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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Mechanism of silver nano-particles formation on α-alumina using supercritical water

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Abstract Supercritical water impregnation is a novel method, which utilizes high diffusivity of the fluid with hydrothermal synthesis allowing nano-particles to deposit on porous materials in well-dispersed condition. In this work, silver nano-particles were deposited on the surface of α-alumina supports using metal acetate solution. TEM-EDS analyses clearly identified the silver particle of two kinds, those deposited on α-alumina surface and those gathering in bulk phase. Their particle size distribution showed differences in propensity, implying that particle formation were via different mechanism. The difference in particle deposition mechanism was also confirmed from the results of other operational factors investigated. Furthermore, the mechanism of particle deposition to alumina support surface have been proposed based on the experimental results and reported observation of nucleation and particle growth steps during the hydrothermal synthesis. In addition, the mechanism of silver particle formation has been discussed in detail.

Introduction

Supercritical water has drawn many of researcher's attention as a new chemical reaction field over the past few decades. Unique properties of supercritical water and the ability to control those kinds of parameters by varying temperature and pressure conditions seem to have captivated their interests.

Applications to inorganic syntheses are especially focused, being the recent trend. Among them, supercritical hydrothermal synthesis is generally acknowledged as a method for preparing metal and metal oxide crystals from metal salts via hydrolysis and dehydration [1–4]. Studies have revealed that high reaction rates and metal oxide solubilities in supercritical water will lead to high supersaturations and thus forming fine metal oxide particles from metal aqueous salt solutions. Moreover, "Supercritical water impregnation", a novel catalyst preparation method reported lately, utilizes high diffusivity of supercritical water in addition to the former fine particle preparation method. The method allows nano-particles to deposit on support surfaces as well as inside the pores in highly dispersed condition [5]. Several reports introducing particles into porous substrates facilitated by gas-like transport properties of supercritical water have been made as well. Morley et al. [6] have deposited silver nano-particles on poly beads and silica aerogels with supercritical carbon dioxide followed by depressurization and addition of H_2 gas, whereas Chang et al. [7] reported the deposition of silver nano-particles onto functionized multiwall carbon nanotube using supercritical water. Dhepe et al. [8, 9] have reported improvements in dispersity when the catalysts were prepared with supercritical carbon dioxide.

However, much of these reports have focused mainly on transport properties, and have not exploited chemical reaction as its characteristics in neither of their methods. From the perspective of catalyst preparation, simultaneous proceeding of transport process and chemical reactions will directly lead to the shortening of preparation steps and

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resolve complicated matters related with post-treatments such as calcinations.

In this work, we elucidated the mechanism of supercritical water impregnation, particularly focusing on particle deposition on support surface, to be served as a guideline for the proposal of unified methodology which enables us to control size, dispersion and composition of deposited particles only with the change of temperature and pressure. Effect of operational factors such as reaction time, presence of support on particle size, on morphology and composition were also investigated respectively.

Experimental

Materials

Ag/α-alumina, catalyst commonly used in ethylene oxide synthesis, was chosen as a model material to demonstrate the supercritical water impregnation. The catalyst is reported to have dramatic change in activity with silver particle sizes [10, 11]. The aqueous feed solution was prepared by dissolving silver acetate Ag(CH_3COOH) (purchased from Wako Pure Chemicals Industries, Ltd.) in distilled water (purchased from Yamamoto Yakuhin Co., Ltd). Silver dispersed in acetic acid and distilled water were also used as a feed solution in particular experiments. Both chemicals were purchased from Wako Pure Chemicals Industries, Ltd. As a support, alpha type alumina (purchased from Soekawa Chemical Co., Ltd.) was used in this work. All materials were used without further treatment.

Procedure

All experiments were performed using batch type reactor made of 3/8-inch tube of stainless steel (SUS316) with inner volume of 4.65 mL. The reactor was loaded with silver acetate aqueous solution and 2 wt.% of α-alumina support. Concentration of the metal acetate solution was set at 0.01 mol/L in standard. The reaction was started when the reactor was immersed into temperature controlled fluidized sand bath. All reactions were conducted under the condition of 673 K and 30 MPa. After a lapse of predefined time, the reactor was cooled to ambient conditions by water bath to stop the reaction. Reaction time, defined as the time from which the reactor was immersed into the sand bath until it was taken out, was varied from 1 to 60 min. Products were then washed out from the reactor by distilled water. No additional treatments such as drying and filtration were carried out in order to avoid unexpected aggregation of the particles during post processing. For microscopic determination, a droplet of product mixture dispersed in methanol was placed onto a carbon coated copper grid (purchased from Nisshin EM Co. Ltd.). The grid was then dried in desiccators kept at ambient condition prior to analysis. Bulk solution, supernatant skimmed from product mixture, was analyzed as well.

