# CHAPTER 1

## INTRODUCTION

# 1. Introduction

This introductory chapter on catalysis is sub divided into three parts. The first one deals mainly with fundamental aspects of catalysis. The second part elaborately discusses in the sol – gel process of oxide material synthesis, with a special focus on its chemistry and factors affecting the morphology of the final material. In the third part, the application of the sol – gel method on the synthesis of alumina and related catalysts, their chemistry and applications are widely considered.

## PART 1: General Catalysis

### 1.1. Fundamentals of catalytic phenomena

*"A catalyst is a substance that increases the rate at which a chemical reaction approaches equilibrium without itself becoming permanently involved in the reaction"*

### 1.2. Catalysts and catalysis and their classification

A catalyst, in simplest terms, is a material, which enhances the rate, and selectivity of a chemical reaction and in the process is cyclically regenerated.

Catalysts are broadly classified into homogeneous, heterogeneous and enzyme catalysts.

In *Homogeneous catalysis*, the catalyst and the reactants are in the same phase. For example: hydrolysis of ester *by acids* (liquid – liquid), oxidation of $SO_2$ by $NO_2$ (gas-gas) and decomposition of $KClO_3$ by $MnO_2$ (solid – solid). Usually, the liquid phase is the most common, with both the catalyst and the reactant being present in solution.

In heterogeneous catalysis, as the name indicates, the catalyst and the reactant(s) exist in different phases. The primary step, in this case, is the adsorption of reactant(s) onto the surface of the catalyst. Adsorbed reactant molecules, thus activated by interaction with the catalyst surface are rapidly and selectively transformed into adsorbed products. Finally the adsorbed products leave the surface in a desorption step. Once the product is desorbed from its surface the catalyst momentarily returns to its original state until the next set of molecules adsorb, repeating the catalytic cycle. These interactions provide a "chemical shortcut" in which reactants are converted to products more rapidly and in several cases, under much milder conditions than if no interaction occurred.

The second aspect of the definition indicates that the reactants can be directed down a certain a chemical transformation path to generate a specific product. In this respect, the catalyst provides *selectivity* or *specificity*. It is these aspects of the definition, "enhancing rate and directing reactants to specific products" that makes catalysis play such a major role in the chemical, petroleum, petrochemical, fertilizer ,pharmaceutical and fine chemicals industries and in solving environmental and energy related problems therein.

Automobile emissions control provides an interesting example of how rate enhancement by a catalyst is put to useful practice. The internal combustion engine in automobiles burns a gasoline – air mixture to generate heat, which is converted to mechanical work in the engine (*piston movement*). The combustion process, however, is stoichiometrically less than 100% efficient; that is, undesirable byproducts such as carbon monoxide (CO) and unburnt hydrocarbons (HC) are produced, which pollute the atmosphere.

At moderately high temperatures and high flow rates typical of auto – exhausts there is insufficient time for CO and HC to react further with available oxygen to form $CO_2$ and water before they exit the tailpipe. However, placing a catalyst in the exhaust manifold allows these reactions to occur within the limited residence time and at the moderate reaction conditions of the catalytic converter. Thus, this catalyst provides an alternative chemical path leading to the destruction of the pollutants.

Another consequence of combustion processes is the generation of nitrogen oxides ($NO_x$), which can be catalytically, converted to harmless nitrogen, and safely emitted into the atmosphere.

Enzymes are protein molecules of colloidal size. They are the driving forces of biochemical reactions. Present in life processes, they are characterized by tremendous efficiencies and selectivity. For example, an enzyme, *catalase*, decomposes hydrogen peroxide $10^9$ times faster than any inorganic catalyst **(1)**.

In this thesis, the emphasis is on heterogeneous catalysts, especially concerning the catalysts for petrochemical processes such as reforming, dehydrogenation hydrogenation etc.

## 1.3. Catalyst Components

Although some catalytic materials are composed of single substances, most catalysts have three types of easily distinguishable components:

### 1.3.1. Active components

Active components are responsible for the principal chemical reaction/activation. These could be in the form of metals, metal oxides or metal salts, crystalline or amorphous in nature. Based on the electronic theory of catalysis one can catalogue active components according to the type of electrical conductivity, i.e., metals, semiconductors and insulators. Since charge transfer is common for both electrical conductivity and catalysis, many aspects of catalysis could be explained on the basis of the theories for electrical conductivity of solids and electronic configurations of elements. Depending on their electronic structure, active components could catalyze different reactions as shown below in Table 1.

**Table 1 Classification of active components**

| Class | Conductivity | Property | Reactions | Examples |
|---|---|---|---|---|
| Metals | Conductors | With metals, overlapping electronic energy bands promote electron transfer with adsorbing molecule **(2)**. | Hydrogenation,<br>Hydrogenolysis,<br>Oxidation | Fe, Ni, Pt, Pd, Cu, Ag |
| Metal oxides | Semiconductors | Electron donor and acceptor levels provide redox type activation but surface configurations are more complex than with metals. Greater geometric complexity leads to more selective redox reactions. | Selective hydrogenation,<br>Hydrogenolysis,<br>Dehydrosufurization | NiO, ZnO, CuO |

### 1.3.2. Catalytic support

An important question that looms over a catalyst researcher at this juncture is the choice of an appropriate support. This critical choice has to be made on the basis of the properties of the active species, the nature and conditions of the reaction under investigation, mobility of reactants / products. The options are infinite; for they range from naturally occurring materials such as diatomaceous earth, kieselghur, activated carbon, pumice, kaolin, bentonite, etc to synthetic inorganic supports such as alumina, silica, magnesia, zirconia, titania, alumino-silicates, etc.

How does the support contribute to catalysis? It provides a means to prepare a large particle or tablet of catalyst. Active phase, when incorporated on a suitable support gains stability against sintering. The support material, acting as walls between independent active species, helps in achieving this **(3)**. Thus, a high surface area is an important prerequisite. High surface area leads to increased dispersion and hence high activity. Often the loss of selectivity is an outcome of high activity and hence one should choose an optimum surface area rather than high surface area so as to maintain optimum activity **(4, 5)**. The selection of pore structure of the support should be such that the transport / mobility of reactants and products through the pores should not be restrained. This choice purely depends upon the reactant molecular size. Increased porosity will lead to thin wall formation, thus adversely affecting the mechanical strength. An optimum porosity should be selected, such that the catalyst is suitable for continuous operations during the course of which, it should withstand immense thermal shocks, attrition, and tendency for crumbling/powder formation etc.

Another aspect to be considered at this stage is the intrinsic catalytic activity of the support. One, must therefore select a support, keeping in mind, whether this inherent activity is desirable or not, with reference to the selected reaction.

In the case of the reforming catalyst (Pt/acidic alumina), while, the inherent acidity of alumina is necessary for dehydrocyclisation activity **(6)**, the same is undesirable for the dehydrogenation of paraffins (Pt/neutral alumina), since it promotes side reactions **(7)**. Apart from this, the support may have some interaction with the active species, which may modify the catalytic action (commonly termed as Strong Metal Support Interaction (or simply *SMSI*). In many a systems, SMSI aids in stabilizing the active species and improve the activity **(8, 9, 10, 11, 12)**. Hence the metal-support system should be chosen in such a way that the optimum level of SMSI exist.

