CHAPTER II

BACKGROUND AND LITERATURE SURVEY

Zirconium oxide or zirconia has the high melting point of 2700°C. It occurs naturally in three crystal phases at different temperatures. At very high (>2370 °C), intermediate (1170 to 2370 °C), and low (< 1170°C) temperature, the material has cubic, tetragonal and monoclinic structure, respectively. Different structure of zirconia makes it suitable for different application (Ward *et al.*,1993).

Zirconia is used commercially in chemical refineries and in environmental catalysts. It is one of the most widely used support because it is stable at high temperatures. Additionally, zirconia has good mechanical properties that include high compressive strength, hardness and attrition resistance. For many reactions, the maximum temperature could reach up to 500 to 600 °C in a reactor or upon regenerator. The zirconia generally has good stability under these conditions. For many uses, such as pollution control where oxidation reactions are required at a very high temperature, catalyst supports reasonably stable up to temperatures as high as 1000 °C may be needed. Examples of processes using zirconia as a support are oxidation, polymerisation for polypropylene and polyethylene productions, reduction, and steam reforming.

2.1 Zirconia Application

2.1.1 Conversion of Natural Gas : Synthesis Gas Chemistry

Natural gas is very worldwide attainably and will continue being important resource in the next centuries, after reserves of oil are overtired. There is, thus, strong interest in the conversion of natural gas, whose main component is methane, into chemicals and liquid transportation fuels. Direct conversion, for example, through oxidative coupling,
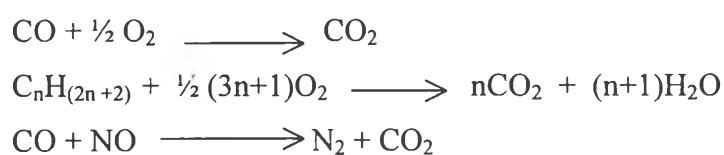
$$2CH_4 + \tfrac{1}{2} O_2 \longrightarrow C_2H_6 + H_2O$$

is in the research stage, and shows no immediate commercial potential.

Pracital processes for the utilisation of natural gas will, therefore, rely on the intial conversion of the feedstock to synthesis gas, through the well-established technology of steam reforming. Synthesis gas is a mixture of carbon monoxide, carbon dioxide and hydrogen with a composition, depending on the feedstock and details of the conversion process.

Methanol synthesis is a large-scale commercial process, dominated by the ICI copper/zinc/alumina catalyst. A number of interesting academic studies showed that zirconia on its own was an effective methanol synthesis catalyst. The synthesis of both synthetic fuels and higher alcohols are the subject of active research and development, and zirconia has a prominent role to play in each. Researchers have now spent over ten years developing catalysts suitable for the production of waxy hydrocarbons from synthesis gas, and have filed a wide range of patents worldwide. The best catalysts contain cobalt, zirconia and silica yielding excellent activity and selectivity. The role of zirconia component is to increase the activity of the catalyst without changing the high level of selectivity to higher hydrocarbons.

2.1.2 Automotive Exhaust Applications

The exhaust from the spark-ignition internal combustion engine of an automobile contains small concentrations of hydrocarbons, CO, and NO. These contaminants are major contributors to air pollution and one of particular concern in urban area. A detail analysis of publications in the year 1995 reveals that about 50 % of contributions deal with the use of catalysts in the treatment of emissions from mobile and stationary sources, and that the majority of articles deal with the application of catalysts in TWCs. The catalysts must be carried out in three chemical reactions:

$$CO + \frac{1}{2} O_2 \longrightarrow CO_2$$

$$C_nH_{(2n+2)} + \frac{1}{2}(3n+1)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

$$CO + NO \longrightarrow N_2 + CO_2$$

The catalyst application to automobiles is unique. It was the large-scale use of a catalyst in a consumer product. Rare earth oxides are widely investigated with ceria providing a number of benefits in automotive catalysis properties, especially oxygen storage capacity (OSC), the ability to store oxygen under fuel-lean operating condition. However, the OSC of pure ceria has been known to degrade with time in the automotive exhaust environment. This has forced researchers to seek new catalyst compositions with the aim of (i) increasing thermal stability, and ii) enhancing low-temperature redox performances. New catalyst composition involves the use of ceria doped with zirconia. CeO_2/ZrO_2 catalysts showed no loss of metal surface area, and zirconia imparts added thermal stability to support ceria catalysts. Zirconia helped to promote the OSC of ceria in an automotive emissions catalytic converter by promoting the formation and the stabilization of more active ceria site than those present for bulk ceria (Rossignal *et al.*, 1999).

