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A comparative study of Ag/Al₂O₃ and Cu/Al₂O₃ catalysts for the selective catalytic reduction of NO by C₃H₆

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Abstract

The selective catalytic reduction (SCR) of NO by C_3H_6 in excess oxygen was evaluated and compared over Ag/Al_2O_3 and Cu/Al_2O_3 catalysts. Ag/Al_2O_3 showed a high activity for NO reduction. However, Cu/Al_2O_3 showed a high activity for C_3H_6 oxidation. The partial oxidation of C_3H_6 gave surface enolic species and acetate species on the Ag/Al_2O_3 , but only an acetate species was clearly observed on the Cu/Al_2O_3 . The enolic species is a more active intermediate towards $NO + O_2$ to yield—NCO species than the acetate species on the Ag/Al_2O_3 catalyst. The Ag and Cu metal loadings and phase changes on Al_2O_3 support can affect the activity and selectivity of Ag/Al_2O_3 and Cu/Al_2O_3 catalysts, but the formation of enolic species is the main reason why the activity of the Ag/Al_2O_3 catalyst for NO reduction is higher than that of the Cu/Al_2O_3 catalyst.

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Keywords: Enolic species; Selective catalytic reduction of NO (SCR of NO); In situ DRIFTS; Reaction mechanism

1. Introduction

The selective catalytic reduction (SCR) of NO by hydrocarbons is a potential method to remove NO_x from oxygen rich exhausts. Since Iwamoto and Held and co-workers [1,2] first reported that the copper-exchanged ZSM-5 catalyst is an effective catalyst for the SCR of NO, much effort in the last decade has been placed on the investigation of a more suitable catalyst. Although many studies have focused on zeolitic catalysts, the metal oxides are the most promising catalysts because of their high stability. In 1993, Miyadera [3] found that an alumina-supported silver (Ag/Al₂O₃) catalyst is highly effective for the SCR of NO by C₃H₆ and C_2H_5OH . In our previous study [4], we also found that the Ag/Al₂O₃ catalyst exhibited a high activity for the reduction of NO with C₃H₆ and C₂H₅OH even in the presence of water vapor and SO₂. The reaction mechanism of the SCR of NO was proposed on the basis of vacuum and in situ studies on Ag/Al₂O₃ [4–9], and R-ONO, R-NO₂ and NCO were suggested as the key intermediates. The alumina-supported

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copper (Cu/Al₂O₃) catalyst has recently become another focus as a metal oxide catalyst for the SCR of NO. Bethke et al. [10] reported that a Cu/ZrO2 catalyst, which contains highly dispersed Cu²⁺ species in a nonreducible oxide matrix, showed NO conversion comparable to Cu-ZSM-5. Afterwards, Shimizu et al. [11] found that Cu/Al₂O₃ with a high Cu content showed higher activity at low temperature and higher hydrothermal stability than Cu-ZSM-5. Recently, Kim et al. [12] reported that the 10 wt.% Cu/Al₂O₃ catalyst with a CuAl₂O₄ phase exhibited a high reactivity for the SCR of NO by C₃H₆. It has also been reported that the SCR of NO by C₃H₆ over Ag/Al₂O₃ [4–9] and Cu/Al₂O₃ [11,13] catalysts undergoes a similar mechanism. However, the similar mechanism is unconvincing to explain the obvious difference between Ag/Al₂O₃ catalysts and Cu/Al₂O₃ catalysts for the SCR of NO by hydrocarbon.

In this study, Ag/Al₂O₃ and Cu/Al₂O₃ catalysts with different Ag and Cu loadings were prepared and characterized by BET and XRD methods. The catalytic performance of Ag/Al₂O₃ and Cu/Al₂O₃ catalysts for the SCR of NO by C₃H₆ was evaluated and compared. In addition, the difference between Ag/Al₂O₃ and Cu/Al₂O₃ for the SCR of NO were studied with respect to the behavior of adsorbed species on the catalyst surface using in situ DRIFTS spectra.

