CHAPTER II
LITERATURE REVIEWS

Hydrothemal methods have been widely applied for the synthesis of a variety of ceramic materials [1-3]. However, only a few papers have dealt with the use of organic media instead of water in hydrothermal method. Inoue et al. have developed novel method for the synthesis of several metal oxides in organic media (non-aqueous solution). These methods have the advantage that the products consist of microcrystalline particles but are sufficiently high thermal stability; they still remain large surface areas after post-calcination at even higher temperature.

Inoue et al. [4] reported that the thermal reaction of gibbsite in ethylene glycol at 250°C yielded an ethylene glycol derivative of boehmite, in which organic moiety is incorporated covalently between the layer structure of boehmite. This reaction has been extended to the reaction of gibbsite in higher homologues of ethylene glycol, and they have found that microcrystalline χ -alumina is formed under quite mild condition [5]. The synthetic process as mentioned above, the use of glycol (organic solvent) instead of water in the synthetic system is different method from the conventional methods. This method was called " **Glycothermal method** ".

Inoue et al. [6] also found that this reaction in inert organic solvents such as toluene, benzene and/or others, thermal decomposition of aluminum alkoxide occurred and yielded a product compose of 4 to 20 nm particles having the χ -alumina mixture. The χ -alumina was stable and maintained a surface area above 100 m^2g^{-1} until its transformation at 1150°C to be α -alumina. With this result, they have applied this method for zirconia synthesis and reported that thermal decomposition of zirconium alkoxides in organic solvents yielded tetragonal zirconia, which had a large surface area and a fairly high thermal stability. However, zirconium n-alkoxide, which decomposed into glycols, did not decompose at 300°C in inert organic solvent [7]. Therefore they tried to hydrolyze the zirconium n-alkoxide in the inert organic solvent with a limited amount of water dissolved in the solvent from the gas phase and found

that this method gave microcrystalline monoclinic zirconia having a much higher thermal stability [8].

Recently, Inoue et al. [9] reported that microcrystalline binary oxide were directly formed when a mixture of two alkoxides, acetylacetonate, and/or acetates was heated in 1,4 butanediol at elevated temperature under autogenous pressure of the glycol (glycothermal reaction). An example was synthesis of gadolinium gallium garnets (GGG) by reaction of mixed gallium acetylacetinate with gadolinium acetate. This reaction has been extended to the reaction of a stoichiometric mixture of aluminium isopropoxide (AIP) and yittrium acetate, and found that crystalline yittrium aluminium garnet (YAG) is formed under similar condition. No other phases were detected. The uncalcined YAG had a large surface area (107 m^2 g^{-1}) which decreased to 44 m^2 g^{-1} and 10 m^2 g^{-1} after calcination at $1000^{\circ}C$ and $1300^{\circ}C$. YAG was composed of agglomerates of almost spherical particles having a relatively narrow size distribution with an average particle size of approximately 30 nm. The use of ethylene glycol instead of 1,4 butainediol in the synthetic system afforded amorphous product [10].

The reaction of aluminium isopropoxide (AIP) and other rare earth acetates have been studied. Inoue et al. [10] reported that the reaction of AIP and acetates of the lanthanide elements from Gd to Lu in 1,4 butanediol at $300^{\circ}C$ yielded the corresponding lanthanide aluminuim garnets. The reaction of AIP with samarium or europium acetate gave a mixture of the corresponding garnets phase and lanthanide acetate oxide ($REOOCOCH_3$). However, the reaction of AIP with neodymium acetate gave only neodymium acetate oxide as the sole crystalline product.

As described above, samarium and europium garnets have never been reported except as solid solutions with YAG, and this paper is the first report of the synthesis of these garnets. Because of the metastability of these garnets, thermal methods such as ceramic processes would not give these garnets. Ease in crystallization of the perovskite phase seems to be another reason for the difficulty in the synthesis of these garnets by the thermal methods.

The stability of lanthanide hydroxide under the hydrothermal conditions increases in ionic size of the lanthanide element This may be one reason for the increase in lower temperature limit for the hydrothermal synthesis of aluminium garnet with the increase in ionic size of the lanthanide element. The aluminium garnet with the large-size lanthanide ion hydrothermally prepared so far was $Tb_3Al_5O_{12}$ and $Gd_3Al_5O_{12}$ could not be prepared by the hydrothermal method. Since the ionic size of samarium and europium are still larger than gadolinium, there seems to be no possibility that samarium and europium garnets can be prepared by the hydrothermal method.

The previous paper as mentioned above, glycothermal treatment of microcrystalline gibbsite yield α -alumina at $280^{o}C$, a much lower temperature than the α -alumina formation temperature by the hydrothermal method. The difference between glycothrmal and hydrothermal reaction was attributed to the difference in stabilities of the intermediate phases, i.e. the glycol derivative of boehmite vs. well – crystallized boehmite. Similarly, the success if the synthesis of samarium and europium garnets by the glycothermal method may be attributed to the instability of intermediate species. Under glycothermal, aluminium alkoxide is easily converted to glycoxide. Thermal decomposition of the glycoxide molecule proceeds by intramolecular participation of the remaining hydroxyl group of glycol moiety, yielding an $>Al-O^-$ anion. In the absence of RE acetate, nucleophilic attack of this aluminate ion on another glycoxide molecule takes place, finally yielding the glycol derivative of boehmite. In presence of RE acetate, this aluminate anion attacks the RE ion forming the Al-O-RE bond, which finally yields the garnet crystals under the glycothermal conditions.

