

CHAPTER I



INTRODUCTION

Majority of the product volume from chemical process industries directly originates from catalytic technology. In recent years, catalytic technology was improved to find the most suitable catalyst for each work. Catalytic technology can separate in 2 parts for material science and chemical reaction engineering.

Recently, much attention has been denoted to catalytic combustion at high temperature for gas turbines, boilers and jet engines, and therefore synthesis of catalytic supports stable at high temperatures has become of important

Alumina is an important material in field of catalytic technology because of the good importance property. Alumina has high melting point (slightly over than 2000°C) which is also desirable characteristic for a support. Alumina can use in three types: use as catalyst, use as co-catalyst and use as support. For example, alumina is used as catalyst in the reaction of steam reforming and clause process using to eliminate hydrogen sulfite at high temperature. Alumina is used as co-catalyst in the catalytic reforming of gasoline. And alumina can use as support in many cases: use in catalytic converter, use in membrane technology.

Transition aluminas have large surface areas with reasonable mechanical strength and are widely used as catalyst supports in industry. However because of metastable nature of transition aluminas, they usually transform to α -alumina at around 1000°C which causes a drastic decrease in the surface area. For the purpose of increasing the thermal stability of transition alumina, the effect of dopants has investigated and success with ThO_2 , ZrO_2 , SiO_2 , etc., in to the alumina matrix

Iler (1964) found the addition of silicic acid to fibrillar colloidal boehmite increased the thermal stability of the resultant alumina. Yoldas (1976) examined the thermal stabilities of silica-modified aluminas prepared by sol-gel method and

reported that the alumina doped with 6% silica had the maximum temperature (1380°C) for α -alumina transformation. Murrell and Dispenziere (1988) reported that the alumina doped with 5% silica by reaction with tetraethyl orthosilicate (TEOS) led to mark stabilization against loss of the surface area by vanadium attack at high temperature. In another papers in this field, Johnson (1990) and Beguin (1991) prepared silica modified alumina confirmed the addition of silica in alumina increase the thermal stability of resultant alumina.

The synthesis of inorganic material by using organic media, Inoue (1988-1992) found that the glycothermal treatment (the use of glycol instead of water for hydrothermal treatment) of gibbsite at 250°C. It yielded the product had structure of boehmite with ethylene glycol moiety incorporated between the boehmite layer with the covalent bonding. Inoue (1988) found that when gibbsite was treated in various glycols at 300°C yielded the glycol derivative on boehmite. Inoue (1995) prepared the silica-modified alumina by the reaction of aluminum isopropoxide and tetraethoxysilane in 1,4 butanediol at 300°C and at Al/Si ratio of 8, This product surface area was lower than the product that prepared by glycothermal method. Inoue (1993) synthesized thermally zirconia by thermal decomposition of zirconium alkoxide. By the thermal treatment of zirconium n-propoxide in organic solvent at 300°C yielded microcrystalline tetragonal zirconia. The crystallite size depended on carbon number of organic solvent by $2 < 6 < 4$. When toluene was used at synthesis, zirconium isopropoxide reacted in toluene and zirconium tert-butoxide decomposed at 200°C yielding amorphous zirconia. Inoue (1993) synthesized thermally zirconia by hydrolysis of zirconium alkoxides. Zirconium n-butoxide suspended in toluene. In the gap 30 ml of toluene was added and then heated to 200-300°C. And then microcrystalline (5.8 nm) monoclinic zirconia that showed high thermal stability. Kominami (1997) synthesized the microcrystalline titanium (IV) oxide in the anatase form by thermal decomposition of titanium (IV) alkoxide in organic solvent. The products shown high surface area $>100\text{m}^2/\text{g}$ even after calcination at 823K. This product had high photocatalytic activity in the photocatalytic mineralization of acetic acid in aerated aqueous solutions because of the high crystallinity and high surface area. Kominami (1999) synthesized the nanosized titanium (IV) oxide in the anatase

form by hydrolysis of titanium (IV) alkoxide. Titanium n-butoxide dissolved in toluene in test tube. In the gap between the autoclave wall and test tube, mixture of toluene and water was added. When the temperature rose, water was dissolved at high temperature (150-300°C). In this method, rutile transformation temperature was higher and the thermal stability was improved. For example product obtained by the reaction at 300 °C for 24 h possessed a surface area of 54 m²/g even after calcination at 900°C and began to transform to the rutile phase at around 1000°C

Highly porous solids prepared by the removal of solvent from a wet gel at a temperature above critical temperature of the solvent. Over the recent years, researchers have built up the strong technical background in such materials. Fanelli and Anthony (1983) found the new polymerization catalyst system comprising an aluminum compound and a transition metal compound on an alumina-based aerogel support, Armor and Carlson (1984) prepared a catalyst composition comprising a uniform dispersion of individual metallic palladium particles. Armor and Carlson (1989) prepared high pore volume alumina by hydrolysis of aluminum isopropoxide and the fluid phase was removed hypercritically. Aerogel had good properties of high pore volume, high surface area and high thermal stability. These properties result from this method that obviate the inherent shrinkage or structural collapse that occurs when precursor gel are conventionally dried to a solid form. Such shrinkage or compaction results from the surface tension of residual liquid trapped within the fragile gel structure.

In the present works, Mixture of AIP and TEOS were treated in 1-butanol, toluene and toluene that toluene in the gap is replaced with water and separate the fluid phase by supercritical drying. The properties of products are examined. Then the products are calcined at various temperatures, and then thermal stability of the resultant silica-modified aluminas are investigated. The reaction mechanism is investigated by the different solvents. While the silica effect on products surface area and other properties is investigated by amounts of TEOS in the reaction.