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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

DeNO$_x$ activity of Ag/γ–Al$_2$O$_3$ nanocomposites prepared via the solvothermal route

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Abstract Ag/γ–Al$_2$O$_3$ with silver loading of 3 wt.% were prepared by the solvothermal-calcination reaction of AgNO$_3$ in mixed water-alcohol solutions at 50–250 °C for 0–120 min, followed by calcinations at 550 °C for 2 h using γ-Al$_2$O$_3$ (SSA: 120–409 m^2 g^{-1}), γ-AlOOH (SSA: 270 m^2 g^{-1}), Al(OH)$_3$ (SSA 10 m^2 g^{-1}), Al(OCH(CH$_3$)$_2$)$_3$ and Al(NO$_3$)$_3$ as an aluminum source. The resultant product produced by the solvothermal reaction was Ag/γ–AlOOH even though a different aluminum source was used and Ag/γ–AlOOH was converted to Ag/γ–Al$_2$O$_3$ by the following calcinations. However, the characteristics of them changed greatly depending on the alumina source. The deNO$_x$ catalytic performance of Ag/γ–Al$_2$O$_3$ also greatly changed depending on the aluminum precursor and solvothermal solvent in the order γ-AlOOH = γ-Al$_2$O$_3$ >> Al(OCH(CH$_3$)$_2$)$_3$ >> Al(NO$_3$)$_3$ > Al(OH)$_3$ and methanol = ethanol > 1-propanol > butanol >> hexanol, since the amount and size of silver particle impregnated and specific surface area of the product changed markedly. Ag/γ–Al$_2$O$_3$ prepared by solvothermal-calcination method consisted of homogeneously dispersed fine particles of silver and showed better performance for NO$_x$ decomposition than that by conventional impregnation-calcination method.

Introduction

Since Cu-ZSM-5 was reported as being an effective catalyst for the selective catalytic reduction (SCR) of NO by hydrocarbons in the presence of excess oxygen, the SCR of NO$_x$ has received much attention as a kind of potential technology for cleaning NO$_x$ in the various oxygen-rich exhausts produced by diesel engine, lean burn gasoline engine and gas engine. Although a number of catalysts have been tested, it seems apparently difficult to find a catalyst that is completely suitable for the removal of NO$_x$ in diesel fuel applications. For practical use, the catalysts are required to be stable and active at a relatively low temperature region [1, 2]. Ag/γ–Al$_2$O$_3$ has received attention as a potential candidate catalyst for the decomposition of NO$_x$ in the exhaust gases in an oxygen-rich environment particularly at lower temperatures [3–7]. However, the existence of the relatively large and inactive agglomerations as well as the non-uniform distribution of silver on alumina matrix in Ag/γ–Al$_2$O$_3$ may result in relatively lower catalytic activity for NO$_x$ decomposition especially at lower temperatures. The impregnation-calcination method which is currently being widely used for loading active metals on supports [8–13] has the advantage of simplicity. However, it may result in a non-uniform distribution and agglomeration of active substances in relation to a meso-scale or even macro-scale due to the solvent-driven capillary force during drying of samples [14]. The solvothermal process is a powerful method for the precipitation of metallic or ceramic nanoparticles to produce well dispersed nanosized composites [15, 16]. Thus, the solvothermal process seems to enable the in-situ localization of the active substance before drying and to solve the problem of deactivation. In the present study, Ag/γ–Al$_2$O$_3$ catalysts were prepared by the solvothermal-calcination

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process using various aluminum sources and alcohol solutions, and their catalytic performance and microstructure were investigated comparatively with those prepared by the imprenation-calcination process.

Experimental

Sample preparation

Ag/γ–Al_2O_3 with silver loading of 3 wt.% were prepared as follows. Aluminum source, $AgNO_3$, alcohol and water were placed in a autoclave and were heated at 50–250 °C for 0–2 h, and then the products were separated by centrifugation followed by calcinations at 550 °C for 2 h. γ-Al_2O_3 (SSA: 120–409 $m^2\ g^{-1}$), γ-AlOOH (SSA: 270 $m^2\ g^{-1}$), $Al(OH)_3$ (SSA 10 $m^2\ g^{-1}$), $Al(OCH(CH_3)_2)_3$ and $Al(NO_3)_3$ were used as an aluminum source. For the purpose of comparison, the sample was also prepared by impregnating the γ-AlOOH powders with an aqueous solution of silver nitrate followed by vacuum evaporation to dryness at 333 K for 12 h and by calcination in air at 550 °C for 2 h. The sample thus formed was designated as the impregnation-calcination sample.