2.1.3 Environmental Protection Catalysis

Environmental protection catalysis has an important and wide-ranging part to play in the drive to protect the environment. Zirconia has potential uses for the removal atmospheric pollution. In United States, the more limitations have been set for NO_x emission from automobiles since 1981, and later a major change in catalyst design was required. A homogeneous gas-phase reduction process in which NO_x is selectively reduced to N_2 and H_2O by NH_3 is the following reaction.

$$6NO + 4NH_3 \longrightarrow 6H_2O + 5N_2$$

The most active catalyst was formed when vanadia was supported on titania or zirconia. The catalyst application of this type was utilized for reducing NO_x and CO in exhaust gases. The designed catalyst was typically vanadium pentoxide on zirconia and cobalt (II) oxide, with mullite as an inert medium, operated at temperature of about 380 ^{o}C and at atmosperic pressure. This catalyst was treated with a composition of flue gas containing 100 ppm of NOx and 150 ppm of CO. Typically, about 100 ppm concentration of NH_3 was also introduced to the catalyst in which 90 % of both CO and nitrogen oxide were removed.

Another application of zirconia catalysis in pollution control uses is for the removal of sulfur oxides from the atmosphere. It is well-known that SO_2 is a cause of acid rain, and that their emission constitutes a global threat to the atmosphere. An ideal catalyst should have the following characterristics to be of interest for this reaction: (i) basic site for adsorption of SO_2/SO_3, (ii) active centers for oxidation of SO_2 to SO_3, and (iii) redox properties for the reductive decomposition of sulfates to H_2S under reducing atmosphere.

In gasification of wet wastes, zirconia can also serve as a catalyst. Addition of zirconia completely prevents both tar and coke formation during occurred of gasification, resulting in significant engineering advantages and a reusable catalyst.

2.1.4 Polymerisation Catalysis

Titanium and zirconium compounds are active catalysts for the Ziegler – Natta polymerisation of olefins using zirconium combining with an alkyl aluminoxane oligomer. The catalyst can be obtained by mixing $2ZrCl_2$ or $2Zr(CH_3)_2$ with a cyclic or linear aluminium compound. Additional zirconia had a positive effect on the final products. It enhances the lifetime of the catalyst system in ethylene polymerization. Another advantage of the system was the very narrow molecular weight distribution, and high molecular weight ideally atactic polymers synthesized from propylene.

2.1.5 Miscellaneous Applications

Zirconia has important applications in both pillared clays and strong acid catalysts. When pillars are added between the layers of smectite clays, catalysts are produced which have many of the characteristics of zeolites, particularly high surface area and acidity. Hydroxy zirconium compounds are effective pillars, and zirconium is one of a few transition metals, which can be used in this manner. Zirconia itself shows useful acidity, and it is well known as a dehydration catalyst. Zirconia has some unique properties for hydrogenation reactions, and it has been commercialized in Japan. Researchers have concentrated on the study of strong acid catalysts by introducing small quantities of sulfate to other solid acidic properties.

Sulphated zirconias are well known for exhibiting very strong acidic properties after activation. The active species was expected to be surface sulphate ions. A typical example found in literature was the isomerisation of alkane, such as n-butane to iso-butane at temperature as low as 100 $^\circ$ C. The strong acid properties of sulphated zirconias can be used to replace the environmentally unfavorable aluminium chloride in Friedel-Craft reactions.

