



CHAPTER 4

PREPARATION OF ISOPROPANOL SYNTHESIS CATALYSTS

4.1 General Knowledge of Isopropanol Synthesis Catalysts

Isopropanol has been produced via hydration of propylene with zeolites as catalyst. Several generations of catalysts have been developed. Here we have selected three types of zeolites as catalyst. One was mordenite (studied by W.Tanthapanichakoon) and the others were offretite/erionite and NaY.

In 1972, Leonard reported in his study of the hydrothermal reaction between feldspars and alkali carbonates that mordenite was formed in 7 days at 200°C and at 15 atm pressure. He also claimed to have prepared a phillipsite-type zeolite at 350°C from feldspars in the presence of fluorides and superheated water vapor at atmospheric pressure. Although Leonard was one of the first to use x-ray powder data to characterize the products, they were not unambiguously identified.

The first substantiated synthesis of a mordenite-type zeolite was made by Barrer. An aqueous sodium aluminate solution, which contained sodium carbonate, was stirred into an aqueous suspension of silicic acid gel containing some dryness at temperature below 110°C, thereby producing, when certain proportions were used, a gel of chemical composition similar to that of mordenite. Crystallization was accomplished by heating the gel with water in an autoclave at temperature up to 300°C. Although an alkaline medium is necessary to crystallize mordenite, in strongly alkaline solution the crystals which first precipitated tended to dissolve and convert to

other unidentified species when left in contact with the mother liquor at high temperatures. At a pH of between 7 and 8 crystallization was retarded and the crystals which formed were fewer and smaller.

Mordenite, with a nearly constant ratio, indicates an ordered distribution of Si and Al in the framework structure.

The structure consists of chain crosslinked by the sharing of neighboring oxygens. Each tetrahedron belongs to one or more 5-member rings in the framework. The high degree of thermal stability shown by mordenite is probably due to the large number of 5-member rings which are energetically favored in terms of stability. For the diffusion of small molecules, the dehydrated zeolite has a two-dimensional channel system but for larger molecule the channel system is one dimensional and may be subjected to diffusion blocks produced by crystal stacking faults in the presence of amorphous material or cation in the channels. Gases such as nitrogen and oxygen are rapidly adsorbed by dehydrated mordenite, whereas hydrocarbons such as CH_4 or ethane are slowly adsorbed. This is inconsistent with the channel dimension of 6.7 Å. Because the main channel system is in one direction, any blockage will completely shut off the main channel. A synthetic type of mordenite, known as "large port" mordenite has been prepared which exhibits the adsorption characteristics expected for the free diffusion of molecules in the main 6.7 Å diameter channel. The extraneous matter which is assumed to block the main channels in the mineral is apparently not present in this synthetic form. Synthetic types of mordenite of the small-port variety can be partially converted to the large-port by acid leaching. This treatment presumably remove the extraneous matter and open up the main channels

Offretite/erionite has a hexagonal structure consisting of parallel arrangements of the $(\text{Al, Si})_6\text{O}_{12}$ rings. In order to diffuse from one cavity to another, molecules must pass through an 8-member ring aperture into an adjacent cavity in the original column. Continuous diffusion paths are available for molecules of appropriate size. Offretite/erionite readily adsorbs normal hydrocarbons which have a minimum kinetic diameter of 4.3 Å

The Kinetic Diameter

For spherical and nonpolar molecules, the potential energy of interaction, $\phi(r)$ is well described by the Lennard-Jones potential

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

The parameters σ and ϵ , are constants which are characteristic of the molecular species and are determined from the second virial coefficients. At large separation the attractive component, $(\sigma/r)^6$, is dominant and describes the induced dipole-induced dipole interaction. At small separations the repulsive component is dominant. When the potential equal to 0 the diameter, r , is equal to σ . The kinetic diameter is the intermolecular distance of closest approach for two molecules colliding with zero initial kinetic energy. The maximum energy of attraction, ϵ , occurs at $r_{\text{min}} = 2^{1/6}\sigma$.

In assessing the apparent pore size of molecular sieve zeolites, the critical dimensions for spherical molecules are given by the value of r_{min} . For diatomic molecules, r_{min} is based upon the van der Waals length, and represents the molecule in all orientations. For long molecules, such as hydrocarbons, the dimension is the minimum

cross sectional diameter. It is preferred to use values, where available, for nonpolar spherical molecules and values, obtained from minimum cross-sectional diameter for more complex molecules.