For the synthesis of catalyst and catalyst supports, metal alkoxides are widely used as the starting material to avoid contamination of the inorganic counter anion from the corresponding metal salts which affects the activity and selectivity of the catalyst. In a series of Inoue's studies on the use of organic media in inorganic synthesis [6-10], metal alkoxides are used as the starting material and the effect of the structure of the alkyl group in the starting alkoxide was examined. They have found

that the formation of the product required direct cleavage of the C-O bonds in alkoxides, and therefore the thermal stability of C-O bonds may be a decisive factor for decomposition of metal alkoxide.

In the previous paper, Inoue et al. [11] found that thermal decomposition of titanium acetylacetonate in toluene at 250°C yielded nanocrystalline anatase titanium (IV) oxide (anatase titania) free from counter anion contamination, and that the sample calcine at 550°C had relatively high surface area (>50 m^2g^{-1}). Kominami et al. [12] reported that nanocrystalline anatase titanium (IV) oxide prepared by the reaction of titanium (IV) tetra-tert butoxide with inert organic solvents at 300 °C under autoclave condition yielded nanocrystalline anatase titanium (IV) oxide with a crystallite size of ca. 9 nm and a surface area of > 100 m^2 g^{-1}. The product was produced by this method was called as " **TD -TiO$_2$** " (Thermal Decomposition – Titania). The titanium (IV) oxide prepared from titanium (IV) tetra-tert butoxide by this manner was thermally stable upon calcination in air and retained high surface area of ca.100 m^2 g^{-1} even after calcination at 550°C.

They also found that primary and secondary alkoxide of titanium (IV) were not decomposed under similar condition indicating that the thermal stability of C-O bonds in the alkoxides was a decisive factor for their decomposition. On the other hand, when water was fed in the autoclave separately from the organic solvent, the alkoxides was hydrolyzed at high temperature with water dissolved in the organic solvent from gas phase and thereby nanocrystalline titanium (IV) oxide was produced. The product prepared by this method was called as "**HyCOM -TiO$_2$**" (Hydrothermal Crystallization in Organic Media –Titania) [13,14]. In this HyCOM method, the structure of alkyl group was not a decisive factor for the TiO$_2$ formation. The resulting highly–crystallized nanoparticles also exhibited the highest, as far as they examined photocatalytic activity in several reaction systems [15-17].

Kominami et al. [18] intended to hydrolyzed titanium alkoxide more homogeneously in organic solvents at high temperature and developed a novel method, i.e., hydrolysis of titanium alkoxide with water homogeneously from alcohols

used as the solvent. They reported that thermal treatment of titanium (IV) alkoxide dissolved in alcohols at temperature of 250 to 300°C yielded nanocrystalline anatase titanium (IV) oxide with diameter of 11 to 31 nm and surface area of 42 to 138 $m^2 g^{-1}$ depended on the reaction condition and kind of alcohols. The titanium (IV) oxide samples prepared by this method is called "**THyCA –TiO$_2$**" (Transfer Hydrolytic Crystallization in Alcohols -Titania).

Similar treatment in hydrocarbons such as toluene gave no solid products, indicating that both hydrolysis of alkoxide with water liberated homogeneously from solvent alcohols and crystallization of anatase phase occurred simultaneously. These titanium (IV) oxides were thermally stable, e.g., BET surface area of titanium (IV) oxide synthesized at 300°C, 63 $m^2 g^{-1}$, was reduced only 30% (45 $m^2 g^{-1}$) even by calcination at 700 °C. Their photocatalytic activity was examined in mineralization of acetic acid in aqueous solutions under aerated conditions and dehydrogenation of 2-propanol under deaerated condition; almost all the samples showed the activity more than twice higher than those of representative active photocatalysts, Degussa P-25 and Ishihara ST-01.

In many studies have been devoted to improve the thermal stability of titanium (IV) oxide using additives such as Al [19], La [20], Si [21] and others. The effect of these additives are quite different by the procedures of the doping and amounts the additives, and the mechanisms for the stabilization effects of these dopants are not yet full elucidated. To improve the thermal stability of titanium (IV) oxide, Kondo et al. [21] prepared the silica–modified titanium (IV) oxide by glycothermal method and have found that reaction of titanium tetraisopropoxide (TIP) and tetraethyl orthosilicate (TEOS) in 1,4 butanediol at 300°C afforded nanocrystals having an anatase structure. With increasing the amount of TEOS added the crystallite size of the product decrease and BET surface area increased. The thus –obtained silica – modified titanium (IV) oxide preserved quite a large surface area even after calcination at high temperature (> 180 $m^2 g^{-1}$ 600°C)

Many papers as mentioned above, the synthesis of several metal oxides and binary metal oxides in organic solvents are explained. The product was produced by this novel method have a large surface area and high thermal stability. This novel method may be a new route to prepare micro- and nanocrystalline metal oxides [22-24]. Physical properties of the product can be controlled by the choice of the solvent, reaction conditions and structure of the alkyl group of the metal alkoxides.