

CHAPTER II

LITERATURE REVIEW

Recently, much attention has been denoted on the catalyst preparation. Today the chemical products are so important for living. Therefore catalyst that had the good properties was important in the chemical process. As the year passed, the catalyst preparation was improved. The catalytic preparation that used organic solvent was improved in many years to found the catalyst that had better properties than another methods.

Iler (1964) tried to prepare silica modified alumina and suggested that silica react with alumina to form an extremely vicious glassy phase, which coats the alumina surface and retards the migration of alumina.

Yoldas (1976) devised a new preparation process. He prepared silica-modified alumina by partial hydrolysis of a mixture of aluminum sec-butoxide (ASB) and TEOS or by adding ASB to the partially hydrolyzed TEOS solution. And then solution was heated to 60°C, followed by complete hydrolysis with a large excess water, gelation, drying and calcination. The silica modified alumina by this method showed high α -alumina crystallization temperature (1380°C). He explained that silica goes into certain sites in the structure of alumina, causing no disturbance in the lattice and the stabilization of the products depend on the optimal silica contents and explained by saturation sites.

Gani and Mcpherson (1977) prepared silica modified alumina by plasma decomposition of aluminum and silicon chloride. The powders were formed from melt and powders were cooled rapidly. Aluminum and silicon were formed homogeneously in atomic scale. And this α -alumina crystallization temperature was 1500°C. He explained that silicon atoms are strongly bound within the tetrahedral sites of the spinel structure, which retards the rearrangement of oxygen atom from

face centered-cubic closet packing of alumina. However the powders had low surface area. So this products was not suitable to be the catalyst or support.

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, a process for preparing the polymerization catalyst system and use of the catalyst system for polymerization and co-polymerization of alpha-olefins are disclosed. A heat-activated alumina-based aerogel useful as a catalyst support and having a morphology by transmission electron microcopy comprising extremely thin folded film-like ribbons or plates and having a high BET surface area, high pore volume, and low bulk density is also disclosed.

Armor and Carlson (1984) prepared a catalyst composition comprising a uniform dispersion of individual metallic palladium particles. Substantially free of clusters of said particles, on and throughout an alumina aerogel support. The products had a BET surface area in the range of about 20 to about 700 m² /g, a pore volume in the range of about 1.5 to about 12 cm³ /g, a bulk density in the range of about 0.003 to about 0.5 g/cm³. Pd/Al₂ O₃ weight ratio of about 1:1000 to about 1:5 is disclosed. A process of preparing the catalyst composition having metallic palladium impregnated on alumina aerogel and a process of using same as a hydrogenation catalyst are also disclosed.

Murrell and Dispenziere (1988) prepared silica modified alumina that the alumina doped with 5% silica by reaction with tetraethyl orthosilicate (TEOS) and boehmite led to marked stabilization against loss of the surface area by vanadium attack at high temperature

Armor and Carlson (1989) prepared high pore volume alumina by hydrolysis of aluminum isopropoxide. This work summarized successful effort to obtained high pore volume alumina. Aluminum isopropoxide suspended in the mixture of water and methanol. The suspension was set in the 225cm³ pyrex linear tube in 300cm³ autoclave. The fluid phase was removed hypercritically. Thus generating the alumina

aerogel. This preparation method was very sensitive to the amount of water and alcohol employed in the synthesis. An unexpectedly large ratio of water and alkoxide yielded the highest pore volume of $8.6\text{cm}^3/\text{g}$. When the heating rate and holding time were changed. It was no effect on the surface area of the products. But when pregelation became before the reaction product's pore volume was decreased.

Johnson (1990) prepared silica-modified alumina and explained the stabilizing effect of silica modified alumina by the reduction of the number of surface hydroxyl because of the formation of Al-O-Si bounds from hydroxyl.

Beguin (1991) prepared silica-modified alumina and reported silica-modified alumina has high thermal stability. He explained that a silica layer grafted to alumina is able to fill the anionic vacancies of alumina.

Inoue (1989) found the reaction of gibbsite with ethylene glycol at $250\text{ }^\circ\text{C}$ at the rate $2^\circ\text{C}/\text{min}$ for 2 h yielded the product had an empirical formula of $\text{AlO}(\text{OCH}_2\text{CH}_2\text{OH})_{0.31}(\text{OH})_{0.69}$. This product had unique honeycomb-like texture by using scanning electron microscope, and had high surface area. The XRD pattern and IR spectrum suggest that the product had structure of boehmite with ethylene glycol moiety incorporated between the boehmite layer with the covalent bonding. When product was calcined. The basal spacing of boehmite gradually decreased because the ethylene glycol moiety was decomposed to be carbonyl compound. Suggesting that the ethylene glycol moiety be placed between the boehmite layer.

