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The synthesis, characterization and application of Ag–SiO₂–Al₂O₃ sol–gel composites

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Abstract

A new type of tertiary Ag–SiO₂–Al₂O₃ sol–gel composite with various silver concentrations has been prepared and characterized using combined spectroscopic techniques of XRD, XPS, TPR, UV–VIS, DRS and SEM. It was found that the homogeneous Ag–SiO₂–Al₂O₃ glass composites with transparent appearance could be obtained when the silver content is controlled below 20 wt.%. The silver ion species are found to be highly dispersed in the framework of the glass composites and exhibited a unique thermal stability in air. In addition, the use of the Ag–SiO₂–Al₂O₃ sol–gel composite material as promising silver catalysts for the catalytic oxidation of methanol to formaldehyde was demonstrated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Sol–gel; Ag–SiO₂–Al₂O₃; Tertiary composites; Silver catalyst; Catalytic oxidation; Methanol; Formaldehyde

1. Introduction

Composites formed by silver ions or nano-clusters embedded in ceramics or glasses have recently attracted much attention as promising materials for applications in optoelectronics [1], separation membranes [2], and catalysts [3]. The sol–gel technique is of particular interest since it offers opportunity to develop various kinds of new composite materials with tunable properties in a controlled way [4]. For instance, composite systems formed by the silver clusters or ions imbedded in a sol–gel network as promising materials for optoelectronics [5] and catalytic [6,7] applications have been intensively inves-

tigated. These previous studies have focused on the investigation of the dual composite systems comprising the silver species and the sol–gel derived materials. Alternatively, it may be more interesting and significant to carry out investigation on more complicated composite systems. In this letter, we present a study on a tertiary composite system, formed by the silver ions dispersed in a silica–alumina glass matrix, prepared by the sol–gel technique. The aims of this research were to synthesize and characterize the Ag–SiO₂–Al₂O₃ sol–gel composite materials containing various silver concentrations. The structural properties of the novel Ag–SiO₂–Al₂O₃ sol–gel composites have been characterized using XRD, XPS, TPR, UV–VIS, DRS and SEM. Additionally, the use of the present tertiary silver composite materials as a promising silver catalyst for partial oxidation of methanol to formaldehyde was demonstrated.

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2. Experimental

The Ag–SiO₂–Al₂O₃ sol–gel composites were prepared from Si(OC₂H₅)₄ (TEOS), Al(NO₃)₃ · 9H₂O, AgNO₃. A partially hydrolyzed silica sol was first prepared in the following way: TEOS (67 ml) was dissolved in iso-propanol (100 ml) and to this, a solution containing water and nitric acid was added with stirring at room temperature. The stirring was continued for 1 h. To this sol, the desired amount of AgNO₃ and 7.36 g Al(NO₃)₃ · 9H₂O dissolved in 50 ml water was added with vigorous stirring. The resulting mixed sol was stirred at 75°C for additional 12 h. Finally, the gel was air dried at 120°C overnight followed by calcination at 1100°C for 6 h in air. The as-prepared samples were colorless and transparent in appearance.

The X-ray diffraction (XRD) patterns were recorded using a Rigaku Dmax-rA X-ray diffractometer with Cu K α radiation. The X-ray Photoelectron Spectroscopy (XPS) experiments were carried out in a Perkin-Elmer PHI 5000C ESCA system using Al K α radiation (14,846.6 eV). The ultra-violet visible diffuse reflectance spectra (UV–VIS DRS) were obtained on a Hitachi Uv-330 spectrometer. The surface morphology was observed by a scanning

electron microscopy (SEM) on a JSM-840 scanning electron microscope.

The catalytic oxidation of methanol over the Ag–SiO₂–Al₂O₃ sol–gel composites was carried out in a flow-type quartz reactor (i.d. = 16 mm) at a reaction temperature of 550–700°C with the space velocity (GHSV) at $1.2 \times 10^5 \text{ h}^{-1}$. Aqueous solution of methanol (60 wt.%) was pumped into the evaporator (keeping at 493 K) and then fed into the reactor after being mixed with air. Gaseous products (CO, CO₂, etc.) and formaldehyde in solution were analyzed by using GC analysis and chemical titration methods, respectively.