Typical crystals of erionite are fibrous. Unlike other fibrous zeolites, however, dehydrated offretite/erionite has a very stable framework structure. Specimens of offretite/erionite exposed to H₂O vapor at 375°C over a long period of time showed essentially no change in adsorption capacity, which confirms a high degree of structural stability.

Zeolites Y are prepared by using a colloidal silicasol or amorphous silica as the silica source. Additional zeolites are formed which do not readily crystallize from the homogeneous sodium silicate-aluminosilicate gels. When an aqueous colloidal silica sol is employed as the major source of silica, the SiO₂ content of the starting reaction mixture is higher than that normally employed in the case of the other sodium zeolites. Typically for zeolite Y, the composition ranges within the limit as follows: Na₂O/SiO₂ = .4-.6, SiO₂/Al₂O₃ = 15-25 and H₂O/Na₂O = 20-50

It appears that the gel prepared from the colloidal silica sol is heterogeneous on a molecular scale and contains a hydrous aluminosilicate phase together with a solution. After the initial gel formation, an aging step is necessary in order to equilibrate the heterogeneous gel mixture with the solution. Room temperature equilibration or aging reduces the SiO₂/Al₂O₃ ratio in the gel necessary to form zeolite Y which has composition: Na₂O/Al₂O₃ = 1, SiO₂/Al₂O₃ = 3-6, H₂O/Al₂O₃ = 9.

4.2 Preparation of isopropanol synthesis catalyst

Catalysts used for isopropanol synthesis can be divided as follows

1. Na-mordenite (TSZ-640 NAA) containing these metal oxides, SiO_2 , Al_2O_3 , Na_2O , with mole ratio $\text{SiO}_2/\text{Al}_2\text{O}_3=20.3$
2. Offretite/erionite (TSZ-410KOA) containing four metal oxides, SiO_2 , Al_2O_3 , Na_2O , K_2O with mole ratios, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 7.7$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.25$ and $\text{K}_2\text{O}/\text{Al}_2\text{O}_3 = 0.78$
3. Na-Y containing these metal oxides, $\text{SiO}_2 = 66.7 \%$, $\text{Al}_2\text{O}_3 = 20.3 \%$, $\text{Na}_2\text{O} = 12.3 \%$ by wt., $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.6$ by mole.

The catalysts were obtained from Chemical Research Laboratory of Toyo Soda Manufacturing Co., Ltd., in Japan Since they obtained in the Na form, we must ion-change them to the H-form the procedure was as follows.

1. Prepare 1 litre of 1-Molar NH_4NO_3 solution.
2. Add 3 gm of the catalyst powder of interest to 45 ml of the 1-Molar NH_4NO_3 solution.
3. Heat the mixture on the hot plate and stir continuously at 80°C for 2 hours.
4. Take out the mixture and centrifuge for 10 minutes to separate the catalyst from the liquid solution.
5. Wash the catalyst with distilled water (50 ml) and centrifuge out the catalyst for 10 minute. Repeat several times.
6. Pour 45 ml of 1-Molar NH_4NO_3 solution in the catalyst and repeat step 3 to step 5.
7. Dry the catalyst in an oven at 120°C for 24 hours.
8. Calcine the catalyst for 15 hours by heating in atmospheric air at approximately 500°C .

To use in the experiment, the catalyst was weighed and then compressed to obtain a pellet with density of 0.866 gm/1cc. The pellet was next cut up and screened to select fragments of size between mesh # 10 and # 15. Then classified fragments were packed into the middle section of reactor for isopropanol synthesis.



Figure 4.1 Set of Ion-changing for Isopropanol Synthesis Catalysts.

