CHAPTER II
LITERATURE SURVEY

2.1 Sol-gel process

Sol-gel technique has been extensively used to prepare amorphous and crystalline materials. The handling of precursor by heat treatment is a factor needed to be considered. In general, the sol-gel process is the synthesis of an organic network at low temperatures by a chemical reaction in solution. This technique involves the transition characterized by a relatively rapid change from a liquid (solution or colloidal solution) into a solid (gel-like state).

Sol-gel technology can be divided into two types. The first type is colloidal method. This method involves the suspension of solid particles in a liquid to form a sol (Schmidt, 1994). The second type is polymeric method. This method involves the polymerization of organometallic compounds, such as alkoxides that provide a convinient source for "inorganic" monomers to form a gel with three-dimensional network structure. The metal alkoxides, $M(OR)_n$, generally consist of metal atom, M, bonded through oxygen to one or more alkyl groups, where n is the valence of the cation. Cerium glycolate is also an organometallic compound that consists of metal alkoxide, thus, sol-gel processing for this substance is possible.

Generally, the precursor is dissolved in a suitable organic solvent in order to form a solution. The solvent must be carefully selected so that a solution with high concentration of the required component is obtained (Yi *et al*, 1991).

Sol- gel processing involves the following steps:
1. precursor formation
2. hydrolysis to form solution (sol)
3. polycondensation
4. film and gel formation
5. organic pyrolysis by heat treatment
6. densification and crystallization by annealing process

In the first step, starting material (metal alkoxides) are mixed in the selected solvent system to form a solution. In the gelation process, the transition from a solution into solid involves the simultaneous hydrolysis and polycondensation of metal alkoxide precursor. The following step, pyrolysis, involves in the removal of all organic compounds.

Sol-gel process is a deposition technique that offers the advantages of molecular homogeniety, high deposition rate and excellent compositional control. Because of mixing of components on nanoscale in the solution, it is easy to introduce trace element by adding it in the form of organometallic compounds, soluble organic or inorganic salts (Kwork *et al,* 1993).
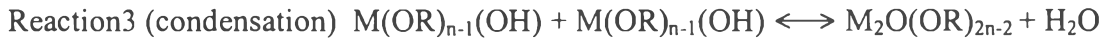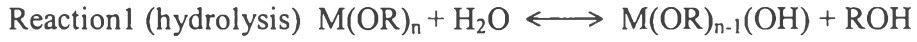
In addition, sol-gel process can be achieved at the ambient condition (vacuum is not needed.). Another advantage of this process is that it is inexpensive as compared to other techniques. Materials can be produced in a variety of forms, such as fine powders, thin films, monoliths and fibers. However, a drawback of the sol-gel process is excessive shrinkage that can cause cracking. A solution is selected to ensure that organic compounds are completely removed.

In the present time, metal alkoxides are used as the precursors for polymeric gel in sol-gel processing. These precursors are readily used with a suitable organic solvent, which is usually alcohol, in order to get a solution. The metal alkoxide bond is, in general, extremely susceptible to hydrolytic reaction leading to metal hydroxides or hydrated oxides. The choice of an alkoxide can be considered by many factors including metal content, reactivity, availability, cost, sensitivity to moisture and decomposition temperature.

A compound with less organic content and high metal content is proper precursor. Less organic solvent content causes in less volumetric shrinkage during drying and annealing. Therefore, film has less tendency to crack. However, a compound with high metal content is usually much more reactive, it may be difficult to prepare a stable solution. For alkoxides with different alkyl groups, the reactivity usually increases in the order of methyl > ethyl > propyl > butyl > higher order alkyl groups (Kwok *et al,* 1993).

There are two important reactions in polymeric gel formation. These reactions are partially hydrolysis, followed by condensation polymerization.