3. Results and discussions

Fig. 1 presents the XRD patterns for the Ag–SiO₂–Al₂O₃ sol–gel composites as a function of silver concentration. For the Ag–SiO₂–Al₂O₃ composites with silver contents below 20 wt.%, clear diffraction peaks were not observed and the sample had an amorphous structure. The absence of crystalline peaks associated with metallic silver indicates that the silver species are either highly dispersed or present as ionic state. However, with increasing sil-

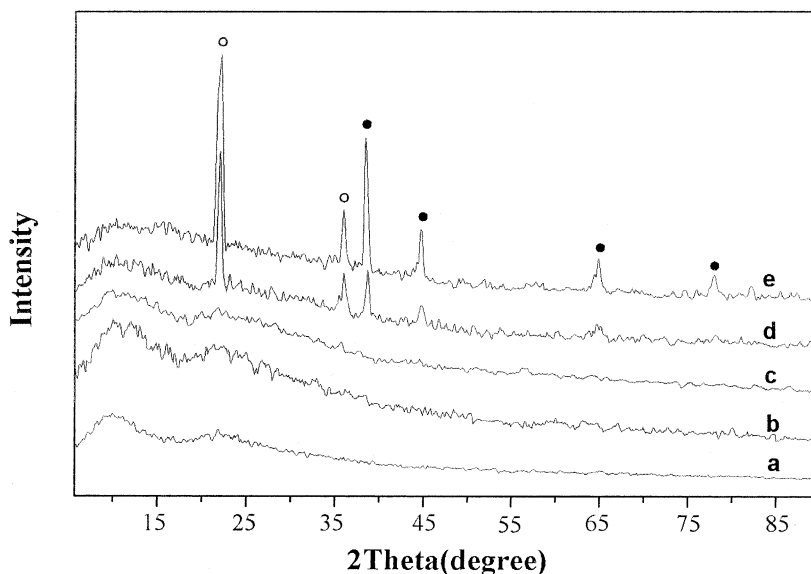


Fig. 1. XRD spectra of Ag–SiO₂–Al₂O₃ composite with various silver concentrations. (a) 2 wt.%, (b) 10 wt.%, (c) 20 wt.%, (d) 30 wt.%, (e) 40 wt.%. ●—metallic silver, ○—cristobalite (low syn).

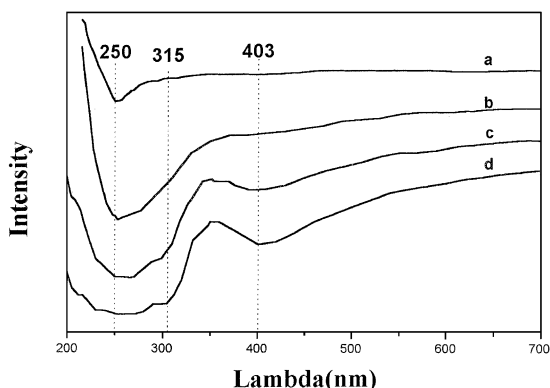


Fig. 2. UV-VIS DRS spectra of Ag-SiO₂-Al₂O₃ composite with various silver concentration. (a) 10 wt.%, (b) 20 wt.%, (c) 30 wt.%, (d) 40 wt.%.

ver concentration, the characteristic diffraction peaks due to the crystalline Ag(111) (38.1°), Ag(200) (44.3°), Ag(220) (64.4°) and Ag(311) (77.5°), respectively, appear in the XRD spectra [6]. This indicates the presence of metallic silver particles in the Ag-SiO₂-Al₂O₃ so-gel composites with silver content higher than 20 wt.%. In addition, two crystalline peaks (21.9° and 36.1°) ascribed to ceramic cristobalite (low syn) were also observed [3], suggesting a

crystallization of the amorphous material at a temperature much lower than that of required occurred. The appearance of the sol-gel composites with silver concentration lower than 20 wt.% is colorless and transparent, indicative of the formation of the homogeneous Ag-SiO₂-Al₂O₃ glass composites. However, an even higher silver concentration (> 20 wt.%) was shown to result in the formation of a yellow sample with many small white particles incorporated in the opaque composites. The failure of the formation of a homogeneous sol-gel composite at high silver containing conditions would be discussed in the following section.