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2. Experimental

2.1. Catalyst preparation

Utilized Al_2O_3 (gamma type) has a total BET surface area of $250\,\mathrm{m}^2\,\mathrm{g}^{-1}$. The supported catalysts, Ag/Al_2O_3 and Cu/Al_2O_3 , were prepared by an impregnation method with an aqueous solution of silver and copper nitrate, followed by evaporation to dryness in a rotary evaporator under pressure reduction at 333 K. The wet sample was dried at 393 K for 12 h, and then calcined in air at 873 K for 3 h. Before the catalytic test, the catalysts were sieved into 20–40 meshes.

2.2. Catalyst characterization

BET surface area, pore volume and pore diameter were obtained from N_2 adsorption isotherms measured at 83 K using an ASAP 2000 instrument (Micromeritics Co., USA). The data of the $\text{Cu/Al}_2\text{O}_3$ and $\text{Ag/Al}_2\text{O}_3$ catalysts with different loadings are given in Table 1.

Powder X-ray diffraction (XRD) measurements of catalysts were carried out on a Rigaku D/max-RB X-Ray Diffractometer (Japan) with a Cu K α radiation and operated at $40\,\mathrm{kV}$ and $40\,\mathrm{mA}$. The patterns were taken in the 2θ range of $10\text{--}70^\circ$ at a scan speed of 6° min⁻¹.

2.3. Catalytic tests

The activity tests for the SCR of NO by C_3H_6 over Ag/Al_2O_3 and Cu/Al_2O_3 catalysts were performed with a fixed-bed quartz flow reactor by passing a mixture gas of $NO/C_3H_6/O_2/N_2=800\,\mathrm{ppm}/1714\,\mathrm{ppm}/10\,\mathrm{vol.\%/balance}$ at a flow rate of $4000\,\mathrm{cm^3\,min^{-1}}$ (W/F = $0.018\,\mathrm{g\,s\,ml^{-1}}$, GHSV: $50,000\,\mathrm{h^{-1}}$) within the temperature range of $400-900\,\mathrm{K}$. After reaching the steady state, the effluent gas was analyzed by (AVL Di Gas, $4000\,\mathrm{light}$) for HC and CO_2 conversion analysis and a chemiluminescence based $NO/NO_2/NO_x$ analyzer (42C-HL, Thermo Environmental Instrument Inc.) for NO_x conversion analysis.

Table 1 BET surface area, pore volume and pore diameter of Ag/Al_2O_3 and Cu/Al_2O_3 catalysts with different Ag and Cu loadings

Catalyst	BET surface area (m^2/g)	Pore volume (cc/g)	Pore diameter (A)
2 wt.% Ag/Al ₂ O ₃	239.8	0.7235	122.9
4 wt.% Ag/Al ₂ O ₃	222.4	0.7107	124.9
6 wt.% Ag/Al ₂ O ₃	211.8	0.6950	126.2
8 wt.% Ag/Al ₂ O ₃	209.9	0.6493	130.3
1 wt.% Cu/Al ₂ O ₃	235.1	0.7214	122.8
5 wt.% Cu/Al ₂ O ₃	205.1	0.6280	122.58
10 wt.% Cu/Al ₂ O ₃	171.9	0.5298	123.3
15 wt.% Cu/Al ₂ O ₃	147.7	0.4839	128.5

2.4. In situ DRIFTS

In situ DRIFTS spectra were recorded in a NEXUS 670-FTIR equipped with a smart collector and a liquid N_2 cooled MCT detector. The sample (about 30 mg) for study was placed in a ceramic crucible. Before the experiment, the catalyst was firstly pre-treated in a flow of 10% $O_2 + N_2$ for 60 min at 573 and 873 K, respectively, then cooled to a suitable temperature in a flow of $O_2 + N_2$ for 30 min, and a spectrum of the catalyst in the flow of $N_2 + O_2$ was recorded as the background. A flow of feed gas mixture controlled by mass flow meters was fed at a flow rate of 300 ml/min. All spectra were measured under real reaction conditions with a resolution of $4 \, \mathrm{cm}^{-1}$ and accumulating 100 scans. A background spectrum was subtracted from each spectrum, respectively.

