The Influence of the Preparing Method of a Ag/Ga$_2$O$_3$ Catalyst on its Activity for Photocatalytic Reduction of CO$_2$ with Water

Naoto Yamamoto
Department of Materials, Physics and Energy Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Tomoko Yoshida and Shinya Yagi
EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Zhang Like
Department of Applied Chemistry, Chemical Engineering and Biotechnology, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Tsuyoushi Mizutani and Satoshi Ogawa
Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Hirofumi Nameki
Aichi Center for Industry and Science Technology, Onda-cho, Kariya 448-0013, Japan

Hisao Yoshida
Graduate School of Human and Environmental Studies, Kyoto University, Yoshida-nishinomatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan

(Received 9 January 2014; Accepted 25 March 2014; Published 7 June 2014)

We have prepared silver-loaded gallium oxide (Ag/Ga$_2$O$_3$) photocatalysts by the solution plasma method (SPM) and impregnation method (imp), and investigate the effects of the chemical states and the size of the Ag nanoparticles on their photocatalytic activities. The photocatalytic reduction of CO$_2$ with water proceeds over all the Ag/Ga$_2$O$_3$ photocatalysts to produce CO, however the CO production rates decrease during photocatalytic reaction. Measurements of UV-VIS diffuse reflectance spectra, XANES spectra and TEM images reveal the followings: the Ag oxide nanoparticles in the as-prepared Ag/Ga$_2$O$_3$ (imp) samples exist and their size distribution is wide from 5 to 10 nm. They become a lot of metallic nanoparticles by UV light-irradiation, and become larger particles with the size of ca. 20 nm during the photocatalytic reaction. On the other hand, the Ag nanoparticles in the as-prepared Ag/Ga$_2$O$_3$ (SPM) samples are metallic with the size of less than 10 nm. The size does not change under UV light irradiation, while become larger particles during the photocatalytic reaction as similar to the case of the Ag/Ga$_2$O$_3$ (imp) samples. Such small metallic Ag nanoparticles with the size of 5-10 nm are suitable for CO production. However, they aggregate during the reaction for 5 h to degrade the photocatalytic activity.

[DOI: 10.1380/ejssnt.2014.263]

Keywords: Carbon dioxide; Water; Gallium; Reduction of carbon dioxide; Solution plasma; Ag loaded Ga$_2$O$_3$ photocatalyst

I. INTRODUCTION

Reduction of carbon dioxide (CO$_2$) with photocatalysts has been widely studied from the viewpoints of environmental issues and artificial photosynthesis [1–7]. We propose gallium oxide (Ga$_2$O$_3$) photocatalysts that possess activity for photocatalytic reduction of CO$_2$ with water. The photocatalytic reduction of CO$_2$ with water is one of the challenging reactions, because the reduction ability of water is weaker as compared to other reduction reagents such as hydrogen (H$_2$) [8]. However, recently, we found that the photocatalytic reduction of CO$_2$ with water proceeded over a bare Ga$_2$O$_3$ and the activity increased by loading Ag nanoparticles on Ga$_2$O$_3$ (Ag/Ga$_2$O$_3$) [9, 10]. The photocatalytic activity is likely to correlate with the chemical states and/or the size of the Ag nanoparticles which depend on the preparing method of the photocatalysts [11].

In this study, we prepare Ag/Ga$_2$O$_3$ photocatalysts by using solution plasma method (SPM) or impregnation method (imp), and refer these Ag/Ga$_2$O$_3$ photocatalysts to Ag/Ga$_2$O$_3$ (SPM) and Ag/Ga$_2$O$_3$ (imp). The SPM is a new preparing method of metal nanoparticles without any dispersants in an aqueous solution with electrolytes [12–17]. These metal nanoparticles are synthesized by glow discharge between metal rods in an aqueous solution. The SPM has an advantage of controlling the size of the metal nanoparticles with clean surface by changing the amount of electrolytes [13–15]. The suitable size and clean surface of the Ag nanoparticles are important for the good photocatalytic properties [18, 19]. Therefore, we tried to apply this SPM to the preparation of the photocatalysts. On the other hand, it has been reported that the Ag/Ga$_2$O$_3$ (imp) photocatalysts possess the high activity for the reduction of CO$_2$ [11]. This high activity would be caused by dispersing the Ag nanoparticles on Ga$_2$O$_3$ in the impregnation process [20, 21]. Therefore, it is important...
FIG. 1: Schematic of the experimental set-up for the Ag nanoparticles.

