CHAPTER 3

GENERAL METHODS OF CATALYST PREPARATION

The art of catalysis includes a very extensive " know how "
of the procedures and experimental techniques employed in the pre-
paration of solid catalysts. The chemical and physical properties
of a catalyst are determined by the total history of its prepara-
tion. To obtain active catalysts it is important to use established
procedures 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 specia-
lized manner. The various methods of catalyst preparations may ge-
nerally be considered as combinations of certain unit operations.
The unit operations most frequently involved will be discussed in
the following pages. The actual choice of methods may be guided by
ease of preparation, homogeneity of the product, stability of cata-
lyst and ease of duplication. Before going into the preparation of
methanol synthesis catalyst, we shall review here the general methods
of catalyst preparation.

Methods of Preparation

Precipitation and Gel Formation. 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 phenomenon 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 oxide 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.

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, sulfides, 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 bench 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 adsorbed 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 precipitants along 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 nitrates 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, revising 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 solutions of aluminum 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 techniques as will be discussed subsequently.

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. Specifi-cally, 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 com-posites will be produced by gelation.

The general conditions required for gel formation were des-cribed long ago by Von 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 gelled either in the alcoholic or alcohol-water media. Certain gels such as those of magnesia and $Cd(OH)_2$ or $Zn(OH)_2$ 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.

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. 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 supports one may use either a powdered or granular material. A granular support is usually preferred since it eliminates pelleting or extrusion of the finished catalyst.

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 and (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.

Evacuation 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 componen 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 consti- tuent and then to wash out the undesired material. For example, a cracking catalyst may be prepared by impregnating silica gel with aluminum sulfate. Since sulfate is not desirable in the final product, it is necessary to precipitate the aluminum as the hydrated oxide by adding ammonia. The sulfate ion is then removed by washing.

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 distri- buted throughout the catalyst pores. Occasionally, this may be used where the active component is expensive and high area is not important.

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 analagous process for maintaining the activity of an alumina-boria cracking catalyst. The variation involves passing an admixture of steam 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.

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.

Methods with Limited Application. Certain well known catalysts are prepared by methods which have little general applicability. Examples of these are: (1) thermal fusion, (2) chemical reaction, and (3) evaporation of metals. Let us consider a few examples of these methods with a brief description of each.

Thermal Fusion. The best known examples of catalysts prepared by thermal fusion are some of the fused iron catalysts used for the synthesis of hydrocarbons and ammonia. These catalysts may be prepared by the "schmeltz" method, electric fusion, or use of an induction furnance. The first of these involves burning iron powder in a stream of oxygen. Promoters are added directly to the melt. Electric fusion of Fe_3O_4 may be accomplished by the use of water-cooled electrodes immersed in a bed of the oxide. For very small laboratory batches fusion of the desired powdered mixtures may be carried out in an induction furnace.

Chemical Reaction . Catalysts prepared by precipitation or gelation techniques usually involve simple metathetical reactions. Other chemical reactions such as decomposition, oxidation and reduction, etc., are frequently employed to prepare catalysts. These preparatory methods are best illustrated by the following examples. Copper chromite catalysts are prepared by the thermal decomposition of a precipitated copper ammonium chromate. The copper ammonium chromate is preferably precipitated in the presence of a support. A chromia-alumina catalyst is prepared by adding chromic acid to a concentrated solution of aluminum sulfate. A solid mass is obtained on heating the mixture at 150 to 400°C. The finished catalyst is obtained by decomposing the dried solid in a reducing atmosphere at 350 to 650°C to remove all the sulfur as sulfur dioxide or hydrogen sulfide.

Another example is the preparation of cracking catalysts from montmorillonite clays. These catalysts are made by leaching the natural clays with dilute sulfuric acid, washing and drying the product. Increased surface area is produced by leaching out part of the alumina and other constituents of the clay. Active surface groups are produced which are acidic in nature and are probably amorphous as contrasted to the crystalline structure of the clay base.

In the case of Raney nickel, an active catalyst is prepared by leaching aluminum from a nickel-aluminum alloy with a base. Usually about a 20 per cent solution of sodium hydroxide is used to remove the aluminum from a 50-50 nickel-aluminum alloy. The washed product is an extremely active hydrogenation catalyst. The finished catalyst is pyrophoric and should not be allowed to dry in air.

Activated magnesia is prepared by alternate hydration of the oxide to the hydroxide at low temperature and dehydration of the hydroxide at temperatures up to $875^{\circ}C$. The final activated magnesia may have an area of over $100 \ m^2/g$.

An alternate oxidation-reduction procedure is used to prepare the copper-iron catalyst used in the Caterole process. Here a mixture of copper and iron turnings in the ratio of 5:1 is placed in a steel tube and alternately oxidized with air at about $400^{\circ}C$ and reduced with hydrogen at about $250^{\circ}C$.

Evaporation of Metals. The work of Beeck, Smith and Wheeler (.C.E.,1954)has helped to bring into prominence the study of metal films as an aid to fundametal catalytic work. The films used by these investigators were prepared by evaporating the metal from a wire onto a glass support.

Another particularly interesting application of metal evaporation has been described by Rhodin (C.F.,1954). In this work single crystals of Zn were produced by an evacuation technique described earlier by Bridgman. The crystals so produced were used in adsorption studies.

Processing Operations

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 blocks 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 when the concentration of the contaminating ion reaches a specified concentration in the filtrate at the end of a wash period. This concentration is usually defined by addition of a counter-ion in sufficient quantity to precipitate the undersired ion when present in the filtrate above the prescribed 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 less than $60^{o}C$.

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 slurrying 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. This 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 also free from that contaminant. This can only be proved by analysis.

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 cata-
lytic properties of the catalyst. Of course, extreme changes in
physical properties should be avoided as they may change the cataly-
tic 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
cannot be tested without being pelleted.

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

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 connec-
tion with catalysts having surface area and small pores. Some scien-
tists have stressed the importance of this factor in catalytic reac-
tions. Hence, it is important to insure freedom from diffusion limi-
tations 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 cata-
lysts 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 structue 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.

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 temperatures 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.