# On the promotion of $Ag/\gamma\text{-}Al_2O_3$ by Cs for the SCR of NO by $C_3H_6$

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The promotion of $Ag/\gamma\text{-}Al_2O_3$ by adding alkali metals (Li, Na, K, Cs) for selective catalytic reduction of NO with $C_3H_6$ was studied in this work. The activity of NO reduction was enhanced by addition of Cs to $Ag/\gamma\text{-}Al_2O_3$ in the presence of excess oxygen and $SO_2$. The stability and growth of silver oxide particles were promoted and the dispersion of silver particles on $\gamma\text{-}Al_2O_3$ was improved by the addition of 0.5 wt% Cs and 1 wt% Cs to 2 wt% $Ag/\gamma\text{-}Al_2O_3$, respectively. The results were confirmed by $H_2$ TPR, UV-Vis DRS, TEM, and XPS.

**KEY WORDS:** silver; alumina; Cs; NO reduction; $C_3H_6$

## 1. Introduction

Diesel engines are used for trucks and trains to deliver heavy loads because they produce a lot of power. On the other hand, diesel engines generate many kinds of air pollutants like carbon monoxide, hydrocarbons and $NO_x$. Especially, the diesel engines generate much $NO_x$. The reduction of $NO_x$ in a diesel engine system requires special conditions such as durability of heat, wide temperature range and deactivation by $SO_2$ and water. Recently, the selective catalytic reduction of $NO_x$ by hydrocarbons has been researched for the removal of nitrogen oxide in the excess oxygen exhaust of diesel and lean burn gasoline [1]. Moreover, using secondary fuel as a reductant has been studied for the reduction of $NO_x$ from diesel engines [23]. After Miyadera [2–4] reported that alumina-supported silver showed high activity for NO reduction in the presence of water and $SO_2$, many researchers have been studying for improving the activity by modifying supports and preparation methods. Researchers are also working to verify the mechanism and kinetics [5–25]. However, the narrow temperature window of $NO_x$ conversion and low $NO_x$ conversion at low temperature still pose a problem for alumina-supported silver catalysts.

Bethke and Kung [16] reported that metallic silver can combust a lot of hydrocarbons when large amounts of silver were loaded on the alumina. Therefore, the catalyst with large amounts of silver loaded on alumina showed low activity of NO reduction; while, the 1+ oxide state of silver showed high reduction ability of NO. Ukisu and Miyadera [5] also indicated that the oxide state of silver is very important for generating isocyanate (–NCO), which is an intermediate of lean $NO_x$ reduction. Seker *et al.* [22] could improve reduction of $NO_x$ by making oxide state silver through a sol–gel preparation method. Therefore, we thought that loading the stable oxide state of silver on alumina could more generate isocyanate, thus, improving the activity of $NO_x$ reduction and expanding the narrow $NO_x$ conversion temperature window.

Alkali metals can be used to improve the stability of silver. Generally, in heterogeneous catalysis, the alkali doping method has been used for increasing selectivity and prolonging the effective lifetime of catalyst. This is due to its intrinsic catalytic effect, the creation of basic sites, neutralization of acidic centers and modification of the electronic properties of the catalyst surface [26]. Actually, Ukisu *et al.* [27] reported that the reduction of NO by propylene could be enhanced by the addition of cesium. Their results also indicated that the effect of an electron donation by cesium to copper on alumina enhanced generation of an intermediate of $NO_x$ reduction, improving the activity of NO conversion. In addition, the crystallization and growth of Ag oxide were promoted by the addition of Cs to $Ag/\alpha\text{-}Al_2O_3$ in the ethylene oxide reaction. Moreover, the selectivity and conversion were also improved [26,29–33].

In this study, we describe the reduction of NO by the addition of alkali metals to $Ag/Al_2O_3$ and the effects of additional sulfur dioxide in the presence of excess oxygen over the catalysts. In addition, X-ray diffraction (XRD), UV-Vis diffuse reflectance spectroscopy (UV-Vis DR), $H_2$ TPR, X-ray photoelectron spectroscopy (XPS) and TEM tests were performed to understand the role of addition of alkali metals.

## 2. Experimental

All catalysts were prepared by the step-excess wet impregnation method using a vacuum rotary evaporator and then dried in an oven at 120 °C for 24 h. The catalysts were reduced in $H_2$ at 300 °C for 3 h and then calcined in $O_2$ at 600 °C for 3 h. Several kinds of alkali metals salts (lithium

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nitrate (Junsei, extra pure), sodium carbonate anhydrous (Duksan, first grade), potassium nitrate (Duksan, first grade), and cesium nitrate (Aldrich, 99.99%)) were added after Ag nitrate (Aldrich, 99+%) was impregnated on $\gamma$-$Al_2O_3$. The spherical $\gamma$-$Al_2O_3$ (2–5 mm ∅, 332 $m^2/g$, Procatalysis Co., Ltd.) was used as a support after crushing into 60–100 meshes sized particles. The catalysts were named using the following notation ($X$Ag$Y$alkali metal/$Al_2O_3$, where $X =$ weight percents of Ag, $Y =$ weight percents of alkali metal, and $Al_2O_3$ is $\gamma$-$Al_2O_3$).