Considering all the afore-discussed factors, alumina is found to be the most compliant support. This is because the preparation variables can be modified in such a way that the desired surface area, pore size distribution, pore volume, acidity etc. can be achieved **(13)**.

As discussed earlier, the most important function of support / carrier is to provide a high surface area required for the active component. This is best illustrated with platinum, an important active component used widely for catalytic reforming **(14)**. For high activity, platinum crystallites must have the highest surface area possible. Ideally, Pt crystallites should be as small as possible in the 0.5 – 5.0 nm range. But when platinum crystallites of this size are used directly as catalysts at very high temperatures, rapid agglomeration occurs resulting in sintering.

These crystallites, at very high temperatures, migrate and contact each other through thermal motion. Above the Tamn temperature, (i.e., at $0.5T_m$, where $T_m$ is the melting point of the metal), bulk metal atoms acquire enough thermal energy to migrate within the crystallite. Even at $0.3\ T_m$, (called the Huttig temperature) surface atoms have enough energy to overcome weaker surface crystal forces, diffuse and form necks. If surface and bulk atoms are mobile enough, two smaller crystallites coalesce to a larger one, thereby decreasing the surface energy. This phenomena is termed as "sintering".

Supports also function as stable surfaces over which the active component is dispersed in such a way that sintering is reduced **(15)**. The support itself must be secure from thermal growth, which means that it should have a high melting point – at least higher than that of the active component. High melting points are found in oxides normally considered as ceramic materials. But, all high melting oxide materials cannot be utilized as catalytic supports. A good support – the oxide material, must be amenable to preparations yielding high surface area. Examples of such supports are $\gamma$ – alumina, silica, diatomaceous clay, silica – alumina etc.

The level of active metal loading on the support is an important factor, since crystallites, even though isolated from each other, may sinter via the migration mechanism. Thus, sintering may not only be caused by high temperatures, but also by factors such as crystallite size, concentration, interaction of active metal with the support, and atomic mobility **(16)**.

Porosity is necessary for high surface area within the support, and pore shape and pore size distributions are critical when the reaction under consideration is diffusion controlled **(17)**.

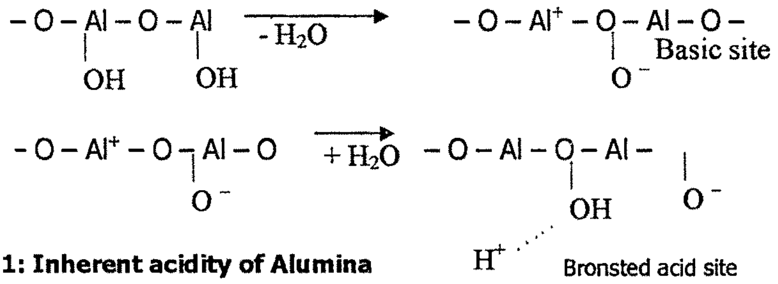


**Figure 1: Inherent acidity of Alumina**

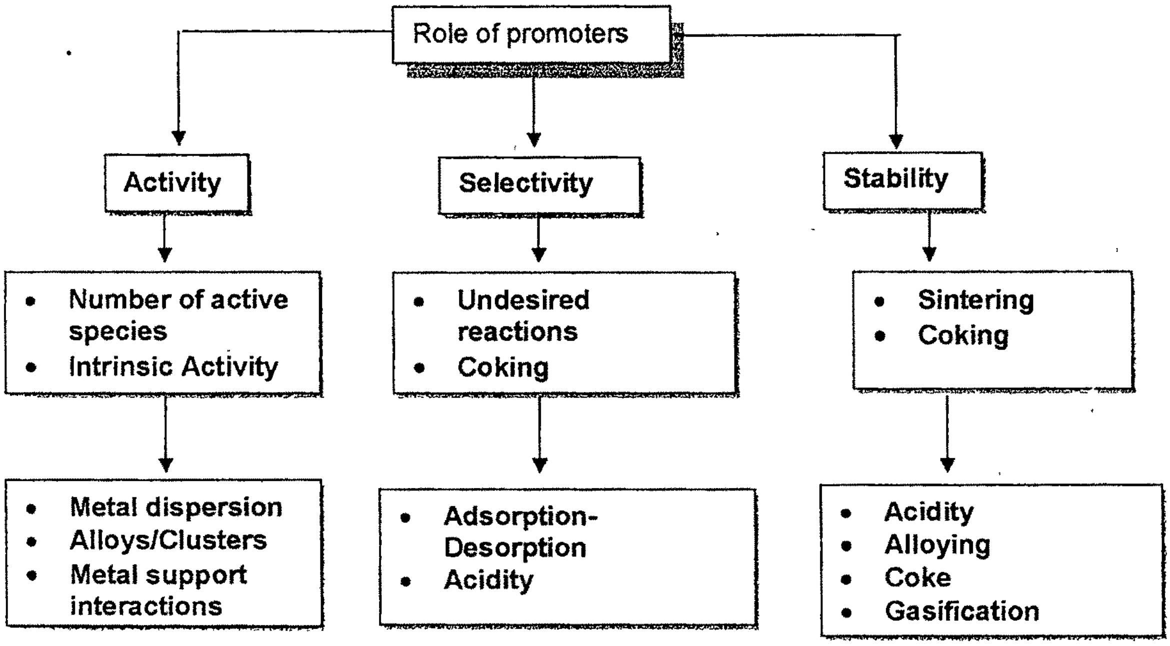
The inherent acidity of the support also plays a vital role. In the case of alumina, the Bronsted sites, (Figure 1) that initiate carbonium ion reactions, giving ion radical reactions, coexist, although it appears that in practice Bronsted acidity predominates **(18)**. It is relevant to mention here that when using $\gamma$ – alumina as a support, undesirable side reactions such as cracking and isomerization leading to "coke" formation always occur. This coke formation is one of the principal reasons that lead to the deactivation of the catalyst.

In some cases, support acidity also has a positive influence, by directly controlling the main reaction. The catalytic dual functionality (– the metal function and the acid function) is illustrated in catalytic reforming, wherein the objective is to convert low octane components of naphtha (a mixture of normal paraffins and naphthenes) into high-octane isoparaffins and aromatics. Typically, the catalytic system employed here is a low loading of platinum on alumina support. Platinum dehydrogenates naphthenes to aromatics but cannot isomerize or cyclize normal paraffins. This is accomplished by the acidic function of the support. This dual functionality becomes an important aspect of catalyst design. Depending upon the nature of our reaction, we can attenuate both or either of these functions to suit our needs.

Metal dispersion on the support is an important factor that affects the catalytic activity directly. But in actual practice there are various factors that contribute to the poor dispersion of active metal on support. Contaminated commercial agents could contain impurities that act as poison, or spillover (a phenomenon, in which a reactive species is generated in a metal site and then migrates over the support to other sites where further reaction occurs) can take place.