FIG. 2: Variation of CO production rate with the amount of Ag loading (a) after 1 h and (b) after 5 h.

FIG. 3: Time dependence of the production rate for CO.

II. EXPERIMENTAL

Ag/Ga₂O₃ (SPM) were prepared by filtration of the Ag nanoparticles solution on Ga₂O₃ (degree of purity: 99.99%, Kojundo Chemical Laboratory Corporation, Ltd.). We synthesized the Ag nanoparticles by glow discharge in aqueous solution in a reactor cell under an open environment. Distilled water (content: 180 ml) and aqueous solution of ammonia (density: 28 mass%, content: 0.1 ml, Wako Pure Chemical Industries, Ltd.) were poured into the reactor cell. The experimental set-up of the SPM system was shown in Fig. 1. Two Ag rods (diameter: 1.0 mm, degree of purity: 99.99%, The Nilaco Corporation), covered with ceramic tubes were placed between reactor cell sides and the spacing between them was 0.3 mm. An alternate current (AC) pulsed power supply (Kurita Corporation) with 2.7 kV, 2.0 A and 20 kHz maximum peaks voltage, current and a fixed pulse frequency, respectively, was used. When the Ag nanoparticles were synthesized, a Ga₂O₃ powder (mass: 2.0 g) was put into the reaction cell and mixed thoroughly. Subsequently, the aqueous solution was filtered, washed with distilled water and dried in air at 293 K overnight. We measured the amount of Ag loading of Ag/Ga₂O₃ (SPM) photocatalysts with inductively coupled plasma atomic emission spectrometry (ICP-AES). The amount of Ag loading of Ag/Ga₂O₃ (SPM) photocatalysts was 0.02-0.24 wt%. Ag/Ga₂O₃ (imp) photocatalysts (0.06-0.40 wt%) were prepared by impregnation of Ga₂O₃ powder with an aqueous solution of silver (I) nitrate. AgNO₃ (0.0019-0.0126 g) was dissolved in distilled water (100 ml), and Ga₂O₃ (1.9981-1.9874 g) was put into the AgNO₃ aqueous solution. Those were mixed thoroughly and dried at 373 K. Successively, Ag/Ga₂O₃ (imp) photocatalysts were calcined for 2 h at 673 K.

Our photocatalytic reaction system was composed of a CO₂ bomb (flow rate: 3 mL/min), a He bomb (flow rate: 3 mL/min), flow instruments (5850E, Brooks Instrument), a specially designed fixed-bed flow reactor cell made of quartz, sampling valves and a Gas Chromatograph-TCD (GC-8APT, Shimadzu Corporation, and column bulking agent (Shincarbon ST, Shimadzu GLC Corporation)). The photocatalytic reaction was conducted as follows: Ag/Ga₂O₃ powder (0.2 g) was put into the fixed-bed flow reactor cell under CO₂ gas with a flow rate at 3 mL/min. When this reactor cell was exposed under UV light irradiation with a 300 W xenon lamp (light intensity measured in the range of 254±10 nm: 25 mW/cm²) for 1 h, a NaHCO₃ aqueous solution (H₂O (10 ml), NaHCO₃ (0.92 g)) was added to this reactor cell in dark. After 1 h, background measurement was conducted with an online gas chromatograph. Successively, photocatalytic reduction of CO₂ under UV light irradiation was started and we measured CO, H₂ and O₂ production rates every 1 h

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
up to five repetitions.

The size, oxidation and aggregation states of Ag particles were investigated by TEM, Ultraviolet Visible (UV-VIS) diffuse reflectance and X-ray absorption near-edge structure (XANES). TEM images of the samples were measured by electron microscope (JEM-2100M or H-800) with high voltage 200 kV. UV-VIS diffuse reflectance spectra were measured by V-670 spectrophotometer. XANES spectra were recorded in NW-10A at KEK-PF in fluorescence yield method.