A stainless-steel fixed-bed reactor (1.5 cm ID) was used to test the catalysts under the following conditions: catalyst loading 0.6 g, total flow rate 400 ml/min (STP), GHSV 20 000 $h^{-1}$, and atmospheric pressure. The catalysts were held in place with quartz-wool plugs. Reaction temperature was controlled by a thermocouple, which was located in the outlet stream. Before the reaction, the gases (NO 1000 ppm, $C_3H_6$ 1000 ppm, $O_2$ 5–10%, $SO_2$ 0–200 ppm, and balance $N_2$) were mixed in a mixing chamber. The gases were controlled by mass flow controllers (Hoke Co, USA). The concentrations of NO and $NO_2$ were measured by an on-line chemiluminescence-based analyzer (Green Line MK2, Eurotron, Italy). The minimum detectable concentration of NO and $NO_2$ was 2 ppm. Because of the analyzer's analysis range, $O_2$, CO, and $C_3H_6$ could not be measured accurately. The catalysts were tested in the temperature range of 200–500 °C in 50 °C steps. The data were collected for a period of 0.5–1 h in the steady state reaction. $NO_x$ conversions were calculated by the following equation:

$$NO_x \text{ conversion } (\%) = \frac{NO_{in} - NO_{x\,out}}{NO_{in}} \times 100.$$

X-ray diffraction (XRD) was performed on a Rigaku power diffractometer with nickel-filtered Cu K$\alpha$ radiation (40 kV of tube voltage and 30 mA of tube current). For crystal phase identification, the typical operation parameters were used such as the $2\theta$ range of scan was from 20° to 80° and a scan rate was 4°/min with a 0.02° data interval. UV-Vis diffuse reflectance spectra were recorded in air on a UV-2101PC scanning spectrophotometer (Shimadzu). Reference spectra were collected with a pressed high purity alumina disk. The Kubelka–Munk transform was used to show all spectra in the 220–500 nm range. $H_2$ TPR was performed on 0.3 g of catalysts in a quartz reactor. All calcined catalyst samples were purged with argon flowing at 100 °C for 1 h. A 35 ml/min feed of 12% $H_2$ balanced $N_2$ gas was used for the reduction. The temperature was raised from room temperature to 700 °C at a rate of 15 °C/min. The $H_2$ consumptions were monitored by a thermal conductivity detector (TCD). A JEM-200CX transmission electron microscope (Jeol) operating at 200 kV was used to study the morphology of the catalyst samples. ESCALAB 2201-XL (Fision) was used with the aluminum anode for XPS (X-ray photoelectron spectroscopy). It was operated at 1486.6 eV at 10 kV, 15 mA, and fixed analyzer transmission.

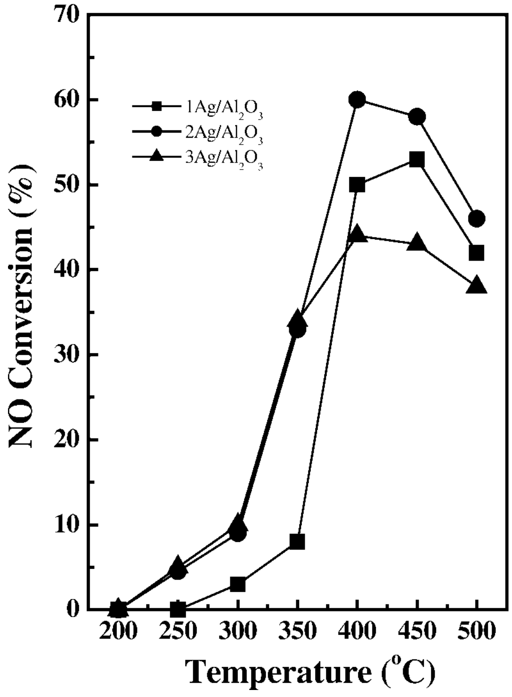

Figure 1. NO conversion profiles of $Ag/Al_2O_3$ catalysts with different silver loading. Catalyst weight 0.6 g; feed: 1000 ppm NO, 1000 ppm $C_3H_6$, 5% $O_2$, $N_2$ balance, 400 ml/min total flow.

## 3. Results and discussion

### 3.1. Activity measurements

Figure 1 shows optimum Ag loading weight on $\gamma$-$Al_2O_3$ for high NO conversion by $C_3H_6$. The results confirmed that $2Ag/Al_2O_3$ had the maximum NO conversion. Moreover, it dramatically increased the NO conversions at 300 °C as noted in previous reports [4,14,16,17]. The NO conversion of $3Ag/Al_2O_3$ was lower than the NO conversions of $2Ag/Al_2O_3$ from 300 to 500 °C. This was caused by the metallic silver on $3Ag/Al_2O_3$, which combusted much $C_3H_6$; leaving $C_3H_6$ to be used as a reductant, as reporting that the metallic silver existed on the alumina support when high loading of Ag on alumina [16].

