapted from Sherman [9] is shown in Table 6.

Table 6
ION EXCHANGE APPLICATIONS [9,5]

Present Applications	**Advantage**
Removal of Cs^+ and Sr^{++} Radioisotopes - LINDE AW-500, mordenite, clinoptilolite	Stable to ionizing radiation Low solubility Dimensional stability High selectivity
Removal of NH_4^+ from waste water - LINDE F, LINDE W, clinoptilolite	NH_4^+ - selective over competing cations
Detergent builder Zeolite A, Zeolite X (ZB—100, ZB—300)	Remove Ca^{++} and Mg^{++} by selective exchange No environmental problem
Potential Applications	**Advantage**
Radioactive waste storage	Same as Cs^+, Sr^{++} removal
Aquaculture AW-500, clinoptilolite	NH_4^+ - selective
Regeneration of artifical kidney dialysate solution	NH_4^+ - selective
Feeding NPN to ruminant animals	Reduces NH_4^+ by selective exchange to nontoxic levels
Metals removal and recovery	High selectivities for various metals
Ion exchange fertilizers	Exchange with plant nutrients such as NH_4^+ and K^+ with slow release in soil.

The single potentially largest ion exchange application as builders in detergents [78] is ironically in the water softening area, the original ion exchange application considered in the 50's. It became a commercial reality due to two changed factors. First, its use to soften water as a builder in detergents in the 70's is non-regenerative and therefore the main earlier disadvantage in regeneration as evaluated in the 50's is absent. Second, there are currently a number of areas in the world in which the use of phospate builders is restricted for environmental reasons. After considerable R and D effort, apparently no other suitable substitute for phosphate has been found to date except the synthetic zeolites A and X.

Replacement of phosphates in detergents by zeolite ion exchangers is also based on performance and cost. The zeolites in powder form provide the same function as phosphates, the removal of hardness ions, Ca^{++} and Mg^{++}, as active ions in the wash water. The maximum ion exchange capacity of the aluminum saturated zeolite A, theoretically the highest possible in zeolites, coupled with a structurally controlled cation selectivity for Ca^{++}, give zeolite A a unique advantage in this application. Projections show a very large volume use and a bulk volume cost that is less than that of phosphates [78a].

Natural zeolites have played an important role in the development of ion exchange applications. The use of the zeolite minerals chabazite, mordenite and clinoptilolite for the removal or recovery of cesium and strontium radioisotopes in the nuclear industry was among the earliest applications of zeolites as ion exchangers. Their superior selectivity and stability characteristics spurred the development of other zeolite ion exchange applications. The high selectivity of clinoptilolite for ammonium ion in waste water treatment and other applications generated interest in developing synthetic zeolites such as Linde F and Linde W. Again these commercial applications were responsive to environmental problems.

The success of the zeolites both natural and synthetic in ammonium removal applications rests principally on their high cation selectivity. In this case their performance is far superior to the organic resin ion exchangers which show poor selectivity for ammonium ions, especially in competition with calcium and magnesium ion [9].

Natural Zeolites. There have been a number of comprehensive and excellent reviews of the uses of natural zeolites in the last five years [1,10,11]. A summary adapted from these references is shown in Table 7. The major use of natural zeolites is in bulk mineral applications [1]: in Europe in the building and construction industry, where proximity to building location makes them cost effective; and in the Far East as filler in the paper industry, largely because of the unavailability of alternate mineral resources. As discussed previously, a modest market for zeolite minerals has developed as a molecular sieve adsorbent in acid gas drying in the natural gas industry, in NH_4 removal in water treatment systems by ion exchange, and in the production of oxygen and nitrogen via adsorptive air separation, especially in Japan [59]. In general, however, their penetration into molecular sieve applications has been quite limited.

