CHAPTER II

LITERATURE REVIEWS

Considerable interest has been shown in nanosize metal oxide because these materials can be used in large number of technological applications. This chapter provides some information for understanding the synthesis of metal oxide in organic media, which is the developed method to find the catalysts that had better properties. These methods have the advantage that the products consist of microcrystalline particles but are sufficiently high thermal stability they still remain large surface area after post calcination at even higher temperature.

Inoue et al. (1988) 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 structures 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 (Inoue et al., 1989). By using Scanning Electron Microscope (SEM), this product had unique honeycomb-like texture. In this connection, they had examined the reaction of aluminum isopropoxide in glycol, and found the formation of the glycol derivatives of boehmite, identical compounds obtained from gibbsite. 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. (1992) 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^2/g until its transformation at 1150°C to be α-alumina. TEM of product showed each α-alumina particle was a single crystal hexagonal plate shape. With this result, they have applied this method for zirconia synthesis and reported that thermal decomposition of zirconium alkoxide in organic solvents yielded microcrystalline tetragonal zirconia, which had a large surface area and a fairly high thermal stability. However, zirconium isopropoxide reacted in toluene and zirconium tert-butoxide decomposed at 200°C yielding amorphous zirconia. While zirconium n-alkoxide, which decomposed into glycol, did not decompose at 300°C in inert organic solvent (Inoue et al., 1993). 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 (Inoue et al., 1995). The obtained zirconia maintained large surface area even after high temperature calcination as 162 and 72 m^2/g at 500 and 900°C, respectively.

Recently, Inoue et al. (1995) reported that microcrystalline binary oxide were directly formed when a mixture of two alkoxide, acetylacetonate, and/or acetate was heated in 1,4-butanediol at elevated temperature under autogeneous pressure of the glycol. An example was synthesis of gadolinium gallium garnets (GGG) by reaction of mixed gallium acetylacetonate with gadolinium acetate. This reaction has been extended to the reaction of a stoichiometric mixture of aluminium isopropoxide (AIP) and yttrium acetate, and found that crystalline yttrium aluminium garnet (YAG) is formed under similar condition. No other phases were detected. The uncalcined YAG had a large surface area ($107 m^2/g$) that decrease to 44 and 10 m^2/g after calcination at 1000 and 1300°C, respectively. 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-butanediol in the synthetic system afforded amorphous product.

The reaction of aluminium isopropoxide (AIP) and other rare earth acetates have been studied. Inoue et al. (1995) reported that the reaction of AIP and acetates of the lanthanide elements from Gd to Lu in 1,4-butanediol at 300°C yielded the corresponding lanthanide aluminium garnets. The reaction of AIP with samarium or europium acetate gave a mixture of the corresponding garnets phase and lanthanide acetate oxide. 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 method.

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 could be formed by the hydrothermal method.

As mentioned above, glycothermal treatment of microcrystalline gibbsite yielded α-alumina at 280°C, a much lower temperature than the α-alumina formation temperature by the hydrothermal method. The difference between glycothermal and hydrothermal reaction was attributed to the difference in the stability of the intermediate phase, i.e. the glycol derivative of boehmite versus well-crystallized boehmite. Similarly, the success of the synthesis of samarium and europium garnets by the glycothermal method may be attributed to the instability of intermediate phase. Under glycothermal, aluminium alkoxide is easily converted to glycoxide. Thermal decomposition of the glycoxide molecules proceeds by intramolecular participation of the remaining hydroxyl group of glycol moiety, yielding an $>Al\text{-}O^-$ 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 garnets crystals under the glycothermal conditions.

For the synthesis of the catalyst and catalyst supports, metal alkoxide are widely uses as the starting materials to avoid contamination of the inorganic counter anion from the corresponding metal salts which effects the activity and selectivity of the catalyst. In a series of Inoue's studies on the use of organic media in inorganic synthesis, metal alkoxide are used as the starting materials 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 requires direct clevage of the C-O bonds in alkoxides, and therefore the thermal stability of C-O bonds maybe a decisive factor for decomposition of metal alkoxide.

