Very Large Pore Zeolites

Krista Finnie Literature Seminar January 30, 1997

In the early 1960's, the catalytic ability of zeolites was discovered, and found to be useful in a variety of areas, especially in the petroleum industry.[1] Since then, industry and academia both have endeavored to expand the body of knowledge on this class of compounds. The result of this effort has been the development of new properties and structures, as well as the development of new uses for these catalysts. One such recent development is the discovery of unusually large pore zeolites. These have the advantage that they can accommodate the larger organic molecules into their pores, but at the expense of selectivity. In order to combat this, industry has resorted to mixing the large pore zeolites with zeolites containing smaller pores. While this method works, the ideal situation would be a zeolite that is capable of both breaking down large organics while retaining the size and shape selectivity desired.

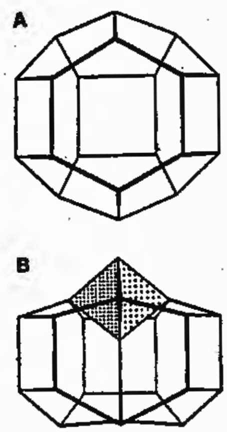

Figure 1

One such way to possibly accomplish this would be to have a zeolite with both types of pores. One such zeolite, MCM-22, has recently been synthesized by a group at Mobil.[2] The XRD pattern and the HREM images of this zeolite have revealed that the structure contains intralayer 10 MR sinusoidal channels as well as 12 MR interlayer cages with 10 MR windows. The topology has been shown to be similar to that of the dodecasil-1H zeolite, with related cage structures (Figure 1). The main difference being that of an additional tetrahedral atom buried inside of the cage. The two pore systems which are formed through the connection of these cages are completely independent, with no communication between them. The zeolite has also been analyzed by NMR and IR, to confirm and refine the proposed structure (Figure 1).[3] This unique structure has the potential for interesting catalytic abilities.

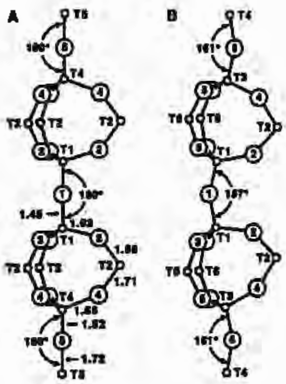

Figure 2

One such test of the catalytic abilities of this zeolite is the isomerization of 1-butene to isobutene.[4] This particular conversion would be useful for isobutene is one of the raw materials used in making gasoline additives. The factors in this test are acidity of the catalyst and geometric restrictions within the pore system. Tests showed that this catalyst remained active for an extended time, with good selectivity to isobutene. The selectivity of the catalyst improved as coking occurred, thereby reducing the number of strong acid sites and the effective free space within the pore system.

Another catalytic study which has been performed is that of isobutane/2-butene alkylation.[5] Addition of alkylation gasoline to the gas pool is one method that has been found to bring gas into compliance with recent regulations. Results of these tests have shown that at high conversions, TMP's make up a large part of the products, however, the catalyst ages rapidly, dropping to 10% after only 15 minutes. This, however, is typical of zeolites, and MCM-22 ages at the same rate as other zeolites.

The catalytic abilities of MCM-22 have also been compared to ZSM-5 and Beta.[6] This test compared the para /ortho-xylene ratio and the isomerization/disproportionation ratio for MCM-22 with other zeolites. These results place MCM-22 between that of 10 MR and 12 MR zeolites, a finding which is consistent with the proposed structure. The other catalytic test, hydroisomerization of n-decane examined the products on the basis of steric bulk. One parameter placed MCM-22 in the category of the 12 MR, while the other parameter suggested 10 MR behavior.

With the catalytic abilities of MCM-22 well established, future work in this area requires building off of this knowledge. One area this can be accomplished is by further investigating a recently synthesized zeolite, MCM-49, which has shown to have a similar structure, before calcination.[7] Another interesting development is the recent synthesis of a silica polymorph of MCM-22.[8] Such a material should have useful properties as a FCC additive. Expansion of these new developments, as well as MCM-22, into industry also needs exploration.