Polymerization steps via hydrolysis and condensation reaction are illustrated (Budd, 1986) by the following reactions (Yi and Sayer, 1991):

Reaction1 (hydrolysis) $M(OR)_n + H_2O \longleftrightarrow M(OR)_{n-1}(OH) + ROH$

Reaction2 (condensation) $M(OR)_n + M(OR)_{n-1}(OH) \longleftrightarrow M_2O(OR)_{2n-2} + ROH$

Reaction3 (condensation) $M(OR)_{n-1}(OH) + M(OR)_{n-1}(OH) \longleftrightarrow M_2O(OR)_{2n-2} + H_2O$

The M-O-M network product is formed by polycondensation reactions as shown in Reaction 2 and 3 in which alcohol and water are produced as the by-products. These reactions lead to a degree of gelation regarding to the appropriate amount of water. Other critical parameters needed to be considered are viscosity of the solutions. Therefore, many applications of controlled hydrolysis to obtain a desired molecular structure and appropriate viscosity of the solution are employed to improve spin ability and coating ability. In addition, solution concentration, viscosity, and surface tension of the solution, and the deposition technique determine the film thickness and uniformity.

Viscosity and rheological properties of the solutions are critical parameters needed to be considered. Therefore, many applications of controlled hydrolysis to obtain a desired molecular structure and appropriate viscosity of the solution are applied to improve spin ability and coating ability. In addition, the solution concentration, viscosity, surface tension of the solution, and the deposition technique determine the film thickness and uniformity.

Chambon and Winter, 1987 proposed a constitutive equation for linear viscoelasticity of incipient gels, which they called the gel equation.

$$\delta(t) = S \int_{-\infty}^{t} (t - t')^{-n} \gamma(t')dt' \qquad (2.1)$$

where δ is the shear stress, γ is the rate of deformation tensor, n is the relaxation exponent, and S is the gel strength parameter (with dimensions Pa.s^n), which depends on the cross-linking density and the molecular chain flexibility. A

more general version of this model has been developed, where the model proposed by Winter and Chambon constitutes a special case.

The storage modulus G' and the loss modulus G" at the gel point will both follow similar power laws in frequency

$$G' = G''/\tan \delta = S \omega^n \Gamma(1-n) \cos \delta \qquad (2.2)$$

where $\Gamma(1-n)$ is the gamma function. The phase angle between stress and strain (δ) is independent of frequency but proportional to the relaxation exponent

$$\delta = n \pi/2 \qquad (2.3)$$

This result suggests that the power law behavior of the dynamic moduli can be expressed as

$$G'(\omega) \sim G''(\omega) \sim \omega^n \qquad (2.4)$$

Theoretical models have been elaborated to rationalize values of the relaxation exponent in the physical accessible range $0 < n < 1$. In the theoretical advances, based on the fractal concept, the dynamic exponent n is associated with information about the molecular structure and connectivity of the incipient gel. The structure may be described by a fractal dimension d_f, which is defined by $R^{d}_f \sim M$, where R is the radius of gyration and M is the mass of a molecular cluster. On the basis of the percolation approach, the Rouse model, which assumes no hydrodynamic interaction between polymeric clusters, predicts $n = d/(d_f + 2)$, and with d = 3 (the space dimension) and $d_f = 2.5$ (percolation statistics) n assumes a value of 0.67. In the electrical analogy, a suggested isomorphism between the complex modulus and the electrical conductivity of a percolation network with randomly distributed resistors and capacitors yields a value of n = 0.72.

If we consider a situation where the strand length between cross-linking points of the incipient gel varies, one may anticipate that increasing strand length

should enhance the excluded volume effect. In order to take this into account, Muthukumar suggested that if the excluded volume interaction is fully screened, the scaling exponent can be expressed as

$$n = d(d + 2 - 2d_f)/2(d + 2 - d_f) \qquad (2.5)$$

Quite recently the relation between the viscoelastic and structural properties of systems of cross-linking polymers near the gel point was considered in the framework of a mechanical ladder model, which predicts a scaling law for the complex shear modulus with an exponent $0 \le n \le 0.5$. It was shown that the parameter n is related to the spectral dimension $d_s \ge 1$ of the fractal through the relationship.

$$n = 1 - d_s/2 \qquad (2.6)$$

Other parameters that need to be considered are aging of gel, removal of solvent, and heat treatment.