The colorless and transparent appearance of the as-prepared samples at low silver concentration indicates that there is no reduction of silver ions during the calcination preparation of the composites in air. This observation is surprising since previous studies have shown that the decomposition of silver compounds occurs at about 500°C in air [8]. Our previous study [6,7] of the sol-gel derived silver-SiO₂ binary composites also showed that the silver is reduced upon calcination at 600°C in air. Further investigation reveals that the silver ions dispersed in the glass matrix are extremely stable even after a long-time heating at 1100°C in air [9]. This phenomenon possi-

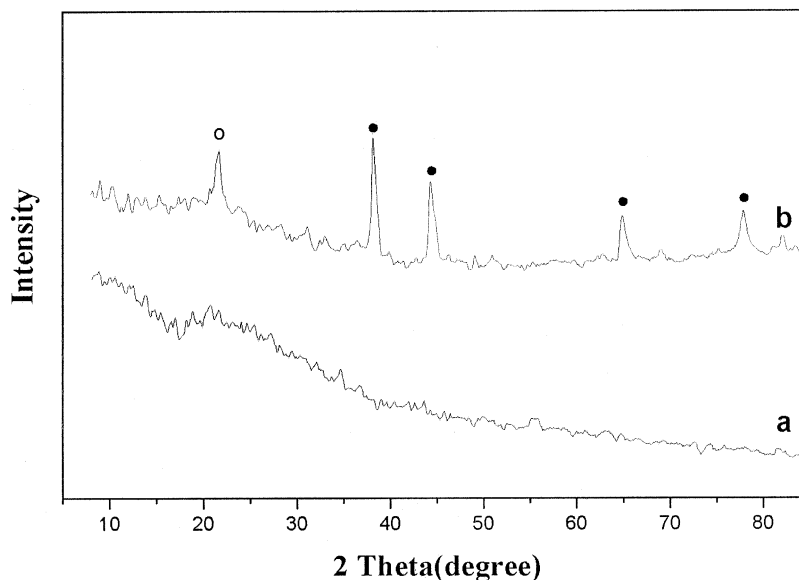


Fig. 3. XRD spectra of Ag-SiO₂-Al₂O₃ composite (20 wt.%) before and after H₂ reduction. (a) Before reduction; (b) after reduction in H₂ for 2 h. ●—metallic silver, ○—cristobalite (low syn).

bly can be attributed to the structural modifying effect of the alumina on the main network of the SiO_2 glass.

The analysis of the structural properties of the as-prepared composites as a function of the silver concentration shows that the homogeneous glass composites can only be obtained at the silver concentration lower than 20 wt.%. This silver concentration implies an interesting relationship between silver and alumina, where the molar ratio of silver to aluminum in the composite is shown to be about 1:1. This ratio suggests that one aluminum ion could stabilize one silver ion in the homogeneous glass composites. We therefore propose that silver ion is stabilized by the tetrahedral $[\text{AlO}_4]^-$ groups incorporated in the framework of the composites.

