CHAPTER II
LITERATURE SURVEY

Nickel aluminate has been studied in many years ago. Chokkaram *et al.* (1997) showed the effect of the calcination temperature on structure in the case of introduction of nickel into alumina, leading to the formation of spinel compound or segregation of oxide phase or a mixture, depending on the experimental conditions. They found that specific surface areas of samples decrease as increasing calcination temperature from 673 K to 1173 K. The pore volume does not depend on the calcination temperature. The interaction between Ni and Al is formed well crystallized nickel-aluminate species above 973 K. Thus, the crystallinity of spinel depends on the calcination temperature and increases with the increase calcination temperature.

The preparation method of metal loaded alumina can be obtained by several methods. Cesteros *et al.* (2000) prepared high surface areas nickel aluminate spinel (110-220 m^2/g) using the co-precipitation method of a stoichiometric mixture of nickel nitrate and aluminium nitrate solution. They found that the higher calcination temperature causes the lower surface areas due to the higher crystallinity of the spinel and the increase in particle size. All samples showed the pore distribution in the mesoporous range.

Loading metal onto alumina can be obtained by other methods. Supported nickel catalysts with low metal loading (0.4-1.7 %wt) were prepared by impregnation of α-alumina with nickel acetylacetonate (Molina *et al.*, 1998). Interactions of metal and support precursor occurred at the impregnation step. For temperature-programmed reduction (TPR), an enhancement of calcination temperature shifted the temperature of maximum reduction values (T_M) to a higher temperature. Two types of metal species could be distinguished according to the calcination temperature. The one (NiO) occurred at calcination temperature below 400°C whereas, at 600°C and above, all nickel was transformed into $NiAl_2O_4$. Two species existed in different proportions in the calcination temperature above 400°C and below 600°C.

Two preparation methods with various nickel loaded alumina were prepared by incipient-wetness impregnation and co-precipitation methods for the TPR study (Li et $al.$, 1995). For impregnation method, more than one species was detected by TPR. At low nickel loading, the Ni-Al_2O_3 interaction is strong, and NiO species is detected at high Ni loading. $NiAl_2O_4$ was not detected at all Ni loadings that were not corresponding to Moiina et $al.$ (1998). For the precipitation method, three nickel species were detected in TPR while $NiAl_2O_4$ was detected at all Ni loadings.

By comparing method for loading metal into alumina using co-precipitation and impregnation (Aksoylu et $al.$, 1997), the co-precipitation method showed increasing total surface areas and total pore volume with increasing metal content due to no metal accumulation on the surface, but occurrence of solid structure integration. On the other hand, for impregnation increase in metal loading caused a decrease in total surface area and total pore volume. It is possibly due to blockage by excess nickel. In addition, co-precipitated samples showed homogeneously distribution of metal in the structural framework even at high metal loading. The increase in total surface area and total pore volume led to smaller crystallite comparing to impregnated samples having similar Ni content, resulting in the higher metal surface area value.

Nanosized nickel aluminate spinel particle was prepared by sonochemical method with the aid of the ultrasound radiation in the process of homogeneous precipitation for the synthesis of a precursor (Jeevanandam et $al.$. 2002), sonicating in aqueous solution of nickel nitrate, aluminium nitrate and urea used as the homogeneous precipitating agent. Urea is a very weak Bronsted base and highly soluble in water. Its hydrolysis rate may be easily controlled by controlling the reaction temperature. $NiAl_2O_4$ nanoparticle can be obtained by heating the precursor at 950°C for 14 h with a particle size of Ca. 13 nm and the specific surface area of 108 m^2/g. If the precursor is heated at the temperature less than 950°C, a mixture of NiO and $NiAl_2O_4$ is obtained. The use of ultrasound radiation during the homogeneous precipitation of the precursor can accelerate the precipitation time of the precursor and control particle size in the nanoscale range.

Rodeghiero et $al.$ (1995) loaded nickel into alumina via the sol-gel route using both polymeric and collidal techniques. The polymeric route involves

introducing nickel formate during the hydrolysis and condensation while the colloidal route involves precipitating $Ni(OH)_2$ onto boehmite (AlOOH) particle. The results exhibited a highly interconnected microstructure of continuous nickel and alumina network, and enhanced fracture properties as compared with pure alumina. For the density and hardness, it was found that the amount of ceramic phase increased, the samples became harder and lighter.