In order to understand the effects of additional alkali metals, 1 wt% of Li, Na, K, and Cs was added, respectively, to $2Ag/Al_2O_3$, the optimum loading weight of Ag for the NO conversion, as the alkali metals (figure 2). $2Ag1Li/Al_2O_3$, $2Ag1Na/Al_2O_3$, and $2Ag1K/Al_2O_3$ showed lower NO conversions than that of $2Ag/Al_2O_3$. $2Ag1Na/Al_2O_3$ showed the lowest NO conversion for the entire temperature region. Therefore, Li, Na, K could not help the activity of $2Ag/Al_2O_3$ for the NO conversion. On the other hand, the NO conversion of $2Ag1Cs/Al_2O_3$ was higher than the NO conversion of $2Ag/Al_2O_3$. In addition, in the low temperature range (300–400 °C), the NO conversion was especially improved by Cs addition. Therefore, we found that Cs was the best alkali metal among the alkali metals to improve the NO conversion of $2Ag/Al_2O_3$. We propose that Cs can help keep oxide silver particles in the reaction and the oxide silver particles can use $C_3H_6$ as a reductant for the NO reduction

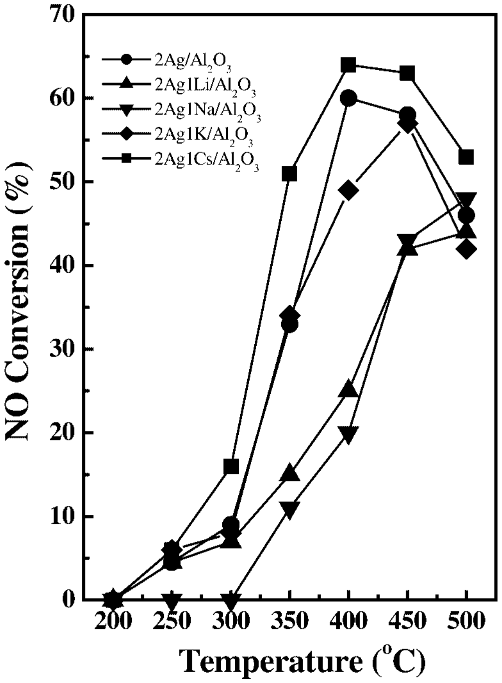

Figure 2. Effect of adding alkali metal to 2Ag/Al$_2$O$_3$ on NO conversion. Catalyst weight 0.6 g; feed: 1000 ppm NO, 1000 ppm $C_3H_6$, 5% $O_2$, $N_2$ balance, 400 ml/min total flow.

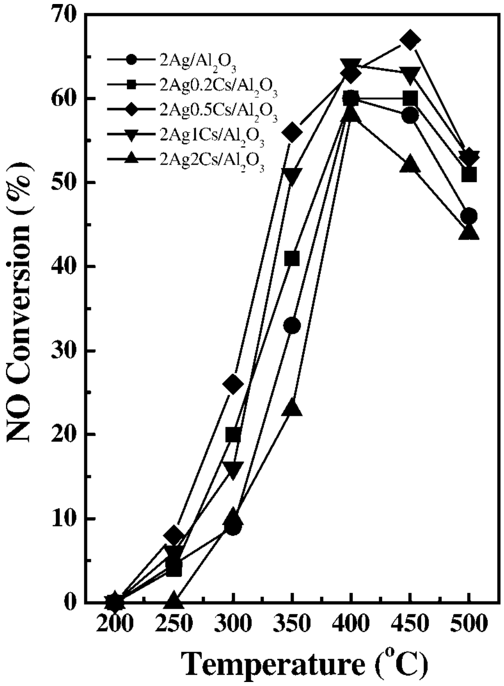

Figure 3. Effect of adding various Cs loading weights to 2Ag/Al$_2$O$_3$ on NO conversion. Catalyst weight 0.6 g; feed: 1000 ppm NO, 1000 ppm $C_3H_6$, 5% $O_2$, $N_2$ balance, 400 ml/min total flow.

reaction. Moreover, the catalysts of Cs on 2Ag/Al$_2$O$_3$ can be suggested as convenient catalysts for the real reaction condition, which requires wider reaction temperature range since it showed much higher NO conversion at low temperature as well as at higher temperature.

Figure 3 shows the effect of adding various Cs loading weights to 2Ag/Al$_2$O$_3$ to find the optimum Cs loading weight for improving the NO conversion. The NO conversions of every catalyst were enhanced by adding Cs except 2Ag2Cs/Al$_2$O$_3$. Therefore, we could make sure that Cs is a good promoter for improving NO conversion on 2Ag/Al$_2$O$_3$. Moreover, the 2Ag0.5Cs/Al$_2$O$_3$ showed the best NO conversion, which was much enhanced (more than 50%) from 350 to 500 °C and adding too much Cs was not helpful to improve activity of 2Ag/Al$_2$O$_3$.

