

CHAPTER III

ZEOLITE CATALYSTS

3.1 General Methods of Catalyst Preparation

3.1.1 Scope and Goals (52)

The goal of this section is to present a lucid and accurate picture of catalyst preparation. It is a further goal of this section to give information which will make it possible for someone skilled in catalytic science to prepare a given catalyst, either in laboratory, semi-works or commercial scale. It, of course, will be impossible to give information for all types of catalysts but it is the intent to give the procedures for all those which are comparatively well known to the practicing catalytic scientist.

The art of catalysis includes a very extensive "know How" of the procedures and experimental techniques employed in the preparation of solid catalysts. The chemical and physical properties of a catalyst are determined by the total history of its preparation. To obtain active catalysts it is important to use established procedure and experimental techniques.

A great many catalysts can be prepared in a variety of ways, while a small number can be prepared in only a very highly specialized manner. The various methods of catalyst preparations may generally be considered as combinations of certain unit operations. The preparative procedures are first given in block outline form and show in Figure 3.1, Figure 3.2, and Figure 3.3

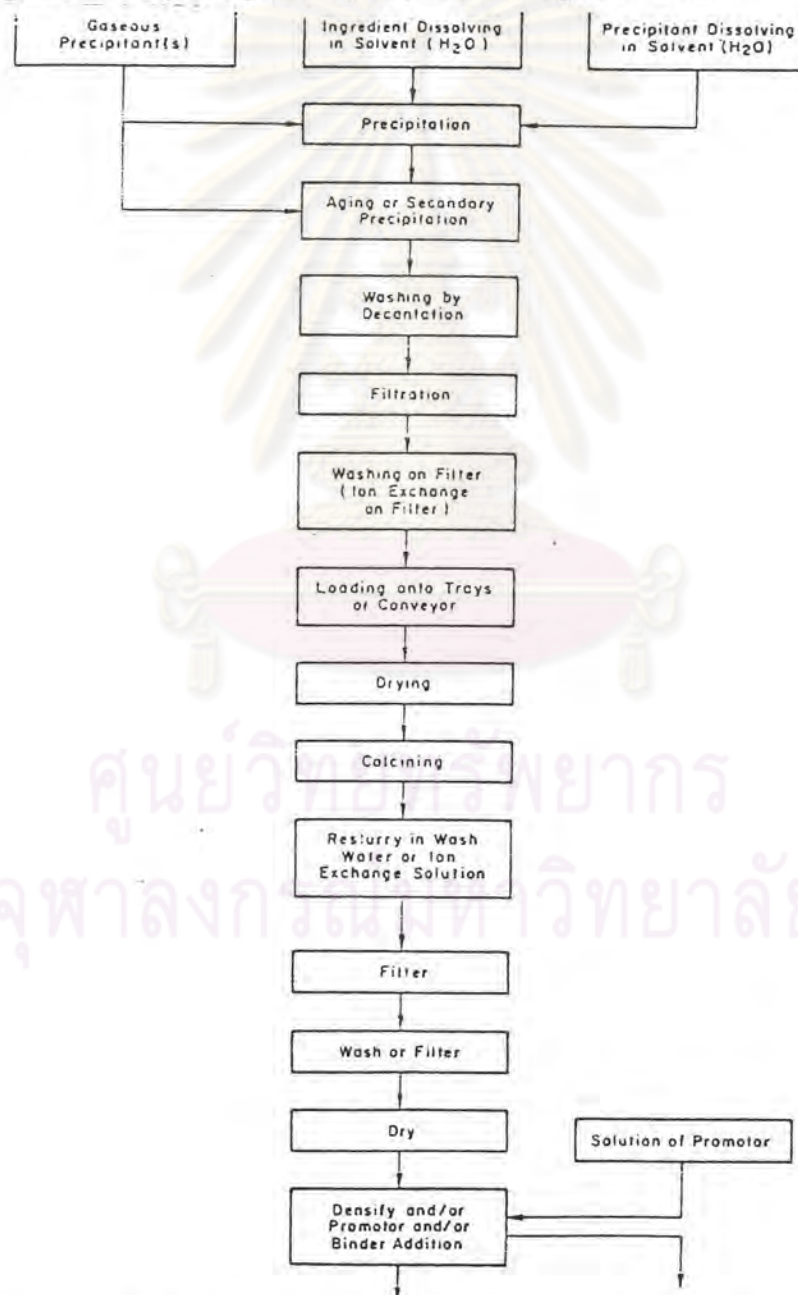


Figure 3.1 Precipitated catalysts flow sheet (52)

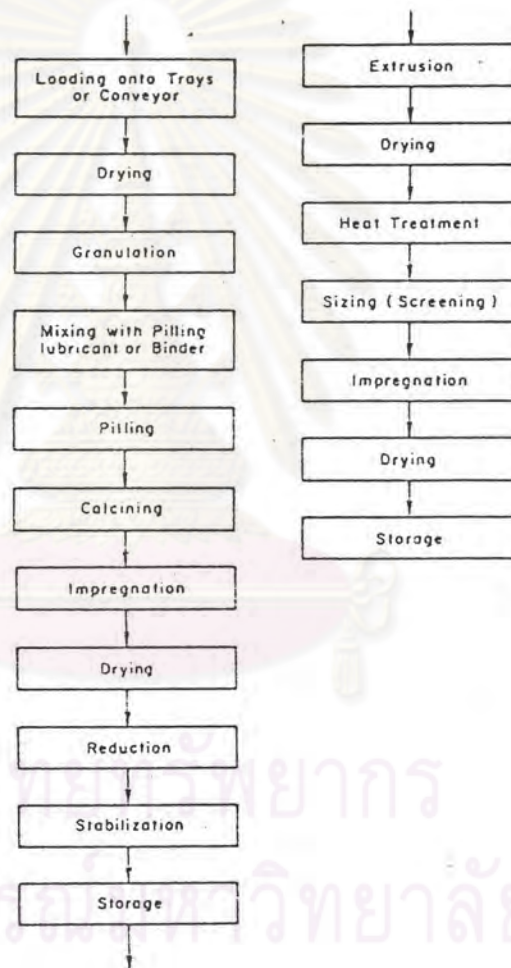


Figure 3.1 (Continued)

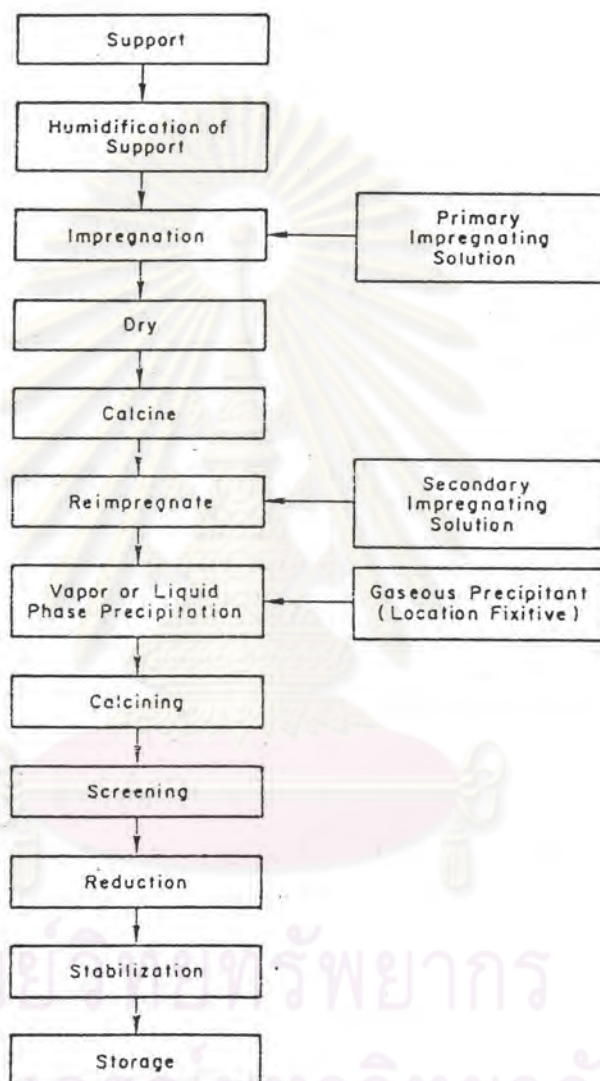


Figure 3.2 Impregnated catalysts (52)