### 1.3.3. Promoters

A promoter is some third agent, which is not a catalyst by itself, but when added, often in small amounts, produces desirable activity, selectivity or stability.



Promoters are designed to assist either the support or the active component. A significant example is that of alumina. Alumina exists in various phases, out of which the γ – alumina phase is the most preferred support. γ –alumina being a defect spinel has a high surface area, a certain degree of acidity and forms solid solutions with transition oxides. This transforms into α – alumina phase, which has an hexagonal structure and low surface area and is not generally preferred as a support material. This transition occurs at about 900°C. This temperature, though not usually encountered during actual reaction, but might become necessary during catalyst regeneration. Addition of promoters such as silica or zirconia in very small amounts would push the transition temperature further beyond 900°C **(19)**. The support is then adequately protected against major thermal upsets and long term changes.

Most often, promoters are added to supports in order to inhibit undesirable activity, such as coke formation. Coking originates from cracking on the Bronsted sites followed by acid catalyzed polymerization to give $(CH_x)_n$ species that cover surface sites and ultimately block pores. Removal of coke by burning may itself lead to activity loss due to sintering. Bases neutralize acidic cracking sites, most effectively by alkali elements **(20)**. Potash, as a promoter, when added to alumina, reduces its coking tendencies.

When dual functionality is needed, as in catalytic reforming, extra acidity is achieved by adding chloride ions to the support **(21)**. A glance at Table 2 gives the effect of promoters in various catalytic processes.

Promotion of active components may either be structural or electronic **(22)**. Addition of Re to Pt in reforming catalysts leads to vastly improved performance, due to decreased hydrogenolysis of the hydrocarbons **(14)**. Chemically, Re preferentially a bond with low coordination sites on crystal plane corners, edges and steps. Since these sites are known to be involved with hydrogenolysis, coke formation reactions are suppressed **(21)**.

In general, any additive, which enhances or inhibits catalytic functions, can be classified as a promoter.

**Table 2 Examples of promoters in major catalytic processes**

| Catalyst | Promoter | Function |
|---|---|---|
| $Al_2O_3$ | $SiO_2$, $ZrO_2$, P | Improves thermal stability |
| | $K_2O$ | Poisons coking sites |
| | HCl | Increases activity |
| | MgO | Retards sintering active components |
| $SiO_2$ - $Al_2O_3$ | Pt | Increases CO oxidation |
| Zeolites | Rare earth ions | Increases acidity and thermal stability |
| | Pd | Increases hydrogenation |
| Pt/ $Al_2O_3$ | Re | Decreases hydrogenolysis and sintering |
| $MoO_3$ / $Al_2O_3$ | Ni, Co | Increases hydrogenolysis of C – S and C – N |
| Cu – ZnO - $Al_2O_3$ | ZnO | Decreases Cu sintering |

## 1.4. Supported metal catalysts

In general, supported catalysts are of two types:

- Supported base metal catalysts
- Supported precious metal catalysts

Both the types are equally important as industrial catalysts in specific applications. In supported catalysts, irrespective of base or precious metal, the catalytically active material is deposited on an inert or active support in a finely divided form **(3)**. As stated in the earlier section, the adsorption of reactants that governs the catalytic activity of a material directly depends on the extent of dispersion of the active species on support. Hence the active species have to be present in a finely divided or micro - crystalline form. Since most of the industrial reactions are carried out at high temperatures, these crystallites rapidly sinter and lose the desired high metal surface area, often leading to deactivation of the catalyst. Hence, they are supported on refractory materials like alumina, silica, clay, carbon etc., having adequate surface area to disperse the material. Some supports may have inherent catalytic properties, which may be desired or undesired **(6, 7)**.

Thermal and mechanical stability of the support materials at the operating conditions is as important as the features of the active species for a specific reaction **(23)**.

## 1.5. Features of Supported Metal Catalysts

As mentioned earlier, factors like, state of the active species (metal / oxide / sulphide / chloride), their location, geometry, etc determine activity, selectivity and specificity of any supported metal catalyst. Two major steps are of great importance at this juncture:

- A suitable mode of incorporating the active phase onto the support in the required form
- Appropriate treatments to generate the necessary active sites and induce interaction between the active phase and support.

In general, the intention of using supported metal catalysts is to achieve a high metal surface area with relatively lesser amount of active material and to maintain it in the active form for the longer duration. In order to achieve this ultimate goal the catalyst should be prepared with:

- Optimum activity and maximum selectivity
- Longer life and easier regenerability
- Appropriate transport, thermal and mechanical properties

The following five aspects are to be considered in detail to design such an ideal catalyst:

- Nature of active metal species
- Nature of support
- Selection of appropriate promoters
- Methods of preparation of catalysts
- Suitable pre-treatments

## 1.6. Catalyst Preparation

The art of the preparation of catalysts lies in how the active species and / or the promoter is incorporated on the support / carrier material. Although some degree of catalytic activity is found in any given material, successful preparations proceed through a series of mysterious steps justifying its description as a Black Art.

## 1.7. Methods of Incorporation of Active Species

Essentially, almost all the preparation procedures **(24)** that involve the incorporation of the active phase on to the support can be divided into the following categories –

(a) Co-precipitation / precipitation

(b) Deposition

(c) Ion Exchange

(d) Impregnation / Adsorption

### 1.7.1. Co-precipitation / precipitation

Co-precipitation / precipitation involve the addition of a precipitating agent to a solution containing both a *support* precursor and *catalyst* precursor. The resulting precipitate contains species, either as a single phase or multiple phases, from which the active component and the support material are eventually produced.

In this case, both the support and the active species are formed simultaneously from solution. The choice of this method has to be done after considering the properties of the support and adsorbate solutions.

### 1.7.2. Deposition

This method involves the precipitation of the active species on to the surface of a carrier, by the addition of alkali to a suspension of the carrier (separately produced) in the metal salt solution. Precipitated metal salt hydroxides distribute over the support. Base metal catalysts like Ni/silica and Cu/alumina are prepared by this method. The concentration and type of metal salt solution, support to metal ratio, nature and rate of precipitant addition, temperature of precipitation and pH of solution are the factors controlling the distribution and dispersion **(25)**.

The inhomogeneous distribution of the precipitant due to the insufficient stirring will cause local supersaturation and nucleation of the metal hydroxide both on the support and in the bulk of the solution, giving rise to uneven distribution of the active species during deposition precipitation.

Hence to avoid this, a modified deposition/precipitation method is used, viz. precipitation from homogeneous solutions (PFHS) **(26)**.

This involves the mixing of two solutions (metal salt solution and the precipitant) under conditions where precipitation cannot occur and then the conditions are gradually and uniformly changed throughout the solution to the region where precipitation is permitted. Here, since the conditions of precipitation are approached gradually, the rate of nucleation and hence surface area can be controlled in a better way. This is generally achieved by using, instead of a base, compounds like urea or HMTA, which can liberate a base on heating by decomposition and cause a pH change **(27, 28)**. There are various other methods such as ion release **(29, 30, 31)**, change of oxidation state **(32)**, change in solubility **(33)**, reagent synthesis **(34)** etc to carryout deposition precipitation.