To understand the effect of excess oxygen on NO conversion, the NO conversion tests were performed in 10% oxygen (figure 4). The NO conversions of all catalysts decreased with increasing oxygen. We think that this trend of NO conversion was caused by increasing complete oxidation of $C_3H_6$ with decreasing generation of intermediates like isocyanate (–NCO) for NO reduction. The complete $C_3H_6$ oxidation can easily occur in the higher oxygen percent reaction condition. We think that if Cs can keep oxide silver particles they can generate more intermediates. Therefore, the NO conversion will increase even in higher oxygen reaction conditions. The catalysts 2Ag0.5Cs/Al$_2$O$_3$ and 2Ag1Cs/Al$_2$O$_3$ showed higher NO conversion than the 2Ag/Al$_2$O$_3$ in the entire temperature region. The 2Ag1Cs/Al$_2$O$_3$ catalyst showed best NO conversion from 300 to 450 °C. The 2Ag0.5Cs/Al$_2$O$_3$ showed the best NO conversion at 5% $O_2$, while the 2Ag1Cs/Al$_2$O$_3$ showed the best NO conversion at 10% $O_2$. Interestingly, the NO conversions of Cs addition catalysts at 10% $O_2$ were higher than the NO conversion of Cs addition catalysts at 5% $O_2$ at 250 °C. In addition, the NO conversions gradually increased with increasing the Cs loading weights at 250 °C

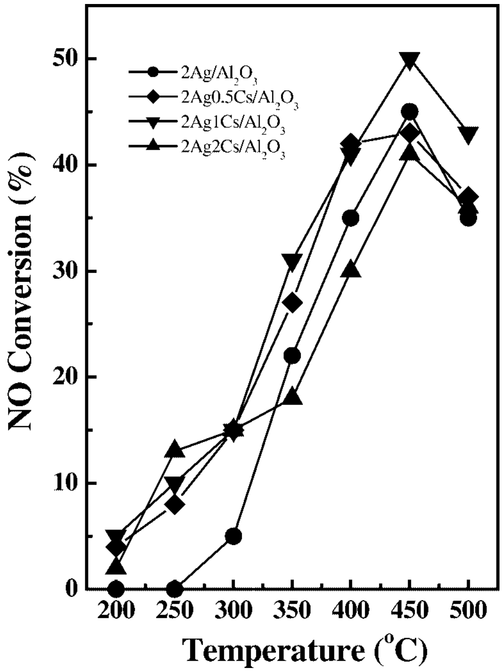

Figure 4. Effect of $O_2$ percent on NO conversion over the Cs loaded 2Ag/Al$_2$O$_3$ catalysts. Catalyst weight 0.6 g; feed: 1000 ppm NO, 1000 ppm $C_3H_6$, 10% $O_2$, $N_2$ balance, 400 ml/min total flow.

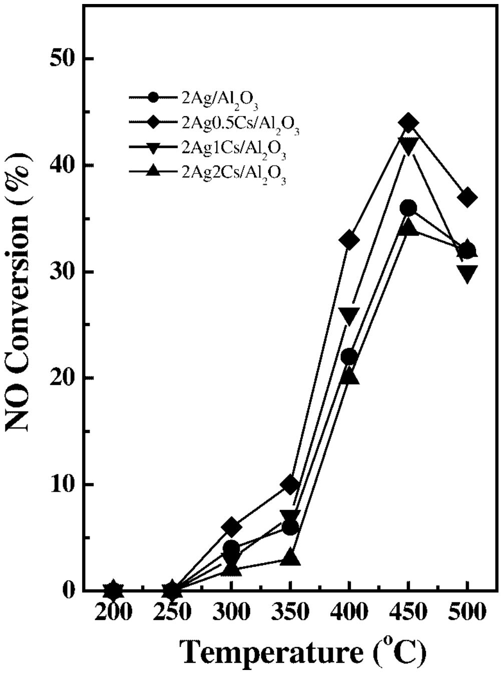

Figure 5. Effect of adding $SO_2$ on NO conversion over the Cs loaded $2Ag/Al_2O_3$ catalysts. Catalyst weight 0.6 g; feed: 1000 ppm NO, 1000 ppm $C_3H_6$, 200 ppm $SO_2$, 10% $O_2$, $N_2$ balance, 400 ml/min total flow.

