CHAPTER I
INTRODUCTION

The uses of supported metal oxide catalysts are applicably important, especially to most of petrochemical industries due to their wide range applications of industrially important reactions, for example, nickel loaded alumina in the form of nickel aluminate ($NiAl_2O_4$). The structure is almost spinel type having nickel atoms distributing over the octahedral and tetrahedral coordination sites (Amini *et al.*, 2002). Several studies on alumina-supporting nickel catalyst (Cesteros *et al.*, 2000 and Arean *et al.*, 2001) revealed the formation of nickel aluminate spinel, $NiAl_2O_4$, being a stable compound with strong resistance to acids, alkalis, and having high melting point and surface area. More importantly, nickel aluminate is capable of resistance to deactivation by coke formation (Pena *et al.*, 1996). Nickel loaded alumina can be prepared by many methods. Those are, a). Solid state reaction of the parent metal oxides (Han *et al.*, 2004) is to mechanically mix all powders followed by sintering. However, to obtain complete reaction, the reaction must be performed at high temperature and maintained for several days. b). Impregnation (Molina *et al.*, 1998) method is to add support to a solution of metal. c). Co-precipitation is to add nickel nitrate and aluminium nitrate in ammonium hydroxide solution (Narayanan *et al.*, 1995, Cesteros *et al.*, 2000). d). Sol-gel process (Arean *et al.*, 2001) is a low temperature synthesis process followed by appropriate heat treatment. e). Microwave induced method (Peelamedu *et al.*, 2002) is used for calcination replacing conventional calcination. f). Sonochemical method (Jeevanandam *et al.*, 2002) with the ultrasound radiation is for preparing precursor followed by heat treatment.

Traditionally dried mixing of ceramics and metal powders followed by heat treatment is often difficult to control, resulting in non-uniform dispersion of the components. In contrast to chemical technique, such as sol-gel process, it offers several advantages. It is low cost and allows greater control in size and morphology. It can design materials of specifically macroscopic morphology, such as ultra-fine particle, fiber, thin film and monolith. The sol-gel process is one of the most interesting ways to synthesize various ceramic materials. This process is performed at low temperature. It provides a uniform microstructure with a high degree of dispersion between the metal and ceramic phase (Rodeghiero *et al.*, 1998). In addition, this process gives high product purity. The sol-gel process involves the hydrolysis reaction, induced by the addition of water, which is known as a sol, and subsequent condensation in which metal oxide (M-O-M) network is obtained leading to a gel formation which alcohol and/or water are produced as a by-products. The sol-gel route with metal alkoxide can be described in term of two classes of reactions (Ertl *et al.*, 1997):

1. Hydrolysis reaction

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

2. Condensation reaction

$$M(OR)_n + M(OR)_{n-1}(OH) \longrightarrow M_2O(OR)_{2n-2} + RO$$

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

There are other parameters to achieve the sol-gel processing: aging of a gel, removing of solvent, and heat treatment.

Aging represents the time between the formation of a gel and 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 be desirable because it leads to a more cross-linked network that is mechanically stronger and easier to handle. However, extensive condensation causes the gel shrink to the point that solvent is expelled.

Drying is evaporation of solvent from a gel network. If the samples is left to dry naturally it will form a xerogel (high density aerogel) and if it is processed at elevated temperature and pressure can form aerogel.

After the removal of pore liquid, further heat treatment is necessary to convert a gel into a catalytically useful form. Heating is done in order to burn off any residual organics. 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 a product depend on parameters such as temperature, heating rate and time.

The advantages of the sol-gel process

1. The ability to maintain high purity
2. The ability to change physical characteristics such as pore size distribution and pore volume
3. The ability to vary compositional homogeneity at a molecular level
4. The ability to prepare samples at low temperatures
5. The ability to introduce several components in a single step
6. The ability to produce samples in different physical forms

There are two different variations of the sol-gel approach (Rodeghiero, 1998, Pierre, 1996). Firstly, the polymeric route allows molecular level mixing by introducing the metal source concurrently with the hydrolysis and condensation of the ceramic precursor. Secondly, the colloidal route involves mixing of a ceramic phase with the metal source. Parameters in the sol-gel process, such as pH, proportion of water used for the hydrolysis and presence of an acid or base catalyst (Ksapabutr *et al.*, 2004) are important. In addition, calcination temperature and duration of calcination also have a significant impact on the final structure and texture of nickel aluminate spinel. Increase in calcination temperature results in development of crytallization of $NiAl_2O_4$ (Pena *et al.*, 1996).

Generally, the metal alkoxides, such as aluminium *sec*-butoxide, aluminium isopropoxide, are popular metal oxides used as ceramic precursors due to the purity of starting materials, the low temperature for a reaction to occur. However, there are also disadvantages from these metal alkoxides, which are expensiveness and low hydrolytic stability. These problems have been resolved by synthesis of simple alkoxide precursors which contain one or more alkoxide ligands having more hydrolytic stability and additionally, blocked coordination site at the metal. The function of chelating agent is to retard the hydrolysis and condensation reaction rate in order to obtain homogeneous gels. Aluminium hydroxide can be used as a precursor, but the gelation of aluminium hydroxide occurs rapidly. It is thus difficult to obtain a uniform gels. It needs a continuously vigorous stir to obtain a homogeneous system preventing the formation a monolithic gel. This problem can be solved by slowing down precursor's reactivity either by using a strong mineral acid (Suh *et al.*, 1998, 2001) or by using chelating such as triisopropanolamine or TIS to form alumatrane complexes (Opornsawad *et al.*, 2001) to be used as a precursor of the preparation of high surface area alumina (Ksapabutr *et al.*, 2004).

In this study preparation of nickel aluminate spinel by means of the sol-gel process starting from alumatrane precursor and nickel acetate will be focused. Optimal conditions to obtain high surface area and high activity of nickel aluminate will be investigated.