Experimental parameters such as the nature of the precipitant (ammonia, ammonium carbonate, sodium hydroxide, sodium carbonate etc), final pH of the solution, hydrothermal treatments, ageing etc., determine the structure of the material formed which is generally a complex one **(35)**. The reducibility and dispersion of the metal depends on these structural modifications.

The reducibility of the catalysts prepared by coprecipitation is generally low, but they give better dispersion. Lower pressure drop and better transport properties of the catalysts, which generally are achieved by a better control of the pore structure, are not possible in co precipitation. Due to the low reducibility of these catalysts, separate high temperature reduction rather than in situ reduction becomes necessary and this leads to sintering. This method is especially useful for high loading of metal/metals.

### 1.7.3. Ion Exchange

Ion Exchange is very similar to ionic adsorption but involves exchange of ions other than protons. For controlled loading of active components or promoters, the catalyst is soaked in excess solutions containing exchangeable ions. Loading or extent of exchange is controlled with soaking time. Even multiple exchanges are possible.

### 1.7.4. Impregnation

In most of the cases, however, the supported catalyst precursors are prepared by a procedure **(36)** that can be described in general terms as impregnation – contacting the solid support with liquid containing of the components to be deposited on the surface. During impregnation, different processes take place with different rates.

- Selective adsorption of species (charged or not) by Coulomb force, van der Waals forces or hydrogen bonds.
- Polymerization / depolymerization of the species (molecules, ions) attached to the surface.
- Ion exchange between charged surface and the electrolyte.
- Partial dissolution of the surface of the solid.

The type of the product depends on nature of both the reactants (the liquid and solid surface) and the reaction conditions.

The main parameters that need to be attenuate are the pH, the nature of the solvent, the nature and concentration of dissolved substances. The first parameter affects ionization and, in many cases, the nature of ions containing the active elements. Second and third parameters influence the solvation.

The main properties of the solid are the texture, the nature of functional groups (e.g. the number and strength of the acidic and basic centers, the isoelectric point), the presence of exchangeable ions, and the reactivity (surface dissolution in acidic or basic solution etc.).

In the overall impregnation process, the following important facts should be noted:

- The properties of the liquid in the pores are different from those measured in the bulk.
- Equilibrium between solid and liquid is established slowly and even distribution of attached species inside the pores is not easy to attain.
- Deposition involves many different types of interaction as described above.

There are various impregnation techniques. Some of them are described below under separate heads.

**Equilibrium adsorption** (*also termed as ion exchange or wet impregnation technique*) – It is so called since the pores of the support are filled with the solvent before coming in contact with the precursor salt **(37)**. In this procedure, a suspension of the support in the salt solution is stirred for a prescribed length of time, followed by separation of the modified support by filtration / centrifugation. The supported salt is then dried and calcined prior to its reduction to the metal.

The notable variables in this technique are:

- Nature of metal salt solution and its concentration
- Equilibration time **(38)**
- The presence of competitive adsorbate ions along with metal salt **(39, 40, 41)**
- The pH of the solution

The distribution and dispersion of the metal in the resultant catalyst depends on the nature of the solution (metal salt/complex) **(42)**, concentration of the solution and equilibration time **(43)**. Thus, depending on the requirement appropriate conditions are to be chosen.

*Competitive Ion Effect*: In solutions like chloroplatinic acid in water competitive anions like chloride are used, which get adsorbed on the highly active centres on the support preferentially, thus forcing the active species into the pores **(39)**. Contrarily, to prevent the deposition of palladium in the pores of alumina, palladium is impregnated by ion exchange on alumina on which sodium / nickel ions have been incorporated earlier **(3)**. This ensures that the palladium species remains on the periphery of the pores resulting in shell type catalyst leading to selective hydrogenation of acetylene to ethylene. Generally inorganic acids (like HCl, $HNO_3$), organic dibasic acids, aromatic acids containing adjacent hydroxyl and carboxylic groups are used as competitive adsorbates **(44)**.

The adsorption capacity of the support and solubility of the salt limit the amount of the active component that can be impregnated by this method. Since it is usually restricted to a mono layer or less, the method is most suitable for precious metals.

**Pore filling** (also *termed as dry impregnation / incipient wetness*)**:** In this technique of impregnation, a predetermined volume of solution, equivalent to the water pore volume of the carrier or support, containing the active constituents is uniformly and slowly sprayed over the support. Alternatively, the support can be "poured" with constant agitation, into the flask containing solution of the active ingredients. Subsequently, drying evaporates the solvent. Here too, the dispersion is controlled by the concentration of the solution.

It is worthwhile to mention here that the drying step is of extreme importance. It is this step that determines the distribution or dispersion of the active species. An inhomogeneous distribution is the consequence of a high rate of temperature rise, since it would cause preferential evaporation of liquid from larger pores. Simultaneously, this concentrated solution will be conveyed to the smaller pores that are already dry, by capillary action. As evaporation makes headway, crystallization of the salt begins in pores still having solution and the crystal size of the metal salt is determined by the amount of the solution present. It is reported that when gamma alumina is impregnated with cuprous chloride, a fast drying results in its migration to the shell of the pellet and hence too uneven distribution **(44)**.

Following are the characteristics of this method:

- The crystallite size distribution is relatively broad and often reflects on the pore size distribution of the support itself.
- An increased metal loading results in loss of specific surface area.
- A narrow choice of metals due to solubility limitation of the salt solution.
- Leads to a concentration slant across the pellet unless conditions are optimized.

## 1.8. Pretreatments

### 1.8.1. Drying of gels

Supported metal catalysts prepared by co-precipitation from solutions containing precursors of support and metal normally form gels that need to be processed further. Drying is necessary in order to remove the large volume of water in the hydrogel **(44)**. Some collapse of the structure is expected, but care must be taken to properly control the drying operations if high porosity is desired.

Initially drying occurs through evaporation of moisture from the outside surface of the hydrogel. The rate of water loss is constant and mass transfer controlled by temperature, relative humidity, and flow rate of air over the surface and particle size of the residue. The process continues until moisture content drops to about 50 %. The residual mass now begins to shrink as most of the external water disappears. The material is now called a *Xerogel*.

Continued moisture loss occurs with declining rate, in which evaporation is controlled by capillary forces. The saturation point decreases as pores become smaller and evaporation slows until water is forced into larger pores by concentration gradients. As evaporation occurs, removal of moisture is blocked by smaller pores, large internal pressures of steam develop and the structure collapses, with loss of pore volume and surface area. Hence, high temperature gradients in the sample must be avoided. Lower temperatures give less surface loss; since evaporation rates are lower **(45)**. Vacuum drying at lower temperatures is a satisfactory laboratory procedure.