Analyses

Qualitative element analysis of solid content subsidenced in product mixture was performed by Energy Dispersive X-ray Spectroscopy (EDS) attached to Transmission Electron Microscope (TEM; JEOL JEM-2000FX). Particle morphology was examined also by TEM (JEOL JEM-2000EX II and JEM-400FX II) in parallel with the investigation on particle sizes. For each sample, more than 300 particles selected at random from the images were investigated to obtain a distribution. Mean size of a particle was estimated from long and short axes measurements [12].

Silver ion remaining in the product mixture was investigated by Inductively Coupled Plasma (ICP; SHIMADZU ICPS-1000III). Supernatant skimmed from product mixture, was analyzed after relevant dilution by distilled water.

Results and Discussion

A representative TEM image of the sample prepared under the reaction time of 1 min is shown in Fig. 1. The figure clearly demonstrates the formation of nano-particles on the surface of a larger particle. Only silver peak was observed in the EDS spectrum of the deposited nano-particles, indicating that the particles were not oxides but metal silver. This result shows a different trend from the reports by

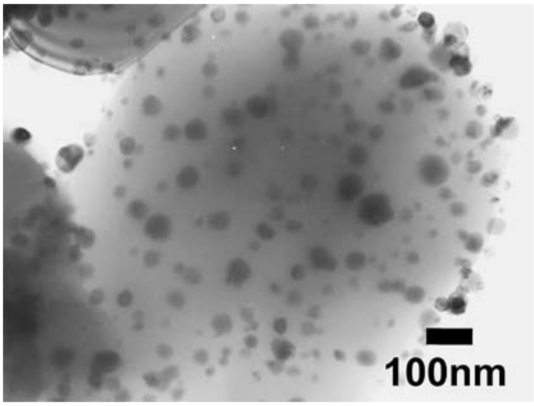

Fig. 1 TEM image of deposited silver particles prepared at 673 K, 30 MPa with reaction time of 1 min

Ziegler et al., in which they suggested reductants as an indispensable additive to obtain metal copper nanocrystals [3].

According to past studies [13–16], a plausible scheme for metal silver formation has been proposed as follows. Hydrothermal synthesis followed by pyrolysis takes place in this scheme, consequently transforming silver oxide Ag_2O to metal silver.

(Step 1: Hydrothermal reaction)

$CH_3COOAg + H_2O = CH_3COOH + AgOH$ (Hydrolysis)

$2\ AgOH = Ag_2O + H_2O$ (Dehydration)

(Step2: Pyrolysis)

$2\ Ag_2O = 4\ Ag + O_2$

On the other hand, gas phase products were not detected from any of the experiment conducted in this work, presumably due to its small amount produced.

Effect of operational factors on particle profile

Reaction time

Reaction time was varied from 1 to 60 min. Representative TEM image of the sample prepared under the reaction time of 5 min is shown in Fig. 2a. Silver particles in the image are apparently larger in size compared to the particles prepared under 1 min (Fig. 1). The particle size distribution shown in Fig. 2b clearly demonstrates the enlargement of mean particle size along with the extension of reaction time. Such particle enlargement is merely explained by particle aggregation. From the graph showing the relationship between reaction time and Ag ion concentration in the residue on Fig. 3, Ag ions originated in silver acetate shows a rapid decrease at 1 min and complete consumption after 5 min of elapse, irrelative to support presence. In other words, the remaining Ag ions in the solution are mostly consumed by the time temperature is elevated to 673 K, which was approximately 1 min. From these facts, it could be speculated that the particle formation and growth (chemical phenomenon) are likely to take place during the heating period. The aggregation (physical phenomenon) is likely to start afterwards, where the amount of Ag ion supply resource is not much abundant. Previously, similar reports have been made by Hakuta et al., in which they theoretically described that particle formation takes place during the heating period and particle growth in the following isothermal period [17]. From 5 min onward, no significant change in particle sizes were observed except for slight changes in morphology due to aggregation as shown in Fig. 4.