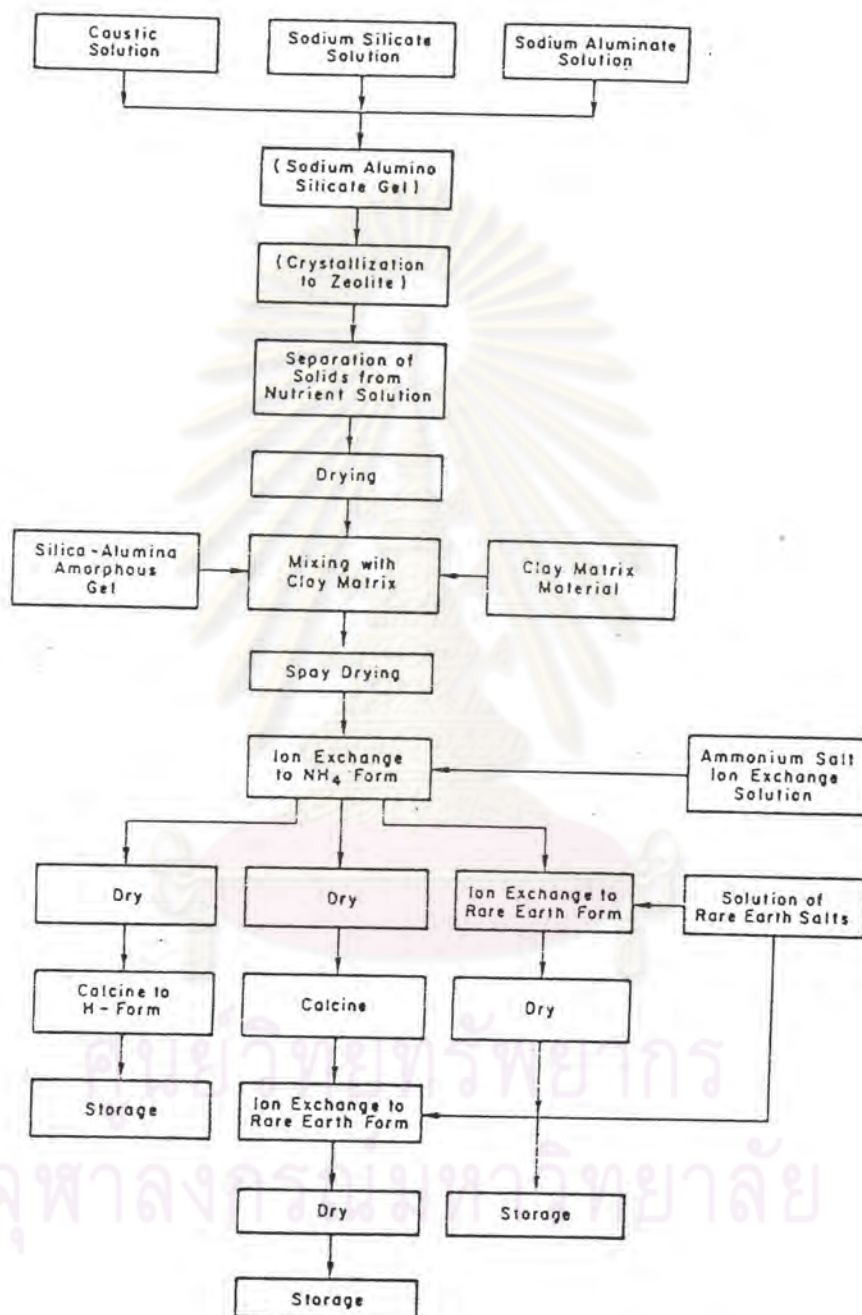


Figure 3.3 Zeolite (fluid cracking) catalysts (52)

The unit operations most frequently involved will be discussed. The actual choice of methods may be guided by ease of preparation, homogeneity of the product, stability of catalyst and ease of duplication. Before going into the preparation of olefin synthesis catalyst, we shall review here the general methods of catalyst preparation.

3.1.2 Precipitation and Gel Formation Methods (53)

These two methods are treated together because they are very closely related chemically. However, the physical characters of the product are usually widely divergent. The phenomena of gelation is a special aspect of precipitation which depends upon the lyophilic properties of the precipitate and the rate of precipitation. A great many hydrous oxides are of interest either as catalysts or catalyst supports, and many of them are amenable to gel formation.

It has often been stressed that the specific details of the preparation of a given catalyst composite are of the utmost importance. Said details may give rise to all-important properties of specificity and stability. However, in spite of the physical differences which show up in catalysts of a given composition when cogelled or coprecipitated, it has frequently been found that the catalytic properties of such products are quite similar. Nevertheless, even when preparing compositions for which



the latter condition holds, there are certain practical advantages to using cogelation techniques. Some of these will be pointed out in the detailed discussions of the compositing methods.

i) Precipitation This method is frequently employed in the preparation of single-and multiple-component catalysts. Precipitation techniques are applicable to materials such as the hydrous oxides, sulfide, carbonates, and phosphates. In general, one starts with aqueous solutions of the desired constituents and adds the required precipitating agent. On a commercial scale, use of aqueous solutions would probably be an economic necessity. However, for tench scale work nonaqueous solutions may be used when advantageous.

One of the primary problems arising in the preparation of a precipitated catalyst is that of purification from occluded or absorbed impurities. One way in which to minimize the presence of such impurities is to carry out the precipitation by mixing very dilute solutions. Another method of minimizing the problem is to use ammonia or ammonium salts as the precipitates alone with nitrates of the desired metals. The resulting precipitate then requires a minimum of washing, since any adsorbed material remaining can be removed by calcination of the product.

The use of nitrated as the source of the desired cations is recommended as a general rule unless otherwise specified. The reason for this is the fact that other anions (e.g., chloride or sulfate) sometimes act as catalyst poisons, if they are present in the final product, for example chloride in precipitated iron catalysts for the Fischer-Tropsch synthesis.

In the case of coprecipitation of two or more components, it is generally desirable to maintain the greatest possible degree of homogeneity in the product. Since normally the solubility products of the constituents are divergent, it is possible to obtain a decidedly heterogeneous product. Such a situation would exist, for example, if one were to add a solution of aqueous ammonia to a solution of two metal nitrates to coprecipitate the two corresponding hydrous oxides. The ammonia would tend to precipitate first one hydroxide then the other. On the other hand, reversing the procedure by adding the solution of the two nitrates to the ammonia solution would tend to give simultaneous precipitation of the two hydrous oxides. It is true that in the latter procedure the pH would change continuously throughout the process of precipitation. If a constant pH is desired the method would have to be modified. To achieve the goal of precipitating at a constant pH it may be necessary to bring together two streams of the reacting solutions in such proportions as to maintain the desired pH.

Alternatively, it is possible to maintain homogeneity of a two-component precipitate by dissolving one of the reactants in an acid solution and the other in a basic solution. For example a silica-alumina coprecipitate may be made by mixing dilute solution of aluminium sulfate (with added acid, if desired) and sodium silicate (water glass).