Aging represents the time between the formation of a gel and the removal of solvent. As long as the pore liquid remains in the matrix, a gel can undergo many transformations. For alkoxide derived gels, condensation between surface functional groups continue to occur after the gel point. This process can actually be desirable because it leads to a more cross-linked network that is mechanically stronger and easier to handled.

Drying is the evaporation of solvent from a gel network. Similar to aging, a gel is not static during drying and, for this reason, drying can be viewed as part of the overall aging process. The properties of product are, thus, dependent on the drying method and drying condition.

Calcination/sintering is often done in the presence of reactive gas (e.g. flowing air, oxygen, or hydrogen in order to burn off any residue organic or to oxidize (or reduce the sample). Exposing the sample to a high temperature over an extended period of time leads to sintering and consequently a decrease in surface

area. The process can also cause the material to crystallize into different structural forms. Thus, the physical characteristics of the product depend on parameters such as temperature, heating rate, time, and gaseous environment.

By varying these parameters, the different product properties will be obtained, for example surface area, pore volume, pore size distribution. Ward and Ko.,1993 studied about effect of sol gel parameters. To determine the effect of sol-gel parameter on formation and properties of zirconia aerogels, they prepared a series of alcogels made with different acid and water contents. They first examined the effect of acid ratio on the gel time and surface area of the aerogel. When a greater amount of acid was used, precipitation was prevented various degrees; instead, a solid gel was formed. After that the above series of gels were extracted and heat treated to 773 K, a common catalyst pretreatment temperature. They obtained the highest surface area of zirconia oxide at the specific acid amount. More or less acid added resulting in decreasing surface area and increasing gel time. The effect of water ratio on the gel time and surface area of the aerogel was examined by performing set of experiments with $H_2O/Zr^{4+} = 2.0$ and varying the acid amount. At each acid amount, decreasing the water content increased the gel time but decreasing surface area. From this work they conclude that At each water ratio, the gel time behavior with respect to acid content was identical, with larger acid contents increasing the gel time. The effect of heat treatment was also studied, the result showed that surface area and pore volume collaps did occur with heat temperature of treatment, the lower surface area, the lower pore volume were obtained.

Intense interest has been focused on the investigation of novel metal alkoxides during the last two decades owing to their remarkable application as precursors in the sol-gel synthesis of inorganic metal oxides for catalytic, composite, and electroceramic material, coatings, and fibers. However, some significant weak point of metal alkoxides make it difficult to investigate their structures. These drawbacks are their high relative cost and low hydrolytic stability or high reactivity towards water. Their high reactivity is the main problem in processing inorganic oxides from alkoxides by sol-gel method.

Many researchers have resolved these problems by modifying the simple alkoxide precursors to reduce hydrolytic reactivity. However, it is not a low-cost and

simple way. The synthesis of new metal alkoxides possessing unique structures and properties is important for the study of sol-gel processes and the evolution of metal alkoxide chemistry.

The precursor used in sol gel process is prepared via the oxide one pot synthesis (OOPS) process. The precursor is inexpensive, and has low hydrolytic stability. Also the chemical reaction is simple and straight forward. The preparation of cerium alkoxide precursor is based on the following reaction (Ksapabutr, 2002):
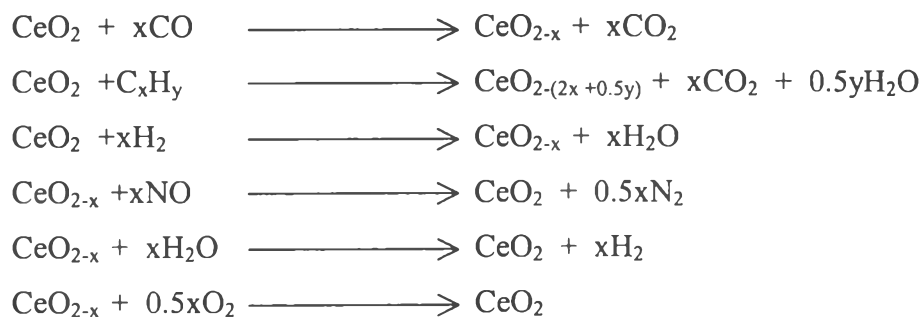
$$Ce(OH)_4 + HOCH_2CH_2OH \xleftrightarrow{\hspace{2cm}} cerium\ glycolate + H_2O$$