Table 7
SUMMARY OF USES OF NATURAL ZEOLITES [1,10,5]

Bulk Applications:
- Filler in Paper
- Pozzolanic Cements and Concrete
- Dimension Stone
- Lightweight Aggregate
- Fertilizers and Soil Conditioners
- Dietary Supplement in Animal Nutrition

Molecular Sieve Applications:
- Separation of Oxygen and Nitrogen from Air
- Acid-resistant Adsorbents in Drying and Purification
- Ion Exchangers in Pollution Abatement Processes

EVOLUTION IN COMMERCE

The synthetic zeolite markets progressed from a relatively small adsorbent market of the order of a million dollars in the late 50's, through a rapid growth which was influenced by the use of zeolites X and Y in catalytic cracking to a published estimate [1] of $40MM in 1970, and a projected $250MM in 1979. The projected market in the large volume, bulk commodity detergent area for zeolite builders is reported to be $25MM, or approximately 100MM lbs. of zeolite A in 1980 [79], and an optimistic projection for growth to a 400MM lb. market in 1982 [78a].

The introduction of zeolites into cracking catalysts caused a commercial as well as a technical revolution in catalytic cracking. It is reported that zeolite cracking catalysts have saved refiners over $250MM per year, and increased gasoline capacity substantially [80]. Today, type Y zeolite has 100% of the U. S. market, and 75-80% of that outside of the United States [68]. The total worldwide consumption of zeolites in catalytic cracking in 1978 is estimated at between 70-90MM pounds per year [68], representing the single largest use of synthetic molecular sieve zeolites to date. It is likely that bulk use of synthetic zeolites in detergents may surpass that volume if projections are realized.

In a recent estimate of the natural zeolite market, Leonard [1] suggests worldwide sales beginning in 1965 of 24MM lbs. at a value of $1MM, 160MM lbs. at $8MM in 1970, and a 1979 projection of 560MM lbs. at a value of $35MM. Greater than 90% of the market is in bulk mineral applications, and only about 2% of that in North America. The major markets are in Europe, Russia, and the Far East, especially Japan.

The synthetic molecular sieve zeolites as industrial materials are appropriately classified as specialty chemicals, or preferably as engineered products. The molecular sieve industry is technology and engineering intensive. The majority of molecular sieve zeolite applications are engineered in all respects, from the synthesis of the zeolite material, the modification of their properties, the selection of a tailormade zeolite product, to a process engineering design and execution that integrates and optimizes the material with the process. The successful growth of molecular sieve zeolites as an industrial chemical depended most strongly on their development as an engineered product.

As developed previously, the effect of "outside" forces in the changing world surrounding molecular sieves had a profound impact on their commercial growth and development. This is especially true in the case of the problems and crises in energy and environment which evolved in the 60's and erupted in the 70's, and which offered opportunities for their uniquely suited properties in separations and catalysis. This is seen in the natural gas purification area where large growth has recently occurred in the treatment of LNG in giant base load facilities in the Middle East [6], in increased FCC production of gasoline and octane improvement for unleaded gasoline, in the fledging use of zeolite ion exchangers in waste water treatment, in insulated window adsorbents, in substitution of zeolites for phosphate in detergents, and possibly in the future, methanol or biomass to gasoline. The normal/iso-paraffin processes using molecular sieve zeolites were influenced by the need for biodegradable detergents. The xylene separation processes were influenced by the industrial need for raw material for polyester fiber production.

THE PAST AS INDICATOR OF THE FUTURE: THE NEXT TWENTY-FIVE YEARS

The initial discoveries of the synthetic molecular sieve zeolites A, X and Y in the late 40's and early 50's spawned an immense worldwide science and technology, utilizing the resources of many major industrial R and D organizations throughout the world. Zeolites are "researched" and used commercially in every major country in the world. (Recently China displayed molecular sieves as one of its industrial products at the Shanghai Industrial Exhibit [81].) Worldwide there are over a dozen manufacturers of zeolites or zeolite-containing products. As an industrial material, their market has grown to hundreds of millions of dollars. Since the mid-1960's, the later developing natural zeolites have reached the status of an important industrial mineral resource [82] with more than 300,000 tons mined worldwide, and used principally in bulk applications.

The Past. What was necessary for the success of the molecular sieve zeolite industry? The development of any new commercial product and process is usually the result of complex interactions among many contributing factors. I will attempt here to highlight some key factors that facilitated the zeolite "explosion".