It is frequently desirable to increase the surface area of the product by precipitating the catalytic material on a support material. The method involves a combination of various catalyst preparation technique as will be discussed subsequently.

The experimental set-up shows in Figure 3.4

ii) Gel Formation. This particular method of catalyst preparation is especially suited to those catalysts whose major components are hydrous oxides. In particular those containing primarily silica or alumina are especially amenable to gel formation. The phenomenon of gel formation is, as mentioned, merely a special case of precipitation. Therefore preparation of a catalyst composite in gel form rather than as a coprecipitate does not necessarily result in a change in specific catalytic activity. However, even when no such change occurs, there are frequently major physical advantages to gel formation. Specifically, the disadvantages inherent in processing

the highly gelatinous precipitates are eliminated. As a result the gel-formed catalyst is usually considerably easier to prepare. In addition, by the very nature of the process, maximum homogeneity in the polycomponent composites will be produced by gelation

The general conditions required for gelformation were described long ago by Van Weimarn. However, for any particular gel, it is usually necessary to specify the conditions very closely. Gels may be prepared not only in aqueous media but also in nonaqueous and mixed media. For example, alcoholates prepared from the various metal chlorides may be dissolved in alcohols and geled either in the alcoholic or alcohol-water media. Certain gels such as those of magnesia and $\text{Cd}(\text{OH})_2$ or $\text{Zn}(\text{OH})_2$ are prepared most easily as organo-gels.

Several examples of gel preparation will be described in detail later in the discussion on specific catalyst preparations. However, it should be pointed out that, as a last resort when other methods of gel formation fail, it is usually possible to form a gel by a dialysis method.

3.1.3 Impregnation Methods

The technique of impregnating an active component (or components) on an inactive support is frequently the simplest possible method of producing a catalyst.

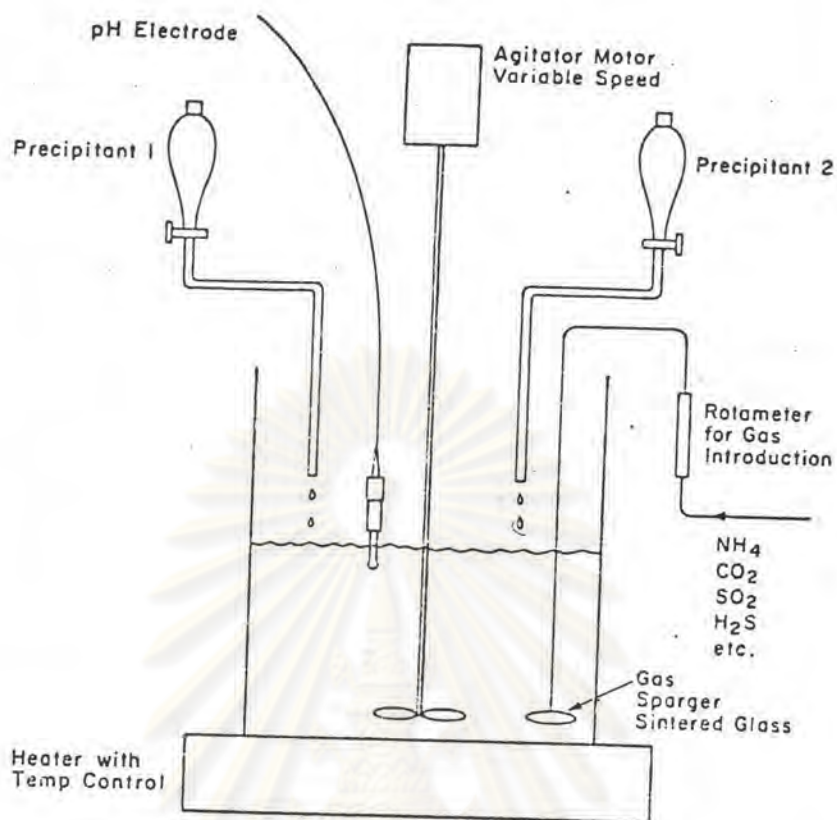


Figure 3.4 Laboratory precipitated catalyst preparation set-up (52)

However, as already stated, a number of complicating factors arise even in such a simple method of preparation.

Impregnation of a support normally involves the use of a soluble compound of the desired constituent dissolved in a liquid, which is usually water. It is also possible to perform a vapor phase impregnation of the support if one can find a volatile compound of the desired constituent. Impregnation by a solution may be carried out on either dried porous supports or on undried

precipitates or gels, In the case of dried support is usually preferred since it eliminates pelleting or extrusion of the finished catalyst.

i) Impregnation of Granular Supports. In its simplest form this method of catalyst preparation may involve the following steps:

- (1) evacuating the support
- (2) contacting the support with the impregnating solution
- (3) removing the excess solution
- (4) drying
- (5) Calcination and activation

Frequently it is necessary to add a precipitation and washing step either before or after drying. In addition, it is generally desirable to obtain preliminary information regarding the equilibrium distribution of the solution between the solid support and the impregnating solution. Such information is necessary to establish the quantity and concentration of the impregnating solution required to obtain the desired concentration of the active component on the support.

Evaluation of the support prior to contacting it with the impregnating solution gives more uniform distribution of the active component. Frequently, trapped air in the pores of the support prevents complete

penetration of the solution. In many cases, this step is unnecessary, provided sufficient time of contact between the support and impregnating solution is allowed. Under certain circumstances it may not be desirable to use a prolonged contact time, e.g., when the support can be hydrolyzed. Thirty minutes to an hour is sufficient time to obtain uniform wetting of the support. An excess of impregnating solution is usually used. Removal of this excess solution can be accomplished by either filtration or decantation. Centrifuging is an effective method of removing liquid between the solid particles.

In several cases, the use of excess impregnating solution is undesirable. In these instances enough solution is added to completely wet the support. This can be done by spraying the solution on the support while it is tumbled in a rotating bottle.

Whether a precipitation step is necessary or not depends on the nature of the impregnating compound. If no undesirable component remains after simple calcination, e.g., as in the case of nitrates or ammonium salts, no precipitation will be required. However, if the impregnating compound involves an undesired component in the final product, it is probably necessary to precipitate the desired constituent and then to wash out the undesired material. For example, a cracking catalyst may be prepared by impregnating silica gel with aluminium

sulfate. Since sulfate is not desirable in the final product, it is necessary to precipitate the aluminium as the hydrated oxide by adding ammonia. The sulfate ion is then removed by washing.

ii) Impregnation of Powdered Supports. Powdered catalyst supports may be impregnated in a manner entirely analogous to that described for granular supports, with the additional steps of pelleting or extruding to form the final particles. Whereas one normally does not impregnate a granular support with a substance which will be precipitated by the support, it may be advantageous to do so with powdered supports. A procedure of this type would, of course, result in the active material on the external geometric surface of the particles rather than distributed throughout the catalyst pores. Occasionally, this may be used where the active component is expensive and high area is not important.

iii) Vapor Phase Impregnation. Under certain circumstances, the simplest method of preparing a catalyst having the desired degree of purity may be to deposit the active material on a support from a vaporized source. Such a method has been employed in the n-butane isomerization process developed jointly by the Anglo-Iranian Oil Co. and the Standard Oil Development Co. In this process the reactor is charged with a low-iron content bauxite ("Porocel"). At the start, a stream of

hot butane is first contacted with AlCl_3 and then passed over the bauxite. When sufficient AlCl_3 has been deposited on the support, hydrogen chloride is added to the incoming n-butane and the charge is passed directly to the reactor. As the catalyst activity decreases, additional amounts of AlCl_3 are intermittently deposited on the bauxite using the hot butane as a carrier.