III. RESULTS AND DISCUSSION

A. Photocatalytic reduction of CO\textsubscript{2} with water over Ag/Ga\textsubscript{2}O\textsubscript{3} photocatalysts

The photocatalytic reduction of CO\textsubscript{2} with water proceeds over all Ag/Ga\textsubscript{2}O\textsubscript{3} photocatalysts to produce CO, H\textsubscript{2} and O\textsubscript{2}. The CO production rates of all Ag/Ga\textsubscript{2}O\textsubscript{3} photocatalysts are faster than that of a bare Ga\textsubscript{2}O\textsubscript{3} (Fig. 2 (a) and (b)). The optimum amount of Ag loading for CO production is 0.06 and 0.20 wt% for Ag/Ga\textsubscript{2}O\textsubscript{3} (SPM) and Ag/Ga\textsubscript{2}O\textsubscript{3} (imp), respectively. The photocatalytic activity of the latter is higher than that of the former. However, the CO production rates decrease during photocatalytic reaction. The CO production rates after 1 h are 2.6 µmol/h for 0.06 wt% Ag/Ga\textsubscript{2}O\textsubscript{3} (SPM) and 3.3 µmol/h for 0.20 wt% Ag/Ga\textsubscript{2}O\textsubscript{3} (imp), while they drop to 1.7 µmol/h and 2.9 µmol/h after 5 h. Especially, the photocatalytic activity of 0.06 wt% Ag/Ga\textsubscript{2}O\textsubscript{3} (SPM) decreases rapidly during initial 3 h (Fig. 3).

Here, we compare the CO production rates among Ag/Ga\textsubscript{2}O\textsubscript{3} (SPM) and Ag/Ga\textsubscript{2}O\textsubscript{3} (imp) with the same amount of Ag loading. In the initial reaction stage after 1 h, the CO production rate of 0.06 wt% Ag/Ga\textsubscript{2}O\textsubscript{3} (SPM) is much faster than that of 0.06 wt% Ag/Ga\textsubscript{2}O\textsubscript{3} (imp), but they become almost equal after 5 h. On the other hand, after 1 h, the CO production rates are 1.8 µmol/h for 0.10 wt% Ag/Ga\textsubscript{2}O\textsubscript{3} (SPM) and 2.1 µmol/h for 0.10 wt% Ag/Ga\textsubscript{2}O\textsubscript{3} (imp), while they drop to 1.4 µmol/h and 2.0 µmol/h, respectively after 5 h. Thus, the Ag/Ga\textsubscript{2}O\textsubscript{3} (SPM) photocatalysts have a pronounced tendency to reduce their photocatalytic activities for the CO production.

B. Characterization of Ag/Ga\textsubscript{2}O\textsubscript{3} samples

Figure 4 shows TEM images and Ag particle size distribution histogram of the Ag/Ga\textsubscript{2}O\textsubscript{3} (SPM) and Ag/Ga\textsubscript{2}O\textsubscript{3} (imp) samples before and after photocatalytic reaction. In all of as-prepared samples, the Ag nanoparticles less than 10 nm are predominantly observed. However, a part of these nanoparticles aggregate and become larger particles with the size of more or less 20 nm, and the particle size distributions are widespread in all the samples after the photocatalytic reaction. In addition, the small hemispherical nanoparticles observed in as-prepared samples change to small and large particles with various shapes after the photocatalytic reaction for 5 h. The changes in the size and shape of the Ag nanoparticles suggest the migration of the Ag nanoparticles on Ga\textsubscript{2}O\textsubscript{3} supports, that is, the Ag nanoparticles repeat the dissolution and re-photodeposition during the photocatalytic reaction.

The chemical states of the Ag nanoparticles in Ag/Ga\textsubscript{2}O\textsubscript{3} (SPM) and Ag/Ga\textsubscript{2}O\textsubscript{3} (imp) samples have been investigated in detailed by measurements of their diffuse reflectance and XANES spectra. Figure 5 (a) shows diffuse reflectance spectra of 0.10 wt% Ag/Ga\textsubscript{2}O\textsubscript{3} (SPM) as an example of the sample prepared by SPM. The absorption with an onset at 320 nm is due to the band gap transition of the Ga\textsubscript{2}O\textsubscript{3}. A surface plasmon absorption
around 400-500 nm due to metallic Ag nanoparticles is slightly observed. The broad bands change rarely after the pretreatment by UV light-irradiation and subsequent introduction of an aqueous NaHCO₃ solution. After the reaction for 5 h, the surface plasmon band around 450 nm and a wide absorption band continuing to a near-infrared region grow, indicating the aggregation of the metallic Ag nanoparticles. In the XANES spectra of 0.06 wt% Ag/Ga₂O₃ (SPM) before and after the photocatalytic reaction (Fig. 6 (b) and (c)), the peaks around 25510, 25530 and 25570 eV characteristic of the metallic Ag appear, suggesting that metallic Ag nanoparticles exist as a major component in Ag/Ga₂O₃ (SPM) samples.