Analysis

The specific surface area was determined using nitrogen adsorption (BET method, Quantachrome Corporation NOVA 1000). The thermal stability was evaluated by TG-DTA analysis (Rigaku, TAS-200). The crystalline phase was determined by X-ray diffraction analysis (Shimadzu, DX-D1) using graphite monochromatized CuKα radiation. The valence state of silver was determined by XPS analysis (Perkin Elmer PHI 5600). Morphology of the samples was observed by using a transmission electron microscopy (JEM-2000EX). UV-VIS spectra were measured using a UV-Visible spectrophotometer (Shimadzu UV-2450). The catalytic test was performed in a fixed-bed flow reactor by passing a mixture of 400 ppm NO, 50 ppm NO_2, 600 ppm n-C_4H_{10} and 5 vol.% O_2 (balanced with N_2) at a rate of 400 $cm^3 \cdot min^{-1}$ over 0.15 g sample. The sample powder was pressed and then the pressed sample was crushed to form granules of 335–600 μm in diameter. After that, the granules were placed into a quartz tube reactor of 6 mm in diameter. The samples were heated at a heating rate of 10 $K \cdot min^{-1}$ from room temperature to ca. 500 °C. A gas FTIR spectrometer (MIDAC Co., IGA-4000) was employed for in-situ analysis of the gas composition. The conversions of NO_x was obtained by using the formula $X_{NOx} = (1-[NO_x]/[NO_x]_0) \times 100$ (%), where $[NO_x]_0$ and $[NO_x]$ were initial and transient concentrations of NO_x, respectively.

Results and discussion

Figure 1 shows the XRD patterns of the samples as-prepared by the solvothermal reaction of γ-Al_2O_3 and $AgNO_3$ mixture in ethanol aqueous solution at 225 °C for 2 h. It was observed that γ-AlOOH appeared after solvothermal treatment. As the ratio of alcohol to water decreased, the γ-AlOOH intensities increased while those of the γ-Al_2O_3 decreased. In the cases having low alcohol content, only peaks of γ-AlOOH could be detected. Therefore, the existence of water promoted the phase change from γ-Al_2O_3 to γ-AlOOH. When γ-AlOOH, $Al(OH)_3$, $Al(OCH(CH_3)_2)_3$ and $Al(NO_3)_3$ were used as an aluminum source, only peaks of γ-AlOOH could be detected.

All samples prepared by solvothermal reaction of γ-Al_2O_3 and $AgNO_3$ mixture in ethanol aqueous solution (shown in Fig. 1) converted to γ-Al_2O_3 by calcinations at 550 °C for 2 h as shown in Fig. 2. It is quite difficult to detect peaks belonging to the silver phase because the total content of silver is too low to be detected by XRD.

Although the sample prepared in the aqueous solution was white, the samples prepared in ethanol aqueous solutions were golden or yellow due to the plasmon absorption by silver nanoparticles. This means that a reducing agent such as ethanol is essential for reducing $AgNO_3$ to form

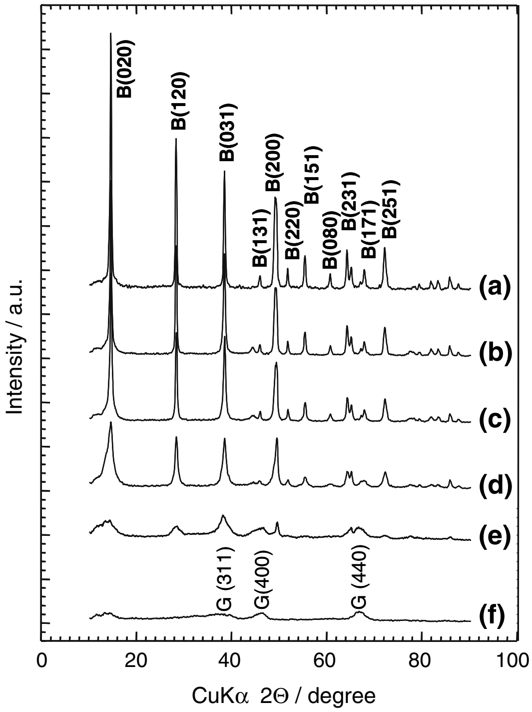


Fig. 1 XRD patterns of γ-Al_2O_3 samples treated at 225 °C for 2 h in $AgNO_3$ ethanol aqueous solutions. G: γ-Al_2O_3, B: γ-AlOOH, Ethanol content (vol.%); (**a**) 0, (**b**) 25, (**c**) 50, (**d**) 75, (**e**) 91, (**f**) original γ-Al_2O_3