In the previous paper, Inoue et al. (1991) 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^2/g). Kominami et al. (1997) used titanium (IV) tetra-tert-butoxide (TTB) to synthesized titania by thermal decomposition reaction in organic solvent at 573 K, the titania sample they prepared by this method will be called TD-TiO_2 (thermal decomposition). They found that TTB was completely decomposition at this condition which yielded anatase without contamination of any other phase. When they changed solvent (toluene) in this reaction, they found that TTB was decomposed in toluene even at 473 K to give anatase having quite large surface area. Since the BET surface area of a sample synthesized at 523 K was larger than that calculated from its crystalline size (they assumed the density of anatase to be 3.84 g/cm^3), it suggested that the product synthesized at lower temperature were contaminated with the amorphous-like hydrated phase. In the effect of the structure of the alkyl group in the starting alkoxide, they found that primary and secondary alkoxides of titanium (IV) were not decomposed even at 573 K. This suggested that the process requires direct cleavage of the C-O bonds in alkoxides, and therefore the thermal stability of the C-O bond may be a decisive factor for the formation of TiO_2 lattice. When TiO_2 calcined, the transformation had occurred to partly from rutile at 973 K and the loss of surface area by calcination was presumably because the as-prepared TiO_2 was well-crystallized having smaller tendency toward sintering and contained lesser amount of amorphous-like phase to be crystallized into anatase upon calcination.

Kominami et al. (1999) 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 alcohol 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 depended on the reaction condition and kind of alcohol.

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, $63m^2/g$,was reduced only 30% ($45m^2/g$) 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.

Kominami et al. (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 the 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 m^2/g even after calcination at 900°C and began to transform to the rutile phase at around 1000°C.

Montoya et al. (1992) studied the effects of the sol-gel synthesis parameters on textural and structure characteristics of TiO_2. They found that TiO_2 had been prepared by sol-gel method, variations in the synthesis conditions produced solids of different characteristics. It was found that parameters such as type of solvent, synthesis temperature, acid addition, alcohol/alkoxide and water/alkoxide molar ratios influence the texture, structure and morphology of the sample. When they calcined the sample at 500°C, its surface area decreased strongly. Microcrystalline anatase was obtained after drying at 80°C in most of the samples. Calcinations at 500°C of microcrystalline anatase brought about the coalescence of the fine material, producing larger size particles. Amorphous titania crystallized to anatase after calcination at 400°C.

Yanagisawa et al. (1997) had synthesized anatase titania at low temperature below 350°C by hydrothermal hot-pressing of amorphous titania consisting of spherical particles prepared by hydrolysis of titanium tetraethoxide. They found that water included in the starting powder was released to produce hydrothermal conditions by heating and the hydrothermal treatment even at 100°C accelerated crystallization of the amorphous titania to anatase. In various temperature, the remarkable decrease in the surface area with increase in reaction temperature from 100°C to 150°C indicated that a large amount of amorphous parts remained in the compacts produced at 100°C. In various reaction pressure, compressive pressure from outside the autoclave, the crystallite size did not change with varying reaction pressure, which suggested that the compression had no effect on the crystallization of anatase.

Inoue et al. (1998) studied glycothermal synthesis of rare earth iron garnets. They synthesized iron oxide products by glycothermal synthesis, the use of organic media in place of water for the hydrothermal method, in 1,4 butnaediol. They reported that in the glycothermal reaction, thermal decomposition of the glycol moiety is directly connected with the crystallization of the products, and therefore starting materials with a high energy level provide a large driving force for the formation of the products. They explained that because of the large driving force available in the glycothermal reaction, crystal growth proceeds rapidly even though the lattice parameter of the grown crystals is much larger than that of the seed crystals. So that, the lattice strain caused by the epitaxial growth of a new crystal on a seed crystal having different lattice parameter is released by edge dislocation and the creation of a number of crystal defect is another characteristic of the glycothermal method. In the same year, Inoue et al. (1998) studied reactions of rare earth acetates with aluminum isopropoxide (AIP) in ethylene glycol. They found that modified-alumina had synthesized by glycothermal method derived amorphous and/or crystal. They reported that a formation of the amorphous product in the reaction can be interpreted by the difficulty in the cleavage of the C-O bond of the intermediate glycoxide formed by the reaction of AIP with ethylene glycol, where the ease in the cleavage of the C-O bond seems to be the prime factor for the formation of crystalline garnets by the reaction in 1,4-BG.