To confirm this conclusion, further characterizations using traditional chemical analysis, H_2 reduction and UV–VIS DRS were carried out. In the chemical analysis experiments, Ag^+ and Ag^0 are separated by hydrofluoric acid and determined by titration method. It was found that all silver was present as ionic state at the silver concentration lower than 20 wt.%. When the silver concentration exceeds 20 wt.%, excessive silver that could not be stabilized by the tetrahedral $[\text{AlO}_4]^-$ groups is present as metallic state. Similar phenomena can also be observed in the temperature programmed reduction (TPR) experiments. It should be noted that one Ag^+ could consume $1/2$ molecular of H_2 . At the case of lower silver containing samples (≤ 20 wt.%), H_2 consumption was found to be increased as a function of the silver content. When the silver content was > 20 wt.%, H_2 consumption did not increase yet. In addition, as shown in Fig. 2, for the sample with lower silver concentration of 10 or 20 wt.%, only one absorption peak at 250 nm could be observed in UV–VIS DRS spectra, which was previously identified as isolated Ag^+ species. If the silver concentration exceeds 20 wt.%, two absorption bands centered around 315 and 403 nm ascribed to metallic silver particles and silver clusters appeared [10,11], respectively, indicating that the excessive silver was present as metallic state on the sample surface at a higher silver concentration. After calculating the molar ratio of Ag to Al in those samples mentioned above, one can find an excellent linear dependence between the molar ratio of Ag and Al. All these

results strongly suggest that all silver species were present as ionic states in the silica–alumina matrix, moreover, one aluminum ion could stabilize one silver ion in the homogeneous glass composites in case of a lower silver concentration (≤ 20 wt.%).

The XRD patterns in Fig. 3 show the presence of sharp diffraction peaks corresponding to metallic silver for the sample treated with H_2 , indicating that the silver ions in the current composite material can be easily reduced to metallic state by using H_2 . There is a remarkable change for the sample in terms of the appearance since the darkening of the present sol–gel composites was noticed after the reduction treatment. Another interesting finding is that the $\text{Ag-SiO}_2\text{-Al}_2\text{O}_3$ sol–gel composites are found to be UV-sensitive although it is shown to be thermally

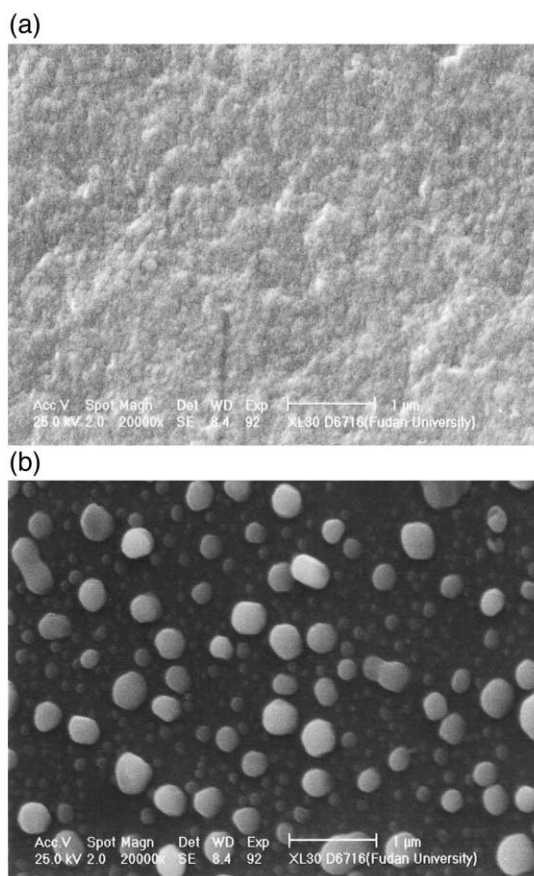


Fig. 4. SEM morphologies of the 10 wt.% $\text{Ag-SiO}_2\text{-Al}_2\text{O}_3$ composite before and after reduction. (a) Before reduction; (b) after reduction in H_2 for 2 h.

Table 1

Catalytic activity test of 20 wt.% Ag–SiO₂–Al₂O₃ composite as comparison to electrolytic silver

| Catalyst | Conversion of CH ₃ OH (%) | Selectivity of HCHO (%) | Yield of HCHO (%) | (CO + CO ₂) yield (%) |
|--|--------------------------------------|-------------------------|-------------------|-----------------------------------|
| Electrolytic silver ^a | 93.6 | 90.2 | 84.4 | 9.2 |
| Ag–SiO ₂ –Al ₂ O ₃ ^b | 97.8 | 92.8 | 90.8 | 7.0 |

^aReaction conditions: GHSV = 1.2×10^5 h⁻¹, reaction temperature = 625°C, O₂/CH₃OH = 0.42, height of catalytic bed = 10 mm, reaction feed = 60 wt.% aqueous solution of methanol.