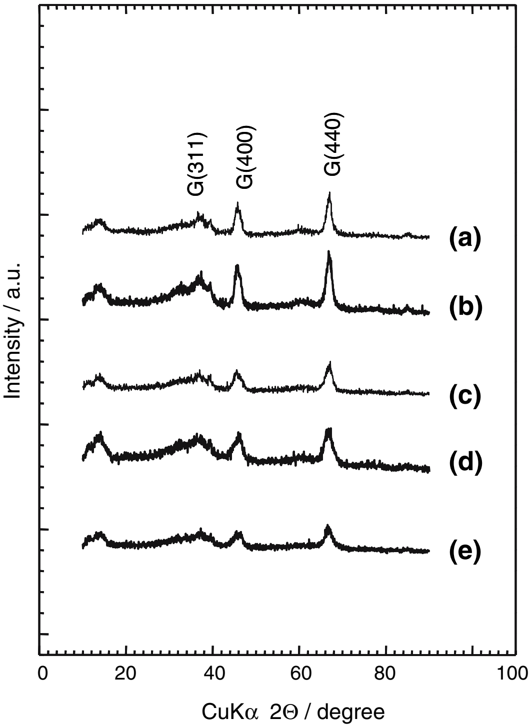
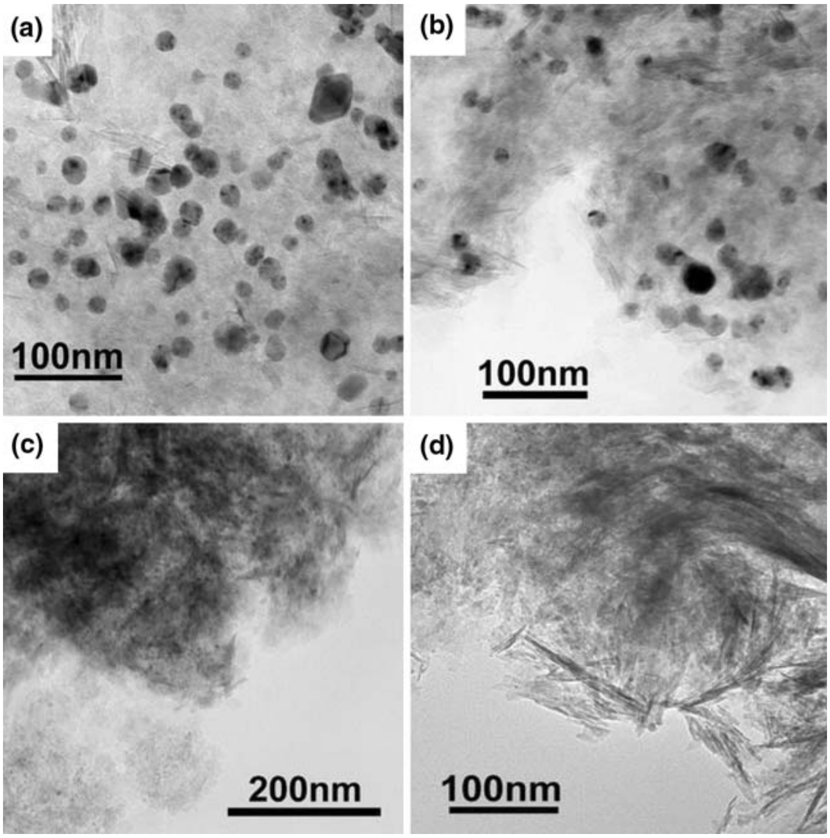