On the other hand, in the diffuse reflectance spectrum of 0.10 wt% Ag/Ga₂O₃ (imp) as prepared, the surface plasmon absorption is not observed. Thus, the spectrum suggests the existence of a large amount of Ag oxide on the sample surface, whereas it increases drastically after the pretreatment. A simple profile of the surface plasmon absorption around 450 nm shows fine metallic Ag nanoparticles with a relatively narrow particle size distribution. We also compare the 450 nm peak with that of 0.10 wt% Ag/Ga₂O₃ (SPM) after the pretreatment, and find that the peak intensity of 0.12 wt% Ag/Ga₂O₃ (imp) is much higher. This result indicates that the Ag/Ga₂O₃ (imp) samples rather than the Ag/Ga₂O₃ (SPM) samples have more metallic Ag nanoparticles in the initial stage of the reaction. After the reaction, however, we confirmed the aggregation of the Ag nanoparticles in the Ag/Ga₂O₃ (imp) in the same way as the Ag/Ga₂O₃ (SPM), by the appearance of the broad band at higher wavelength region.

These results are supported by the measurement of XANES of 0.10 wt% Ag/Ga₂O₃ (imp) before and after the reaction (Fig. 6 (d) and (e)). The profile of the XANES spectrum of the sample as prepared is likely to exhibit the coexistence of metallic Ag, Ag oxides (Ag₂O and/or AgO) and the other components such as Ag–Ga mixed oxide, because we could not reproduce the spectrum by superimposing those of Ag metal and oxides. XANES spectrum also shows that a large amount of metallic Ag nanoparticles exist after the reaction, since the fine structures originated from the metallic Ag can be observed definitely.

C. Relation between the photocatalytic activity and the chemical and aggregation states of the Ag nanoparticles

As mentioned above, measurements of TEM images, UV-VIS diffuse reflectance spectra and XANES spectra reveal the followings.

In the as-prepared Ag/Ga₂O₃ (SPM) samples, the Ag nanoparticles are mostly metallic with the size of less than 10 nm, and few Ag oxide nanoparticles exist. The chemical states and the size of the Ag nanoparticles do not change remarkably by the pretreatment (UV light-irradiation and the introduction of an aq. NaHCO₃ solution). However, a part of the metallic Ag nanoparticles aggregate to become larger particles with the size of more or less 20 nm during the photocatalytic reaction for 5 h.

On another front, in the as-prepared Ag/Ga₂O₃ (imp) samples, the Ag oxide nanoparticles (AgO, Ag₂O and Ag–Ga mixed oxide etc.) exist and their size distribution is
wide from 5 to 10 nm. They become a lot of the metallic Ag nanoparticles by the pretreatment, and become larger particles during the photocatalytic reaction for 5 h as similar to the case of the Ag/Ga$_2$O$_3$ (SPM) samples. Thus, it is likely that the small metallic Ag nanoparticles less than 10 nm are generated in major proportions after the pretreatment (UV light-irradiation), while, they are aggregated by the dissolution and the rephotodeposition during the photocatalytic reaction. Such change in the aggregation states of the Ag nanoparticles should influence the photocatalytic activities for the CO, that is, the aggregation of the small metallic Ag nanoparticles causes to suppress the CO production.