Belin et al. (2002) studied the soft chemistry method using precipitation of chloride salts in stoichiometric proportions to synthesize γ-Fe_2O_3 nanoparticles. They reported that varying synthesis temperature lead to different sizes of nanoparticles from 9 to 14 nm. The surface area decreases when synthesis temperature increase, temperature provides grain growth rather than germination phenomenon. In order to obtain highly divided powder, centrifugation and freeze drying process have been used before thermal treatment at 250°C under air atmosphere. X-ray diffraction and surface area measurements confirmed the nanometric scale. They also found that TEM and XRD showed both their narrow size distribution and their spherical shape.

Diamandescu et al. (1999) synthesized hematite powders with distinct particle morphology by hydrothermal synthesis, in the temperature range of 160-300°C. Goethite and ferric hydroxide precursors prepared by precipitation oxidation under different reaction conditions were used. The hydrothermal reactions were developed in aqueous neutral or alkaline suspensions. By changing and controlling the reaction parameters, oxide powders with desired particle shapes (acicular, polyhedral, platelike, spherical, hexagonal) and dimensions (0.1-30 μm) were obtained. They reported that the decrease of specific surface as the mean diameter of particle increases. The density of sintered oxides depends significantly on the particle size. The smaller the particle diameter, the higher becomes the density of the sintered bodies.

Xu et al. (2003) synthesized crystalline zinc oxide powders with various morphology by hydrothermal treatment of zinc acetate in pure water, potassiumhydroxide or ammonia aqueous solution. They prepared the product by adopting zinc acetate as the source material for zinc species. Zinc acetate was dissolved in deionized water for preparing zinc cation solution. Deionized water, potassium hydroxide and ammonia solution are employed as the solvent. The reaction was maintained at 200°C for 2 h and then cooled to room temperature. The precipitate was flitted off wash with deionized water dried in air at 120°C for 30 min. They found that phase-pure hexagonal structure ZnO has been successfully synthesized in various solutions via this hydrothermal method at 200°C and the selected solvents play a different role in controlling the morphologies of the obtained powder. In pure water the pencil-like ZnO particles are obtained. The morphology of ZnO powders prepared of different concentration on KOH solution changes in turn from twinned pyramidal, shortened prismatic, sheet-like to prismatic-like, as as the concentration of KOH solution varies from 0.25 to 2.00 mol/l. If ammonia solutions of different concentrations are employed as the solvents, the shapes of the ZnO particles are ellipsoidal and long prismatic-like.

Li et al. (2003) reported that ZnO powders with different morphologies were synthesized by alkali precipitation, organo zinc hydrolysis, and spray pyrolysis. They used acetaldehyde decomposition as a probe reaction to evaluate the photocatalysis of these ZnO powders and investigated the relationship between photocatalytic activity and crystallinity, surface area, or morphology. They found that the photocatalytic activity of ZnO powder depends on crystallinity rather than surface area for the same original ZnO powders prepared by equal conditions other than the difference in calcination temperature. However, no direct relationship between photocatalytic activity and crystallinity or surface area was found for the differently original ZnO powders prepared by different methods, or the same method with different conditions. Instead, they found that the particle morphology significantly affects its photocatalysis.

Lu et al. (2000) prepared crystalline zinc oxide powder by adopting ammonia as the base source via the hydrothermal process at temperature ≥ 100°C. The temperature for synthesizing zinc oxide powder is around 200°C lower than of conventional heating process.The formation and growth zinc oxide powder under hydrothermal environment progress rapidly as soon as the temperature reaches 100°C. Prolonging the reaction time at 100°C does not significantly influence the characteristics of obtained powder; however, raising the reaction temperature slightly reduces the particle size and the production yield of zinc oxide powder. On the other hand, as the pH of the starting solution increases from 9 to 12, the morphology of zinc oxide powder markedly varies from an ellipsoidal shape to a rod-like shape. In addition, the crystallinity and particle size of zinc oxide powder increase with rise in the pH of solutions, but the yield of production decreases. The reason for the variation of morphology and characteristics of obtained powder with pH mainly depends on the nucleation states occuring in the hydrothermal reaction.