Precursor concentration

Effect of precursor concentration on silver particles under the reaction time of 1 min was examined. Representative TEM image of the sample prepared from 0.001 M metal solution, 1/10 times the concentration of the original metal solution, under the reaction time of 1 min is shown in Fig. 5a. Although silver particles did not show significant change in size, the number of particles decreased ambiguously compared to the sample prepared from 0.01 M metal solution at identical condition (Fig. 1). Comparison of particle size distribution is shown in Fig. 5b. Results simply indicated that the downsizing of silver particles can be achieved by lowering precursor concentration in exchange for the decrease of particle deposition amount per support. Morphology and element composition of particle have shown no change in the variation of precursor concentration which is consistent with the results of Xu et al., where they have discussed the effect of precursor concentration to particle deposition on activated carbon pellets [18].

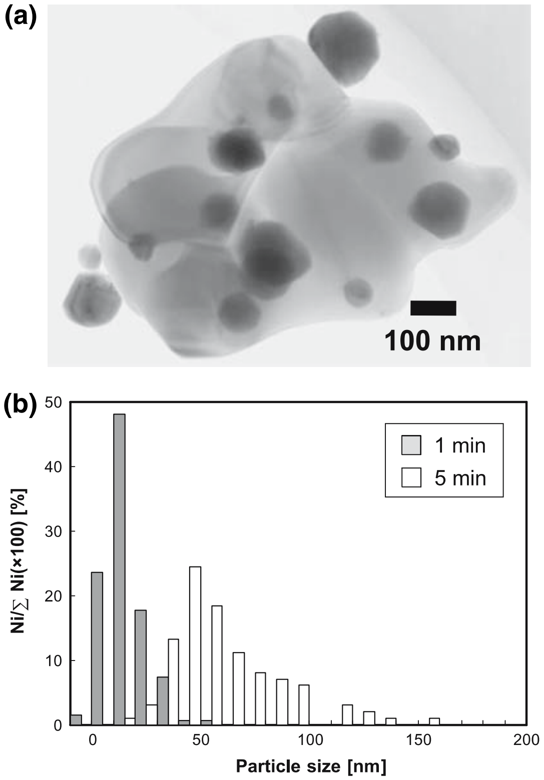

Fig. 2 Sample prepared at reaction time of 5 min; (**a**) TEM image of silver particles on α-alumina and (**b**) particle size distribution compared to particles prepared at reaction time of 1 min

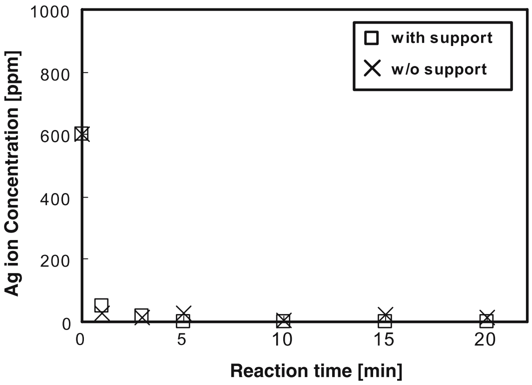

Fig. 3 Concentration change of silver ions remaining in the solution

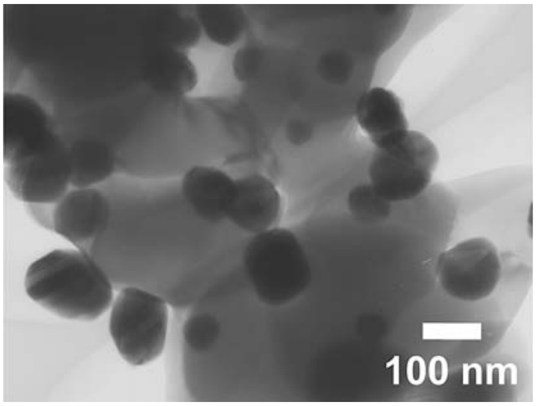

Fig. 4 TEM image of deposited silver particles prepared at 673 K, 30 MPa with reaction time of 5 min

Presence of α-alumina support

Effect of alumina presence on particle formation behavior under the reaction time of 1 min was examined. Representative TEM image of the sample collected from reaction performed without loading of alumina support is shown in Fig. 6a. Spherically uniformed particles observed in the image were characterized as metal silver by EDS analysis. The particles were apparently larger than the particles prepared with support presence at same reaction conditions (Fig. 1). Difference in size can be quantitatively verified from particle size distribution shown in Fig. 6b.