Fig. 2 XRD patterns of the samples by the solvothermal reaction of γ-Al_2O_3 at 225°C for 2 h in $AgNO_3$ ethanol aqueous solutions followed by calcination at 550 °C for 2 h. Ethanol content (vol.%); (**a**) 0, (**b**) 25, (**c**) 50, (**d**) 75, (**e**) 91

silver under hydrothermal conditions. The formation of silver nanoparticles 5–20 nm in diameter by the solvothermal reaction in 75 vol.% ethanol aqueous solution was confirmed by TEM (Fig. 3a). The silver nanoparticles existed after calcination in air below 280 °C (Fig. 3b), however, they disappeared above 390 °C (Fig. 3c, d). Therefore, it is suspected that the nanoparticles of silver were oxidized and reacted with γ-Al_2O_3 during the calcinations process exceeding 390 °C.

In order to determine the valence state of silver in the sample, XPS analysis (Perkin Elmer PHI 5600) was performed. Because of no distinct difference between the peak positions of 3d core levels of Ag, Ag_2O and AgO, their Auger peaks were assigned as shown in Fig. 4 together with the peaks of the standard samples of Ag, AgO and Ag_2O. It is seen that silver exists as the metallic state in the sample (a) before calcinations, but after calcinations (b), silver existed as AgO or Ag_2O although silver oxides are unstable at temperature higher than 300 °C. Therefore, γ-Al_2O_3 seems to play an important role in improving the thermal stability of silver oxide. The silver compound retained a higher valence state which may oxidize NO to an active state to quickly react with reductive species such as n-C_4H_{10}. This may be the reason why Ag/γ–Al_2O_3 shows excellent deNO$_x$ catalytic activity in the presence of excess oxygen.

Fig. 3 Transmission electron micrographs of Ag/γ–Al_2O_3 (**a**) as-prepared by the hydrothermal reaction in 75 vol.% ethanol aqueous solution at 225 °C for 2 h and (**b**) after calcination at 280, (**c**) 390 and (**d**) 550°C for 10 min



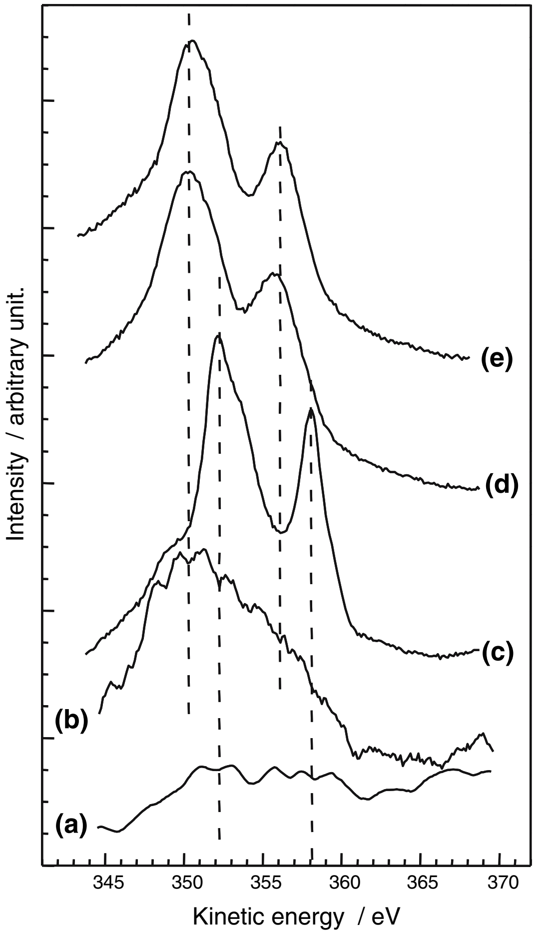


Fig. 4 Ag Auger peaks of samples (**a**) as prepared by the solvothermal treatment of γ-Al_2O_3 at 225 °C for 2 h in a 50 vol.% ethanol aqueous solution with $AgNO_3$ and (**b**) calcined at 550 °C for 2 h. Curves (**c**), (**d**) and (**e**) are Auger peaks of Ag, Ag_2O and AgO, respectively

