

## Preparation of Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Nanocomposite by Solvothermal Process

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Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocomposite was prepared by solvothermal process at 498 K for 2 h in an alcohol (methanol or ethanol)-water medium with AgNO<sub>3</sub> followed by calcination at 823 K for 2 h. The influence of the composition of solvent on the microstructure of Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocomposite was investigated by using XRD, TEM, XPS, TG-DTA, BET, etc. It is found that with decreasing the ratio of alcohol to water, the matrix phase of  $\gamma$ -alumina gradually changed from smaller fibrous to rhombic shape, and the BET specific surface area decreases. These phenomena may be attributed to the formation of rhombic  $\gamma$ -AlOOH during the solvothermal process in the presence of water which results in the decrease of the total pore volume and a shift of the characteristic pore size and a double peak pore size distribution. The state of silver in composites changed from Ag<sup>0</sup> to AgO and/or Ag<sub>2</sub>O after calcination

Key words: Silver/ $\gamma$ -alumina, Nanocomposites, Solvothermal process, Preparation, Microstructure

### 1. INTRODUCTION

Me/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Me=Pt, Sn, Co, Cu, Ag and In etc.) composite material is one of the most important catalysts especially used in the environmental purification.<sup>[1-3]</sup> In recent years, special interest has been focused on Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst due to its relatively lower cost compared with noble metals, good resistance against catalytic poisoning and excellent deNO<sub>x</sub> behaviour.<sup>[4-6]</sup>

Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> material is believed to be a potential candidate catalyst for the decomposition of NO<sub>x</sub> in the exhaust gases from the lean burn engine with the oxygen rich environment and diesel engine particularly at lower temperature. However, there are some problems such as the relatively lower catalytic activity for NO<sub>x</sub> decomposition. The existence of the relatively large and inactive agglomerations as well as nonuniform distribution of silver on alumina matrix in Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has been considered as the main reason of the problem. An impregnation method is currently widely used for loading of active metals on supports because of the advantage of simplicity, but may result in a nonuniform distribution and agglomeration of active substance on the support in a mesoscale or even macroscale due to the solute transition with solvent driven capillary force during drying of samples. The *in-situ* localization of the active substance or solute before drying is an acceptable approach to solve the problem.

Solvothermal process is a powerful method for the precipitation of micro-particles or nanoparticles of metallic or ceramic material and has been widely used to produce well dispersed metallic and both structural and functional ceramic nanoparticles. It is possible to make

the active substance *in-situ* deposit on the substrate by suitable design of the reaction system.

In the present study Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> materials were prepared by the solvothermal-calcination process in alcohol aqueous solutions and the influence of the ratio of alcohol to water on the microstructure of materials was investigated.

### 2. EXPERIMENTAL

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder (G025, Sumitomo Chemical Co., Ltd., 5 g) and AgNO<sub>3</sub> (0.2435 g, AR) were added into 165 cm<sup>3</sup> of alcohol-deionized water mixed solution and ultrasonically mixed for 30 min, then the suspended liquid was poured into an autoclave chamber of 200 cm<sup>3</sup> of internal volume. The autoclave was placed in an electric furnace and heated to 498K. After maintaining at the temperature for 2 h, the autoclave was taken out from the furnace and cooled in air. Stirring with 350 rpm rotation speed was applied during the reaction. After reactions the products were separated by centrifugation, washed with alcohol or water and vacuum dried at 333K for 18 h. Then samples were calcined at 823K in an electric furnace (Motoyama SB-1415) for 2 h.

The specific surface area and pores size of the sample were determined using nitrogen adsorption method (BET, Yuasa Ionics Co. NOVA 1000). The pore size distribution was determined by BJH method using desorption isotherm. The thermal stability was evaluated by TG-DTA analysis (Rigaku, TAS-200). The morphology and particle size of sample were observed by a transmission electron microscope (JEOL, JEM-2000EX). The crystalline phase was determined by X-ray diffraction analysis (Shimadzu, DX-D1) using graphite monochromatized Cu K $\alpha$  radiation. Valence

state of silver was determined by XPS analysis (Perkin Elmer, Phi 5600).