Heating rate

Reactions were conducted under the average heating rate of 6.7 (standard heating rate), 10.2 and 15.5 K/s. Representative TEM image of the sample prepared with heating rate of 10.2 and 15.5 K/s are shown in Fig. 7 and 6.7 K/s in Fig. 1. Images showed no remarkable difference in morphology and size of the deposited particles in different heating rates.

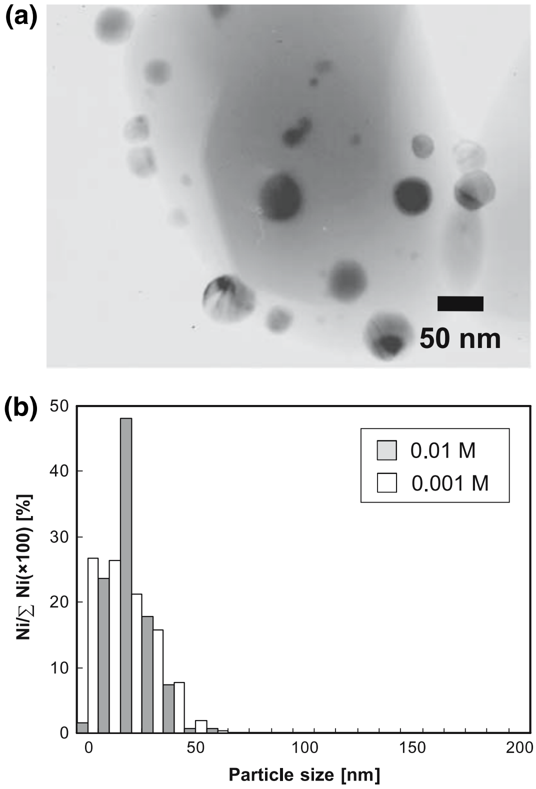

Fig. 5 Sample prepared from 0.001 M solution with reaction time of 1 min; (**a**) TEM image of silver particles on α-alumina and (**b**) particle size distribution compared to particles prepared from 0.01 M solution

Particle deposition mechanism

The mechanism of particle deposition on support surface, which constitutes an essential part in supercritical impregnation, was elucidated experimentally. Correlation with reported observation of nucleation and particle growth steps during the hydrothermal synthesis has been worked on, proposing a mechanism of particle deposition to alumina support surfaces.

Strategically, two schemes for particle deposition have been hypothesized and experimentally verified accordingly.

> Particle formation in bulk phase followed by adsorption to support surfaces (Scheme A).
> Particle formation at support surfaces followed by particle growth (Scheme B).

To evaluate the contribution of (Scheme A), behavior of particles in the bulk phase under the presence of support was investigated. In this particular experiment, preliminary synthesized silver particles dispersed in 0.01 M-acetic acid or in distilled water were packed in the reactor replacing silver acetate solution. Silver particles used in this experiment were either purchased or supercritical hydrothermal

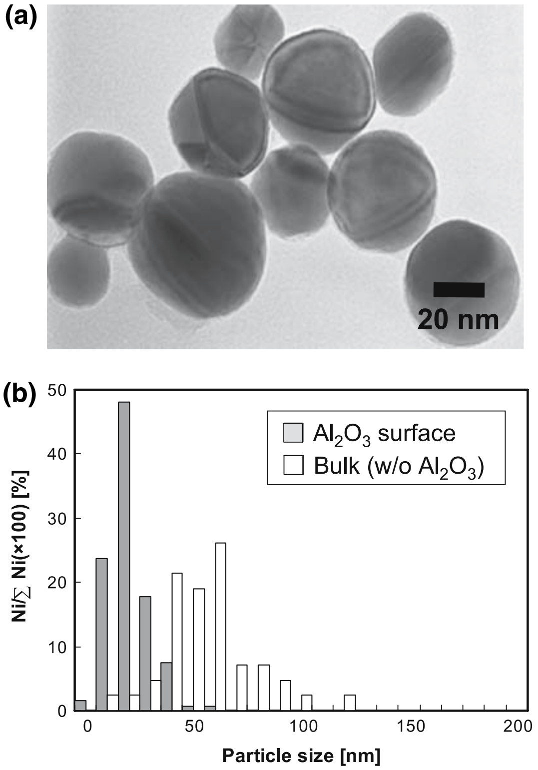

Fig. 6 Sample prepared at reaction time of 1 min without α-alumina; (**a**) TEM image of silver particles in bulk phase and (**b**) particle size distribution compared to deposited particles prepared at reaction time of 1 min with α-alumina