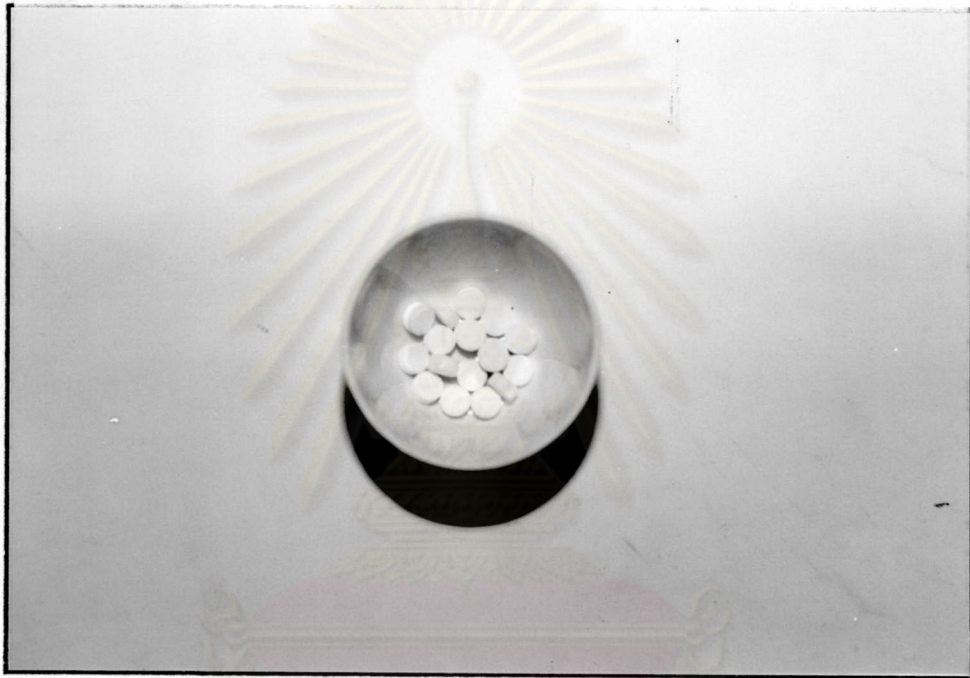


Figure 4.2 Pellet Catalysts after Compressed.

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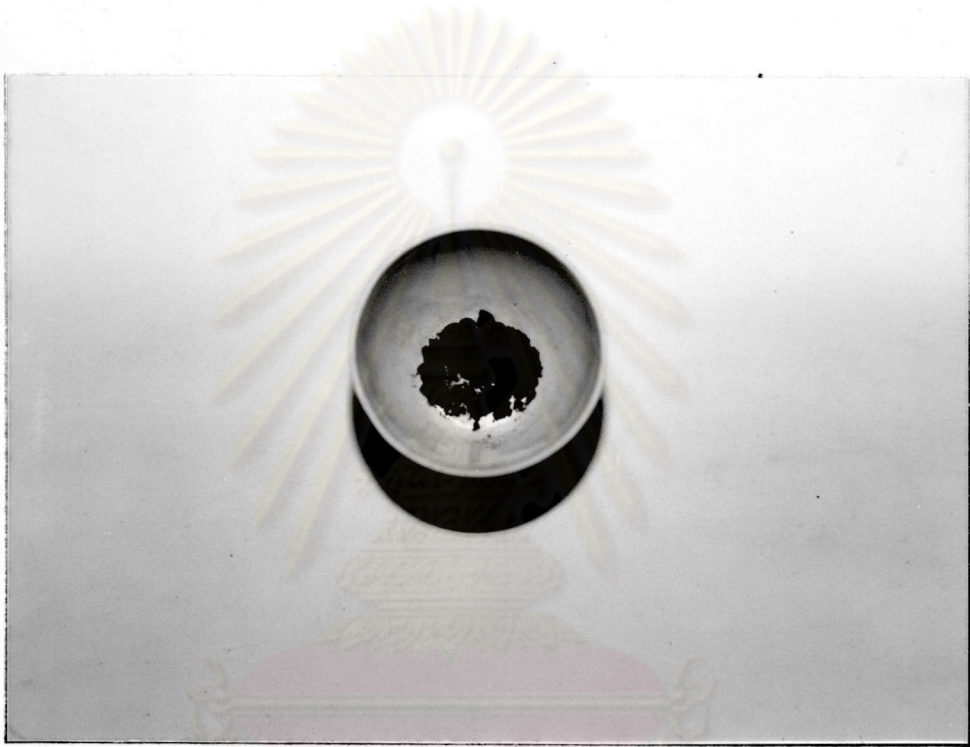


Figure 4.3 The Reacted Catalyst.

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