An analogous process for maintaining the activity of an alumina-boria cracking catalyst. The variation involves passing an admixture of setam plus boric oxide with a hydrocarbon cracking charge over the alumina-boria catalyst. This catalyst is prepared initially by a simple impregnation technique. The catalyst loses boria rapidly in operation. Thus, the process serves to maintain the boria content and, therefore, the activity, much more nearly constant.

iv) Wet Mixing of Catalyst Components. One technique of catalyst preparation frequently used is that of wet-mixing two or more components. The components may be hydrogels or hydrous precipitates or they may be dried materials, or both. Ball milling of the components represents the simplest technique for the preparation of small batches of catalysts. For example, Bailie and See prepared an active silica-magnesia cracking catalyst by ball milling finely divided magnesia with a washed silica hydrogel.



3.1.4 Processing Operations

i) Washing. The object of the washing step is primarily to remove impurities from the catalyst. For this reason many impregnated catalysts need not be washed. These materials usually involve decomposable compounds whose solid decomposition products are desired on the catalyst and whose gaseous products disappear. When working with precipitates or gels, washing is usually essential.

Washing techniques vary to a great extent the method is as follows. The hydrogel is either formed originally in bead form or cut into blocks after gelation. The beads or block are placed in a large Buchner funnel which is closed at the bottom with a stopper. Using this simple apparatus, a batch-type washing operation is carried out. Washing is discontinued with the concentration in the filtrate at the end of a when period. This concentration is usually defined by addition of a counter-ion in sufficient quantity to precipitate the undesired ion when present in the filtrate above the prescribe limit. In the washing of certain hydrogels, such as zirconia, peptization is so serious that the temperature of the wash water must be controlled, for example, that zirconia gels must be washed at temperatures not lees than 60°C.

The procedure just described probably represents the simplest possible washing method. However, as previously mentioned a great majority of catalysts cannot be formed as gels. Precipitates are washed most efficiently by slurring the filter cake in a large volume of water (usually 5 to 10 times the volume of the cake) with vigorous stirring. The slurry is then filtered in a large Buchner funnel. The washing technique is repeated until the concentration of the contaminating ions in the filtrates, as determined by the addition of a counter-ion, is very low. When the precipitate peptizes on washing, the addition of a small amount of ammonia to the wash water helps to prevent the peptization. Elkin et al. have described such a technique in the preparation of alumina. If the products are to be pelleted, some workers prefer to oven dry the precipitates before washing them.

It should be mentioned that when a coprecipitate possesses zeolitic properties, washing alone will probably not be sufficient to remove all contaminating ions. In this case an ion-exchanging operation will be required prior to washing. Such a situation arises in the preparation of cogelled silica-alumina cracking catalysts. These are exchanged with NH_4^+ or Al^{3+} ions prior to washing. A number of oxide combinations possess zeolitic properties. For example, that silica-zirconia gels may possess considerable base exchange capacity. Thus, the observation that the wash water shows no contaminating

ions is no proof that the precipitate is no proof that the precipitate is also free from that contaminate. This can only be proved by analysis.

ii) Drying. In the preparation of industrial catalysts the drying operation is frequently a complicated one. Many patents have been granted on specialized drying techniques for particular catalytic products. However, in general, these closely controlled operations are used to insure certain desired physical characteristics in the products. They are not usually important to the chemical and catalytic properties of the catalyst. Of course, extreme changes in physical properties should be avoided as they may change the catalytic properties.

Usually drying is carried out in air, in laboratory electric or steam ovens. The temperatures used vary from possibly 60 to 200°C. If one is not concerned with the structural qualities of his product he could use practically any temperature within this range. A safe working would be from 100 to 150°C. Higher drying temperatures may result in severe fracturing of the gel particles so that, the product can not be tested without being pelleted.

Certain catalysts like Raney nickel or colloidal platinum used for low temperature hydrogenation are not dried at all.

iii) Catalyst Forming or Sizing. The ultimate end of a catalyst preparation is its use in a catalytic reactor. Recently, attention has been focused on the problem of diffusion, particularly in connection with catalysts having surface area and small pores. Some scientists have stressed the importance of this factor in catalytic reaction. Hence, it is important to insure freedom from diffusion limitations by sizing of the catalyst.

If properly handled, many of the gelled and precipitated catalysts can be obtained as hard lumps after drying. Grinding and sieving to the proper mesh size are the only operations required prior to calcination and activation. For most small scale testing of catalysts in fixed bed reactors, particle sizes between 6 and 30 mesh are used. The size range is normally defined in terms of the Standard Screen Scale. During the sieving operation catalyst fines which cause large pressure drops through a catalyst bed are eliminated. The shrinkage factor on calcination should be considered in sizing the dried catalyst.

If the dried catalyst crumbles to a powder, or its structure is too weak to withstand the grinding or sieving operation, pelleting or extrusion is required. These latter operations require specialized equipment and knowhow to obtain the catalyst in the desired shape and size.

iv) Calcination and Activation. Calcination and activation take several forms depending on the type of catalyst being prepared. These steps represent the final operations in catalyst preparation. In general, the dried catalyst is calcined and activated at temperatures at least as high as those used in the reaction. This treatment is carried out while a large volume of purge gas is passed through or over the catalyst to maintain a low partial pressure of the evolved vapors.

The hydrous oxide catalysts prepared by the techniques previously discussed require only a calcination treatment at temperature of 350 to 750°C. For example, the activity of silica-alumina cracking catalysts is stabilized by heating in an inert or air atmosphere at approximately 650 to 750°C. The calcination may be carried out in a catalytic reactor or in a muffle furnace. If a muffle furnace is used, the catalyst should be placed in a shallow bed to insure uniform treatment.

Catalysts which are to be used for hydrogenation or dehydrogenation reactions are calcined and activated in a reducing atmosphere. Nickel, Cobalt, iron, or copper catalysts are prepared by reduction of the corresponding oxides in a hydrogen atmosphere at 300 to 500°C. The initial activity of these metallic catalysts, as well as those of platinum and palladium, is a function of the extent of reduction and the temperature used. For the

nonreducible oxides of the transition metals, such as chromium, molybdenum, and tungsten oxides, activation in a stream of hydrogen at high temperatures results in a reduction of the valence of the metal ion.

After reduction, these catalysts should be handled in an inert atmosphere such as nitrogen or carbon dioxide to avoid oxidation. Exposure of finely divided metallic catalysts to air frequently destroys their activity.

In the laboratory, the reduction step is normally performed in the catalytic reactor prior to the introduction of the reactants. If exact knowledge of catalyst weight and volume is required the reduced catalyst should be cooled in a stream of nitrogen to minimize the amount of hydrogen adsorbed on the catalyst surface.

Several catalysts require special activation and conditioning treatments to show maximum activity.

3.2 Physical Characterization and Examination (54)

Most practical catalysts are highly complex materials, and a basic problem is how to correlate catalyst behavior with physical and chemical structure. Only a few methods of characterization are standardized or nearly so. These include determination of total surface

area, and in some cases specific metal area by selective chemisorption. Crystallite size may be determined by X-ray line broadening or by direct observation in electron microscopy.

Measurement of Surface Area: In comparing different catalysts or the effect of various treatments on catalytic activity, it is necessary to know the extent to which a change in activity is caused by a change in the area of a catalyst, in contrast to a change in intrinsic reactivity.

The principal method of measuring total surface area of porous structures is by adsorption of a particular molecular species from a gas or liquid onto the surface. If the conditions under which a complete adsorbed layer, averaging one molecule thick, can be established and the area covered per molecule is known, then the quantity of adsorbed material gives directly the total surface area of the sample.