^bReaction conditions: GHSV = 1.2×10^5 h⁻¹, reaction temperature = 635°C, O₂/CH₃OH = 0.39, height of catalytic bed = 10 mm, reaction feed = 60 wt.% aqueous solution of methanol.

stable in air. The incorporated Ag⁺ can be gradually reduced to ultra fine silver particles after a period of irradiation under UV light. The transparent samples will be darkened after UV irradiation. We note that this phenomena can provide an alternative approach for preparation of ultrafine silver clusters, probably at several nanometer scale, imbedded in the sol–gel matrix, which has recently received increasing attention as promising materials for optoelectronics [1,5].

Fig. 4 shows the representative SEM of the morphology of the 10 wt.% Ag–SiO₂–Al₂O₃ sol–gel composite before and after H₂ reduction. Almost no silver particles were observed on the sample before reduction, while a great many of isolated metallic silver appeared regularly with an average size of about 500 nm on the surface after its reduction. This observation suggests that silver ions are reduced and migrated to the surface from the bulk during the reduction process. Similar silver diffusion behavior was observed on a silver–soda–lime glass system prepared by ion-exchanging method [12]. XPS results indicated that the surface concentration of silver after reduction increased by at least 50 times in comparison to that before reduction. All these experimental results demonstrate that silver will be enriched on the surface of the support after H₂ reduction. We note that this process provides a new approach to prepare new silver catalysts with strong interaction between the supported metal and the SiO₂–Al₂O₃ supports.

To explore the possible application of the present glass composites as potential silver catalysts in catalytic reaction, one representative Ag–SiO₂–Al₂O₃ sol–gel composite (silver concentration: 20 wt.%) has been used as a supported silver catalyst in the catalytic oxidation reaction of methanol to formaldehyde. Our results show that an excellent overall

conversion of the methanol as well as a higher selectivity to formaldehyde was achieved over the present Ag–SiO₂–Al₂O₃ sol–gel composite. It should be noted that metallic silver would be produced in situ on the surface of the Ag–SiO₂–Al₂O₃ sol–gel composite by the methanol vapor during the initial reaction stages. Hence, the metallic silver covered on the surface of the sol–gel composite serves as the intrinsic silver catalyst in the following catalytic oxidation of methanol to formaldehyde. Table 1 compares the catalytic performance of the 20 wt.% Ag–SiO₂–Al₂O₃ composite and that of a commercial electrolytic silver catalyst. As shown in Table 1, the yield of formaldehyde on this novel catalytic material was 6.4% higher than that of the commercial electrolytic silver. The result that the catalytic performance of the present Ag–SiO₂–Al₂O₃ sol–gel composites is much better than that for the commercial electrolytic silver catalyst may be possibly attributed to the unique nature of the metallic silver particles generated in situ at the initial stage of the catalytic reaction. The present results shown here suggest that the present tertiary Ag–SiO₂–Al₂O₃ sol–gel composites are promising catalysts for formaldehyde production from the catalytic oxidation of methanol.

4. Conclusions

In conclusions, we have demonstrated that the tertiary Ag–SiO₂–Al₂O₃ glass composites can be prepared using a sol–gel processing approach. The Ag–SiO₂–Al₂O₃ sol–gel composites are homogeneous and transparent in appearance. The structural characterization of the as-prepared composites shows that the silver is highly dispersed and present as

stable positive ions in the homogeneous glass matrix. It was also found that the present Ag–SiO₂–Al₂O₃ sol–gel composites systems exhibit remarkable thermal stability in air upon high temperature calcination. The present Ag–SiO₂–Al₂O₃ sol–gel composites have shown to be a new type of supported silver catalysts that are promising for the formaldehyde production from the catalytic oxidation of methanol.

Acknowledgements

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