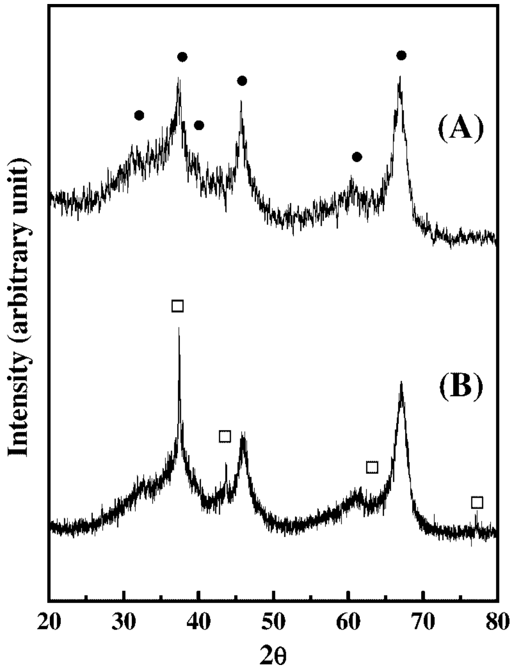

Figure 6. XRD spectra of $3Ag/Al_2O_3$ after calcination (A) and, $3Ag/Al_2O_3$ after reaction (B). (●) $\gamma$-$Al_2O_3$ peak, (□) metallic Ag peak. Reaction conditions: 1000 ppm NO, 1000 ppm $C_3H_6$, 5% $O_2$, $N_2$ balance, 400 ml/min total flow.

at 10% $O_2$. It seems that adding Cs can improve generation of intermediates for NO reduction at the temperature in higher $O_2$% which is a good condition for complete oxidation of $C_3H_6$. Therefore, NO conversion was improved at low temperatures. However $2Ag2Cs/Al_2O_3$ showed low NO conversion except at 250 °C like the NO conversion at 5% $O_2$.

Figure 5 shows the effect on NO conversion by the addition of $SO_2$ to the reaction gas because the $SO_2$, which is produced in the diesel engine emission, can affect the deactivation of de $NO_x$ catalysts. The NO conversions of catalysts with Cs addition and without Cs addition decreased when $SO_2$ was added to the reaction gas. Especially, they were suppressed in the low temperature range (250–350 °C). We think that this deactivation was caused by sulfate formations on the catalysts like the aluminum sulfate ($Al_2(SO_4)_3$) and $Ag_2SO_4$. However, $2Ag0.5Cs/Al_2O_3$ and $2Ag1Cs/Al_2O_3$ showed higher NO conversion from 400 to 450 °C than $2Ag/Al_2O_3$, while $2Ag2Cs/Al_2O_3$ showed the lowest NO conversion. Therefore, by adding Cs the promoted $2Ag/Al_2O_3$ was less deactivated by $SO_2$. We observed that the Cs on $2Ag/Al_2O_3$ catalyst had higher NO conversions than $2Ag/Al_2O_3$ even though they were in the presence of excess oxygen and $SO_2$.

### 3.2. Catalyst characterization

To find the differences of silver crystallites after calcination and after reaction, XRD tests were performed. The XRD spectra of the $2Ag/Al_2O_3$ and the various weight percent of Cs loaded on $2Ag/Al_2O_3$ catalysts revealed neither the presence of silver oxide peaks nor metallic silver peaks after calcination and after reaction. Moreover, the Cs peaks were not seen. Only $\gamma$-$Al_2O_3$ reflections were found. Thus, it seems that there were well dispersed amorphous oxide silver particles, or very small metallic silver particles, which were too small to be detected by X-ray diffraction methods on the alumina. After reaction, the XRD patterns of the $3Ag/Al_2O_3$ revealed the presence of metallic Ag, however neither the presence of silver oxide nor metallic silver over $3Ag/Al_2O_3$ were detected after calcinations (figure 6). After reaction at 500 °C, the color of $3Ag/Al_2O_3$ was darker than the colors of $2Ag/Al_2O_3$. This showed that the silver particles of $3Ag/Al_2O_3$ changed to metallic silver during the reaction. Therefore, we think that the low NO conversions of those catalysts were caused by the metallic Ag like previous reports' results [14,16].

In order to understand the changing states of silver on the catalysts, the catalysts were characterized through a UV-Vis DR spectrophotometer. Figure 7 shows UV-Vis DR spectra of the various weight percents of Cs loaded on $2Ag/Al_2O_3$ after calcination and after reaction. Flytzani-Stephanopoulos *et al.* reported that on the catalysts of silver loaded on alumina or ZSM-5, the band at 220 nm is assigned to isolated $Ag^+$ ion, which cannot be determined because of strong absorption of alumina. Moreover, the peak at ~250 nm and the broad peak are seen at ~350 nm (the oxidized Ag cluster ($Ag_n^{\delta+}$)) in oxidized state. On the other hand, the peak at 295 nm with a shoulder at 335 nm, which are caused by the electronic transition of reduced Ag species and the broad peak at ~420 nm (metallic silver particles) are seen in reduced state [20,21].