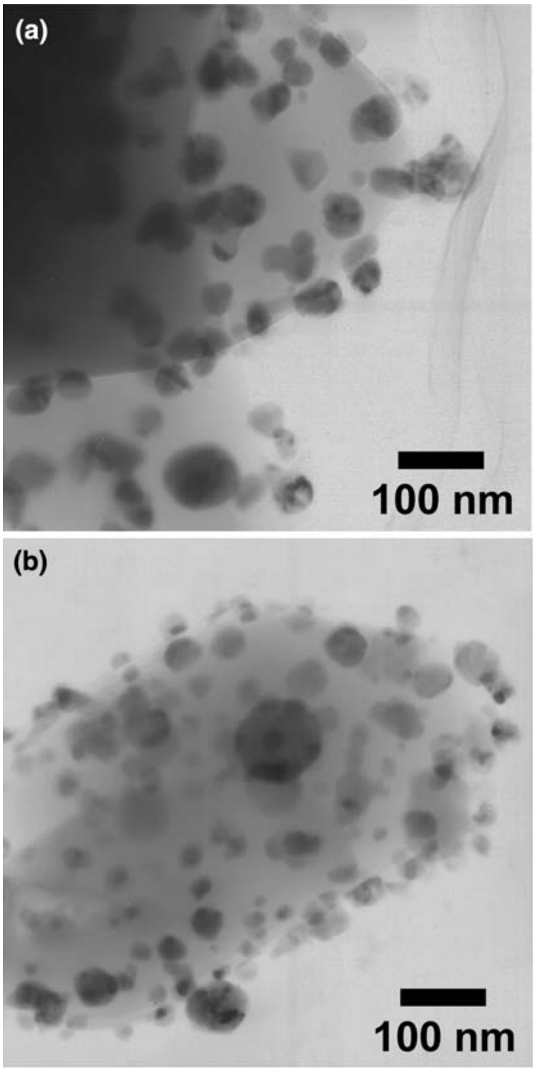

Fig. 7 TEM images of deposited silver particles prepared in rapidly heated conditions; (**a**) 10.2 K/s and (**b**) 15.5 K/s

synthesized (TEM image and size distribution of the particle shown in Fig. 6) in the laboratory. Purchased silver contained 0.1 μm particles in mean size. Reactions were performed under the reaction time of 5 min. From the representative TEM images shown in Fig. 8a and b, no particles were found to be deposited on the support surface in either condition testifying that the deposition of preformed particles is physically an impractical phenomenon. Undeposited silver particles were aggregated forming a cloud-like figure in the bulk phase as shown in Fig. 8a. This result implies that silver particles formed in bulk phase would not be adsorbed on the support surface, suggesting the particle deposition mechanism via (Scheme B) is plausible than (Scheme A).

Particles in bulk phase

Particles in bulk phase were also observed from every product mixtures. EDS spectrum exhibited the particles as silver, identified similarly as the particles on support surface. Representative TEM image of the particles in bulk phase prepared under the reaction time of 1 min is shown in Fig. 9a. The particle size were apparently disorganized compared to particles deposited on support surface (Fig. 1) and particles prepared in the absence of alumina support (Fig. 6a). Comparison of the particle size distribution in three phases is shown in Fig. 9b. Particles formed in bulk phase in the presence of support were apparently smaller in size, but showed wider distribution than particles in the absence of support. On the other hand, deposited particles and particles in bulk with support presence showed noticeable difference in propensity indicating the specificity of particles formation in the bulk phase.