### 3. RESULTS AND DISCUSSION

#### 3.1 Phase constitutions and morphologies of solvothermal products

Figure 1 shows the XRD patterns of the samples obtained by solvothermal reaction in ethanol-water mixed solution both before and after calcination at 823 K for 2 h. It can be found that  $\gamma$ -AlOOH appeared after solvothermal treatment of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and AgNO<sub>3</sub> in the mixture of alcohol and water at 498 K for 2 h. As the ratio of alcohol to water decreased, the  $\gamma$ -AlOOH intensities increased while those of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

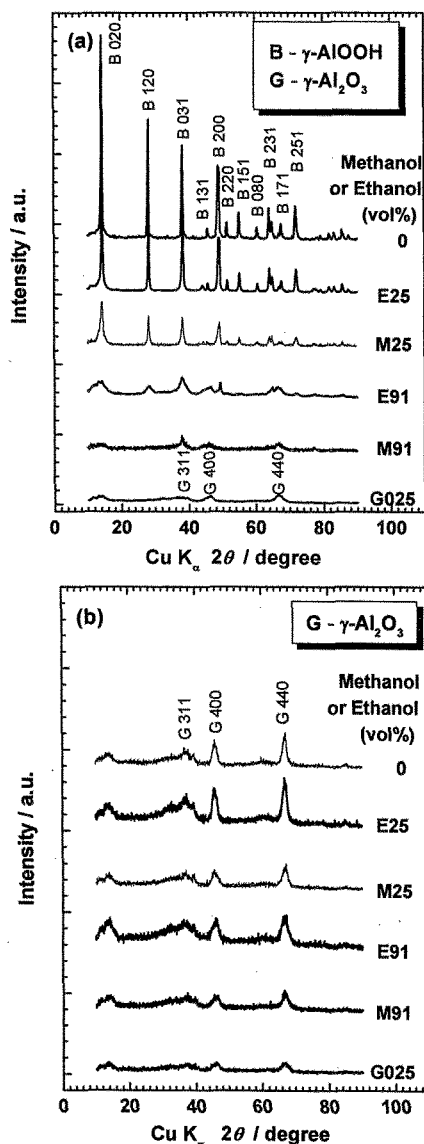


Fig1. XRD patterns of (a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples treated at 498 K for 2 h in AgNO<sub>3</sub> alcohol aqueous solutions, and (b) then calcined at 823 K for 2 h. "M" and "E" refer to methanol and ethanol, and the followed numbers refer to the volume percentage of alcohol in solutions, "0" refers to aqueous solution.

decreased. In the cases with low content of alcohol or without alcohol, only peaks of  $\gamma$ -AlOOH could be detected. Therefore, the existence of water influenced to the conversion of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\gamma$ -AlOOH, and alcohol seemed to act as an inhibition agent on the phase change. After calcination at 823 K for 2 h, only  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> peaks were detected as shown in Fig.1(b).

It is quite difficult to detect peaks belonging to silver phase because the total content of silver is too low to detect by XRD.

Figure 2 presents the transmission electron micrographs of samples as-prepared in 25 and 85 vol% methanol at 498 K for 2 h and after calcination at 823 K. The sample obtained using 85 vol% methanol aqueous solution (Fig. 2(c)(d)) showed somewhat similar morphology to that of the raw material which possessed a needle-like morphology. There was a pronounced change in morphology in the cases of lower ratio of methanol to water, i.e., as-prepared sample was rhombic (Fig. 2(a)) whereas calcined sample (see Fig. 2 (b)) was a mixture of needle-like and rhombic particles. The rhombic platy particles are similar to those produced under hydrothermal treatment of aluminum trihydroxides or pseudoboehmite.<sup>[7]</sup> According to the results of XRD analysis and TEM observation, the needle-like and rhombic particles are found to be  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and  $\gamma$ -AlOOH, respectively.

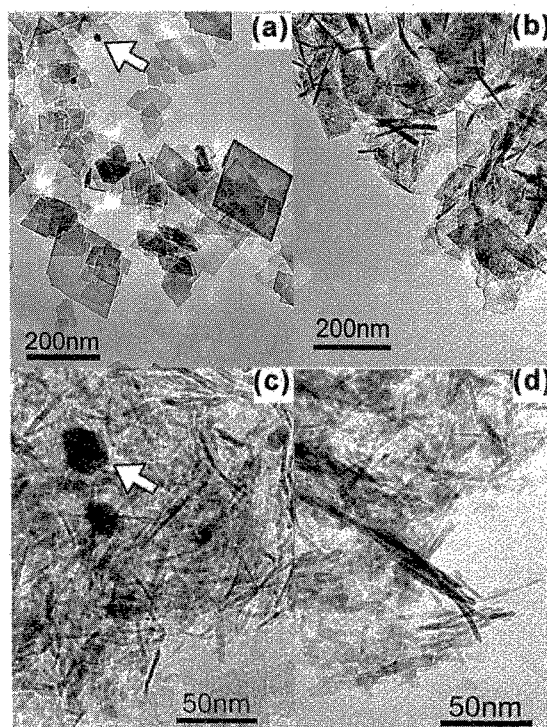


Fig.2 TEM micrograph of samples. (a) and (c): as prepared by solvothermal treatment of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (G025) in 25 and 85 vol% methanol at 498 K for 2 h, (b) and (d): calcined (a) and (c) at 823 K for 2 h, respectively.