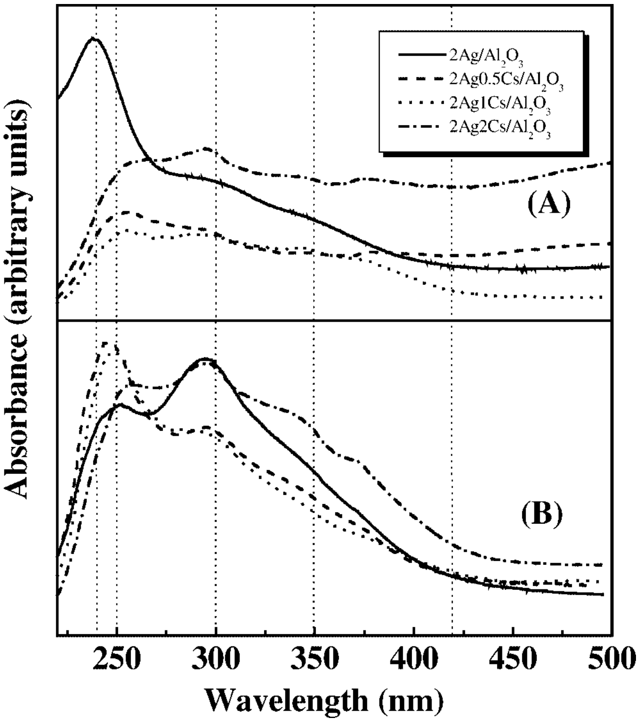

Figure 7. UV-Vis DR spectra of Cs loaded 2Ag/$Al_2O_3$. (A) after calcination and (B) after reaction. Reaction conditions: 1000 ppm NO, 1000 ppm $C_3H_6$, 200 ppm $SO_2$, 10% $O_2$, $N_2$ balance, 400 ml/min total flow.

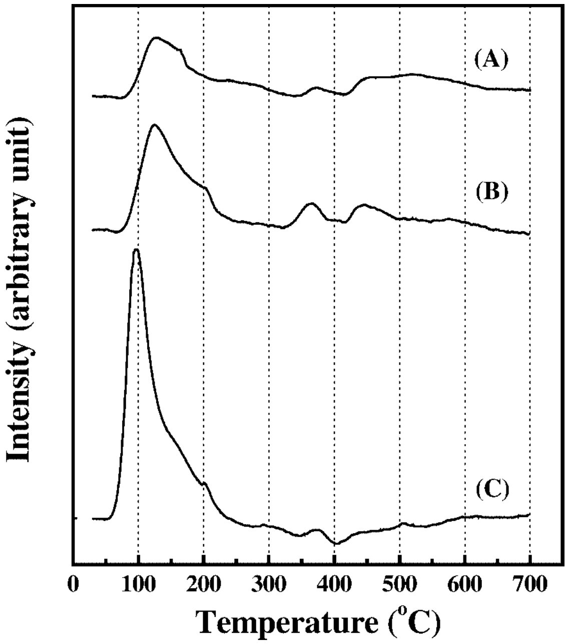

Figure 8. TPR profiles: (A) 1Ag/$Al_2O_3$, (B) 2Ag/$Al_2O_3$ and (C) 3Ag/$Al_2O_3$.

In 2Ag/$Al_2O_3$, a strong peak was seen at ~250 nm (the oxidized Ag cluster ($Ag_n^{\delta+}$)) after calcination. On the other hand, after reaction the peak at ~250 nm was decreased, while the peak at 295 nm with a shoulder at 335 nm was much increased. Therefore, the characteristic of silver on 2Ag/$Al_2O_3$ changed from oxidized silver to metallic silver during reaction. The XRD results of 2Ag/$Al_2O_3$ could not show differences between after calcination and after reaction. However, the UV-Vis DR spectra of 2Ag/$Al_2O_3$ revealed a changing silver state during the reaction. The low and broad peaks were seen at ~250, 295, and 335 nm after calcination with the catalysts of 2Ag0.5Cs/$Al_2O_3$ and 2Ag1Cs/$Al_2O_3$, while those peaks increased after the reaction. Especially, the peaks at ~250 nm increased a lot compared to other peaks. Thus, the characteristic of oxidized silver on the 2Ag0.5Cs/$Al_2O_3$ and 2Ag1Cs/$Al_2O_3$ catalysts showed more stability than the characteristic of oxidized silver of Cs on 2Ag/$Al_2O_3$ since the peaks of 2Ag0.5Cs/$Al_2O_3$ and 2Ag1Cs/$Al_2O_3$ at ~250 nm were higher than the peak of 2Ag/$Al_2O_3$ after the reaction.

The 2Ag2Cs/$Al_2O_3$ showed high and broad peaks at 295 and 420 nm after calcinations and after reaction. Therefore, a conclusion can be drawn that the 2Ag2Cs/$Al_2O_3$, which is the worst catalyst for NO conversion among all of the other catalysts, showed higher characteristics of metallic silver between after calcination and after reaction. Therefore, we assumed that too much Cs addition inhibited the formation of silver oxide. In contrast, it preferred to form metallic Ag. This explains why the NO conversion of 2Ag2Cs/$Al_2O_3$ was so low. The broad peak at 420 was not seen clearly on the 2Ag/$Al_2O_3$, 2Ag0.5Cs/$Al_2O_3$, and 2Ag1Cs/$Al_2O_3$ since the surface of silver particles was covered by adsorbed oxygen [19].