$$200\ °C$$
$$TETA/with\ NaOH$$
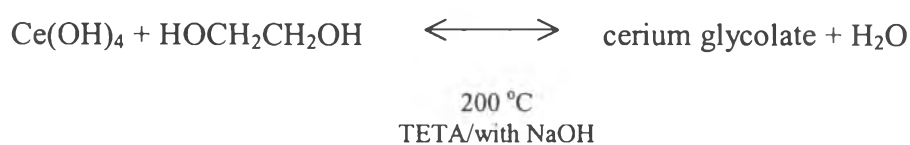
2.2 Application of CeO$_2$

2.2.1 Three-Way-Catalyst (TWC)

The most important application of ceria in catalysis is certainly the treatment of exhaust gases (CO, NO, hydrocarbons) from spark-ignited internal combustion engines. It is not the intention of this review to fully describe the utilization of ceria in TWC as a number of papers have been recently published on the role of ceria in TWC technology.

TWC catalyst formulation consists primarily of noble metals and metal oxides dispersed either on the surface of alumina pellets or on an alumina wash anchored to a monolithic ceramic substrate. It is very well-known that the main role of ceria in this complex mixture is to provide oxygen buffering capacity during the rich/lean oscillation of exhaust gases. A typical closed-loop control system causes the air/fuel ratio (A/F) to cycle rapidly around the stoichiometric composition with a frequency of the order of Hertz (Hz). Under these conditions, the catalyst is exposed a constantly varying feed stream compositions going alternately from rich exhaust stoichiometry (deficient O$_2$) to lean stoichiometry (excess O$_2$). In this environment, ceria has the ability to donate its oxygen for the removal of CO and hydrocarbons (HCs) during the oxygen-deficient portion of the cycle while adsorbing and storing oxygen from O$_2$, NO and water during excursion into the lean part of the cycle.

These reactions positively affect the conversion of the three major pollutants (CO, HCs and NO) under conditions typically encountered in the normal operation of a three-way catalyst.

$$CeO_2 + xCO \longrightarrow CeO_{2-x} + xCO_2$$

$$CeO_2 + C_xH_y \longrightarrow CeO_{2-(2x+0.5y)} + xCO_2 + 0.5yH_2O$$

$$CeO_2 + xH_2 \longrightarrow CeO_{2-x} + xH_2O$$

$$CeO_{2-x} + xNO \longrightarrow CeO_2 + 0.5xN_2$$

$$CeO_{2-x} + xH_2O \longrightarrow CeO_2 + xH_2$$

$$CeO_{2-x} + 0.5xO_2 \longrightarrow CeO_2$$

This ability derives from the ease with which ceria can deviate from a stoichiometric format to give a continuum of oxygen deficient nonstoichiometric oxides CeO_{2-x}. If the atmospheric environment in which CeO_2 operates changing continuously from a net oxidizing to a net reduction composition, the oxidation state of cerium correspondingly shifts from +4 to +3 , enhancing the conversion of CO and hydrocarbons during rich oscillations, and that of NO during lean oscillations. This feature of ceria is called oxygen storage capacity, and its uniqueness derives from the kinetics and thermodynamics of the redox processes which allow a good fit of the extent and the rate of the redox processes on the ceria surface and the timescale of fluctuation of composition in the exhaust. This feature is enhanced if ceria is in contact with noble metals (such as Rh), which can help the transfer of oxygen from the bulk to the surface.

2.2.2 Catalytic Wet Oxidation (CWO)

The use of ceria in environmental applications also involves aqueous phase in catalytic wet oxidation(CWO), a destruction method applied to waste streams. The aim is catalytic abatement of organic pollutants present in wastewater to less toxic compounds that are then amenable to biological treatment for final purification. Catalytic wet oxidation is carried out at high oxygen pressure and high temperature to oxidize a significantly high concentration of organic compounds in aqueous phase.

