New Vistas in Zeolite and Molecular Sieve Catalysis

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Zeolites and zeolite-like molecular sieves are able to recognize, discriminate, and organize molecules with precisions that can be less than 1 Å.[1] Because these structures (Figure 1) contain uniformly sized pores in the range of 4–13 Å, they have been exploited by the petrochemical industries to perform many large-scale, shape-selective hydrocarbon reactions.[2] Further information on the materials listed in Figure 1 is provided in Table I. The pore sizes listed are the crystallographic free diameters from each structure. Additionally, the dimensionality of the pore systems is provided. (A simple way to think about the dimensionality of the pore system is to place an organic molecule into the void space and observe in how many different directions it can move. For example, an *n*-hexane molecule can move in one direction in the channels of VPI-5 whereas it can travel in all three directions in NaX.) For more details on the structures of zeolites and molecular sieves, see ref 3.

Typically, zeolite catalysis involves acid-catalyzed reactions or bifunctional (acid–metal function) processes. The first report of shape-selective acid catalysis using a zeolite catalyst was by Weisz et al., who selectively dehydrated *n*-butanol in the presence of isobutanol (difference in kinetic diameter less than 1 Å).[5] The shape-selective properties of these catalysts are due to the confinement of acid sites within the zeolite pore architecture. Additionally, the zeolite can serve as a host for small metal particles that can work in concert with the acid functionality, e.g., hydrocracking and hydroisomerization.[2b]

There is a close connection between the microscopic structures and the macroscopic properties of zeolite catalysts. The commercial success of zeolites is largely due to the continual discovery of new materials that have enabled process improvements and the development of new technologies. The ability to control the zeolite properties through synthetic efforts will continue to be of great importance. At present, the control of zeolite properties mainly involves molecular level manipulations of structural features, e.g., pore size and location of active sites. That is to say, the chemical and/or electronic nature of the catalytically active site is not normally controlled. Rather, the three-dimensional structure surrounding this active site is fabricated. In the 1970s and 1980s, catalyst "design" implied the manipulation of the porous support material to affect the mass and energy transport properties (length

scales of 10^{-2}–10^{-9} m). Now, with zeolite catalysts, "design" implies manipulation at the 10^{-10}-m length scale and involves complementarity between the active site and reactant geometries, i.e., docking of reactants to the active site. Current zeolite-mediated conversions rely on reactant or product shape selectivity (size discrimination between reactants or products, respectively).[5] Future, high-selectivity reactions will proceed with transition-state shape selectivity[6] that attempts to mimic the behavior observed in enzyme- and antibody-catalyzed conversions.[7]

It is likely that new zeolite catalysts will require greater complexity in their preparation. Also, they will be able to catalyze a broader spectrum of reaction chemistries, e.g., oxidations (vide infra). These factors may induce cost factors that are prohibitive for use in the fuel industries. However, new and widespread opportunities exist in the production of bulk and especially specialty (vide infra) chemicals. Below, four new areas of zeolite and molecular sieve catalysis in which we have been involved are briefly described. These areas are (i) catalysis in extra-large-pore molecular sieves, (ii) base catalysis with zeolites, (iii) oxidation–reduction chemistries in molecular sieves, and (iv) asymmetric catalysis with zeolites.

Extra-Large-Pore Molecular Sieve Catalysis

Zeolites have been known for quite some time and have been used as industrial catalysts since the 1960s.[1,2] Zeolites CaA, ZSM-5, and NaX illustrated in Figure 1 contain rings (that construct the pores) comprising 8, 10, and 12 oxygen atoms (likewise 8, 10, and 12 silicon and aluminum atoms), respectively. These zeolites are denoted as small-, medium-, and large-pore materials. Small-, medium-, and large-pore zeolites are all currently being employed as industrial catalysts. In 1988, we reported a material called VPI-5[8,9] that contained an 18-membered ring with a pore size of approximately 13 Å. This material significantly expands the pore size