Results emphasizing such peculiarity were obtained from other operational factors investigated. Size enlargement observed in particles on support surfaces caused by the extension of reaction time was uncertified in the particles in bulk phase. Sample prepared at rapidly heated conditions showed difference in morphology, obtaining spherical figure in deposited particles (Fig. 7) and rod-like figure in bulk phase, as shown in Fig. 10. As for the

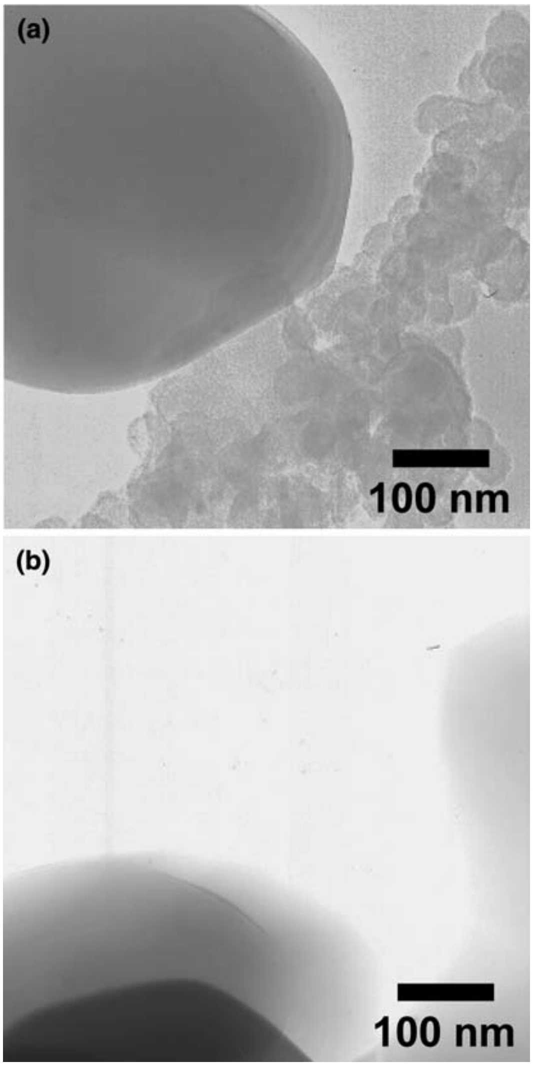

Fig. 8 TEM images of samples prepared with preliminary synthesized particles; (**a**) hydrothermally synthesized silver particles dispersed in distilled water and (**b**) purchased silver particles dispersed in 0.01 M acetic acid

composition, particles in both phases were metal silver, in spite of the fact that Hakuta et al. have reported intermediates in various composition at slower heating conditions in the case of phosphor particle preparation in supercritical water [19].

Cited differences observed in size distributions and morphology of particles between support surface and bulk phase, presumably implies that the particle formation is via different mechanism.

Conclusion

Silver nano-particles were deposited on the surface of α-alumina supports from silver acetate solutions using supercritical water. Besides particles deposited on support surface, silver nano-particles were also observed in the bulk phase. The particle size distribution was apparently different, suggesting that particle formation was via different mechanism respectively. Difference in particle deposition mechanism was also confirmed when mean size of the particles on support was compared to particles in bulk phase without the presence of support. Extension of reaction time enlarged the average size of particles on the support whereas the particles in bulk phase showed no remarkable difference in size. Particle morphology difference observed from support surface and bulk phase of samples prepared in rapidly heated condition also suggest the difference in particle deposition mechanism. In parallel, the scheme for metal silver formation was collaterally discussed, concluded as a scheme proceeding via hydrothermal synthesis, subsequently followed by pyrolysis.