Figure 8 shows $H_2$ TPR profiles of various loading weights of Ag on alumina. As the loading weight of Ag increased, the peak around 100 °C was increased and was shifted down to lower temperatures. As it was mentioned [16], the peak at around 100 °C was caused by large $Ag_2O$ oxide clusters; therefore, we assumed that many large $Ag_2O$ oxide clusters were on 3Ag/$Al_2O_3$ before reaction and it can easily change to metallic silver, which can favor low NO conversion in the reaction. The biggest two peaks were clearly seen at 350 and 450 °C with 2Ag/$Al_2O_3$ among the catalysts. We think that those peaks are assigned to stable and well dispersed $Ag_2O$ particles or $Ag^+$ ions [16]. The silver oxide might be more stable than large $Ag_2O$ oxide clusters on 3Ag/$Al_2O_3$ during the reaction; therefore, it could yield a higher NO conversion.

Figure 9 shows TPR profiles of catalysts with various loading weights of Cs on 2Ag/$Al_2O_3$. The results show that the peaks gradually decreased at lower temperatures, while the peaks gradually increased at higher temperatures as the loading weights of Cs increased up to 0.5 wt%. Moreover, the high temperature peaks decreased as the loading weight of Cs increased more than 0.5 wt%. Especially, 2Ag2Cs/$Al_2O_3$ had small peaks at the high temperatures and the form of the peak at the low temperatures was also quite different. Therefore, we assumed that 2Ag2Cs/$Al_2O_3$ had many unstable $Ag_2O$ oxide clusters, which easily changed to metallic silver in the reaction. This is consistent with UV-Vis DR spectra results. Thus, the addition of Cs on 2Ag/$Al_2O_3$ enhances the stability of $Ag_2O$ particles or $Ag^+$ ions.

Figure 10 shows morphologies of silver particles on $Al_2O_3$ through transmission electron microscopy images after reaction. The silver on $3Ag/Al_2O_3$ were small particles (<2 nm) after the reaction. We assumed that the metallic silver existed in the small particles on $3Ag/Al_2O_3$. The silver particles grew by addition of Cs as shown by the TEM images of $2Ag/Al_2O_3$ (1–10 nm) and $2Ag0.5Cs/Al_2O_3$ (10–20 nm). In addition, we can easily see in the TEM image of $2Ag0.5Cs/Al_2O_3$ that Cs addition causes good dispersion of the silver particles. This is similar to the effect of Cs on $\alpha$-$Al_2O_3$ when the addition of Cs helped the crystallization and growth of Ag oxide for the ethylene oxide reaction [29–33]. We assumed that the growth of Ag particles were stable Ag oxide particles such as ions of $Ag^+$ and oligometric $Ag_n$ clusters. It seems that the high NO conversion catalysts with Cs were caused by the promoted crystallization and growth of stable oxide silver particles. It was reported that stable oxide Ag catalysts had high NO conversion [16,20]. In addition, selective reduction of nitric oxide over alumina was seriously deactivated by the accumulation of aluminum sulfate ($Al_2(SO_4)_3$) on the surface of alumina in the presence of $SO_2$ [34–40]. The catalysts with Cs were less affected, possibly caused by the growth of stable Ag oxide particles, which were less covered than small Ag oxide particles by aluminum sulfate.

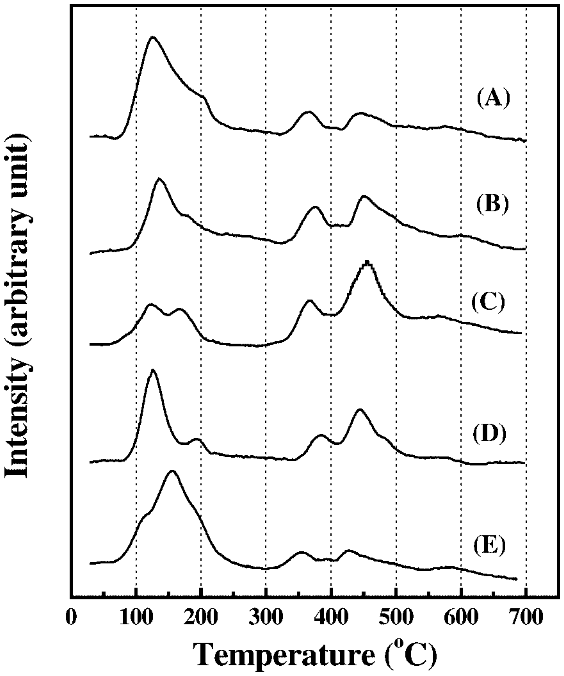

Figure 9. TPR profiles: (A) $2Ag/Al_2O_3$, (B) $2Ag0.2Cs/Al_2O_3$, (C) 2Ag $0.5Cs/Al_2O_3$, (D) $2Ag1Cs/Al_2O_3$ and (E) $2Ag2Cs/Al_2O_3$.