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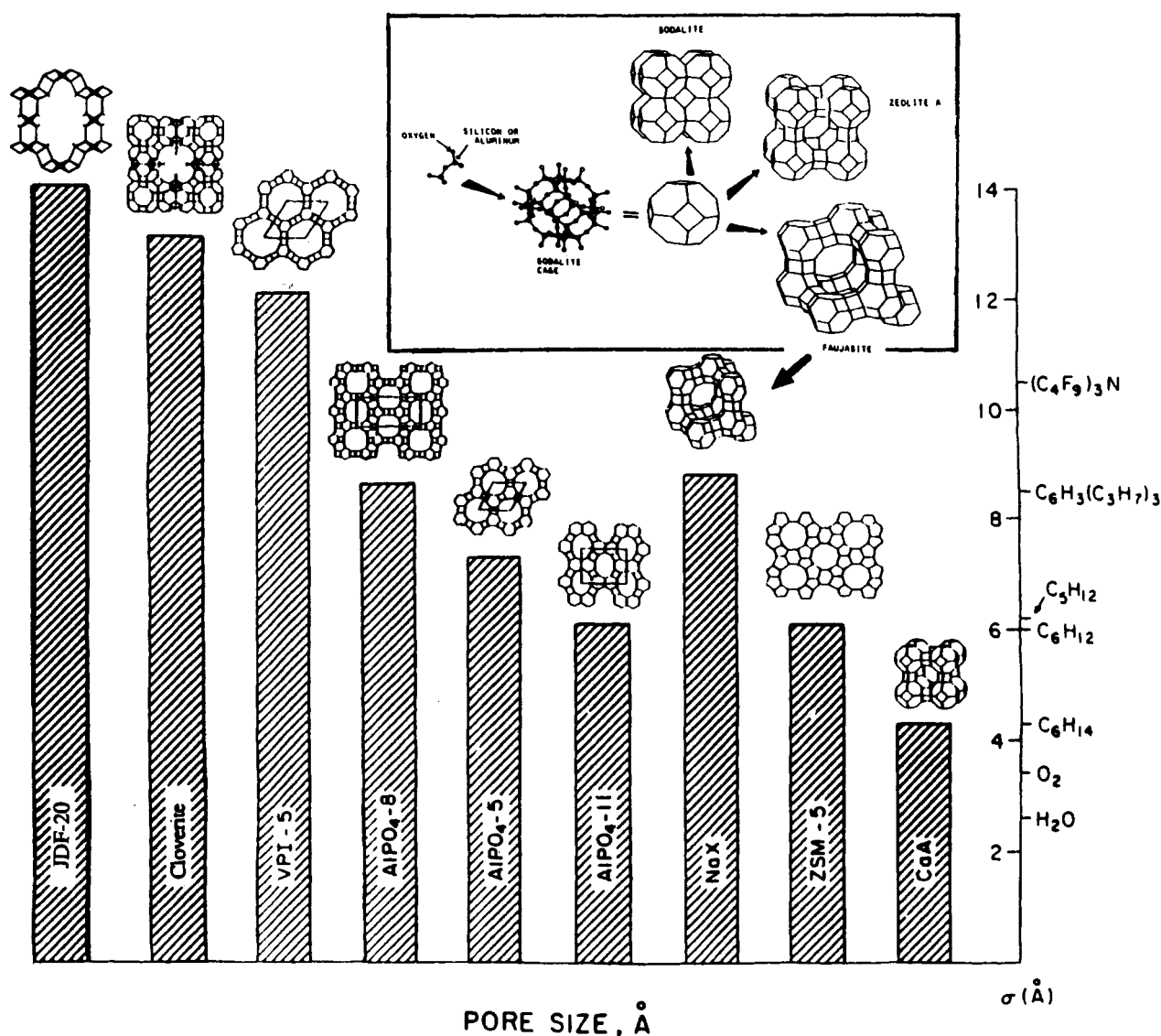(5) Weisz, P. B.; Frilette, V. J.; Mastman, R. W.; Mower, E. B. *J. Catal.* **1962,** *1,* 307–312.
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PORE SIZE, Å

Figure 1. Correlation between pore size of molecular sieves (an oxide framework of aluminum and silicon alone is classified as a zeolite; the term molecular sieve can describe frameworks of any composition) and the kinetic diameter (δ) of various molecules. Inset: Schematic of zeolite frameworks. The synthetic faujasites are zeolites NaX (Si/Al = ~1.1) and NaY (Si/Al = ~2.1). From ref 1b.