The specific surface areas of the samples as prepared by the solvothermal reaction of γ-Al_2O_3 and $AgNO_3$ mixture in various concentrations of ethanol aqueous solutions at 225 °C for 2 h and after calcination at 550 °C for 2 h are shown in Fig. 5. It can be seen that as the proportion of ethanol in the solution increased, the specific surface area of both samples before and after calcination monotonously increased. This is attributed to the phase changes of γ-Al_2O_3 → γ-AlOOH → γ-Al_2O_3 during solvothermal reaction and calcination. When ethanol content is low, most of γ-Al_2O_3 transformed to γ-AlOOH as shown in Fig. 1 and the specific surface area decreased. The phase change from γ-AlOOH to γ-Al_2O_3 by calcinations resulted in increase of the specific surface area, but the values did not attain the value of the original γ-Al_2O_3. For the sample having 91 vol.% ethanol, the percentage of γ-AlOOH was quite low and γ-Al_2O_3 was the main phase. Therefore, there was no clear change in the specific surface area before and after calcination.

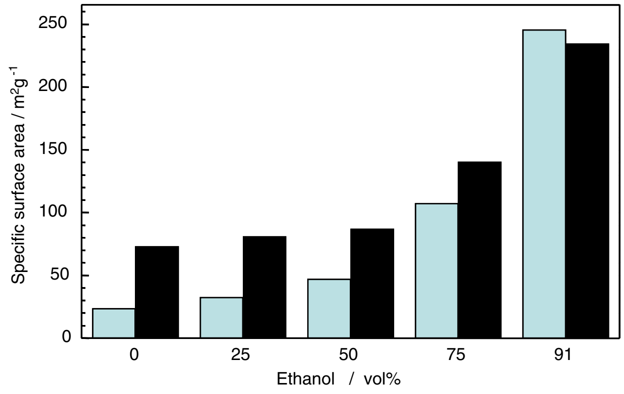


Fig. 5 Specific surface areas of Ag/γ–Al_2O_3 samples as prepared by the solvothermal reaction of γ-Al_2O_3 in various concentrations of ethanol aqueous solution at 225 °C for 2 h and after calcination at 550 °C for 2 h. □: as prepared, ■: after calcination

Plots of NO_x conversion vs. temperature for Ag/γ–Al_2O_3 prepared by solvothermal processes in (b) 25, (c) 50, (d) 75 and (e) 91 vol.% of ethanol aqueous solution at 225 °C for 2 h followed by calcination at 550 °C for 2 h are shown in Fig. 6 together with that of the original γ-Al_2O_3 without Ag loading. NO_x conversion with γ-Al_2O_3 alone was quite low, but by loading silver, NO_x conversion greatly increased. It can be deduced that the NO_x conversion performance at low temperature increased with increasing the ethanol content in the solvent, i.e., the increase in the specific surface area of γ-Al_2O_3 support.

Figure 7 shows plots of NO_x conversion vs. temperature for Ag/γ-Al_2O_3 prepared by solvothermal treatments of (a) γ-AlOOH, (b) γ-Al_2O_3, (c) $Al(OCH(CH_3)_2)_3$, (d) $Al(NO_3)_3$ and (e) $Al(OH)_3$ in 91 vol.% of ethanol aqueous solutions containing $AgNO_3$ at 225 °C for 2 h followed by calcination at 550 °C for 2 h. The samples as prepared by

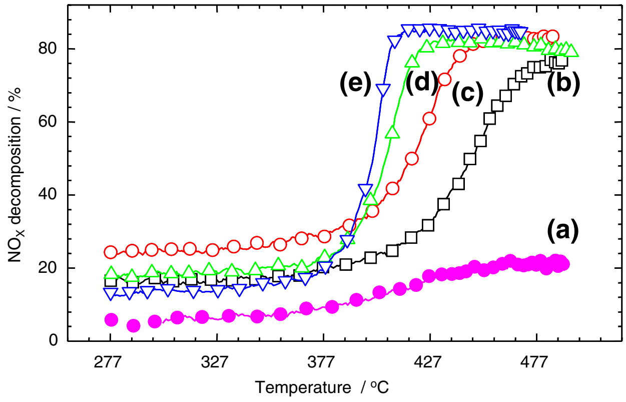


Fig. 6 Plots of NO_x conversion vs. temperature for (**a**) γ-Al_2O_3 without Ag loading and Ag/γ–Al_2O_3 prepared by solvothermal processes in (**b**) 25, (**c**) 50, (**d**) 75 and (**e**) 91 vol.% of ethanol aqueous solution at 225 °C for 2 h followed by calcinations at 550 °C for 2 h