Control of evaporation rates is easier with large-scale equipment such as spray dryers, rotary kilns etc. These are known to give consistent and uniform results than laboratory ovens, hot plates etc. **(46, 47)**.

Dried xerogels contain 25% to 30% water, encapsulated in fine pores or chemically bound to the oxide. In this moist state, the material is sometimes easier to form into pellets and extrudates.

### 1.8.2. Calcination

Calcination is further heat treatment beyond drying during which several processes occur **(12, 48, 49)**: (1) Loss of chemically bound water, (2) changes in pore size distribution, (3) active phase generation, (4) surface conditioning and (5) stabilization of mechanical properties.

Alumina is a good example with which to demonstrate all of these features **(50)**. On drying of the hydrogel, a hydrous oxide known as "boehmite" is produced with the structure $Al_2O_3.nH_2O$. With pure boehmite, n = 1, but values up to 1.8 are found. The structure of boehmite is distinctive and the surface is hydrated. Upon calcination above 300°C, a series of phase change occurs, simultaneously with the loss of hydroxyl groups. This results in $\eta-, \gamma$ and $\delta -$ phases approximately at 300°C, 450°C and 900°C respectively. The transition from $\delta$ phase to $\theta$ - phase occurs when the former is calcined at about 1,000°C. Further calcination (up to 1200°C) of the $\theta -$ alumina leads to the formation of $\alpha -$ phase.

The temperature of calcination has to be chosen keeping in view, the required species on the surface like chloride, oxide or mixed phases. However, the support characteristics also determine the temperature and duration of calcination. Sulphiding, chloriding, ammonia treatment etc are steps required in some cases where undesired reactions are suppressed and selectivity for a particular reaction path / product is optimized.

### 1.8.3. Reduction

Reduction is the ultimate treatment given to a supported metal catalyst. This step ensures that the active species exists on the support in the zero (or near – zero) oxidation state. It is this state of the active species that makes it catalytically conducive for a specified reaction. If a metal species is required on the surface, the catalyst should be reduced preferably *in situ* as far as possible.

An EXAFS study of the impregnation of $\gamma$ - alumina with chloroplatinic acid **(51)**, and its subsequent treatment has provided some information concerning the nature of platinum species present at the various stages of the impregnation process. After impregnation and separation of the impregnated alumina, the resulting material composed of $PtCl_6^{2-}$ complexes that are weakly held on the alumina. After calcining at 530°C the platinum atoms are surrounded, on average, by five oxygens and 2.5 chlorines. At this temperature the platinum oxide particles are relatively small, but calcination at 700°C leads to larger platinum oxide agglomerates. Reduction of 530°C calcined material in a hydrogen stream, at 480°C gave platinum crystallites having an average coordination number of six as compared with twelve for a platinum atom in the bulk material. This data indicates that the reduction of small oxide particles leads to the formation of small platinum crystallite **(51)**.

Of recent, several novel methods of preparation of supported metal catalysts have been developed. Solvated metal atom dispersion, electron beam lithography, sol – gel methods are few to be named. Amongst these, sol – gel route has gained more acceptability, since it is easy to adapt and has the potential for preparation of tailor made catalysts. Since the emphasis of the thesis is on the application of sol – gel chemistry in catalysis, details on sol – gel chemistry in general and its applications in catalysis are presented below.

# PART 2: Sol – Gel Chemistry

## 1.9. Introduction

A century and a half year ago, in 1846, Ebelmann **(52)** accidentally obtained a silica gel from the interaction of silicic acid with humid air. This gave birth to a novel approach to the synthesis of oxide materials. This methodology is now known as the *sol – gel* technique. Nevertheless, it was during and after World War II that this soft chemistry materials synthesis method rapidly developed, first in the fields of ceramics and later catalysis.

As mentioned earlier, the sol – gel method provides a new approach to the synthesis of oxide materials **(53, 54, 55)**. Starting from molecular precursors, such as metal alkoxides, an oxide network is obtained via inorganic polymerization reaction **(56)**. These reactions occur in solutions and the term *sol – gel processing* is often used to describe the synthesis of inorganic oxides by *wet chemistry* methods. These processing offer many advantages as compared to the conventional *powder* route. A low temperature processing allows the synthesis of metastable oxide phases and evenly mixed organic – inorganic materials. The rheological properties of sols and gels allow the fabrication of fibers, films or composites by techniques such as spinning, dip – coating or impregnation.

Indeed, there are numerous advantages, in preparing solid catalysts by a sol – gel route, namely the particularly high rate of division, the flexibility of the synthesis conditions and needless to say, the large porosity – all parameters of paramount importance for heterogeneously catalyzed reactions. Finally, the sol – gel process allows the fabrication of multiphasic catalysts in a tailor made manner.

One unique property of the sol gel process is the ability to go all the way from the molecular precursor to the product, allowing a better control of the whole process and the synthesis of *tailor – made* materials. Mono dispersed, sub micron size colloids or transparent monolithic gels can be obtained by a careful control of its chemistry.

## 1.10. Sol – gel chemistry

The chemistry is based on the formation of a sol, i.e. a suspension of colloidal particles, typically in the dimension range of 1 to 100 nm **(57)**. When the sol is destabilized, this can lead to the formation of a flocculate or a gel.

The immediate and main characteristics of a gel are first its elastic property, which makes it appear as a solid system and second the fact that it occupies whole volume of the starting liquid mixtures i.e. there is no phase separation between solid and liquid as with a precipitate. Roughly speaking, the gel is a one – phase continuous mixture of a liquid and a solid. In other words, it can be considered as a liquid dispersed into a solid and vice versa **(58)**.

For example, silica gels can be easily made from a solution of sodium silicate and HCl in water through two main chemical reactions, namely hydrolysis and condensation, as follows:

$Na_2SiO_3 + 2HCl \rightarrow SiO_2 + 2NaCl + H_2O$ ........................................................(1)

Equation (1) is in fact results from a mass balance which is the sum of the following two processes:

$2(Na+ + SiO^{3-}) + 3(H+ OH) \rightarrow Si(OH)^4 + 2(Na+OH-)$ ................................(2)

Equation (2) indicates the sol formation of silicic acid through hydrolysis

$n.Si(OH)_4 \rightarrow n.(SiO_2, 2H_2O)$ ......................................................................(3)

The above equation is the result of condensation.

Since the late 1960s, organic precursors such as Tetra Methoxy Silane (TMOS) and Tetra Ethoxy Silane TEOS have been available. These alkoxides are soluble in organic solvents. They are hydrolyzed stoichiometrically by water molecule in the presence of acid or base catalysts. The following two equations show the corresponding hydrolysis and polymerization steps leading to the preparation of silica from an $Si(OR)_4$ precursor, where R is an alkyl group:

$Si(OR)_4H \rightarrow HO - Si(OR)_3 + RO^-$ ..................................................................(4)

Or

$Si(OR)_4OH- \rightarrow HO - Si(OR)_3 + ROH$ ..............................................................(5)

Equations (5) and (6) show the hydrolysis steps for base and acid catalysts respectively. The corresponding condensation steps are represented by the following two equations (7) and (8) respectively.