Table I. Details of Structures Given in Figure 1

structure	pore size, Å[a]	pore dimensionality	ref
zeolite A	4.1 (circular)	3-dimensional	3
ZSM-5	5.1–5.5 (elliptical)	3-dimensional	3
NaX	7.4 (circular)	3-dimensional	3
AlPO₄-11	3.9–6.3 (elliptical)	1-dimensional	3
AlPO₄-5	7.3 (circular)	1-dimensional	3
AlPO₄-8	7.9–8.7 (elliptical)[b]	1-dimensional[b]	3
VPI-5	12.1 (circular)	1-dimensional	3
cloverite	6.0–13.2 (cloverleaf)[b]	3-dimensional[b]	3
JDF-20	6.2–14.5 (elliptical)[b]	3-dimensional[b]	4

[a] From crystal structure. [b] From crystal structure. No adsorption data available to confirm these properties.

range of crystalline molecular sieves. We proposed that molecular sieves containing ring sizes above 12 be called extra-large-pore materials.[10] Since 1988, three other extra-large-pore materials have appeared: AlPO₄-8, cloverite, and JDF-20. The pore size values listed in Figure 1 for these materials are the maximum diameters obtained from the crystal structures since no reports on adsorption have appeared.

There are many reasons for desiring uniformly sized, extra-large-pore molecular sieves.[11-13] The most obvious reason is to perform shape-selective catalysis on reactants too large to enter the pores of large-pore molecular sieves. We first illustrated this concept by the liquid-phase hydrogenation of cyclooctene with rhodium-containing VPI-5.[9] Since then, other liquid-phase reactions, e.g., octane oxidation by iron phthalocyanine-containing VPI-5,[14] have been reported. Extra-large-pore molecular sieve catalysis is not limited to liquid-phase conversions. Recently, we demonstrated the reactions of *n*-hexane over platinum-containing VPI-5 at temperatures as high as 525 °C,[15] and Martens et al. have isomerized decane over VPI-5-based catalysts at 250–450 °C.[16]

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Zeolite and Molecular Sieve Catalysis

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It is clear that the trend toward the catalytic application of larger pore molecular sieves is occurring and will continue to occur in the future.[13] As the size and dimensionality, e.g., unidimensional (VPI-5) vs tridimensional (NaX), of the pore system increase, the framework density (number of atoms per volume) declines. Brunner and Meier have shown that there appears to be a correlation between framework density and the smallest rings in the structure.[17] This correlation suggests that extra-large-pore structures with multidimensional pore systems may likely contain three-membered rings. (The reasons for desiring multidimensional pores can be found elsewhere.[11]) Annen has recently concentrated on this problem.[18] It appears that molecular sieves comprising zinc and silicon[18,19] may provide a viable route to obtaining very low density structures.

Base Catalysis with Zeolites

Zeolites are cation exchangers. Because of this, it is easy to make zeolites solid acids by substituting all cations with H^+. Shape-selective base catalysis is of great current interest. As a first thought, a molecular sieve that has a positively charged framework could provide a basis for producing a shape-selective base catalyst.

Pure silica molecular sieves are neutral, and it is the substitution of trivalent aluminum for tetravalent silicon that produces the negatively charged frameworks in zeolites. If silicon could be substituted with pentavalent phosphorus, then a positive framework may result. We investigated the atomic ordering of silicon, aluminum, and phosphorus in silicoaluminophosphate molecular sieves.[20,21] At no time is silicon in the second-coordination sphere of phosphorus (first-coordination sphere always oxygen.) We rationalized these arrangements according to Pauling's bonding rules.[22] Referring to Figure 2, tetrahedral silicon cannot form an oxygen bridge to tetrahedral phosphorus without violating bond strength concepts (bond strength on oxygen should not exceed 2). However, it is expected that octahedral silicon (very rare in oxides) can reside next to tetrahedral phosphorus. Since octahedral silicon is not observed in molecular sieves, a silicophosphate molecular sieve is unexpected. The atomic arrangements of silicon, aluminum, and phosphorus in oxide glasses have been inferred from NMR studies.[23] Interestingly, the results are fully consistent with the orderings observed in molecular sieves, and for the case where only silicon and phosphorus are used, octahedral silicon appears. Thus, it is unlikely that a zeolite-like material with a positive framework will exist.