3. Results and discussion

3.1. Catalytic test

Fig. 1 shows the NO conversions for the SCR of NO by C_3H_6 over Ag/Al_2O_3 and Cu/Al_2O_3 catalysts with different loadings at various temperatures. As shown in Fig. 1(A), the maximum of NO conversion increased significantly with increasing silver loading from 2 to 4 wt.%, and the temperature at which the maximum of NO conversion is obtained (i.e. T_{max}) was shifted towards a lower temperature. Further increase of the silver loading from 4 to 8 wt.% did not show any promotion of low temperature NO conversion but lowered the high temperature conversion. As shown in Fig. 1(B), the maximum of NO conversion increased with the increase of copper loading until 10 wt.%, but decreased at 15 wt.%.

BET results of the catalysts are shown in Table 1. The surface area of both Ag/Al₂O₃ and Cu/Al₂O₃ catalysts gradually decreased with increasing the loading. XRD patterns of a series of Ag/Al₂O₃ (A) and Cu/Al₂O₃ (B) catalysts are shown in Fig. 2. Only the γ -Al₂O₃ phase was detected as the Ag loading increased from 2 to 6 wt.%, but the Ag₂O phase was also observed at 2θ of 19.26, 33.76 and 38.12°, etc. with the 8 wt.% Ag loading (Fig. 2(A)). Likewise, the CuO phase could not be detected until the Cu loading up to 15 wt.% in Cu/Al₂O₃ (Fig. 2(B)). On the other hand, the test data in Fig. 1 shows that the optimum Ag and Cu loadings for Ag/Al₂O₃ and Cu/Al₂O₃ during the SCR of NO are 4 wt.% Ag/Al₂O₃ and 10 wt.% Cu/Al₂O₃, respectively. This implied that both catalysts have the highest catalytic activity for the SCR of NO with the highest Ag or Cu loading before the presence of Ag and Cu metal oxide phases.

Fig. 3 shows the NO (A) and C₃H₆ (B) conversions for the SCR of NO by C₃H₆ over 4 wt.% Ag/Al₂O₃, 10 wt.% Cu/Al₂O₃, Al₂O₃ catalyst and blank reactor at various temperatures. As shown in Fig. 3(A), the blank reactor had almost no activity for the SCR of NO by C₃H₆. The Al₂O₃ showed a better activity than 10 wt.% Cu/Al₂O₃ catalysts,

70

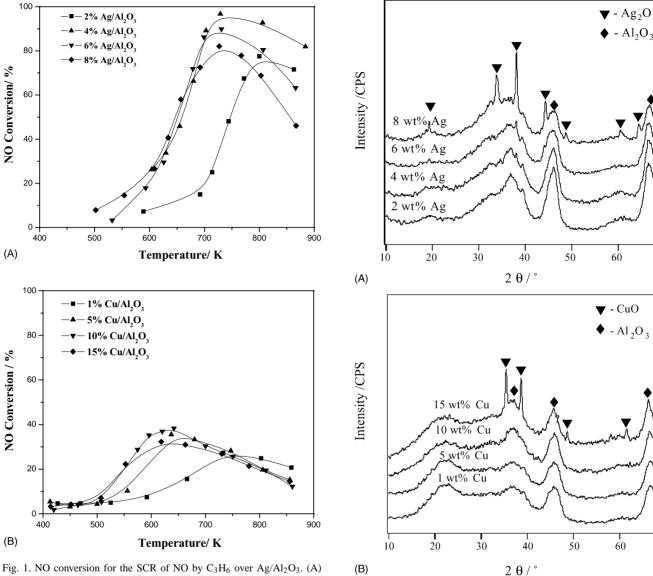


Fig. 1. NO conversion for the SCR of NO by C_3H_6 over Ag/Al_2O_3 . (A) (\blacksquare) 2 wt.%, (\blacktriangle) 4 wt.%, (\blacktriangledown) 6 wt.%, (\spadesuit) 8 wt.%, and Cu/Al_2O_3 . (B) (\blacksquare) 1 wt.%, (\blacktriangle) 5 wt.%, (\blacktriangledown) 10 wt.%, (\spadesuit) 15 wt.%, at various temperatures.