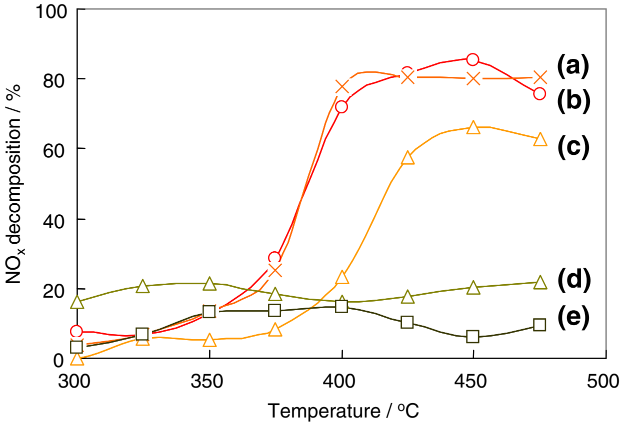


Fig. 7 Plots of NO_x conversion vs. temperature for Ag/γ–Al_2O_3 prepared by solvothermal processes in 91 vol.% of ethanol aqueous solution at 225 °C for 2 h followed by calcination at 550 °C for 2 h using (**a**) γ-AlOOH, (**b**) γ-Al_2O_3, (**c**) $Al(OCH(CH_3)_2)_3$, (**d**) $Al(NO_3)_3$ and (**e**) $Al(OH)_3$ as an aluminum source

Table 1 Characteristics of products by the solvothermal reactions at 250 °C for 2 h using various aluminum sources

Al source	Ag content/wt.%	Ag particle size/nm	SSA/m^2 g^{-1}
γ-AlOOH	2.77	10	165
γ-Al_2O_3	1.71	12	171
$Al(OCH(CH_3)_2)_3$	1.72	50	143
$Al(NO_3)_3$	0.68	–	129
$Al(OH)_3$	1.96	–	18

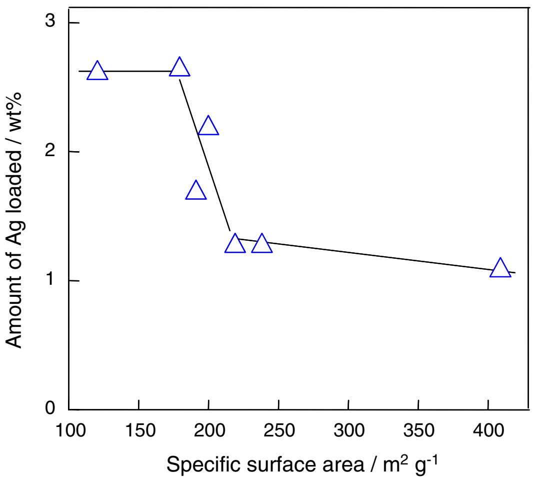


Fig. 8 Relationship between the amount of Ag loaded by solvothermal processes in 91 vol.% of ethanol aqueous solution at 225 °C for 2 h and the specific surface area of γ-Al_2O_3 used as an aluminum source

solvothermal reaction of γ-AlOOH, $Al(OCH(CH_3)_2)_3$, $Al(NO_3)_3$ and $Al(OH)_3$ consisted of γ-AlOOH wheras that of γ-Al_2O_3 consisted of a mixture of γ-AlOOH and γ-Al_2O_3, and all of them transformed to γ-Al_2O_3 after calcination, but the deNO_x performance greatly changed depending on the aluminum source used in the order γ-AlOOH = γ-Al_2O_3 > $Al(OCH(CH_3)_2)_3$ >> $Al(NO_3)_3$ > $Al(OH)_3$ (Fig. 7).

The amounts of silver loaded, particle sizes of silver and the specific surface areas of the samples are shown in Table 1. When γ-AlOOH was used, most of silver (ca. 3 wt.%) was loaded in the sample, but in all other cases a lesser quantity of silver was loaded. The amount of silver loaded was in the order γ-AlOOH > $Al(OH)_3$ > $Al(OCH(CH_3)_2)_3$ = γ-Al_2O_3 >> $Al(NO_3)_3$. In addition, the particle size of silver loaded using γ-AlOOH and γ-Al_2O_3 was ca. 10 nm in diameter, and that using $Al(OCH(CH_3)_2)_3$ was 50 nm. In the case of $Al(NO_3)_3$ and $Al(OH)_3$, silver particles could not be clearly observed. The specific surface area also changed depending on the aluminum source as γ-Al_2O_3 = γ-AlOOH > $Al(OCH(CH_3)_2)_3$ > $Al(NO_3)_3$ >> $Al(OH)_3$. These differences may be responsible for the difference in the deNO_x performance of the sample.