In addition, the average particle size of the Ag nanoparticles would be an important factor to control the photocatalytic activity for the CO production. As shown in Fig. 2 (a), initial CO production rates are faster for 0.06 wt% Ag/Ga$_2$O$_3$ (SPM) and 0.20 wt% Ag/Ga$_2$O$_3$ (imp) than that for 0.06 wt% Ag/Ga$_2$O$_3$ (imp). The major particle sizes in 0.06 wt% Ag/Ga$_2$O$_3$ (SPM), 0.20 wt% Ag/Ga$_2$O$_3$ (imp) and 0.06 wt% Ag/Ga$_2$O$_3$ (imp) could be estimated from the TEM measurements (Fig. 4 (a), (c), and (e)) as 5-8 nm, 8-10 nm and 3-5 nm, respectively. Therefore, the metallic Ag nanoparticles with the size of 5-10 nm are probably suitable for the CO production. The size of the Ag nanoparticles may influence on the chemical states and the amount of adsorbed CO$_2$ molecules.

The impregnation method rather than SPM would be suited for the formation of the moderate sized (5-10 nm) Ag nanoparticles. Actually, the measurements of diffuse reflectance spectra of 0.10 wt% Ag/Ga$_2$O$_3$ (imp) and Ag/Ga$_2$O$_3$ (SPM) exhibit that the former sample has more metallic Ag nanoparticles in the initial stage of the reaction. In the sample preparation by impregnation method, Ag ions connect with the Ga$_2$O$_3$ support to form highly dispersed the small Ag oxide nanoparticles and/or Ag–Ga mixed oxides by calcination. Under UV light-irradiation, these Ag oxide nanoparticles are probably reduced to highly dispersed metallic Ag nanoparticles. This strong interaction between the Ag nanoparticles and Ga$_2$O$_3$ somewhat prevent the aggregation of Ag nanoparticles to inhibit the catalytic degradation for CO production.

On the other hand, in the sample preparation by SPM, the metallic Ag nanoparticles are directly supported on the Ga$_2$O$_3$. Therefore, these metallic Ag nanoparticles tend to aggregate and do not change their chemical states by the photo-reduction under UV light-irradiation. We also speculate that the Ag nanoparticles are not strongly fixed on the Ga$_2$O$_3$, because they are loaded only by filtration. Therefore, binding force of the Ag nanoparticles on the Ga$_2$O$_3$ would be too weak to prevent their migration and aggregation. Therefore, photocatalytic activities of the Ag/Ga$_2$O$_3$ (SPM) samples decreased rapidly with the reaction time.

Thus, the chemical and aggregation states of the Ag nanoparticles depend on the Ag loading processes, and which possibly cause the differences in the optimum amount of Ag loading for the CO production and the change of the photocatalytic activity during the reaction among Ag/Ga$_2$O$_3$ (SPM) and Ag/Ga$_2$O$_3$ (imp). On the other hand, the initial high activity of 0.06 wt% Ag/Ga$_2$O$_3$ (SPM) is remarkable (Fig. 2 (a)), and the stabilization of metal Ag nanoparticles on supports must be improved in the sample preparation by SPM. This is one of the important subjects in our future’s study.

IV. CONCLUSIONS

We have prepared silver-loaded gallium oxide (Ag/Ga$_2$O$_3$) photocatalysts by the solution plasma method (SPM) and impregnation method (imp), and investigate the effects of the chemical states and the size of the Ag nanoparticles on their photocatalytic activities.

The photocatalytic reduction of CO$_2$ with water proceeds over all Ag/Ga$_2$O$_3$ photocatalysts to produce CO, H$_2$, and O$_2$. The optimum amount of Ag loading for CO production is 0.06 and 0.20 wt% for Ag/Ga$_2$O$_3$ (SPM) and Ag/Ga$_2$O$_3$ (imp), respectively, and the photocatalytic activity of the latter is higher than that of the former. However, the CO production rates decrease with the reaction time, and the decrease in the CO production rates is remarkable for Ag/Ga$_2$O$_3$ (SPM) samples.

Measurements of UV-VIS diffuse reflectance spectra, XANES spectra and TEM images reveal the followings: Ag particles in the as-prepared Ag/Ga$_2$O$_3$ (SPM) samples are metallic with the size of less than 10 nm, and the size does not change under UV light irradiation. However, a part of the metallic Ag nanoparticles aggregate to become larger particles with the size of ca. 20 nm during the photocatalytic reaction.