Specific Area by Selective Chemisorption: With a supported metal catalyst it is frequently desirable to be able to determine the exposed metal area in distinction to the total surface area. This may be achieved by measuring the uptake of a gas that is chemisorbed on the metal but negligibly so on the support, under conditions that allow the coverage corresponding to a monolayer to be

determined. Most useful for this purpose is hydrogen, but carbon monoxide and oxygen have also been used. Although simple in concept, the method can be complex in application. The most suitable experimental conditions vary considerably with the nature of the metal and the nature of the support.

As a prerequisite, it is necessary to know the chemisorption stoichiometry, that is, the number of surface atoms covered for each molecule of gas adsorbed, and the surface area occupied per metal atom. For hydrogen the stoichiometric number is almost always 2 since the hydrogen molecule usually dissociates upon adsorption and each hydrogen atom is adsorbed on one metal atom. Carbonmonoxide can adsorb in either a linear form in which it covers one metal atom (stoichiometric number of 1) or in a bridged form covering two metal atoms (stoichiometric number of 2). The number of surface atoms per unit area of metal varies slightly with the crystallographic plane, but for all metals it is about 10^{19} atoms per square meter. Specific representative values are 1.5 to 1.6×10^{19} atom per square meter for Fe, Co, and Ni; 1.25 to 1.33×10^{19} atoms per square meter for Pt, Pd, Ir, and 1.15×10^{19} atoms per square meter for Ag.

Crush Tests: Crush tests may be made in a variety of way on individual pellets or on beds of catalyst. A generally useful procedure is to slowly force a piston

down onto a bed of catalyst pellets of several hundred cubic centimeters volume and measure displacement as a function of applied pressure. The flow rate of a gas through the bed is sometimes measured simultaneously to indicate the degree of increased flow resistance caused by catalyst breakup, since formation of a small amount of fines may be more deleterious to operation than a larger amount of partially fractured pellets. The increase in pressure drop with a fixed rate of gas flow or, more easily, the decrease in flow rate of a gas supplied to both fresh catalyst and catalyst that has been subjected to an accelerated deactivation procedure designed to simulate long-time use in plant.

Particle-Size Distribution: The average particle size and particle-size distribution can markedly affect fluidization characteristics in a fluid-bed reactor and affect settling and filtering characteristics in a slurry reactor. Size fractions of a powder are commonly separated for measurement by shaking the powder through a stack of sieves of standard construction, the opening size decreasing from top to bottom. In the United States this is the Tyler Standard Sieve Series in which the sieve is identified by the nominal number of meshes per linear inch. The finer the sieve, the finer the wire diameter used. Table 3.1 gives the sieve opening for a number of sieves commonly used.

Table 3.1 Tyler standard sieve series. (54)

Sieve size, Tyler designation	Sieve opening, mm
4	4.76
8	2.38
12	1.41
20	0.841
35	0.420
60	0.250
80	0.177
100	0.149
150	0.105
200	0.074
270	0.053
325	0.044

A 60-to 80-mesh powder, for example, consists of particles that pass through a screen with openings of 0.250 mm but are retained on a screen of openings 0.177 mm. Since the finer particles in a container will settle towards the bottom upon handling, suitable procedures for obtaining a representative sample must be used.

Microscopy: Light microscopy helps to characterize materials and to define problems by revealing

such features as size, shape, surface markings, occurrence of occlusions or other discontinuities, and color. It is particularly helpful to identify the characteristics of single particles and to determine particle-size distribution.

Scanning electron microscopy (SEM) In the scanning microscope the electron spot focused on the sample is moved over a small area by means of a set of deflecting coils. This area is displayed highly magnified on a cathode ray tube (CRT) by causing the currents passing through the scanning coil to pass through the corresponding deflecting coils of the cathode ray tube while the electrons emitted from the sample are collected, amplified, and used to modulate the brightness of the CRT. Scanning microscopy has been used primarily for examination of the topology framework of catalyst surfaces.

X-Ray Diffraction Crystallography: X-ray diffraction may be used to obtain information about the structure and composition of crystalline materials. Common compounds can be identified using tabulations of reference patterns. The minimal limit of detection is approximately 5 percent for compounds and approximately 1 percent for elements. With calibration procedures it is possible to obtain quantitative information and thus determine the approximate amount of a particular phase in a sample.

The mean crystallite size of a material can also be determined from the broadening of an X-ray diffraction peak. The line broadening is inversely proportional to crystallite size, and can be used to give the microcrystalline size in the range of about 3 to 10 nm.

Small-angle scattering (about 0.5° from the incident beam) may be used to give the particle-size distribution in the range of 5 to 100 nm.

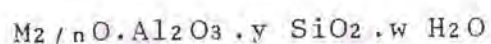
Calorimetry: Calorimetry may be employed to observe various types of chemical transformations that are accompanied by significant energy changes. For example, if a catalyst or catalyst support undergoes several irreversible phase changes at different temperatures, such as alumina does, calorimetry may indicate the maximum temperature to which the material has been subjected. With a poisoned catalyst, the disappearance of a deposit at a low temperature may indicate that the poison is organic rather than inorganic.

Gravimetric Methods: The change in weight of a catalyst with changing experimental conditions can be used for a variety of studies. Modern microbalance instruments can be used with catalyst samples of from a few milligrams up to gram quantities and can detect changes in weight of the order of 0.05 mg. or less. Measurements can be made

at temperatures up to 1000°C, which can be programmed, at constant or variable pressures, and under static or flow conditions. The method has been applied for adsorption-desorption studies and has been particularly useful for studying the rate of coking, dehydration, sorption of poisons, catalyst regeneration, etc., as a function of reaction conditions. It is also useful for catalyst characterization, e.g., of oxidation catalysts in which weight gain or loss may reveal the state of oxidation and hence stability as a function of environment.

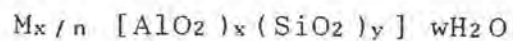
3.3 Zeolite (55)

Zeolites are crystalline aluminosilicates of group IA and group II A elements such as sodium, potassium, magnesium, and calcium. Chemically, they are represented by the empirical formula:



where y is 2 or greater, n is the cation valence, and w represents the water contained in the voids of the zeolite. Structurally, zeolites are complex, crystalline inorganic polymers based on an infinitely extending framework of AlO_4 and SiO_4 tetrahedra linked to each other by the sharing of oxygen ions. This framework structure contains channels or interconnected voids that are occupied by the cations and water molecules.

The structural formula of a zeolite is based on the crystal unit cell, the smallest unit of structure, represented by



where n is the valence of cation M , w is the number of water molecules per unit cell, x and y are the total number of tetrahedra per unit cell, and y/x usually has values of 1-5. Many new crystalline zeolites have been synthesized and several fulfill important functions in the chemical and petroleum industries and consumer products such as detergents. More than 150 synthetic zeolite types and 40 zeolite minerals are known.