Instead of forcing the oxide framework to accommodate the base site, alternatively a nonacidic molecular sieve could host guest materials that have basicity.
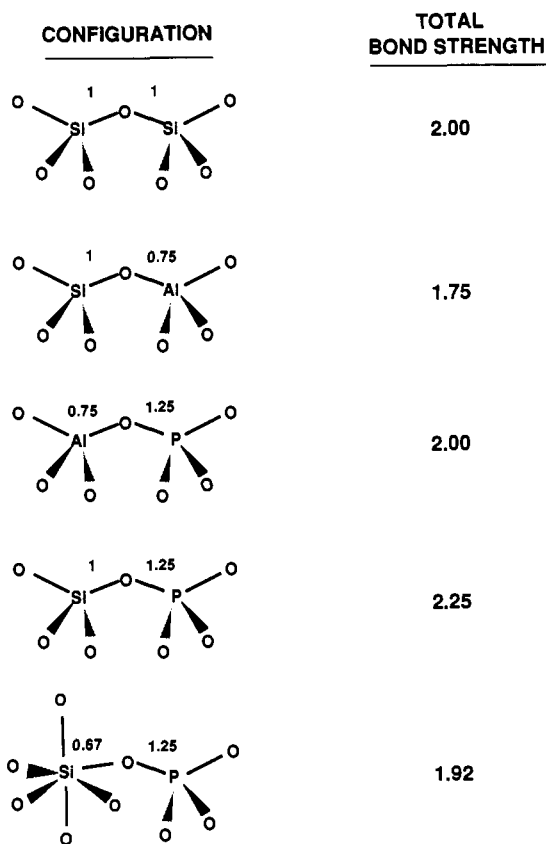

CONFIGURATION	TOTAL BOND STRENGTH
	2.00
	1.75
	2.00
	2.25
	1.92

Figure 2. Bond strengths on bridging oxygen atoms. From ref 1a.

Martens et al. formed metallic sodium particles in zeolites by the decomposition of occluded sodium azide.[24] These sodium zeolites are capable of performing base-catalyzed reactions. However, the materials are difficult to prepare and are oxygen sensitive. Hathaway and Davis synthesized nanophase cesium oxide within the pores of zeolites and showed that these air stable materials are excellent base catalysts.[25] Hathaway and Davis could not distinguish the catalytic properties of the cesium zeolite from cesium oxide. However, Tsuji et al. recently followed the synthesis procedure of Hathaway and Davis and found the cesium zeolite catalysts to be the first known alkali oxide to catalyze the isomerization of 1-butene at 0 °C (pure cesium oxide does not).[26] Therefore the cesium zeolite material is a solid superbase with the ability to perform shape-selective catalysis.

A very important example of base catalysis using zeolites has recently been reported by workers at Merck and Company.[27] The compound 4-methylthiazole (4-MT) is an intermediate in the synthesis of thiabendazole, which is used as a systemic fungicide.[28] The industrial route to 4-MT involves a multistep process that uses several hazardous chemicals (see Figure 3A).[27] Gortsema et al. report a new environmentally sound

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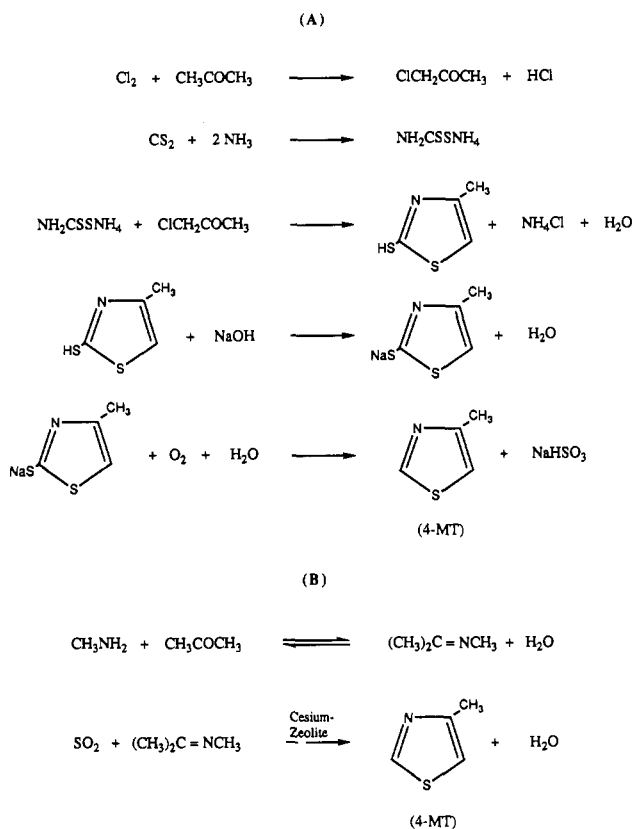
Figure 3. (A) Industrial route to 4-MT. (B) New Merck route to 4-MT. From ref 27.