$ROSi(OH)_2O- + ROSi(OH)_3 \rightarrow RO\,(HO)_2 - Si - O - Si - (HO)_2\,RO + OH^-$ ........(6)

$ROSi\,(OH)_2(OH)_2+ + ROSi(OH)_3 \rightarrow RO\,(HO)_2{-}Si{-}O{-}Si{-}(HO)_2\,RO{+}H_3O^+$ ..........(7)

In fact, the dimer and the trimer resulting from the condensation of silicic acid are linear. Further polymerization develops in the entire volume and leads to a three dimensional network.

When water is the solvent, then *aquagel* (or *hydrogel*) is formed, while when the solvent is organic, an organogel (viz. acetogel, benzogel etc.) is formed. A complete review of organic precursor synthesis can be had from Mehrotra's **(59, 60)** work. Livage et al **(53, 56)** has explained the chemistry of sol – gel pertaining to metallic alkoxide precursors in terms of oxolation or olation reactions, which are nucleophilic substitutions involving nucleophilic entering entities ($H_2O$, $OH^-$, MOH) and neucleophilic leaving groups (ROH, $H_2O$) around the central metallic cations (Si, Al, Zr, Ti etc.).

Sol – gel chemistry is based on inorganic polymerization reaction **(56)**. Initiation is performed via the hydroxylation of metal alkoxides through the hydrolysis of alkoxy groups as shown below:

$$M - OR + HOH \rightarrow M - OH + ROH$$

As soon as hydroxyl groups are generated, propagation occurs through a polycondensation process. Depending on experimental conditions, two competitive mechanisms have to be considered that can be described as follows:

1. Formation of hydroxyl bridges by the elimination of solvent molecules via olation mechanism:

   $M - OH + M - OHX \rightarrow M - OH - M + XOH$ (X = H or alkyl group)

2. Formation of oxygen bridges by the elimination of water or ROH molecules via oxolation mechanism:

   $M - OH + M - OX \rightarrow M - O - M + XOH$ (X = H or alkyl group)

These three reactions (hydrolysis, oxolation, olation) can be involved in the transformation of a metal alkoxide precursor into an oxide network. The structure and the morphology of the resulting network strongly depend on the relative contribution of each reaction. These reactions can be described as nucleophilic substitutions. They involve three main reactive species – nucleophilic entering molecule ($H_2O$, $OH^-$, HO–M-), the nucleofugal leaving group (ROH, $H_2O$) and the metal atom (Si, Al, Zr, Ti etc.). Therefore, sol – gel chemistry could be tailored via the control of these reactive centers. However, this may not be as simple as it sounds here. Many other chemical species are involved. Metal alkoxides, for e.g. can be used neat or dissolved in a solvent. Moreover, literature survey indicates that foreign species such as organic acids and β - diketones or allied derivatives are commonly used to improve the process **(53, 61)**.

While on this discussion about introductory sol – gel, it is worthwhile to mention that a gel is only a state of matter, i.e. it is theoretically always possible to obtain a gel either by a chemical or by a physical means. Considering sol – gel chemistry, both hydrolysis and condensation reactions take place simultaneously during this synthesis, but it is generally possible to favor one step over the other by selecting a convenient catalyst. Alternatively, one can proceed through a two step sol – gel procedure, varying the catalyst in each step. First, one can develop essentially the hydrolysis step (nucleation or seeding), by first using acid catalysts and then changing the catalytic system from acid to base in the subsequent step to promote the condensation reactions (chain growth). The choice of the catalyst very important in the making of co-gels of different metallic cations precursor, because, depending on the respective gellation rates, either a co-gel or a gel coating can be obtained as a result. A good example of this is the preparation of silica-alumina gels from their respective alkoxide.

The physical and chemical properties of the final oxide material depend on various factors. Each of them is discussed in depth in the following paragraphs.

## 1.11. Factors influencing sol – gel chemistry

### 1.11.1. Nature of the metal

Literature reveals that the metals alkoxides, (other than silicon alkoxide) behave in a similar fashion. It has also been observed that, transition metal elements are very effective. This may be due the following two points –

- Transition metals have a lower electronegativity and exhibit a much higher electrophilic character.

- Most of these metal atoms can have several co ordinations and tend to expand their coordination number when full coordination is not satisfied.

Consider the electrophilic character of some transition metal alkoxides $M(OR)_n$. If the partial charge on the metal atom be expressed as the δM **(56, 62)** and their degree of unsaturation be expressed by the difference (N – n), where N is the coordination number usually found in the oxide. Table 3 **(53)** below shows the dependence of δM and {N – n} on rate of hydrolysis of the transition metal alkoxide.

**Table 3: Effect of degree of unsaturation on the rate of hydrolysis**

| **Alkoxide** | **δM** | **{N – n}** | **Hydrolysis** |
|---|---|---|---|
| $Zr(Oeth)_4$ | + 0.64 | 3.4 | Very Fast |
| $Ti(Oeth)_4$ | + 0.60 | 2 | Very Fast |
| $VO(Oeth)_3$ | + 0.46 | 1.2 | Fast |
| $Si(Oeth)_4$ | + 0.32 | 0 | Slow |
| $PO(Oeth)_3$ | + 0.13 | 0 | No |

It is observed that the chemical reactivity of alkoxides, towards nucleophilic reactions increases when both {N - n} and δM increase. Hydrolysis rates decrease from Silicon to phosphorous. Hydrolysis of titanium ethoxide is very fast; those of vanadium ethoxide and silicon ethoxide are respectively fast and slow while phosphorous ethoxide is very difficult to hydrolyze. As a result, transition metal, rare earth and aluminum oxides are much more reactive than the corresponding silicon oxides.

### 1.11.2. Molecular structure of alkoxide precursors

The full coordination of the metal atom is usually not satisfied in the monomeric transition metal alkoxide $M(OR)_n$. Coordination expansion occurs by the use of vacant d – orbitals to accept oxygen or nitrogen lone pairs from nucleophilic ligands. When neat, or dissolved in a polar solvent, coordination expansion of metal alkoxides occurs via the formation of alkoxy bridges. This leads to the formation more or less condensed oligomers. The degree of association depends on the nature of the metal atom. The molecular complexity increases with the atomic size of the metal within the given group **(63, 64)**. The molecular complexity also depends upon the nature of the alkoxy group. It decreases with bulkiness of the OR group because of steric hindrance effects **(63)**. The molecular complexity of liquid metal alkoxides is usually estimated from molecular weight measurements or mass spectrometry **(63, 65)**.

The effects of various alkoxides of titanium are extensively recorded in literature **(53)**. In titanium alkoxides, the primary alkoxy groups are trimeric species with a penta-coordinated metal atom while those with secondary or tertiary alkoxy groups are monomers with titanium in a tetrahedral environment. Differences in the reactivity related differences in structure of the molecular precursors have been observed for titanium alkoxides. The morphology of the sol – gel derived titania powder strongly depends on the nature of the alkoxy group from where it originated.