Zeolite minerals are formed over much of the earth's surface, including the sea bottom. Until about twenty years ago, zeolite minerals were considered as typically occurring in cavities of basaltic and Volcanic rocks. More common types zeolite see Table 3.2

The classification of zeolites is separated into three types ; low, intermediate, and high silica-alumina ratio respectively

Table 3.2 Properties of selected zeolites and feldspathoids (56)

Name	Crystallographic Data	Selected Chemical Composition
A	isometric: a 12.3Å; Pm3m (pseudo)	$\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$
cancrinite	hexagonal: a 12.7 c 5.1Å; P6_3	$\text{Na}_4\text{Al}_6\text{Si}_6\text{O}_{24} \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$
chabazite	rhombohedral: a 9.4Å α 94.5°; $\text{R}\bar{3}\text{m}$	$(\text{Ca}, \text{Na}_2)_{\sim 2}\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 13\text{H}_2\text{O}$
erionite	hexagonal: a 13.3 c 15.1Å; $\text{P6}_3/\text{mmc}$	$(\text{Ca}, \text{K}_2, \text{Na}_2)_{\sim 4}\text{Al}_6\text{Si}_{26}\text{O}_{72} \cdot 27\text{H}_2\text{O}$
faujasite	isometric: a 24.7Å; Fd3m	$\sim \text{Na}_{13}\text{Ca}_{11}\text{Mg}_3\text{K}_2\text{Al}_{55}\text{Si}_{137}\text{O}_{384} \cdot 235\text{H}_2\text{O}$
X	isometric: a 25.0	$\text{Na}_{96}\text{Al}_{86}\text{Si}_{106}\text{O}_{264} \cdot 264\text{H}_2\text{O}$
Y	isometric: a 24.7	$\text{Na}_{56}\text{Al}_{56}\text{Si}_{136}\text{O}_{384} \cdot 250\text{H}_2\text{O}$
gmelinite	hexagonal: a 13.7 c 10.0Å; $\text{P6}_3/\text{mmc}$	$(\text{Na}, \text{etc.})_{\sim 8}\text{Al}_8\text{Si}_{16}\text{O}_{48} \cdot 24\text{H}_2\text{O}$
L	hexagonal: a 18.4 c 7.5Å; $\text{P6}/\text{mmm}$	$\text{K}_9\text{Al}_9\text{Si}_{27}\text{O}_{72} \cdot 22\text{H}_2\text{O}$
mazzite	hexagonal: a 18.4 c 7.6Å; $\text{P6}_3/\text{mmc}$	$\text{K}_{2.5}\text{Mg}_{2.1}\text{Ca}_{1.4}\text{Na}_{0.3}\text{Al}_{10}\text{Si}_{26}\text{O}_{72} \cdot 28\text{H}_2\text{O}$
Ω	do. but a 18.2	$(\text{Na}, \text{etc.})_8\text{Al}_8\text{Si}_{23}\text{O}_{72} \cdot 21\text{H}_2\text{O}$
mordenite	orthorhombic: a 18.1 b 20.5 c 7.5Å Cmcn	$\text{Na}_8\text{Al}_6\text{Si}_{40}\text{O}_{96} \cdot 24\text{H}_2\text{O}$
offretite	hexagonal: a 13.3 c 7.6Å; $\text{P}\bar{6}\text{m}2$	$\text{KCaMgAl}_3\text{Si}_{13}\text{O}_{36} \cdot 15\text{H}_2\text{O}$
sodalite	isometric: a 8.9; $\text{P}\bar{4}3\text{n}$	$\text{Na}_4\text{Al}_6\text{Si}_6\text{O}_{24} \cdot 2\text{NaCl}$
ZK5	isometric: a 18.7Å; Im3m	$\text{Na}_{30}\text{Al}_{30}\text{Si}_{66}\text{O}_{192} \cdot 98\text{H}_2\text{O}$

3.3.1 Structure and Structure Modification (55)

There three structural aspects: the basic arrangement of the individual structural units in space, which defines the framework topology; the location of charge-balancing metal cations; and the channel-filling material, which is water, as the zeolite is formed. After the water is removed, the void space can be used for adsorption of gases, liquids, elements, and many other substances. Modern tools such as x-ray crystallography have provided a very detailed description of many structures.

Table 3.3 The evolution of zeolite (57)

Quantity	Si/Al ratio	Types of Zeolites
Low	1 - 1.5	A , X
Intermediate	2 - 9.5	a) Natural : erionite, chabazite, clinophiloite, mordenite b) Synthesis : Y, L, Large pore mordenite
High	10 - 100	a) By thermal framework modification : high silicious variants of Y, mordenite, erionite b) By direct synthesis : ZSM-5

There are two types of structures, one provides an internal pore system comprised of interconnected cage-like voids; the second provides a system of uniform channels which, in some instances, are one-dimensional and in others intersect with similar channels to provide two- or three-dimensional channel systems. The preferred type has two- or three-dimensional channels to provide rapid intracrystalline diffusion in adsorption and catalytic applications.



In most zeolite structures, the primary structural units—the tetrahedra are assembled into secondary building units which may be simple polyhedra such as cubes, hexagonal prisms, or octahedra. The final structure framework consists of assemblages of the secondary units. Models of the structures are often constructed of skeletal tetrahedra.

Several types of structural defects or variants can occur which figure in adsorption and catalysis:

Surface defects due to termination of crystal surface and hydrolysis of surface cations.

Structural defects due to imperfect stacking of the secondary units, which may result in blocked channels.

Ionic species may be left stranded in the structure during synthesis (eg, OH^- , AlO_2^- , Na^+ , SiO_3^{2-})

The cation form, acting as the salt of a weak acid, hydrolyzes in water suspension to produce free hydroxide and cations in solution.

Hydroxyl groups in place of metal cations may be introduced by ammonium ion exchange followed by thermal deammoniation. These impart acidity to the zeolite, which

is important in hydrocarbon-conversion reaction.

Tetrahedral aluminum atoms can be removed from the frame work by internal hydrolysis to produce $Al(OH)_3$ when heated in steam. Chemical treatment with acids or chelating agents may also be used to carry out dealumination, but this may cause severe structural damage.

3.3.2 Properties (54)

Adsorption: Zeolites selectively adsorb or reject molecules based upon differences in molecular size, shape, and other properties such as polarity.

Acidity of zeolite : The primary requirement for catalytic activity is that the solid be acidic and be capable of forming carbonium ions by reaction with hydrocarbon, carbonium ions are intermediates in such reaction as cracking, polymerization, and isomerization.

Source of acidity; For structure of aluminosilicate, aluminum ion, which is trivalent, and is substituted isomorphously for a silicon ion, which is quadrivalent (shown in the Figure 3.5)

The net negative charge must be stabilized by a nearby positive ion. The aluminium atom is electrophilic and can react with hydrocarbon or oxygenated compound

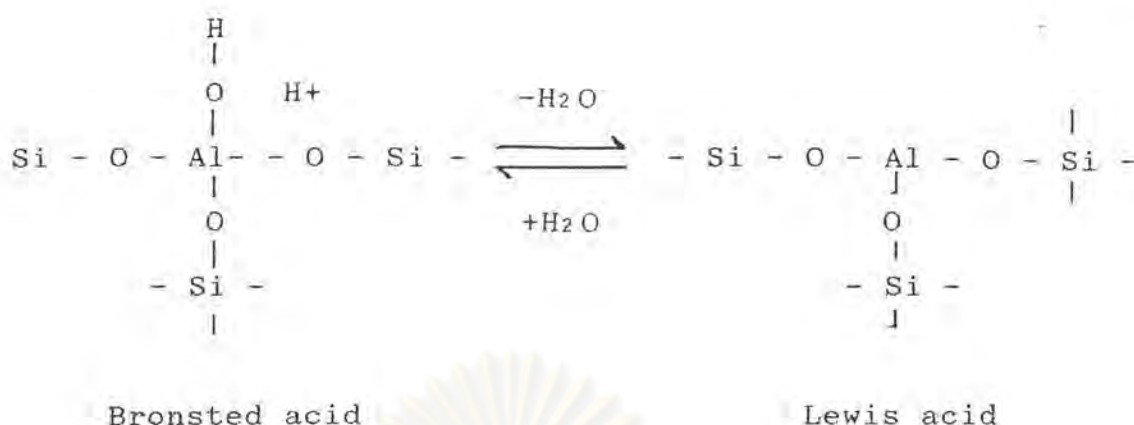


Figure 3.5 Postulated structure of silica-alumina Bronsted and Lewis acidity (54)

to form an adsorbed carbonium ion, as illustrated below for the low kinds of sites (Figure 3.6)