References

1. Dyer, A., An Introduction to Zeolite Molecular Sieves, John Wiley & Sons, New York, 1988, 1-3, 12-51.

2. (a) Leonowicz, M.; Lawton, J., Lawton, S.; Rubin, M., "MCM-22: A Molecular Sieve with Two Independent Multidimensional Channel Systems," *Science*, **1994**, *264*, 1910-1913. (b) Corma, A.; Corell, C.; Perez-Pariente, J., "Synthesis and Characterization of the MCM-22 Zeolite," *Zeolites*, **1995**, *15*, 2-8.

3. (a) Kolodziesjski, W.; Zicovich-Wilson, C.; Corell, C.; Perez-Pariente, J.; Corma, A., "^{27}Al and ^{29}Si MAS NMR Study of Zeolite MCM-22," *J. Phys. Chem*, **1995**, *99*, 7002-7008. (b) Corma, A.; Corell, C.; Fornes, V.; Kolodziejski, W.; Perez-Pariente, J., "Infrared Spectroscopy, Thermoprogrammed Desorption, and Nuclear Magnetic Resonance Study of the Acidity, Structure, and Stability of Zeolite MCM-22," *Zeolites*, **1995**, *15*, 576-582. (c) Hunger, M.; Ernst, S.; Steuernagel, S.; Weitkamp, J., "High-field 1-H Mas NMR Investigations of Acidic and Non-acidic Hydroxyl Groups in Zeolites H-Beta, H-ZSM-5, H-ZSM-58 and H-MCM-22," *Microporous Mat.*, **1996**, *6*, 349-353. (d) Kennedy, G.; Lawton, S.; Rubin, M., "^{29}Si MAS NMR Studies of a High Silica Form of the Novel Molecular Sieve: MCM-22," *J. Am. Chem Soc.*, **1994**, *116*, 11000-11003.

4. Asensi, M.; Corma, A.; Martinez, A., "Skeletal Isomerization of 1-Butene on MCM-22 Zeolite Catalyst," *J. of Catalysis*, **1996**, *158*, 561-569.

5. Corma, A.; Martinez, A.; Martinez, C., "Isobutane/2-Butene Alkylation on MCM-22 Catalyst. Influence of Zeolite Structure and Acidity on Activity and Selectivity," *Cat. Letters*, **1994**, *28*, 187-201.

6. (a) Corma, A.; Corell, C.; Perez-Pariente, J.; Guil, J.; Guil-Lopez, R.; Nicolopoulos, S.; Calbet, J.; Vallet-Regi, M., "Adsorption and Catalytic Properties of MCM-22: The Influence of Zeolite Structure," *Zeolites*, **1996**, *16*, 7-14. (b) Corma, A.; Corell, C.; Llopis, F.; Perez-Pariente, J., "Proposed Pore Volume Topology of Zeolite MCM-22 Based on Catalytic Tests," *App. Cat. A*, **1994**, *115*, 121-134. (c) Souverijns, W.; Verrlst, W.; Vanbutsele, G.; Martens, J.; Jacobs, P., "Micropore Structure of Zeolite MCM-22 as Determined by the Decane Catalytic Test Reaction," *J. Chem. Soc., Chem. Commun.*, **1994**, 1671-1672.

7. Lawton, S.; Fung, A.; Kennedy, G.; Alemany, L.; Chang, C.; Hatzikos, G.; Lissy, D.; Rubin, M.; Timken, H.; Steuernagel, S.; Woessner, D., "Zeolite MCM-49: A Three-Dimensional MCM-22 Analogue Synthesized by *in Situ* Crystallization," *J. Phys. Chem*, **1996**, *100*, 3788-3798.

8. Camblor, M.; Corell, C.; Corma, A.; Diaz-Cabanas, M.; Nicolopoulos, S.; Gonzales-Calbet, J.; Vallet-Regi, M., "A New Microporous Polymorph of Silica Isomorphous to Zeolite MCM-22," *Chem. Mater.*, **1996**, *8*, 2415-2417.