Mesoporous nickel loaded alumina aerogel catalyst could be prepared by CO_2 supercritical drying of alcogels obtained from the fast sol-gel process (Suh *et al.*, 1998). The effects of two different nickel precursors, nickel nitrate and nickel acetate, were studied. Nickel nitrate gave relatively inhomogeneous gel containing precipitation. The behavior of the wet gel prepared using nickel acetate was similar to that of the blank alumina gel. Thus, the same sol-gel conditions for obtaining clear alumina wet gel were prepared by using nickel acetate. The sample obtained from nickel nitrate giving inhomogeneous gel did not have a good thermal stability as the sample obtained from nickel acetate. For the effect of loading methods, impregnation method showed the nickel phase was not uniformly distributed in three-dimensional gel network. On the other hand, the sol-gel process had textural properties comparable to blank alumina aerogel support, indicating the nickel metal was uniformly distributed in the final product. In addition, it showed stability against coke formation because the uniform distribution helped to reduce coke formation physically seperating carbon species from the nickel surface. As for the effect of two different alumina supported, alumina obtained from synthesis and commercial γ-alumina, the former showed resistant to coke formation and exhibited a better activity and excellent stability in the reaction of reforming of methane and in the liquid-phase hydrogenation of benzophenone and soybean oil (Suh *et al.*, 2001) in comparison with the commercial γ-alumina that deactivated immediately due to the coke formation.

The sol-gel process is used to prepare the high specific surface area $NiAl_2O_4$ containing different Ni/Al ratios (1:2, 1:4 and 1:8) by using nickel aluminium isoproxide, $NiAl(OC_3H_7)_2$, and aluminium isoproxide mixed in the the appropriate ratios (Arean *et al.*, 2001). The reactions were prepared by controlled hydrolysis of mixed metal alkoxide followed by calcination at 773 K for samples having Ni/Al =

1:2 and 1:8 and 1073 K. All samples were found to be $NiAl_2O_4$ and Al_2O_3-$NiAl_2O_4$ spinel solid solutions having high specific surface areas in the range of 200-300 m^2/g. Mixing at the molecular level between the precursor materials allowing spinel solid solution formation at low temperature, avoiding severe sintering, leads to high specific surface areas. The products were found to be mesoporous region.

Piao *et al.* (2002) also prepared alumina supported nickel aerogel catalyst by the sol-gel followed by supercritical drying method. The samples favor the formation of spinel structure $NiAl_2O_4$ or α-Al_2O_3 phases in a wide range of the calcination temperature. They have a high specific surface area (about 200-300 m^2/g), high porosity and ultra-low-density. The specific surface areas of this method are much larger than the Ni/Al_2O_3 catalyst obtained from co-precipitation method, and reduce with the increase the calcination temperature.

$NiAl_2O_4$ showed poor crystallinity from the calcination temperature at 773 K for 5 h (Cesteros *et al.*, 2000) and by increasing calcination temperature to 1273 K, crystallinity of $NiAl_2O_4$ was enhanced (Pena *et al.*, 1996). Thus, different calcination temperature can alter the texture of nickel aluminate. Calcination by microwave is an alternative processing route.

Using the sol-gel process, the elements become uniformly distributed during the gel formation step. However, the disadvantages of the sol-gel process are the relatively high costs of the metal alkoxide and the release of large amount of alcohol during the calcination step (Jeevanandam *et al.*, 2002). Ksapabutr *et al.* (2004) prepared alumina from tris(alumatranyloxy-*i*-propyl) or alumatrane precursor. Alumatrane was synthesized via one step process or the Oxide One Pot Synthesis (OOPS) process from the reaction of inexpensive and readily starting materials, aluminium hydroxide and triisopropanolymine (TIS) in ethylene glycol solvent (Opornsawad *et al.*, 2001). Triethylenetetramine (TETA), a stronger base than TIS, can be used as a catalyst to accelerate the rate of $Al(OH)_3$ dissolution. The results showed the oligomer product. The main product was pentamer bonded with one molecule of TIS lost one molecule of water. Alumina gels using the sol-gel method (Ksapabutr *et al.*, 2004) were studied the effect of pH, hydrolysis ratio and temperature of reactions. They found that these parameters affected dramatically the

gel time. From the system with pH ranging from 3-11 at hydrolysis ratio = 9 and temperature of 25°C, the values of t_{gel} at around pH 9 corresponding to the isoelectric point of alumina that give the maximum strength of the gel network indicating that intermolecular crosslinks are stronger. For the effect of the hydrolysis ratio (9, 18, 27), a system with a lower hydrolysis ratio grew slowly, resulting in the denser network. From the systems varying the temperature between 20° and 25°C, at lower temperature gelation occurred slower giving higher gel strength. Heat treatment of the alumina gels at 500°C produced a homogeneous mesoporous alumina particle of 70 A° and high specific surface areas.