method for preparing 4-MT (see Figure 3B) that involves the use of a zeolite catalyst to perform a base-catalyzed reaction. The key to success of this new route is the direct synthesis of 4-MT from SO_2 and the imine. This reaction is known to proceed over a base catalyst.[29] Gortsema et al. prepared cesium-loaded zeolites and demonstrated that these base catalysts gave excellent performance characteristics, e.g., activity, selectivity, and lifetime, for the synthesis of 4-MT. Also, the catalysts has been successfully prepared as extrudates and has been investigated through full scale pilot plant studies. There are two very important consequences of this work if this system is implemented at commercial scale. First, it will be the first example of a zeolite catalyst used for the production of a pharmaceutical, and second, it will be the first use of a zeolite to perform base catalysis.

Oxidation–Reduction Chemistries

As previously mentioned, zeolites normally perform acid-catalyzed hydrocarbon reactions. However, in 1983 Taramaso et al. described the synthesis of a titanium-containing zeolite,[30] and this ushered in the area of partial oxidation chemistries with zeolite catalysts. Subsequently, it was shown that titanium occupied framework positions in this material (denoted TS-1 (titanium silicalite-1)).[31] TS-1 is now used commercially to produce catechol and hydroquinone from

phenol and aqueous H_2O_2.[32] The mechanism of this reaction remains unknown although many features have been investigated.[33] TS-1 is a unique material in that it can catalyze a very broad spectrum of oxidation reactions, e.g., alkenes to epoxides, and alkanes to alcohols and ketones. Comparison studies on the oxidations of phenol, 1-alkenes, and n-alkanes are available.[34,35] Interestingly, although each reaction can be catalyzed by TS-1, the physicochemical properties of the catalyst affect each reaction differently. For example, only framework Ti is capable of catalyzing the oxidation of alkanes while framework Ti can work in concert with nanophase TiO_2 to oxidize phenol.[35] Little is known about the fundamental properties of this unique system. However, it is expected that this type of technology will be employed further in the future as aqueous H_2O_2 is expected to be less expensive[36] and greater environmental restrictions are mandated.

There has been no clear evidence that titanium can be incorporated into structures other than ZSM-5 (TS-1) and ZSM-11 (TS-2: very similar to ZSM-5)[33] until recently.[37,38] Titanium-containing ZSM-48 (pores smaller than ZSM-5)[37] and zeolite β (pores larger than ZSM-5)[38] have been reported to possess framework titanium. Thus, after about a 10-year period with no new titanium-containing structures, several are now appearing and should expand the types of catalytic chemistries possible with titanium zeolite catalysts.

Cobalt[39] and vanadium[40-42] zeolites have been synthesized and the vanadium-containing materials investigated as catalysts for high-temperature oxidation reactions. Likewise, cobalt[43-45] and vanadium[46] aluminophosphates have been synthesized. These heteroatom-substituted zeolites and aluminophosphates are very difficult to characterize because of the variety of possible locations, coordinations, and oxidation states of the transition-metal ions. It has been shown that cobalt residing in framework positions of aluminophosphates (Co^{2+} partially substitutes for Al^{3+}) can be reversibly oxidized to Co^{3+} (tetrahedral coordination) and reduced back to Co^{2+}; nonframework Co^{2+} cannot.[45] Thus, the oxide lattice stabilizes Co^{3+} in tetrahedral coordination. Likewise, framework V^{4+} can be reversibly oxidized to V^{5+} and reduced back to V^{4+} in

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aluminophosphates.[46] These examples reveal that isolated (single atom/one electron) redox centers can be formed within microporous environments. Very recently, Rigutto and van Bekkum successfully oxidized a series of liquid-phase organics, e.g., allyl alcohol, geraniol, toluene, and ethylbenzene, with *tert*-butyl hydroperoxide using a vanadium-substituted aluminophosphate catalyst.[47] Also, Rao and Ramaswamy recently reported the oxyfunctionalization of alkanes with aqueous H_2O_2 using vanadium-substituted puresilica ZSM-5.[42] Unlike TS-1, the vanadium catalyst oxidized primary carbons and toluene to benzyl alcohol. This fascinating difference between titanium- and vanadium-substituted pure-silica ZSM-5 demands further study.

Another recent application of zeolite catalysis for oxidation–reduction reactions is the decomposition of NO by copper-containing ZSM-5.[48,49] ZSM-5 that contains occluded copper is able to decompose NO in the presence of O_2. This exciting new catalyst system may be useful in future environmentally benign processes.