As a general rule, the formation of mono-dispersed particles is highly favored when the nucleation and the growth steps can be separated **(66, 67, 68)**. Spherical mono-dispersed $TiO_2$ particles can be obtained via controlled hydrolysis of dilute ethanolic solutions of titanium ethoxide **(69)** whereas poly dispersed particles of irregular shapes are obtained from titanium iso propoxide **(70)**.

The above phenomenon can be explained based on the differences on the molecular structures of the parent alkoxides. These differences lead to different behaviors towards hydrolysis and condensation. The tetra – coordinated monomeric species $Ti(Pr^i)_4$, is very reactive. As a result, as soon as one isopropyl group is hydrolyzed, condensation occurs. It is worthwhile to mention here that hydrolyzed precursors correspond closely to an alkoxide to water ratio of 3 **(71)**. Hydrolysis and condensation proceed simultaneously so that precipitation leads to small poly dispersed particles.

### 1.11.3. Hydrolysis ratio

This is one parameter that can be easily toyed with. Called as the hydrolysis ratio, it is defined as $h = H_2O/M$. Three cases for the value of $h$ are possible.

**(i) h < 1**

In this range, the condensation is mainly governed by alkoxy bridging oxolation, with preferential elimination of alcohol molecule. Sometimes, olation is also observed. Since the quantity of water is less, the hydrolysis step proceeds in a controlled manner. As a consequence of this, polymerization / gellation can occur as long as hydrolysis occurs. Once the water for hydrolysis is exhausted, polymerization terminates.

**(ii) $1 < h < n$**

This is a case when the hydrolysis ratio is between one and *n*. This means that quantity of water necessary for hydrolysis is $n^{-1}$ times the amount of the central metallic species. Polymeric gels are obtained.

**(iii) $h > n$**

Here is a case when excess of water is used. Resultant is obviously the formation of cross linked polymers, particulate gels and precipitates.

### 1.11.4. Catalysts (pH)

During the formation of a sol – gel material, say silica, it is often observed that $Si(OR)_4$ is not reactive since all its coordination points are fulfilled. To make a reactive center out of such species, one needs to manipulate the pH of the system. Inorganic acids protonate alkoxy ligands, which therefore become better leaving groups. Basic medium increases the neucleophilic prowess of the entering molecule.

Hydrolysis rates increase under acidic conditions, while condensation proceeds faster at pH greater than 7 **(53)**. It can be inferred that pH values much lesser than 7 are conducive to promote decoupling between hydrolysis and condensation.

### 1.11.5. The solvent

Metal alkoxides are often dissolved in organic solvents before hydrolysis is performed. These solvents usually correspond to the parent alcohol and are far from being chemically inert with respect to the alkoxide. Dilution leads to lower association.

Alkoxy bridging is not the only way for coordination expansion. The alternative process is the addition of a solvent donor molecule. In presence of such donor species, the metal alkoxides function as Lewis acids and react with the entrant bases (donor molecules). This leads to an extensive solvation. The stability of such solvates increases with the positive charge of the metal atom.

Starting from a given alkoxide, different molecular precursors can be obtained depending on the solvent used. For example, Zirconium alkoxides prefer to extend their coordination to the alcohol molecules (the solvent) rather than form alkoxy bridges. Thus it shows a reduced molecular complexity when dissolved in their parent alcohol instead of an inert solvent, say, benzene. Alkoxy bridges appear to be more stable towards hydrolysis than solvate bonds; different hydrolysis rates are therefore expected which would in turn lead to different oxide materials. As for example, precipitation occurs when Zr – n – propoxide is dissolved in n – propanol. It can, however, be avoided when zirconium propoxide is dissolved in a non – polar aprotic solvent such as cyclohexane. Hydrolysis and condensation rates are much faster in the former solvent than in cyclohexane. This may be attributed to the presence of solvent bond in the former and alkoxy bridges in the later.

Alcohol interchange reactions are known to occur when alkoxides are dissolved in alcohols other than the parent one **(57, 72, 73)**. Alcohol interchange strongly affects hydrolysis and condensation rates. Hence, it is possible to adjust gellation times by using different alcohols as solvents **(57, 74)**. For example, Titania precipitates are readily formed when a stoichiometric amount of water ($h = 2$) is added to Titanium isopropoxide, whereas stable sols are obtained with $Ti(OAm^{i})_4$. On the other hand, within a few minutes, gels made of complex polymeric species are rapidly formed when Titanium isopropoxide is dissolved in isoamyl alcohol prior to hydrolysis. The formation of mixed $Ti(OisoPr)_{4-x}(OisoAm)_x$ alkoxides occurs, leading to a decrease of the apparent functionality of the precursor that promotes anisotropic growth.

It is to be mentioned here that solvent modification not only effects gellation rates, but also morphology and porosity **(75)** of the resulting oxide.

To summarize, the chemistry of sol – gel process can be described as follows: Metal alkoxides, often used in the sol – gel process, are very reactive species. Hence, hydrolysis and condensation reactions occur rapidly when water is added. However, chemical modifications can be easily performed that can lead to new molecular precursors that exhibit a wide range of new properties. All these chemical reactions can be described as nucleophilic mechanism of addition or substitution reactions. Addition reactions lead to the formation of solvates or coordination complexes. Substitution occurs when highly electrophilic metal alkoxides react with nucleophilic hydroxylated ligands. The complexing behaviour of the organic ligands towards alkoxides depends upon their nucleophilic power and ability to form chelates **(76)**. As a general rule, complexation is favored when the electronegativity of the metal decreases and its ionic size increases, i.e., when going down the periodic table.

Alkoxy groups can be replaced by new ligands that can be removed on hydrolysis. Less electronegative ligands are first and rather quickly removed upon hydrolysis while more electronegative ones should mainly be removed during condensation reactions. Upon hydrolysis, a metal oxide is still obtained when the new ligand is hydrolysable. Whereas when the metal – ligand bond cannot be broken during hydrolysis, the resulting material is a mixed inorganic - organic network. It is these materials that open up wide possibilities of novel sol – gel based materials **(77)**

The synthesis of transparent sols, monolithic gels and mono dispersed powders requires a careful control of chemistry. In any case, uncontrolled precipitation must be avoided. Therefore, the first condition to fulfill this is to perform a homogeneous generation of water. Water for hydrolysis of alkoxides should be diluted in a solvent or provided in situ very slowly via a chemical reaction such as esterification, tertiary alcohol dehydration etc. Condensation must be rather slow compared to hydrolysis. This can be achieved by using organic ligands (acetate etc.) that decrease the functionality. Their removal by hydrolysis is difficult and is mainly removed during condensation. Hydrolysis with sub – stoichiometric hydrolysis ratios in the acidic medium also leads to a decrease of the functionality together with an acceleration of the hydrolysis rate that promotes de – coupling between hydrolysis and condition.

## 1.12. Role of sol – gel materials in heterogeneous catalysis

It has been reported that due to very high degree of metal dispersion (up to 90%) sol –gel catalysts are more active than their impregnated counterparts and less prone to deactivation with time on stream.