In the as-prepared Ag/Ga$_2$O$_3$ (imp) samples, the Ag oxide nanoparticles (AgO, Ag$_2$O and Ag–Ga mixed oxide etc.) exist and their size distribution is wide from 5 to 10 nm. They become a lot of metallic Ag nanoparticles by UV light irradiation, and become larger particles during the photocatalytic reaction as similar to the case of the Ag/Ga$_2$O$_3$ (SPM) samples.

Such differences of the chemical and aggregation states of the Ag nanoparticles among the Ag/Ga$_2$O$_3$ (SPM) and Ag/Ga$_2$O$_3$ (imp) possibly cause the differences in the optimum amount of Ag loading for the CO production. We also found that the metallic Ag nanoparticles with the size of 5-10 nm are suitable for the CO production. The stabilization of the small nanoparticles on supports is important to improve the photocatalytic properties of the Ag/Ga$_2$O$_3$ samples.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research (B) (No. 24360332) from the Japan Society for the Promotion of Science (JSPS). The authors are grateful for Muto laboratory and High Voltage Electron Microscope Laboratory of Nagoya university, Aichi Center for Industry and Science Technology and KEK-PF.
[1] O. K. Varghese, M. Paulose, T. J. Latempa, and C. A. Grimes, Nano Lett. 9, 731 (2009).
[2] Y. R. Smith, V. Subramanian, and B. Viswanathan, Photo-Electrochemistry & Photo-Biology for the Sustainability (Union Press, Osaka, 2010) p. 225.
[3] A. Nishimura, G. Mitsui, K. Nakamura, M. Hirota, and E. Hu, Int. J. Photoenergy 2012, 184169 (2012).
[4] D. Luo, N. Zhang, S. Hong, H. Wu, and Z. Liu, Int. J. Mol. Sci. 2010, 2792 (2010).
[5] W. Lin, H. Han, and H. Frei, J. Phys. Chem. B 108, 18269 (2004).
[6] J. Z. Y. Tan, Y. Fernandez, D. Liu, M. Maroto-Valer, J. Bian, and X. Zhang, Chem. Phys. Lett. 531, 149 (2012).
[7] H. Takeda, K. Koike, H. Inoue, and O. Ishitani, J. Am. Chem. Soc. 130, 2013 (2008).
[8] K. Teramura, H. Tsuneoka, T. Shishido, and T. Tanaka, Chem. Phys. Lett. 467, 191 (2008).
[9] K. Koci, K. Mateju, L. Obalova, S. Krejcikova, Z. Lacny, D. Placha, and L. Capek, Appl. Catal. B: Environ. 96, 239 (2010).
[10] K. Iizuka, T. Wato, Y. Miseki, K. Saito, and A. Kudo, J. Am. Chem. Soc. 133, 20863 (2011).
[11] Z. Like, E. Tanabe, K. Morikawa, T. Kazino, T. Sekihuzi, S. Matumoto, Y. Hirata, and H. Yoshida, 108th Symposium of Catal. Soc. (A), 1D15 (2011) (in Japanese).
[12] O. Takai, Pure Appl. Chem. 80, 2003 (2008).
[13] N. Saito, J. Hieda, and O. Takai, Thin Solid Films 518, 912 (2009).
[14] T. Mizutani, Y. Abe, H. Hamaguchi, H. Nameki, and S. Yagi, Proc. Int. Conf. NANOCON (2012).
[15] M. A. Bratescu, S. Cho, O. Takai, and N. Saito, J. Phys. Chem. 115, 24569 (2011).
[16] S. M. Kim, G. S. Kim, and S. Y. Lee, Mater. Lett. 62, 4354 (2008).
[17] J. Lung, J. Huang, D. Tien, C. Liao, K. Tseng, T. Tsung, W. Kuo, T. Tsai, C. Jwo, H. Lie, and L. Stobinski, J. Alloys Compd. 434-435, 655 (2007).
[18] H. D. Jang, S-K. Kim, and S-J. Kim, J. Nanopart. Res. 3, 141 (2001).
[19] F. Zhao, Y. Ikushima, and M. Arai, J. Catal. 224, 479 (2004).
[20] Q. Xu, K. C. C. Kharas, and A. K. Datye, Catal. Lett. 85, 229 (2003).
[21] H. A. Bensesi, R. M. Curtis, and H. P. Studer, J. Catal. 10, 328 (1968).