It has to be pointed out that there existed spherical particles of about 5-20 nm in diameter in the samples as-prepared in methanol-water system (see Fig. 2(a) and (c), indicated by arrows). No such spherical particle can be found in both raw material and sample prepared in water. Although samples prepared in alcohol-aqueous solutions were golden or yellow, the sample prepared in aqueous solution was white. XPS analysis did not show any peaks of silver in the sample obtained in aqueous solution, while samples obtained in alcohol-aqueous solutions showed clear peaks of silver (see Fig. 3). This means that  $\text{AgNO}_3$  cannot be decomposed to form silver under hydrothermal conditions without any reductant. Thus, alcohol works to reduce  $\text{AgNO}_3$  to silver. Therefore, it is reasonable to believe that the spherical particles in Fig. 2(a) and (c) are silver containing phase. After calcination, the Ag particles disappeared (see Fig. 2(b) and (d)). In order to determine the valence state of silver in their samples, XPS analysis was performed. Because there is no distinct difference between the peak positions of 3d core levels of Ag,  $\text{Ag}_2\text{O}$  and  $\text{AgO}$ , their Auger peaks were assigned as shown in Fig. 3. Because of diverse in the reported data of Auger peaks,<sup>[8]</sup> the standard samples of pure silver and silver oxides have also been examined. Silver exists as the metallic state in the sample before calcination. After calcination, silver existed as  $\text{AgO}$  or  $\text{Ag}_2\text{O}$  though it is believed that silver oxides are unstable at temperature higher than 573 K.

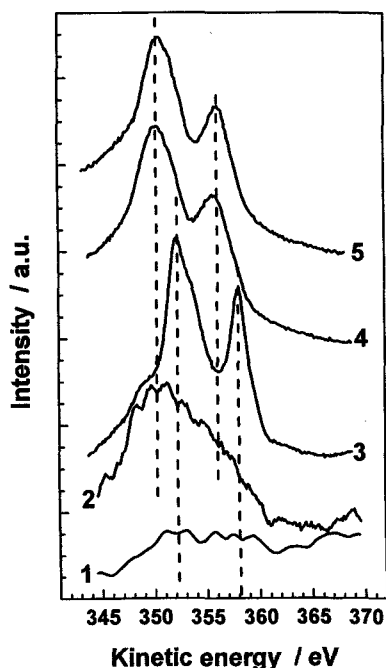


Fig.3 Ag Auger peaks of samples prepared by solvothermal treatment of  $\gamma\text{-Al}_2\text{O}_3$  at 498K for 2 h in a 91 vol% methanol aqueous solution with  $\text{AgNO}_3$  before (curve 1) and after (curve 2) calcination at 823K for 2 h. Curves 3, 4 and 5 are Auger peaks of Ag,  $\text{Ag}_2\text{O}$  and  $\text{AgO}$ , respectively.

In the case of ethanol the situation was similar to that of methanol.

### 3.2 Phase change between $\gamma\text{-Al}_2\text{O}_3$ and $\gamma\text{-AlOOH}$

The TG-DTA results for samples prepared in alcohol-aqueous solutions with various alcohol contents are shown in Fig. 4. An exothermic peak observed around 500K might be due to the combustion of alcohol and/or some organic compounds adsorbed on the surface. On the other hand, the sharp endothermic peak around 743 to 773K accompanied with large weight loss could be attributed to the dehydration of  $\gamma\text{-AlOOH}$  to form  $\gamma\text{-Al}_2\text{O}_3$  which was confirmed by XRD analysis of all the samples calcined at 823K for 2 h (see Fig.1(b)). The transition temperature of  $\gamma\text{-AlOOH}$  to  $\gamma\text{-Al}_2\text{O}_3$  was quite close to that reported in a literature (793 K).<sup>[9]</sup> The difference in the transition temperature can probably be related with the preparation route as well as geometric feature of powders. At low proportion of alcohol in the mixed solution, the weight losses around 743 to 773K were large and proportionally the DTA peaks were strong, indicating that the content of  $\gamma\text{-AlOOH}$  increased