The relationship between the amount of silver loaded by solvothermal processes in 91 vol.% of ethanol aqueous solution at 225 °C for 2 h and the specific surface area of γ-Al_2O_3 used as a aluminum source is shown in Fig. 8. When the specific surface area of original γ-Al_2O_3 was less than 200 m^2 g^{-1}, most of Ag was loaded on the sample, but the quantity of silver loaded greatly decreased above 200 m^2 g^{-1}. Although the reason for this has not be clarified, it is suspected that the cluster size of the silver compound before reduction may play an important role in determining the amount of silver loading, i.e., Ag^+ may be converted to a precursor cluster such as AgOH, Ag_2O, etc on the surface of the substrate before reducing to silver particle. The cluster size may be decreased by increasing the specific surface area of the substrate because of the increase in the adsorption site. Generally, the solubility of the small cluster is larger than that of the large cluster. Therefore, small silver compound clusters formed on γ-Al_2O_3 with large specific surface area may have a tendency to dissolve in the solution making it difficult for it to be reduced to silver, therefore, the quantity of silver loaded decreased with increasing the specific surface area of γ-Al_2O_3 used. Further study is necessary to clarify the mechanism behind this, but it is confirmed that the amount of silver loaded by the solvothermal reaction changes depending on the characteristic of the aluminum substrate.

Plots of NO_x conversion vs. temperature for Ag/γ–Al_2O_3 prepared by solvothermal treatment of γ-AlOOH in 91 vol.% of (a) methanol, (b) ethanol, (c) 1-propanol, (d) 1-butanol and (e) 1-hexanol aqueous solutions at 225 °C for 2 h followed by calcination at 550 °C for 2 h are shown in Fig. 9 together with that (f) prepared by the

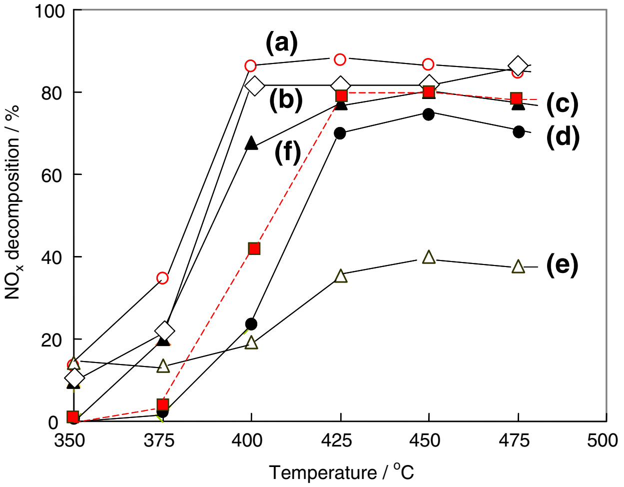


Fig. 9 Plots of NO_x conversion vs. temperature for Ag/γ–Al_2O_3 prepared by solvothermal treatment of γ-AlOOH in 91 vol.% of (**a**) methanol, (**b**) ethanol, (**c**) 1-propanol, (**d**) 1-butanol and (**e**) 1-hexanol aqueous solutions at 225 °C for 2 h followed by calcination at 550 °C for 2 h and (**f**) prepared by the impregnation-calcination method

impregnation-calcination method. The deNO_x performance decreased with increasing the carbon number of the alcohol used as solvent in the order methanol = ethanol > 1-propanol > impregnation > 1-buthanol >> 1-hexanol.