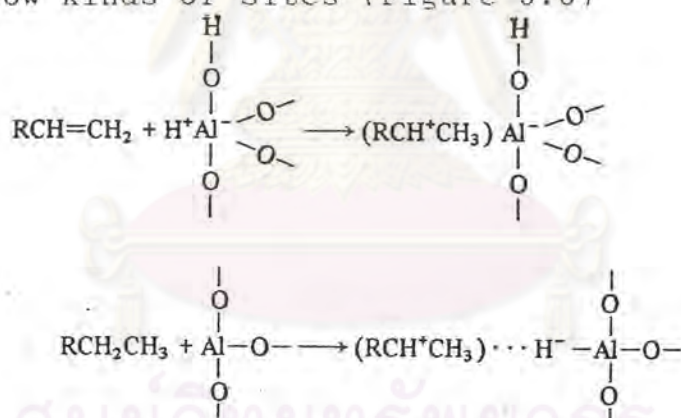


Figure 3.6 Formation of carbonium ion (54)

Acid Strength: The acid strength of a solid may be determined by its ability to change a natural organic base, adsorbed on the solid, into its conjugate acid form. This may occur by transfer of proton from Bronsted acid site to the adsorbed base, or by transfer of an electron pair from the adsorbed molecule to a Lewis acid site, thus forming an acidic addition product. The acid strength can

be expressed by the Hammett acidity function H_0 as

$$H_0 = pK_a + \log \frac{[B]}{[BH^+]}$$

$$\text{or } H_0 = pK_a + \log \frac{[B]}{[AB]}$$

Where K_a is the equilibrium constant of dissociation of the acid and $pK_a = -\log K_a$, B and BH^+ are the concentration of the neutral base and of its conjugated acid, and AB is the concentration of the addition product formed by adsorption of B onto a Lewis site.

Acid Amount: A sample of the solid acid as a powder is suspended in an inert nonaqueous liquid, e.g. benzene, and is titrated with a base, Utilizing an indicator. The titrating base must be stronger base than the indicator, and *n*-butylamine, $pK_a = +1.0$, is often used for this purpose.

The acid amount versus acid strength for Y-type zeolite show in the Figure 3.7. The Y-type zeolite is often used in catalyst preparations, has a high acid strength in the H^+ form or when exchanged with calcium or lanthanum.

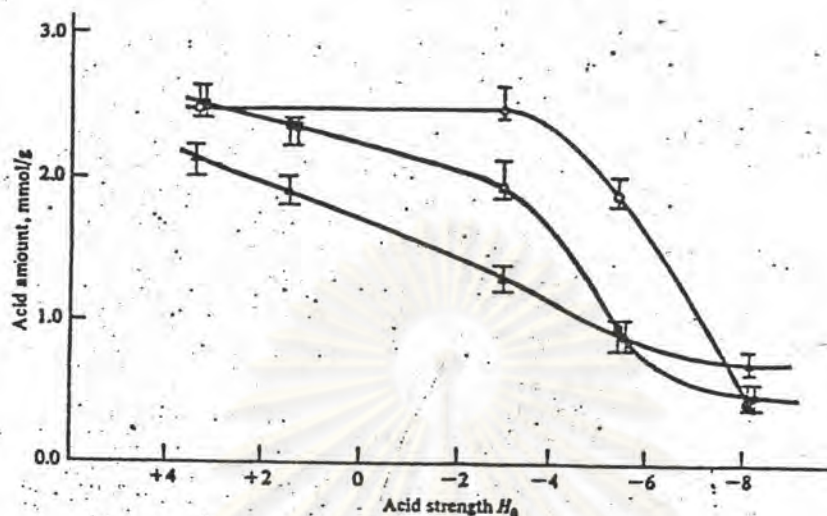


Figure 3.7 Acid amount versus acid strength for a synthetic Y zeolite (54).

Pore Structure: Table 3.4 gives some well-characterized zeolites of interest in catalysis. Of these, especial industrial interest lies in type Y, mordenite, erionite and offretite (which are closely related and frequently intergrown), and zeolites synthesized in the presence of various quaternary alkylammonium compounds. The effective pore diameter may also vary with the nature of the cation present, for example, Na, Ca, H, or with the dehydroxylated form, and with other treatments. The pore structures may be

Table 3.4 Selected well-characterized zeolites of interest in catalysis (54)

Group	Name	Void fraction (from H ₂ O content)	Channel geometry*	Kinetic diameter of dehydrated form [†]
6	Mordenite (Na form), large port	0.28	0.67 × 0.7, one-dimensional interconnecting with 0.29 × 0.57, one-dimensional	0.62
3	Type A (Na form)	0.47	0.42, three-dimensional	0.36–0.39
4	Type X	0.50	0.74, three-dimensional	0.81
	Type Y (both in Na form)	0.48		0.81
4	Chabazite (Ca form)	0.47	0.36 × 0.37, three-dimensional	0.43
2	Erionite	0.35	0.36 × 0.52, three-dimensional (but tortuous)	0.43
2	Offretite ^{‡§}	0.40	0.64, one-dimensional interconnecting with 0.35 × 0.52, one-dimensional	0.6
4	Type L, K ₉ [(AlO ₂) ₉ (SiO ₂) ₂₇] · 22H ₂ O	0.32	0.71, one-dimensional	0.81
2	Omega, Na _{6.8} TMA _{1.6} [(AlO ₂) ₈ (SiO ₂) ₂₈] · 21H ₂ O	0.38	0.75, one-dimensional	1.0

*Breck, 1974, p. 48. Based on structure of hydrated zeolite. Units in nanometers.

[†]Breck, 1974, pp. 133–180. Commercial NaX has a reported pore size of about 1.0 nm, commercial Na mordenite about 0.7, commercial H mordenite about 0.8–0.9 nm (Breck, p. 747).

[‡]TMA offretite is also known as Zeolite O.

[§]Zeolite T is mostly offretite intergrown with some erionite with free aperture sizes probably similar to that of erionite.

designated as one-, two-, or three-dimensional.

Zeolite A, X, Y, erionite and offretite have both channels and cages while ZSM-5 and mordenite only have channels. The intersecting channels of ZSM-5 may allow three dimensional motion for molecules of the proper size while the differentiate pores of mordenite renders the latter structure essentially undimensional with respect to the diffusion of hydrocarbon molecules.

In the Figure 3.8 summarizes the major features of their pore structure and compare their critical dimensions to those of typical hydrocarbon molecules.

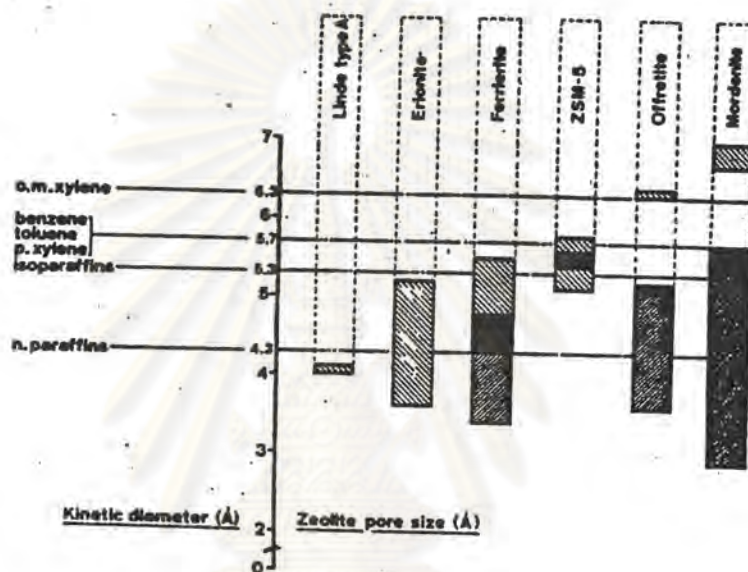


Figure 3.8 Pore structure of industrially important zeolites (58).