The commercial use of zeolites depends on: 1) useful properties controlled by their structural chemistry; 2) availability; and 3) cost [5]. The pioneering work of Barrer in the 40's in outlining the large number of molecular sieve separations possible gave the impetus to the industrial researchers, Milton and associates, who made initial key discoveries in novel synthetic zeolite compositions and a practical method for their manufacture. The scientific and engineering resources were then committed by a large, major chemical corporation, Union Carbide Corporation, with available technical and commercial resources. As a result they became available to the industrial and scientific communities in late 1954.

The major early synthesis efforts in the late 40's and early 50's could not have been successful without the development of rapid, effective characterization techniques to evaluate the synthesized products [2]. Such techniques were developed to determine their structure, chemical composition, purity, and adsorption properties. As a result time efficient analysis of a very large number of synthesis experiments was possible which facilitated the discovery of twenty-some new zeolite species and delineated their optimum synthesis system.

The general synthesis method developed by Milton provided a simple, cost effective manufacturing process, involving readily available, cheap raw materials such as hydrated alumina, soluble alkali silicates, caustic, and water, and process conditions of relatively low temperature and pressure and short crystallization times. The unit operations of batch crystallization, filtration and drying, were well established in the practiced manufacturing art. Thus, molecular sieve zeolites could be manufactured to compete on a cost performance basis with other known commercial adsorbent, catalyst, and ion exchange materials.

The development of formed or bonded zeolite products necessary for commercial application in supported or moving bed systems, required extensive development of forming technology. The as-synthesized 1-5μm zeolite crystals are formed into beads, pellets, or mesh, typically by use of a clay binder. Over the period of twenty-five years, the development of an unsung and little discussed forming technology has resulted in the ability to control particle properties such as strength and attrition resistance and mass and heat transfer characteristics, and to optimize the formed products' properties and performance.

As the new molecular sieve zeolites became known and available and subsequently used, extensive research effort in industrial and academic circles provided a wealth of scientific information on the physical, chemical, and structural characteristics of this unique class of materials. The resulting in-depth understanding of properties allowed the selection of zeolite product for a specific application, the identification of applications for the product, and the design and engineering of the application process.

Their application as adsorbents required a major development in adsorption process design and engineering technology. The unit opera-

Table 8
SOME PROPOSED APPLICATIONS OF ZEOLITES [5]

Adsorption
- New adsorbents for sieving
- Hydrophobic adsorbents
- Gas storage systems
- Carriers of chemicals

Nuclear Industry Applications

Environmental
- Weather modification
- Solar energy

Agricultural
- Fertilizers and soils
- Animal culture

Consumer Applications
- Beverage carbonation
- Laundry detergents
- Flame extinguishers
- Electrical conductors
- Ceramics
- New catalysts

The major trends in future commercial applications will probably comprise substantial growth in most of the presently existing separations and catalysis areas, and the development of new applications. The emergence of zeolite ion exchange applications could parallel that of zeolite adsorption technology over the last twenty-five years. The maturing of the developing ion exchange process design and engineering technology, with the capability of advanced systems design and engineering concepts, should stimulate the growth and acceptance of zeolite ion exchange separations in the chemical process industry alongside those based on adsorption and catalysis.

The growth of bulk chemical and consumer applications for synthetic as well as natural zeolites appears to be certain. In addition to those now prevalent for natural zeolites, Table 8 includes their use in agriculture, beverage carbonation, and raw materials for ceramics.

Natural zeolites should continue to grow as an important industrial mineral resource used principally in bulk application areas. The "engineering" of the mined zeolites, by beneficiation to upgrade purity and chemical modification to tailor properties, will no doubt emerge as the level of technically intensive effort on natural zeolites expands [1]. They should then enjoy a larger share of "engineered" molecular sieve type applications. The extent of such growth will not likely be related to their lower cost but rather improved property and performance characteristics. That expansion will continue to be a relatively minor portion of the total molecular sieve applications market, largely because of the increasing capability in the manufacture and availability of a large number of synthetic zeolites, and the ability to control purity and properties during manufacture.