A Pt – Sn/$Al_2O_3$ catalyst prepared by sol – gel technique was designed for catalyzing n – heptane dehydrocyclization reaction in order to increase gasoline production. Results have shown that the selectivity of various aromatics produced is very high (65 – 75 %) whereas that of benzene, a known carcinogen, does not exceed beyond 13 % **(78)**.

Ru/$SiO_2$ catalysts prepared by the sol – gel technique gave interesting results concerning their textural and mechanical properties. Partial incorporation of Ru in the support network resulted in a strong metal stabilization towards sintering by $O_2$ at 450°C **(79, 80, 81)**. With Rh supported by titania or magnesia, prepared by the sol – gel route exhibited higher BET area in comparison with the corresponding traditional catalysts **(81)**. Lopez et al **(80)** extended similar trend for Pt and Pd supported sol – gel catalysts, using square planer complexes of the type, $MCl_2(NH_3)_2$ with M = Pt or Pd.

**Superacids (58)**prepared by the sol–gel method are environmentally favorable, develop greater acidity than pure $H_2SO_4$ in terms of acid strength and are able to isomerize normal paraffins into branched ones with enhanced octane number, and are of great interest for high-octane (lead – free) gasoline production. Superacids based on zirconia – sulfate systems are very active at low temperatures.

The sol – gel technique is an ideal route to prepare hydrogen transfer catalysts. The quaternary ammonium salts of Rh, Pt and Co are entrapped in silica**(82)** in order to make a highly stable, recyclable and active hydrogen transfer catalyst.

Other examples of sol – gel materials as catalyst **(83)** are enlisted below:

- Enantioselective catalytic activity of an entrapped organic molecule in a sol – gel silica matrix **(84)**.
- A new sol – gel method for hetergenizing a homogeneous catalyst, namely $Rh(Co)Cl(PR_3)$ **(85)**.

## 1.13. Conclusion

LaMer's model **(86)** convincingly summarizes mechanism of the whole sol – gel process. According to him, mono dispersed particles can be obtained when the critical supersaturation of the solute precursors is reached so that only one burst of nuclei occurs. Many nuclei are generated. They grow rapidly, lowering the molecular species concentration to a point below the nucleation concentration but high enough to allow particle growth to occur so that no secondary nucleation takes place during the growth process. The growth of colloidal particles is produced by diffusion of solute species on to the existing nuclei. Mono dispersed particles are favored when the nuclei are small and present in a narrow size distribution. This requires a careful control of the generation of the solute species. Nucleation and particle growth usually take place simultaneously, but it would be better to separate them so that no secondary nucleation takes place. This can be obtained when the nucleation rate remains rather slow while the growth rate is fast. Chemical modification again offers a possibility to modify nucleation and growth rates. Complexation enables good control of nucleation and growth processes and strongly affects parameters such as gellation time, porosity, particle structure and shape.

Mono dispersed particles are mainly spherical in shape. Different processes such as nucleation and growth of an amorphous phase, coiling of linear polymers, reticulation of highly branched polymers, or aggregation of very small crystalline particles could favor sphere formation. However, in all cases, the spherical shape is promoted by the minimization of interfacial energy that exists between a solid and liquid phase.

Among the many methods to prepare catalytic solid materials, i.e. precipitation, impregnation, ion exchange and fuming, the sol-gel process leads to some specific properties that are desirable in heterogeneous catalysis. In particular, the use of organic precursors allows one to obtain a large range of reactivity, chiefly when multi component catalysts are needed. They permit the manufacture of either ultra homogeneous mixture at the nano scale level or, in contrast, coatings of one phase by another. The chemical purity of the precursors is essential in order to control the synthesis of the catalytic materials from the point of view of reproducibility. Moreover, with such organic precursors it is no longer necessary to wash the wet gel before drying. This is considerable advantage too, since it is well known that such washing steps are very tedious and time consuming (weeks or more!). The reason is the very large network of very fine pores full of mother liquids (diffusion and permeability problems). It is also a general rule that dried gels display unusual high specific surface areas, large pore volumes, adjustable pore size distributions in the meso and macropore ranges, and amorphous phases able to undergo solid state chemistry reactions at rather low temperatures. Though it is not always a general rule, gels may exhibit very good resistance to thermal sintering even under severe conditions.

When applied to catalytic reactions, the gels exhibit better activities and/or selectivities. Their specific activities (per gram of material) are in general very high because of their large specific surface areas. If necessary, the porous texture of the still wet gel can be preserved by drying it with the help of the supercritical drying method (aerogel) or by applying the freeze drying process (cryogel).

The catalytic gels can be considered for "traditional" catalysis where selectivity is the principal goal. They can also be considered for more recent applications to environmental problems where much more severe conditions are encountered (reaction temperatures, presence of large quantities of water, etc.) which contribute to sintering and rapid deactivation processes.

## PART 3 : Application Of Sol – Gel Chemistry For Alumina Synthesis

### 1.14. Sol – gel chemistry of Alumina

The sol – gel chemistry of alumina synthesis is very interesting in the sense that it allows extreme flexibility as far as the morphology and texture of the final material is considered. In the case of alumina, numerous investigations have explored the textures and structures of various dry gels as a function of the precursors used. For e.g.: aluminium metal **(87)**, aluminium salts **(88)**, and alkoxides **(89)**. The materials produced range from fibrous gels to monosized spheres **(90, 91)**.

Other investigations have focused on the chemical processes that take place, including influence of anionic group on the formation of alumina **(91)**, hydrolysis and peptization **(92)**, and the chemical properties of alumina with respect to solvation **(93)**.

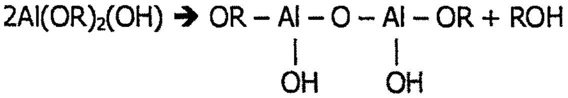
As in any sol – gel reaction, two reactions involved *viz.* hydrolysis and condensation.

The reactions involved in the preparation of alumina can be shown as follows:

Hydrolysis

$Al(OR)_3 + H_2O \rightarrow Al(OR)_2(OH) + ROH$

Condensation



$$2Al(OR)_2(OH) \rightarrow OR - \underset{\displaystyle OH}{\underset{|}{Al}} - O - \underset{\displaystyle OH}{\underset{|}{Al}} - OR + ROH$$

Gellation occurs due to polymerization, branching and cross-linking of molecular chains through chemical reaction. The nature and kinetics of the reaction determine the properties of the gel and the resultant alumina. Controlling the hydrolysis is imperative, otherwise one will end up with fine oxide powder as from colloidal sols. Condensation (a.k.a. polymerization) takes place only when soluble polymerizable species are present in the liquid for sufficient time. This is achieved by making use of mutual solvents like alcohols and controlling the molar ratio of alkoxide to water to catalyst, which can be an acid or a base.

This route has opened up immense possibilities of obtaining transparent bulk alumina gel, film or fiber just by controlling the alkoxide to water to catalyst ratio **(94)**.

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