Catalytic Properties: In Zeolites, catalysis takes place within the intracrystalline voids. The aperture size and channel system affect catalytic reactions caused by diffusion of reactants and products. Activity and selectivity are achieved or altered by modifying the zeolite in several ways. In hydrocarbon reactions in particular, the zeolite with the largest

poresizes are preferred. These include mordenite and zeolites Y, L, and Omega. Modification techniques include ion exchange, composition in terms of Si/Al ratio, hydrothermal dealumination or stabilization which produces lewis acidity introduction of acidic groups such as OH which impart Bronsted acidity and introducing dispersed metal phases such as the noble metals. In addition the zeolite framework structure determines shape-selective effects. Several types have been demonstrated including reactant selectivity, product selectivity and restricted transition-state selectivity.

The pore size and shape in a zeolite may affect the selectivity of a reaction in two main-ways; Reactant selectivity occurs when the aperture size of the zeolite is such that it admits only certain smaller molecules and excludes larger molecules; hence, in a mixture, effectively only the smaller molecules react. Product selectivity occurs when bulkier product molecules cannot diffuse out, and if formed, they are converted to smaller molecules or to carbonaceous deposits within the pore. These eventually may cause pore blockage. It is also possible that pore shape may sterically hinder certain types of reactions and thereby affect selectivity, but the evidence is ambiguous.

In shape-selective catalysis the pore size of the zeolite is important. For example, the ZSM-5 framework

contains 10-membered rings with 0.6 nm. pore size. This material is used in xylene isomerization, ethylbenzene synthesis, and the conversion of methanol to liquid hydrocarbon fuels.

The zeolites used are primarily modified forms of zeolite Y, acid forms of synthetic mordenite, silicalite, and ZSM-5. Smaller-pore-size zeolites such as zeolite T are used in shape-selective catalysis

Some current and possible future zeolite catalyst applications are listed below.

Alkylation	dehydration
cracking	methanol to gasoline
hydrocracking	organic catalysis
isomerization	inorganic reactions
hydrogenation and	H ₂ S oxidation
Dehydrogenation	NH ₃ reduction of NO
hydrodealkylation	
methanation	$\text{H}_2\text{O} \longrightarrow \frac{1}{2}\text{O}_2 + \text{H}_2$
shape-selective reforming	CO oxidation

3.3.3 General Knowledge of Alcohol-Reactivity Study Zeolites.

Reactivity of alcohols has been studied via dehydration reaction of alcohols (C₁ - C₄) with zeolites as catalyst to produce light olefin as main product. Several generations of catalysts have been developed. Here, we have selected two types of zeolites as catalyst. One was Y-type zeolite and the other was mordenite-zeolite, which they have been the different Si/Al ratio.

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 the crystallization was retarded and the crystals which formed were fewer and smaller.

i) Mordenite: The structure consists of chain crosslinked by the sharing of neighboring oxygens. Each tetrahedron belongs to one or more five-member rings in the framework showed in the Figure 3.9.

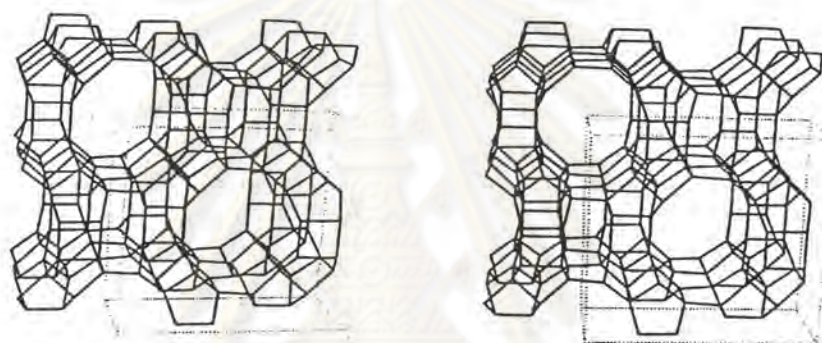


Figure 3.9 Stereodiagram of framework topology of mordenite

(56)

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. Mordenite has a two-dimensional structure in which the large channels are interconnected by other cross channels. These, however, are sufficiently smaller that they do not

generally provide a means for transport of molecules between adjacent passageways. Hence mordenite has effectively a one-dimensional structure that may be regarded as an array of parallel noninterconnecting channels. In the ideal mordenite pore structure these are slightly elliptical, with dimensions of about 0.70×0.67 nm. Unlike type Y, sodium mordenite can be treated directly with acid to produce a highly active and stable hydrogen form. This treatment also may increase channel size, up to about 0.8 to 1.0 nm diameter, by selective leaching of alumina. Si/Al ratios in the leached mordenite can range up to 50:1 or more, if desired, without collapse of structure. 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°A 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.

ii) Y-type Zeolite: Y zeolites 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 sodiumsilicate-aluminosilicate gels. When an aqueous colloidal silicasol is employed as the major source of silica, the SiO_2 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: $\text{Na}_2\text{O}/\text{SiO}_2 = 0.4-0.6$, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.5-2.5$ and $\text{H}_2\text{O}/\text{Na}_2\text{O} = 20-50$

It appears that the gel prepared from the colloidal silicasol 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the gel necessary to form zeolite Y which has composition; $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1$, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0-6.0$, $\text{H}_2\text{O}/\text{Al}_2\text{O}_3 = 9$.

Y zeolite (faujasite-type) has three-dimensional intersecting channels in which the minimum free diameter is the same in each direction. The Y-type consist of an array of cavities having internal diameters of about 1.2 nm. Access to each cavity (also termed a supercage) is through six equispaced necks having a diameter of about 0.74 nm. The Y zeolite has among the largest minimum aperture restrictions of any zeolite, and the highest void

fractions. Their structure may be visualized by the line drawing of Figure 3.10.

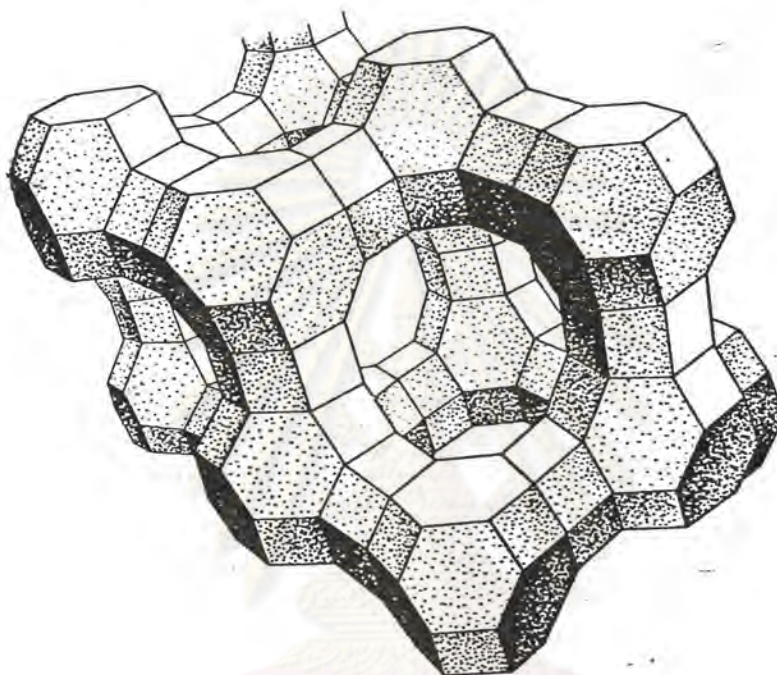


Figure 3.10 The line drawing of faujasite structure (54).

In the foreground is one of the necks, consisting of a ring of 12-oxygen atoms, through which may be seen slight portions of three other necks. The rows of necks comprise an array of passageways perpendicular to one another in three dimensions.