Asymmetric Catalysis with Zeolites

Enantioselective separations and syntheses are of great current importance. Unfortunately, the number of chiral solids that can perform enantioselective catalysis are very limited.[50] This is especially true for inorganic solids.

Recently, zeolite-supported, chiral rhodium complexes were reported to perform asymmetric hydrogenation of N-acyldehydrophenylalanine derivatives with enantioselectivities greater than 95%.[51] Clearly in this case, the enantioselectivity is derived from the metal complex.

Another approach to asymmetric catalysis is the preparation of a chiral zeolite. A chiral zeolite would be able to perform shape-selective, asymmetric, heterogeneous catalysis. To date no zeolite structure is chiral. However, Newsam et al. have shown that zeolite β is a highly intergrown hybrid to two distinct structures, the so-called polymorphs A and B, and polymorph A is chiral.[52] Polymorph A contains a three-dimensional pore system in which the pore along the c-direction of the crystal follows a 4-fold screw axis to define a helix (right- or left-handed: $P4_122$ or $P4_322$, respectively). Newsam et al. immediately recognized the consequences of this structure and stated that it might have potential for effecting chiral catalysis. Since then, we have shown that polymorph A of zeolite β is not unique in that many theoretical chiral zeolite structures can be derived.[1b]

Although theoretical, chiral zeolite structures can be generated, the real challenge is to synthesize a chiral zeolite. We have been attempting to synthesize pure polymorph A of zeolite β by introducing chiral organic
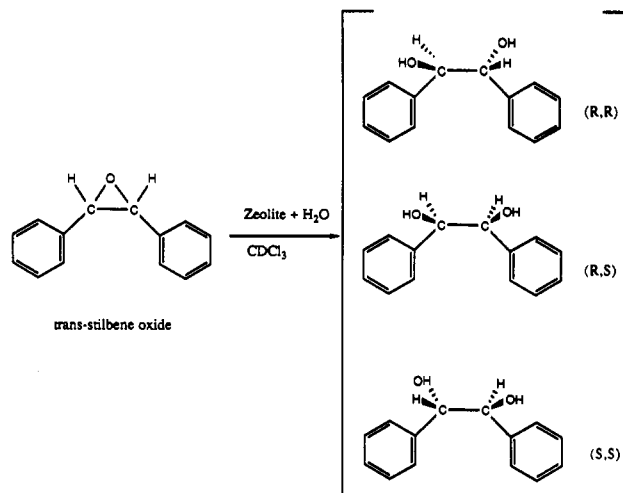

Figure 4. Reactions on zeolite β. From ref 1b.

molecules into the synthesis procedure of zeolite β with hopes of "templating" a chiral zeolite. We have successfully synthesized zeolite β "enriched" in the presence of polymorph A over that of normal zeolite β.[1b] In order to test whether enantioselective catalysis can be performed on this new material, the zeolite was placed in its acid form and contacted with *trans*-stilbene oxide and then water. The reaction products (see Figure 4) gave an enantiomeric excess (ee) of 5% ((R,R)-diol).[1b] "Normal" zeolite β produced an ee of 0. Additionally, a racemic mixture of the diols ((±)-hydrobenzoin) was slurried with the new material and "normal" zeolite β. The new material preferentially adsorbed the R,R isomer (ee again <5%) while "normal" zeolite β did not.[1b] Although the ee's from these experiments are low, they are nonzero and are outside the error limits of the experiments. These results suggest that a chiral zeolite can perform asymmetric catalysis.

It is important to point out that the discovery of transition-metal-catalyzed asymmetric reactions by Noyori and co-workers gave ee's of 10% or less for copper-catalyzed cyclopropanations of olefins.[53] Eventually, the ee's were improved to the point where this reaction is now used for the commercial production of cilastatin. The zeolite β sample we have synthesized is only slightly "enriched" in polymorph A. Thus, large ee's are not expected from this material. However, if an enantiomerically pure polymorph A can be synthesized, our work suggests that highly enantioselective catalysis may be possible with zeolites.

Summary

No longer are zeolite and zeolite-like molecular sieves restricted to performing acid or bifunctional (metal + acid) catalysis. The scope of reaction chemistries accomplished by zeolite catalysts has broadened into areas such as base catalysis, oxidation catalysis, and even asymmetric catalysis. These new vistas in zeolite and molecular sieve catalysis are likely to be implemented in the future for the synthesis of specialty chemicals and pharmaceuticals.

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