The trends in molecular sieve process design should see more compound, multistep process systems utilizing multiple or composite molecular sieve materials and combined unit operations such as integrated adsorption and catalytic systems. The energy savings possible in adsorption separations has received emphasis only recently [83]. It is likely that the energy efficiency in molecular sieve adsorption and catalytic processes will be more fully exploited in the process design.

Over the long range, molecular sieve zeolite technology should continue to be strongly influenced by the new emphasis on clean environment, and energy and renewable resource technology. Cost effective and novel separation and recovery processes will be required to meet pollution standards and material and energy resource limitations in the next several decades. Development of adequate energy resources, especially the presently considered alternate synthetic fuel technologies based on synthesis gas, oil shale, coal, and gasohol among others, all involve technically difficult and complex separations and catalytic problems.

tion of adsorption has undergone a major development in the last twenty years mainly as a result of the introduction of molecular sieves as commercial adsorbents [6,2]. It is now a mature engineering practice that has brought adsorption to the forefront as a major tool of the chemical process industry.

Indispensable to the commercial success of molecular sieve zeolites has been the dedication and contributions of the scientists and engineers who provided the key to their discovery and development, and subsequently unfolded their elegant structural and chemical architecture and novel properties. The zeal with which these molecular sieve "apostles" preached their gospel to the scientific world, to industrial technology management, and to the hard-to-sell chemical process industries, was essential to their success. Hundreds of these apostles and champions became committed, in addition to the original pioneers. The growth of molecular sieve science and technology has evolved a community of outstanding scientists and engineers, whose contributions include creative and practical scientific work, and the successful translation of R and D results to commercial manufacture, sale and utility. It is estimated at the onset of their second twenty-five years, that over five thousand scientists and engineers devote a substantial portion of their technical effort to molecular sieve zeolites.

The Future. The future trends in materials will no doubt see the development of new commercial zeolites selected from newly discovered compositions and structures, chemical modifications of present commercial products to generate new and useful properties, and a reevaluation of the host of known zeolites which never achieved commercial success. It seems likely that with the increasing number of laboratories devoting resources to the search for new structures and compositions, new classes of molecular sieve materials will be discovered. The modification chemistry of zeolites practiced to date, such as steaming and chemical extraction, leaves a vast area of chemical and structural modification of solids as yet unexplored with zeolites. Additional types of natural zeolites will probably not achieve commercial prominence since the large geological exploration efforts for zeolite deposits throughout the world during the last ten to fifteen years have probably identified all of the zeolite mineral species of commercial significance.

The commercialization of "stored" or "shelved" zeolites has largely been hampered by their lack of general availability and their apparent inability to compete performance-wise with the current commercial products. With the worldwide expansion of scientific zeolite centers with the capability of synthesizing non-commercial zeolites and determining their properties and potential applications, it is likely that several "old" zeolites will achieve commercial status.

It is likely that there will be more development and change in zeolite manufacturing processes during the next decade than during the last twenty years, due to the cost incentives of the bulk chemical and consumer markets, and the availability of the natural zeolites.

Breck has recently reviewed [5] a large number of new potential applications areas for zeolites. His compilation of proposed applications based on the reported literature is reproduced in Table 8.

Molecular sieve zeolites are well positioned historically and offer a most appropriate technology because of their unique properties which give them a near-infinite flexibility to tailor product and process. The recent extension of their shape and surface selectivity characteristics with the advent of high silica zeolites and silica molecular sieves offers new opportunities in design parameters, as exemplified by the methanol to gasoline process with ZSM-5. The availability of hydrophobic molecular sieve adsorbents opens up a new application area in removing and recovering organic molecules from aqueous systems. Combined hydrophobic and hydrophilic adsorbent systems would allow the concentration or removal of an organic molecule from an aqueous solution, and efficient drying of the recovered organic. Similar separation schemes are now under investigation in the production of gasohol from grain [84].

The zeolite future looks bright.

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