Inoue (1992) found that when gibbsite was treated in glycol at 300°C , the glycol derivative on boehmite was get. A commercial gibbsite was suspended in 1,4-butanediol. The suspension was set in 300 ml autoclave and then heated to 300°C at rated $2.5^\circ\text{C}/\text{min}$. XRD showed that product comprised with α -alumina and well crystallite boehmite. TEM of product showed each α -alumina particle was a single crystal ahexagonal plate chape. Suggest that microcrystalline α -alumina could prepare from glycothermal reaction of gibbsite.

Inoue (1993) synthesized thermally zirconia by thermal decomposition of zirconium alkoxide. Thermal treatment of zirconium n-propoxide in organic solvent at 300°C yielded microcrystalline tetragonal zirconia. The crystallite size was depend 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, while zirconium n-propoxide was stable at 300 °C. Zirconium n-propoxide didn't react in toluene. Suggesting that reaction in toluene depend on structure of alkyl group of the alkoxide. And the-obtained tetragonal zirconias maintained large surface areas (90-160 m²/g) even after calcination at 500 °C.

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 held at this temperature for 2 h. When autoclave was cooled, 30ml distilled water was added. The autoclave was heated again at 250-300 °C in the same way. And then microcrystalline (5.8nm) monoclinic zirconia, which showed high thermal stability, was retained. And the-obtained zirconias maintained large surface area of 162 and 72 m²/g even after calcination at 500 °C and 900 °C. And the pretreatment in toluene above 250 °C was essential avoid the formation of tetragonal formed.

Inoue (1995) studied to prepare the silica-modified alumina for increased the α transformation. Because of the α transformation was important reason on the decreasing of surface area. The mixture of aluminum isopropoxide and tetraethoxysilane in 1,4 butanediol was autoclaved at 300°C at the rate 2.3°C /min for 2 h yielded the white powder. The XRD pattern and IR spectrum suggest that the product had the structure ethylene glycol moiety incorporated between the boehmite layer with the covalent bonding. But when the tetraethoxysilane increased structure of products were amorphous. When products was calcined at various temperature. Product that had Al/Si ratio of 8,18 had highest thermal stability. And products (Al/Si = 8,18) had the structure of spinel phase. And when he used another methods to

prepare silica-modified alumina at Al/Si ratio of 8, This product's surface area was lower than the product that prepared by glycothermal method.

Kominami (1997) synthesized the microcrystalline titanium (IV) oxide in the anatase form by thermal decomposition of titanium (IV) alkoxide in organic solvent. Titanium-tert-butoxide (TTB) dissolved in organic in test tube. In the gap between the autoclave wall and test tube, 30 ml of solvent was added. Autoclave was heated to 300°C. The products had a crystallite size of 9nm and a surface area >100m²/g. Primary and Secondary alkoxides were not decomposed in the similar conditions, indicating that the thermal stability of C-O bonds in alkoxides was a decisive factor of their decomposition. The products shown high surface area >100m²/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). The elevation of the reaction temperature and an increased of reaction time had effect on the crystallite sized of products. 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

Inoue (1999) synthesized alkoxyalumoxanes by oxidation of aluminum metal in alcohol. Aluminum foil and alcohol were in the pyrex test tube, and then it was set in 300ml autoclave. Heated it 300°C at rate 2.5°C/min and held for 2 h. The product had the layer structure of boehmite with covalently bonded alkyl groups. Basal spacing linearly increased with the carbon number of alcohol.

Kominami (1999) prepared nanosized titanium (IV) oxide in the anatase form by hydrolysis of titanium (IV) alkoxide. Thermal treatment of titanium(IV) alkoxides dissolved in alcohols at temperature of 523-573 K under autogenous pressure yielded microcrystalline anatase titanium(IV) oxide (TiO₂) with diameter of 11-31 nm and surface area of 42-138 m² g⁻¹. Similar treatment in hydrocarbons such as toluene gave no solid products, indicating that both hydrolysis of alkoxides with water liberated homogeneously from solvent alcohols and crystallization of anatase phase occurred simultaneously. These TiO₂'s were thermally stable, e.g., BET surface area of TiO₂ synthesized at 573 K, 63 m² g⁻¹, was reduced only 30% (45 m² g⁻¹) even by calcination at 973 K. Their photocatalytic activity was examined in mineralization of acetic acid in aqueous solutions under aerated conditions and dehydrogenation of 2-propanol under deaerated conditions; almost all the samples showed the activity more than twice higher than those of representative active photocatalysts, Degussa P-25 and Ishihara ST-01. The superior activity of the present TiO₂ photocatalysts was attributable to compatibility of high crystallinity and large surface area owing to the newly developed synthetic procedure.



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