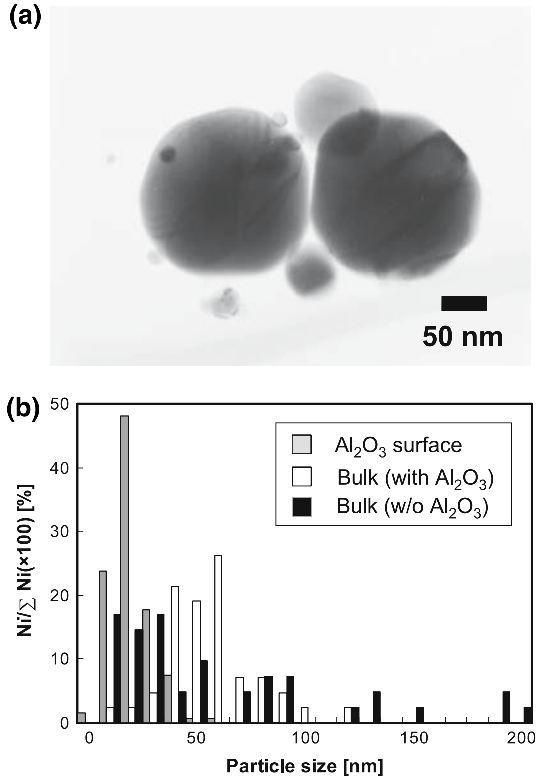

Fig. 9 Sample prepared at 673 K, 30 MPa with reaction time of 1 min; (**a**) TEM image of silver particle in bulk phase and (**b**) particle size distribution comparing particles on α-alumina, in bulk phase with/without α-alumina

On the basis of such experimental results and reported observations of nucleation/particle growth steps during the hydrothermal synthesis, proposal for particle deposition mechanism to alumina support surface have been made. Suspensions of preliminary synthesized silver particles were substituted for metal aqueous solution to examine the deposition from preformed particles in bulk. Experimental

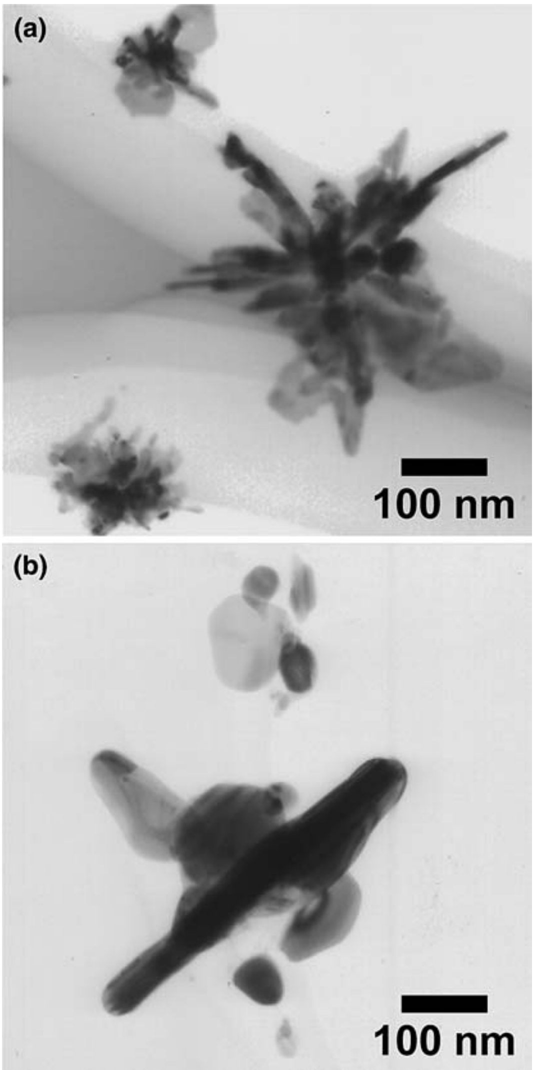

Fig. 10 TEM images of silver particles in bulk phase prepared in rapidly heated conditions; (**a**) 10.2 K/s and (**b**) 15.5 K/s

results implied that the silver particles are likely to start its formation at support surfaces followed by growth.

Effects of operational factors irrelative to the elucidation of deposition mechanism were also organized for fundamental considerations. Extension of reaction time simply enlarged the size of particles on the support. The number and the size of particles deposited on the support increased with higher precursor concentration.

Yet, thorough investigations on respective operational factors are required to actualize the unified methodology in particle deposition, results obtained in this work indicated the possibility of its establishment. From the viewpoint of catalyst preparation, application to porous materials is an unavoidable agenda. Diffusion steps in the pore are to become a crucial issue considered sufficiently, presumably entwined with particle deposition steps altering its mechanism in complex figures.

Continuous production is also an issue that cannot be overlooked. By applying a continuous reactor, enough product amounts can be obtained in a single experimental run, consequently making it possible to analyze the gas phase products. Therefore, the development to continuous production enables us to take into account additional information and factors beyond simple quantitative comparisons. Further investigations on continuous production are currently in study.

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