2.2 Zirconia Preparation

Zirconia is usually produced from the zircon, $ZrSiO_4$. To produce zirconia from zircon, the first step is to convert zircon to zirconyl chloride, $ZrOCl_28H_2O$. There are two methods employed in the production of zirconia from the zirconyl chloride : thermal decomposition and precipitation. For thermal decomposition method, zirconyl chloride ($ZrOCl_2.8H_2O$) is heated to 200 $^\circ$C until it starts dehydration to $ZrOCl_2$ and becomes dehydrated. In the next step, $ZrOCl_2$ decomposes into chlorine gas and becomes zirconia at a much higher temperature. The precipitation method, on the other hand, involves chemical reactions producing zirconia hydroxide as the intermediate. These reactions are accomplished by adding $ZrOCl_2.8H_2O$ to NH_4OH. The precipitate is formed, filtered, washed, dried and calcined (Feng *et al.*, 1995).

2.3 Sol-Gel Process

Sol-gel technology has expanded dramatically since 1800. It generally refers to a low-temperature method using chemical precursors that can produce ceramics and glasses with better purity and homogeneity than high temperature conventional processes. This process has been employed to produce a wide range of compositions (mostly oxides) in various forms, including powders, fibers, coatings, thin films, monoliths and composites, and porous membranes. Organic/inorganic hybrids, where a gel (usually silica) is impregnated with polymers or organic dyes to provide specific properties, can also be made.

The sol-gel technique is a method to produce solid from gel. This well-known technique functions from both colloidal solutions and metal-organic combinations. Metal alkoxides can be reacted with water to produce a finely

distributed sol, followed by polymerization of the hydrolyzed alkoxides through condensation of the hydroxyl groups. When the extent of polymerization and cross-linking of polymeric molecules become extensive, the entire solution becomes rigid, and a solid gel is formed. Controlling the hydrolysis and condensation between particles leads to aggregation and the formation of gel in a three-dimensional network of particles in a polymeric matrix. With an alkoxide ($M(OR)_n$) as a precursor, sol-gel chemistry can be described in terms of two separated reactions (Ward and Ko, 1993) :

Hydrolysis:
$$-MOR + H_2O \longrightarrow MOH + ROH$$

Condensation :
$$-MOH + ROH \longrightarrow -MOM- + ROH$$

$$-MOH + HOM \longrightarrow -MOM- + H_2O$$

During the initial reaction, the reactant hydrolyzes and condenses to form gel. The hydrolysis occurs when water is added to the alkoxide, which is usually dissolved in alcohol. In the condensation or polymerization reactions, alkoxy groups (-MOR) react with hydroxyl groups (-MOH), formed during the hydrolysis step, to form metaloxanes (-MOM-). During this step, the primary structure and the properties of the gel are determined. These reactions occur simultaneously, and usually do not go to completion. It is important to note that the conditions, under which the condensation reaction occurs, are important in determining the nature of the final product as either a gel or a precipitate.

The chemical reactivity of metal alkoxides towards hydrolysis and condensation depends mainly on

- the electronegativity of the metal atom, its ability to increase the coordiantion number,

- the steric hindrance of the alkoxy group,

- the molecular structure of the metal alkoxides (monomeric or oligomeric),

- the amount of added water in the hydrolysis step and how the water is added, and

- pH.

Gomez *et al.* (1997) prepared zirconia-silica mixed oxides in an acid (HCl, pH 3) and basic (NH$_4$OH, pH 9) solutions. The results showed that acid preparation formed solids of high surface area, whereas basic one formed solids of low surface area. Moreover, the effect of the pH on the gelation of ZrO$_2$/SiO$_2$ mixed oxides was of importance on the textural and shape of the solid particles. Small spherical particles were obtained in basic pH, and cubic particles were observed when the catalysts were prepared in acid medium.

The second stage in the sol-gel synthesis including drying and calcination of the gel involves the desorption of water, the evaporation of the solvent, the desorption of organic residues and structural changes. The solvent entrapped in the sol-gel products is removed from gel by either evaporative drying or drying with supercritical extraction leading to the formation of strong capillary forces in order to prepare gels containing uniform-sized pores or at least a narrow pore size distribution.

After the removal of pore liquid, further treatment called calcination/sintering is necessary to convert a gel into a catalytically useful form. Often, heating is performed in the presence of a reactive gas (air, oxygen or hydrogen) in order to burn off any residual organics or oxidize the samples. The physical characteristics of a product depend on parameters, such as temperature, heating rate, time, and gaseous environment.