Transmission electron micrographs of the samples as prepared by the hydrothermal reactions in 91 vol.% of various alcohol aqueous solutions containing $AgNO_3$ at 225 °C for 2 h and impregnation method are shown in Fig. 10, where the values in parentheses are silver contents. The particle size of silver formed in methanol and ethanol were ca. 10 nm in diameter and tended to increase with increasing the carbon number of alcohol. The amount of silver loaded in methanol, ethanol, 1-propanol and 1-butanol was almost identical, but greatly decreased in 1-hexanol probably due to the decrease in the reducing power of the solvent. In the case of impregnation, silver could be completely loaded, but the particle size was larger, ca. 50 nm in diameter due to the particle agglomeration which may be the reason why the sample prepared by impregnation-calcination method was low. These profiles agree with the deNO$_x$ performance of the samples shown in Fig. 9.

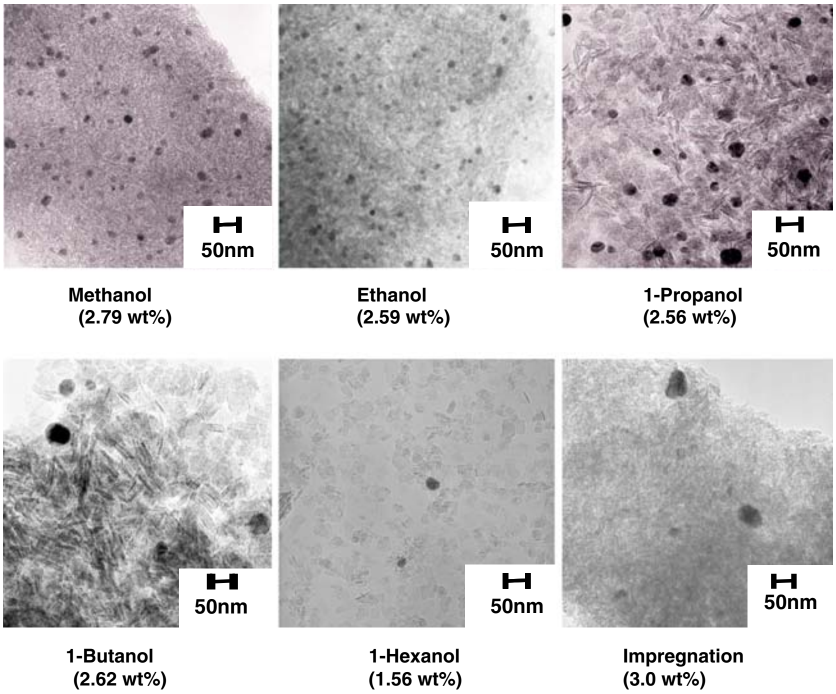
Conclusions

Based on the above results, the following conclusions may be drawn:

(1) Ag/γ–Al_2O_3 with silver loading of ca. 3 wt.% could be prepared by the solvothermal-calcination reaction of $AgNO_3$ in mixed water-alcohol solutions at 50–250 °C for 0–120 min, followed by calcinations at 550 °C for 2 h using γ-Al_2O_3 (SSA: 120–409 $m^2\ g^{-1}$), γ-AlOOH (SSA: 270 $m^2\ g^{-1}$), $Al(OH)_3$ (SSA 10 $m^2\ g^{-1}$), $Al(OCH(CH_3)_2)_3$ and $Al(NO_3)_3$ as an aluminum source.

(2) The product produced by the solvothermal reaction was Ag/γ–AlOOH even though a different aluminum source was used and Ag/γ–AlOOH was converted to Ag/γ–Al_2O_3 by the following calcination, however,

Fig. 10 Transmission electron micrographs of the samples as-prepared by the hydrothermal reactions in 91 vol.% of various alcohol aqueous solutions containing $AgNO_3$ at 225 °C for 2 h and the impregnation method. The values in parentheses are Ag contents



the characteristics of them changed greatly depending on the aluminum source.

(3) The deNO$_x$ catalytic performance of Ag/γ–Al$_2$O$_3$ also changed greatly depending on the aluminum precursor and solvothermal solvent in the order γ-AlOOH = γ-Al$_2$O$_3$ >> Al(OCH(CH$_3$)$_2$)$_3$ >> Al(NO$_3$)$_3$ > Al(OH)$_3$ and methanol = ethanol > 1-propanol > butanol >> 1-hexanol, since the amount and size of silver particle loaded and specific surface area of the product changed greatly.

(4) Ag/γ–Al$_2$O$_3$ prepared by the solvothermal-calcination method consisted of homogeneously dispersed fine particles of silver and showed better performance for NO decomposition than that by conventional impregnation-calcination method.

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