In many studies have been devoted to improve the thermal stability of titanium (IV) oxide using additives such as Al (Ding et al., 1994), La (Ledus et al., 1996), Si (Iwamoto et al., 2000) and others. The effect of these additives are quite different by the procedures of the doping and amount of 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, Iwamoto et al. (2000) synthesized the large-surface area silica-modified titania by glycothermal method. The reaction of titanium tetraisopropoxide (TIP) and an appropriate amount of tetraethyl orthosilicate (TEOS) in 1,4-butanediol at a desired temperature (200-300°C) yielded nanocrystal with an anatase form. The product preserved relatively large surface area even after calcination at high temperatures. The anatase-rutile transformation began at around 1000°C with the increase of the amount of TEOS added, the surface area increased and the crystallite size decreased. The effect of the reaction temperature was examined by fixing the Si/Ti ratio at 0.10. The reaction at 230-250°C also affored products having the anatase structure with large surface area as well as smaller crystallite sizes than the product obtained by the 300°C reaction. A small amount of TEOS added to the reaction mixture caused the anatase-rutile phase transformation to shift markedly toward higher temperatures, and the samples with the silica content higher than 0.20 preserved the anatase structure even after calcination at 1200°C for 30 min.

Iwamoto et al. (2001) also prepared the xerogels of nanocrystalline silica-modified titanias by the glycothermal reaction of titanium tetraisoproxide (TIP) and tetraethyl orthosilicate (TEOS) in 1,4-butanediol at 300°C for 2 h in an autoclave, followed by the removal of the organic phase by flash evaporation at the reaction temperature. The thus-obtained products exhibited extremely high thermal stability on calcination at high temperatures. This is because of the prevention of the coagulations, which takes place by the strong surface tension of the liquid between nanoparticles during drying of wet gels, which contributes to the superior thermal stability and photocatalytic activity of the products.

Yoshinaka et al. (1997) studied in a formation and sintering of TiO_2 (anatase) solid solution in system TiO_2-SiO_2. As-synthesized titania was prepared by hydrazine method, they had developed the new method using hydrazine monohydrate ($(NH_2)_2.H_2O$) in the hydrolysis reaction. The product was form anatase titania. When they added SiO_2 to synthesized titania, they found that transformation of anatase occurred of higher temperature with increased SiO_2 content and a linear decreased in specific surface area was due to the formation of tightly bound aggregated in the primary particle with increase temperature. In the transformation of anatase to rutile they suggest that anatase by transformation decomposed into rutile and amorphous SiO_2, no crystalline SiO_2 was recognized throughout the heating process.

Martucci et al. (1999) studied crystallization of Al_2O_3-TiO_2 sol-gel systems. They found that the presence of a large amount of Al_2O_3 in the system has an inhibitory effect on the crystallization of titania in both anatase and rutile structures which a shift in rutile crystallization temperature with increasing the Al_2O_3 content. In the other hand, they reported that the formation of titania rutile phase in the films may be attributed to be in great part due to the direct transformation amorphous-rutile, rather than anatase-rutile. They had discussed the effect of Al_2O_3 on the crystallization in two conclusions, first, Al_2O_3 could prevent the nucleation of anatase by interfering with the mutual contact between adjacent TiO_2 particles, second, the presence in the film of nanometric TiO_2 clusters allow the formation of mixed Ti-O-Al bonds, localized at the surface of these clusters, which prevents the crystal growth and the anatase phase transformation. In more content Al, they found that sample was calcined at 1000°C the metastable β-Al_2TiO_5 and α-Al_2O_3 were formed they reported that α-Al_2O_3 was formed from amorphous Al_2O_3 and the metastable β-Al_2TiO_5 was form from both amorphous titania and alumina in the film.