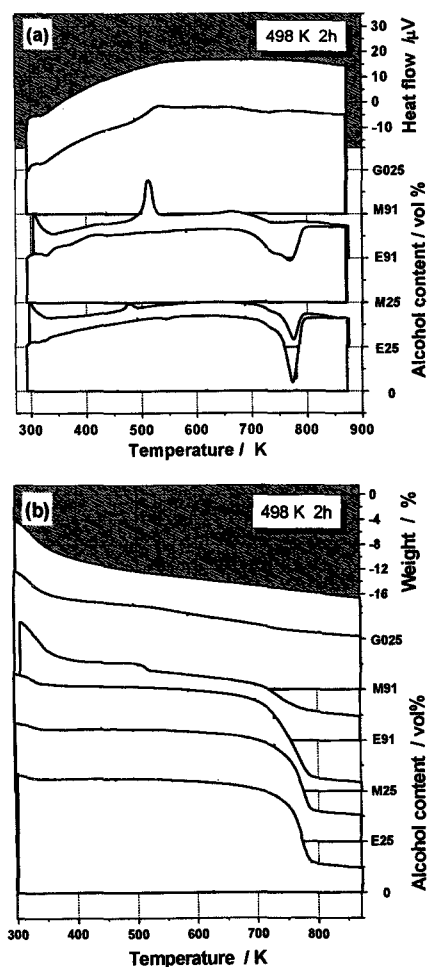


Fig.4. (a) TG and (b) DTA profiles of samples obtained by solvothermal process with various ratios of alcohol to water.

with decreasing alcohol content in the solvothermal solvent.

### 3.3 Characterization of pores in the samples

The correlation between specific surface area (SSA) of the samples before and after calcination at 823K for 2 h of powders prepared at 498K for 2 h and the volume percentage of ethanol in the solvothermal solvent are shown in Fig. 5. It can be found that as the proportion of ethanol in the solution increased, the SSA of both samples before and after calcination monotonously increased. The increase of SSA may be due to the decrease in the proportion of large rhombic  $\gamma$ -AlOOH particles with the increase in the ethanol content (see Fig. 2). On the other hand, the SSA increased after calcination except the sample obtained in the solution with 91 vol% of ethanol which showed a slightly decreased value. This is attributed to the phase change from  $\gamma$ -AlOOH to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. As the percentage of ethanol decreased, the content of  $\gamma$ -AlOOH increased, and smooth and dense rhombic  $\gamma$ -AlOOH changed into rough and loose  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after calcination (see Fig.2(a) and (b)). Therefore, the SSA increased. For the sample with 91 vol% ethanol, the percentage of  $\gamma$ -AlOOH was low, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was the main phase. There was therefore no clear change in SSA after calcination.

The total pore volume (TPV) of the samples without calcination increased from 75 to 1304 dm<sup>3</sup>kg<sup>-1</sup> as the percentage of ethanol in solutions increased from 0 to 91 vol%. The TPV increased from 187 to 1399 dm<sup>3</sup>kg<sup>-1</sup> after calcination. Similar results are also obtained for the case of methanol.

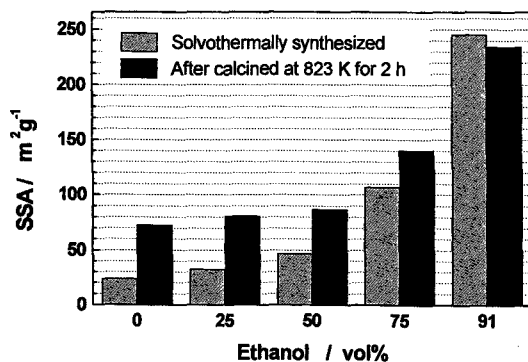


Fig.5. Comparison of BET specific surface area (SSA) of the samples before and after calcination at 823 K for 2 h of powders obtained by solvothermal process at 498 K for 2 h.

The BJH pore size distribution curves of the samples prepared in ethanol aqueous solutions showed double characteristic peaks (not shown here). One peak was located at around 2.9 nm which may be corresponded to the rhombic  $\gamma$ -AlOOH, and the other peak was at around 9.0 nm, the needle-like  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> since the starting material, i.e. G025 showed only the larger

characteristic pore size peak and it disappeared in the sample prepared in water which mainly consisted of  $\gamma$ -AlOOH. The strength of both peaks increased with increasing ethanol content up to 91 vol%, indicating that the powders became more porous with increasing ethanol content.

### 4. CONCLUSIONS

Ag/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocomposites were prepared by solvothermal process using alcohol (methanol or ethanol)-water. With increasing the percentage of alcohol in aqueous solutions, the morphology of  $\gamma$ -alumina gradually changed from submicron rhombic plates to nanometer fibrous particles, and the BET specific surface area increased. These results are attributed to the formation of rhombic  $\gamma$ -AlOOH during the solvothermal process in the presence of water, which resulted to decrease total pore volume and a shift of the characteristic pore size and a bimodal pore size distribution. The Ag in the composites changed from metallic to AgO and/or Ag<sub>2</sub>O after calcination at 823K for 2 h.

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