Attention has been focused on ceria because it can active both in the oxidation of lower carboxylic acids (especially acetic acid) and of ammonia. Ammonia is one of the pollutants, which causes eutrophication of the receiving water system. Moreover, because nitrogen atoms composed in various organic compounds are converted into ammonia during wet oxidation, a further treatment to remove ammonia is necessary even after the carbonaceous part of the organic pollutant has been removed.

Imamura *et al.,* 1999 first found the beneficial effect of CeO_2 addition on a CO_3O_2-BiO(OH) composite catalyst in the oxidation of ammonia. The activity was found to increase by a factor of 2 with the addition of approximately 10% wt. of CeO_2. Similar catalyst compositions containing CO_3O_4-CeO_2 and MnO_x-Ce_2 were also active in this reaction. Generally, it was observed that Co_3O_4 and CeO_2 had no activity in this reaction under the same conditions. Therefore, it was first suggested that the redox properties of the mixed oxide compositions were the main factors contributing to their activities.

Overall, it seems like these ceria-based materials are promising systems for the catalytic depollution of water streams. The main features of these systems are:

1. stability under reaction conditions
2. low catalyst leaching
3. the possibility of varying the composition over an almost unlimited range
4. enhanced textural and redox properties at low temperatures

However, despite the increasing number of studies in this direction, research is generally focused exclusively on the assessment of catalytic behavior and kinetic modeling. Catalyst characterization under reaction conditions has not been adequately addressed, and in our opinion, needs to be investigated in the near future for a better understanding of catalysts of this type and their rational design.

2.2.3 Catalyst Removal of SOₓ

It is very well known that sulfur oxides are precursors of acid rain and that their emissions constitute a global threat to the atmosphere. Environmental

agencies have therefore regulated emissions of SO_2 and SO_3; the limits are becoming increasingly severe. Approximately 5% of all SO_x emissions are from FCC units. In these, the amount of sulfur that is emitted is primarily a function of the sulfur in the feed stream and of conversion in the reactor. Nearly 60% of incoming sulfur remains in the liquid products and 50% is converted to H_2S which is then treated downstream in a Claus plant. The rest (<10%; the amount is highly dependent on feedstock composition) remains trapped in the coke which builds up on the catalyst. This sulfur is then oxidized to SO_3 in the catalyst regeneration step and it is this SO_2/SO_3 mixture that needs to be treated before release into the atmosphere. Desulfurization at this stage can be done by flue gas scrubbing, however, the addition of an SO_x adsorption/reduction additive to the main FCC catalyst formulation is a less costly option. The function of this additive is to transform SO_x back to H_2S which can then be treated directly in the Claus plant.

A catalyst for this purpose should thus perform the following actions :

- oxidation of SO_2 to SO_3 during FCC catalyst regeneration;
- chemisorpton of SO_3 and its storage as sulfate; and
- release of sulfate as H_2S (reduction step) in the FCC riser reactor.

The temperatures for the first and the second step, which are carried out in the catalyst regeneration section of the plant, are in excess of 973 K. Whereas the final step is carried out at around 820 K in the riser reactor. An ideal catalyst should have the following characteristic to be of interest for this section :

1. Basic site for adsorption of SO_2/SO_3
2. Active centers for oxidation of SO_2 to SO_3
3. Redox properties for the reductive decomposition of sulfates to H_2S under reducing atmosphere

One catalytic system which meets all these criteria is a ceria containing magnesium aluminate spinel MgO solid solution of the type $CeO_2/MgAl_2O_4\ MgO$. Several modifications of the basic system have recently appeared containing V and Fe either deposited or incorporated in the solid solution. The role of ceria in this catalyst formulation derives from its basic/redox character. Ceria possesses sufficient oxidation activity to promote oxidation of SO_2 to SO_3 and its basic sites allow the adsorption of SO_2/SO_3 with formation of sulfates.