Xue et al. (2002) synthesized nanocrystalline maghemite (γ-Fe_2O_3) in amorphous silica matrix at room temperature by mechanically activating a precursor gel derived from iron nitrate and tetraethyl orthosilicate in ethanol. The formation of γ-Fe_2O_3 occurs through a reduction-oxidation reaction from the activation-triggered Fe_3O_4 with increasing degree of mechanical activation. The initial 10 h of mechanical activation triggered the formation of nanocrystalline Fe_3O_4 in a highly activated matrix. Increasing the mechanical-activation time led to a phase transformation from Fe_3O_4 to γ-Fe_2O_3. The nanocrystalline γ-Fe_2O_3 phase was well established after mechanical activation of the precursor for 30 h. However, with further extension of mechanical-activation time to 40 hours, γ-Fe_2O_3 was partially converted to α- Fe_2O_3 due to the steady growth in crystallite size of γ-Fe_2O_3, induced by mechanical activation. The mechanical-activation-grown γ-Fe_2O_3 nanocrystallites were 10-12 nm in size and well dispersed in the silica matrix, as observed using TEM. In addition, the activation-derived nanocrystalline γ-Fe_2O_3 exhibits superparamagnetic behavior and a saturation magnetization of 62.6 emu/g.

Solinas et al. (2001) prepared Fe_2O_3-SiO_2 nanocomposites with Fe/Si molar concentrations ranging between 0.25 and 0.57 by sol-gel route. They used tetraethoxysilane mixed with iron (III) nitrate solution in ethanol and hydrolysis reaction was promoted by the hydration water of the salt. The sols were gelated in air and then treated at 400°C for 4 h. The effect of the gelation process on the formation of the final nanocomposites has been investigated by studying different factors, such as temperature and surface of evaporation/volume ratio of the sol. Nanocomposites of γ and/or α iron oxide phase of different size were obtained in the silica matrix depending on the gelation conditions and on the later heat treatment. γ-Fe_2O_3-SiO_2 nanocomposites were obtained only when organic material was present into the pores of the gel silica matrix supporting their formation through a magnetite phase. At temperature > 400°C, the γ-phase begins to transform to the α-phase.

Xu et al. (2004) found that iron oxide-silica nanocomposites (Fe~15 mol%) were synthesized using $Si(OC_2H_5)_4$ and an iron-containing citrate solution. α-Fe_2O_3

nanocrystal is the main form of iron oxide formed in the composites after sintering. For the composites sintered above 1000°C, α-quartz and cristobalite became the main crystalline phase observed. All sintered composites show weak magnetic behavior, but the strongest was the composites after sintering at 1000°C due to more γ- Fe_2O_3 formed at ~1000°C

Clapsaddle et al. (2003) synthesized Fe-Si mixed oxide nanocoposites materials in which the iron (III) oxide is the major component. In a typical synthesis, the iron oxide precursor, $FeCl_3.6H_2O$ was mixed with a silica precursor, tetramethyl or tetraethylorthosilicate in ethanol and gelled using on organic epoxide. The composition of the resulting materials was varied from Fe/Si (mol/mol) 1-5 by adjusting the amount of silica precursor added to the $FeCl_3.6H_2O$ solution. Further processing of the gels in supercritical CO_2 resulted in monolithic, porous aerogel nanocomposite materials with surface areas ranging from 350-450 m^2/g. The bulk materials are composed of iron (III) oxide/silica particles that vary in size from 5-20 nm depending on the epoxide used for gelation. Iron (III) oxide and silica dispersion throughout the bulk material is extremely uniform on the nanoscale. The synthesis method presented is general for the synthesis of several other metal oxide/silicon oxide nanocomposite materials.