In XPS study, analyzing the electronic states of Ag was difficult through XPS spectra because the binding energies of various silver states were too close to analyze (368.3 eV for metallic silver, 367.5 eV for $Ag_2O$, 367.3 eV for AgO and 368.8 eV for $AgOOCF_3$) [22]. Only the Ag $3d_{5/2}$ peak of $3Ag/Al_2O_3$ was significantly shifted to the metallic silver state after the reaction like in the results of XRD and TPR. We think that the promoted stability of well dispersed silver oxide particles by Cs generates better intermediates for NO reduction; therefore, the conversion of NO might have increased.

## 4. Conclusion

It was confirmed that 2 wt% of silver was the optimum Ag loading weight for NO conversion by $C_3H_6$. Alkali metals (Li, Na, K, Cs), respectively, were added to $2Ag/Al_2O_3$

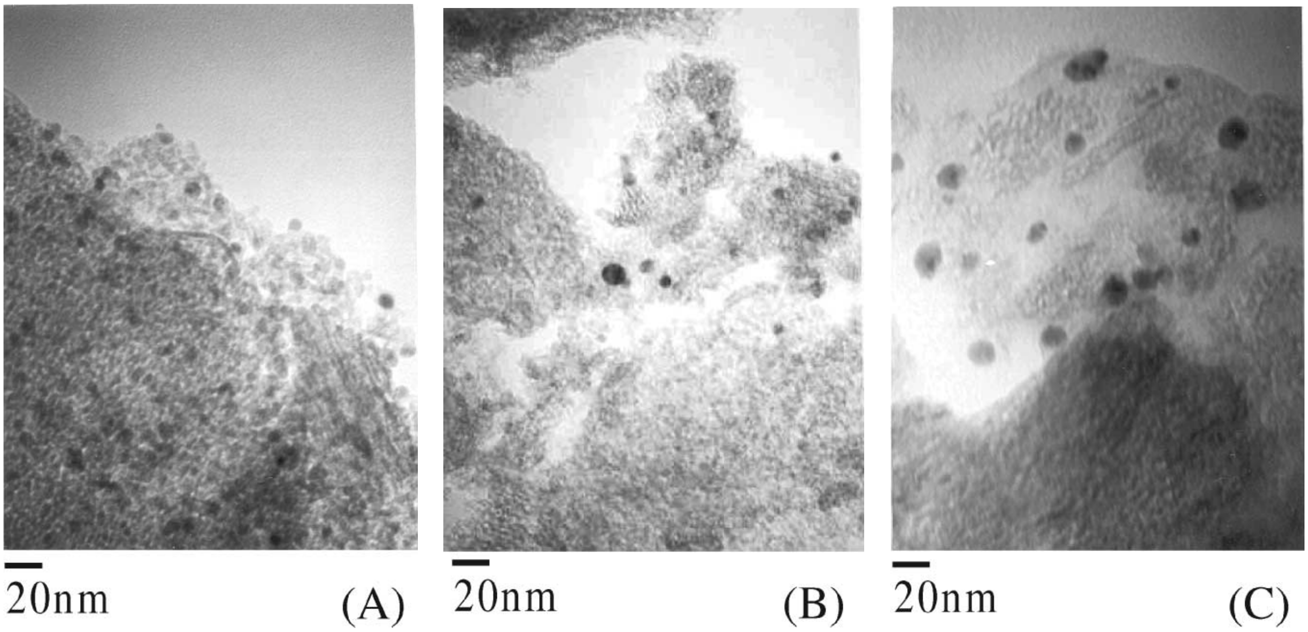

Figure 10. TEM images: (A) $3Ag/Al_2O_3$ after reaction, (B) $2Ag/Al_2O_3$ after reaction, and (C) $2Ag0.5Cs/Al_2O_3$ after reaction. Reaction conditions: 1000 ppm NO, 1000 ppm $C_3H_6$, 200 ppm $SO_2$, 10% $O_2$, $N_2$ balance, 400 ml/min total flow.

to promote the activity of NO reduction. By adding Cs, the NO conversion of $2Ag/Al_2O$ was higher than the NO conversion of $2Ag/Al_2O$ in the presence of excess oxygen and $SO_2$. Especially, the NO reduction at low temperatures was enhanced. It was revealed by XRD that lower NO conversion of $3Ag/Al_2O_3$ was caused by metallic silver. After calcinations large unstable $Ag_2O$ oxide clusters, which easily changed to small metallic silver particles, were on $3Ag/Al_2O_3$. It was confirmed that Cs promoted stability and growth of silver oxide particles. Moreover, the UV-Vis DR spectrometer, $H_2$ TPR, TEM, and XPS showed increase in the dispersion of silver particles in the reaction. We assume that generating intermediates like isocyanate (–NCO) was increased by the stable well dispersed silver oxide particles. Therefore, the NO conversion was increased in the presence of excess oxygen and $SO_2$.

## Acknowledgement

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