In addition, it must facilitate the reductive desorption of sulfates as hydrogen sulfide under reductive conditions. A possible scheme for the reaction is the following :

$$SO_2 + 0.5O_2 \longleftrightarrow SO_3 \tag{1}$$

$$SO_3 + MO \longleftrightarrow MSO_4 \tag{2}$$

$$MSO_4 + red. \longleftrightarrow MO + H_2S + H_2O \tag{3}$$

red. = C_xH_y, H_2

M = sulfur storage component

Cerium dioxide can contribute to all these steps. Its reducibility facilitates the oxidation of SO_2 to SO_3 under FCC regeneration conditions by reacting with SO_2 to give substoichiometric cerium oxide, which is then reoxidized by oxygen:

$$xSO_2 + CeO_2 \longleftrightarrow xSO_3 + CeO_{2-x}$$

$$CeO_{2-x} + 0.5xO_2 \longleftrightarrow CeO_2$$

The next step is the adsorption of SO_3. The best oxides for the storage of SO_3 are those that form stable metal sulfates following SO_3 adsorption.

CeO_2 is also an efficient catalyst for reduction of sulfate to give H_2S (step 3 of the reaction scheme). The direct reaction between SO_2 and hydrocarbons or CO to give sulfer catalyzed by ceria was also found to be of potential interest. In this case, the suggested mechanism implies the alternate reduction and oxidation of the catalyst through the formation of oxygen vacancies. High oxygen mobility in the catalyst is an important requirement facilitating oxygen transfer on the surface and from the bulk to the surface. This high mobility can be obtained through the doping of ceria lattice with transition and rare-earth metal oxides like Zr, Cu, La.

The use of catalyst compositions similar to those of FCC has also been reported to be effective for the treatment of tail gases (SO_2, CO, COS and CS_2) from a Claus plant. In this case, tail gases are oxidatively adsorbed over the catalyst in one

step and reductively desorbed with H_2 to give H_2S, which is recycled to the Claus plant for further processing.

Under FCC conditions, ceria is also able to reduce NO_x emission originating from a cracking unit. Here, the role of ceria is to provide oxygen vacancies for the reduction of NO to N_2. The ceria-containing material can be reduced by H_2 or hydrocarbons in the riser reactor and in the regenerator it serves as a reducing agent for NO.

A substantial amount of reducing is also required in the regenerator to maintain the redox process of cerium between Ce^{3+} and Ce^{4+}. CO originating from incomplete combustion of coke can be used for this purpose and a direct inverse relationship exists between CO concentration in the regenerator and NO emitted by the cracking unit. Reduction of 300 ppm. NO_x to 150 was observed.

One of the important properties of catalyst is the surface area. Normally higher surface area leads to better activity of catalyst, and that brought out an idea to improve surface area and high purity catalyst by using sol-gel technique.

Most of the previous preparation methods of ceria use traditional techniques such as precipitation, hydrothermal synthesis, and sol-gel. Though the sol-gel technique yields products with high purity, homogeneity, and well-controlled properties, the use of expensive organometallic compounds as precursors represents a disadvantage. Hence, a new synthetic approach becomes important. Alternatively, using supramolecular long-range ordered molecular aggregates of surfactants as templating agents, mesostructured aluminosilicates having high surface area were synthesized. This synthetic method makes it possible to synthesize new oxide mesoporous materials, such as ZrO_2, TiO_2, and Nb_2O_5. Recently, by using a hybrid organic route, the preparation of high-surface-area ceria with higher thermal stability was also reported, although a long-range ordered structure was not obtained.

Textural properties of the cerium oxide seem dependent on the preparation methods. Some investigations have sought the relationships between the synthesis methods and surface and bulk structural properties, but to date some questions still remain concerning the crystalline structure of ceria derived from supramecular templates and how it affects the formation of the lattice vacancies in ceria and its catalytic properties. Deniela Terribile *et al.,* 1997 studied a surfactant-assisted

synthesis method is applied to prepare ceria nanophases. The procedure they used to prepare cerium oxide exploits the interaction of hydrous cerium oxide with cationic surfactant under basic condition, where the organic molecule can be easily incorporated within the hydrous oxide by ion exchange with hydroxy group, at a pH well above that of the isoelectric point of the oxide (6.75). For the preparation, an aqueous solution of the appropriate cetyltrimethylammonium bromide and $CeCl_3 \cdot 7H_2O$. From comparing sol-gel method and conventional precipitation method, sol gel process can improve surface area, textural, structural, and redox properties for catalyst applications.