Monte et al. (1997) prepared isolated nanometric particles of γ-Fe_2O_3 in a silica matrix by heating at 400°C the gel formed in the hydrolysis of an ethanol solution of $Fe(NO_3)_3.9H_2O$ and tetraethylorthosilicate (TEOS). However, when $FeCl_3.6H_2O$ was used as precursor, well-developed hematite particles were obtained in the final composite. This different behavior was already manifest in the initial gels. Thus, the gel obtained from iron nitrate salt shows a compact appearance as a result of its higher degree of network connectivity (polymeric gel) whereas the one from the iron chloride appears more loose and highly hygroscopic (colloidal gel). In addition, small superparamagnetic nuclei are formed during the hydrolysis and condensation of the gel obtained from the iron nitrate salt. The γ-Fe_2O_3 nanoparticle formation takes place through a reduction-oxidation reaction which occurs during the burning of the organic species trapped inside the gel pore. The growth mechanism of the γ-Fe_2O_3 nanoparticles in the silica network has been studied as well as the optimum conditions for their preparation. Thus, γ-Fe_2O_3 nanocomposites with different particle sizes and distributions can be prepared by adequate modification of the initial gel microstructure through different gelation times, salt concentrations, and mechanical treatment. Superparamagnetic behavior has been found in all nanocomposites at room temperature, meanwhile at 70 K, a transition from superparamagnetic to ferrimagnetic behavior is observed as the particle size increases. In all cases, the variation in particle size observed by X-ray diffraction corresponds well with changes in the saturation magnetization for the γ-Fe_2O_3 nanocomposites. Similar size effects are also found via the coercivity values at 70 and 5 K.

Kominami et al. (2002) studied the synthesis of perovskite-type lanthanum iron oxide by glycothermal reaction of lanthanum-iron precrsor. They prepared the precursor by reacted a mixture of lanthanum (III) isopropoxide (LIP) and iron (III) n-butoxide (INB) in toluene, this process in toluene they call the solvothermal decomposition process and they used the precursor reacted in 1,4 butanediol (1,4 BG), this solvothermal process in 1,4 BG is called a glycothermal process. Formation of the amorphous phase that prepared by solvothermal decomposition of the mixture of LIP and INB in toluene, they found that it suggested a relative strong interaction between two starting compounds and high homogeneity of lanthanum and iron species in the precursor. When they prepared the product by direct glycothermal reaction of a mixture of LIP and INB without preparation of the precursor using the solvothermal decomposition process they found that the starting materials, LIP and INB, reacted independently under glycothermal condition and yield each related compound.

Chen et al. (2000) successfully prepared zinc oxide powder via hydrothermal process. The reaction of $ZnCl_2$ and NaOH with molar ratio of 1:2 are dissolved in deionized water, and the white $Zn(OH)_2$ precipitate forms. After filtration and washing with deionized water, the white precipitate is dispersed in deionized water and the pH value is adjusted to 5-8 by HCl. After stirring for about 3 h, the homogeneous sol is poured into a teflon-lined autoclave and hydrothermally heated at the designed temperature for a planned period. Then, the autoclave is cooled to room temperature and the product is filtered and washed with deionized water and dried at room temperature. The result reveals that the reaction temperature significantly influences the particle morphology, increasing the temperature from 100 to 220°C, the particle morphologies change from rod-like to polyhedra. Particles with different morphologies and sizes can be obtained by adjusting the template agents while the temperature is held at 160°C.

Kongwudthiti et al. (2002) synthesized the large-surface area of silica-modified zirconia by the glycothermal method. They prepare the product from zirconium n-butoxide and amount of tetraethyl orthosilicate in 1,4 butanediol, they found that the tetragonal was formed for all the products and they reported that the crystallinity of sample prepared by the glycothermal method was not effected by increasing of the Si ratio. All the product were composed of spherical particle when TEOS was added to the reaction, the spherical particle formed aggromerates but the crystallite size of all product not different, they suggested that the nucleation frequency of product was scarcely affected by TEOS content added to the reaction. In thermal stability, the tetragonal to monoclinic phase transformation temperature shifted toward higher temperatures with the addition of TEOS.

Many papers as mentioned above, the synthesis of several metal oxides and binary metal oxides in organic solvents are explained. The product by this novel method has a large surface and high thermal stability. This novel method maybe a new route to prepare micro-and nanocrystalline metal oxides. 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.