The advantages of the sol-gel process, in general, are: (1) higher purity of the product and homogeneity are obtained, and (2) a relatively low temperature is required, reducing loss of volatile components and being more environmental friendly. In addition, this process can produce some materials with thermal and thermodynamic stabilities that can not be made by conventional methods.

The disadvantages of sol-gel process include the need of expensive high-purity alkoxides and the specific of materials because the process relies on the hydrolysis and condensation of alkoxide based precursors. This tends to limit the process compositional flexibility, but the limitation is a minor factor for special applications or those cases where a conventional method fails (Richardson *et al.*, 1989)

Ward *et al.* (1993) prepared zirconia by a sol-gel method using zirconium propoxide ($Zr(n-OC_2H_7)_4$) as a precursor in the addition of n-propanol solution containing the hydrolysis catalyst (HNO_3) into the precursor. The mixed solution was maintained under a covered beaker at room temperature for 2 hours Afterward, the gel was dried by semicontinuous supercritical carbon dioxide (CO_2) at 343 K for 2 hours. and, then, calcined by two different methods. For the first method, powders were calcined in a vacuum oven at 383 K for 3 hours. On the other, powders were calcined in flowing oxygen at 773 K for 2 hours for the second method.

Ward *et al.* (1994) also prepared zirconia using preformed sol as a staring material. Sols were gelled by the addition of NH_4OH/HNO_3 ratio of 0.3-0.4. Stirring was continued until the vortex created by the stirring disappeared. After aging for 2-3 hours, the gel was dried for 3 hours at 383 K under a vacuum of 3.4 kPa. The dried samples were covered and allowed to stay overnight. Next, powders were subsequently calcined to 773 K for 2 hours under flowing of oxygen (24 L/h.)

Stocker *et al.* (1997) prepared zirconia by using tetra-n-butoxy zirconium (IV) (TBOZ; 80 wt% in n-butanol) as a precursor. They studied the effect of nitric acid-to-alkoxide ratios and alcoholic solvents. Increasing the acid-to-alkoxide ratio, R, from 0.3 to 1.6 resulted in smaller pore size distributions and larger monoclinic zirconia fraction. Preparations carried out with EtOH, n-BuOH, and t-BuOH revealed that the steric hindrance of the solvent affects the pore size distribution, BET surface area, and fraction of monoclinic zirconia.

Stocker *et al.* (1997) produced zirconia aerogels from tetra-n-butoxy zirconium (IV) using different types of mono- and dicarboxylic acid catalysts. They also studied the effect of acid to alkoxide ratio on the properties of product. With increasing acid-to-alkoxide ratio, the effect of complexation increased and the acid

as a potent chelating agent (R = 1 and 2). The use of oxalic and adipic acid resulted in lower specific surface area when compared to that of acetic acid.

Sheng Wu *et al.* (2000) improved the method of preparing ZrO_2 sol by controlling the hydrolysis of zirconium alkoxide through the slowly-released esterification water. In addition, the acetic acid also served as a chelating ligand and reduced the rate of hydrolysis. The result showed that the rate of hydrolysis decreased and minimized the agglomeration, meaning that very fine particle of zirconia can be formed.

Pure ZrO_2 and SiO_2, and the mixture of SiO_2-ZrO_2 were prepared by a sol-gel method in the presence of tetrapropyl-ammoniumhydroxide as a gelling agent. The use of a strong base gelling agent led to the preparation of amorphous mesoporous materials. Increasing the amount of Zr in mixed oxides increased the density of the acid sites and lower the strength of the Bronsted acid sites (Flego *et al.*, 2001) .

According to above literature review, one of the difficulties in the sol-gel method is that zirconium alkoxide is highly sensitive to water, because the commercial zirconium alkoxides are generally derived from $ZrCl_4$ and must be kept away from water. In this study, Sodium Tris(glycozirconate) produced by the OOPS method was used as a precursor for preparing zirconia. To obtain the formation of gels with different gel bodies, oxalic acid and NH_4OH were employed to adjust pH along with the variation of molar ratio of water to precursor. The effects of pH and molar ratio of water and precursor on the product properties were examined. Additionally, the influence of different calcination temperatures on the crystal structure of zirconia was investigated as well.