Fig. 2. XRD patterns of Ag/Al_2O_3 (A) and Cu/Al_2O_3 (B) catalysts with different Ag and Cu loadings.

but the curve of NO conversion was shifted towards higher temperatures. The highest NO conversion was 98% for the 4 wt.% Ag/Al₂O₃ catalyst, contrasted with 40% for the 10 wt.% Cu/Al₂O₃ catalyst. However, the activity for C₃H₆ combustion can be arrayed as order of 10 wt.% Cu/Al₂O₃ > 4 wt.% Ag/Al₂O₃ > Al₂O₃ > blank reactor, as shown in Fig. 3(B). The results above all showed the different promoting effects of silver and copper to supporter.

Meunier and co-workers [6,14] reported that the favorable catalysts for the SCR of NO, e.g. low loading (<2 wt.%) Ag supported on alumina, are not significantly active for either oxidation of NO to NO₂ or hydrocarbon combustion during the SCR of NO. Likewise, the reverse is true for high loading (10 wt.%) Ag/Al₂O₃ catalyst, which showed high activity for NO oxidation and hydrocarbon combustion, but was unselective for the SCR of NO. They suggested that the

most efficient catalysts for the SCR of NO should not oxidize NO to NO2 and hydrocarbon to any significant extent. Shimizu et al. [11] also found that the reactivity for the SCR of NO by C₃H₆ over a 8 wt.% Cu/Al₂O₃ catalyst exhibited the highest activity at 623 K, but almost all of the propylene was converted into the CO_X at higher temperature, so they suggested that the decrease of reactivity for NO reduction is due to the consumption of C₃H₆ through the combustion reaction on the catalyst. On the other hand, many studies also showed that the SCR of NO₂ (NO₃⁻) by hydrocarbon is much faster than that of NO [5,7-9,13,15,16]. In fact, the NO₂ route may be the origin of selectivity of NO reduction in excess oxygen. Therefore, this discussion should be further done at mechanistic level since the results published apparently contradicted each other. The steady and transient DRIFTS experiments were carried out over the 4 wt.%

100

4wt.% Ag/Al₂O₃

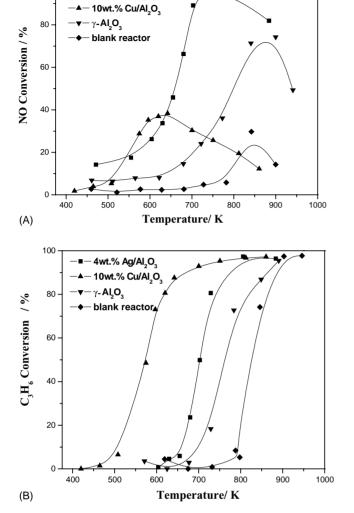
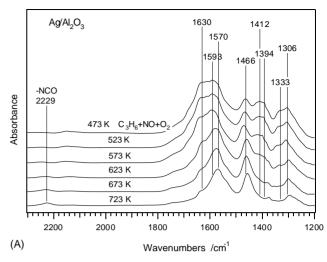


Fig. 3. NO conversion (A) and C_3H_6 conversion (B) for the SCR of NO by C_3H_6 over (\blacksquare) 4 wt.% Ag/Al₂O₃, (\blacktriangle) 10 wt.% Cu/Al₂O₃, (\blacktriangledown) γ -Al₂O₃, (\spadesuit) blank reactor, at various temperatures.

Ag/Al₂O₃ and the 10 wt.% Cu/Al₂O₃ catalysts, which have the best activity for NO reduction in the same series catalysts, respectively.

3.2. In situ steady state DRIFTS

Fig. 4(A) shows the DRIFTS spectra of 4 wt.% Ag/Al₂O₃ catalyst in a flow of NO + C₃H₆ + O₂ at various temperatures (473–723 K) in a steady state. After an exposure of the catalyst to NO + C₃H₆ + O₂ mixture gas for 30 min at 473 K, many bands appeared at 1630, 1593, 1570, 1466, 1412, 1394, 1333 and 1306 cm⁻¹. The strong bands at 1630, 1412 and 1333 cm⁻¹ which were also observed on Ag/Al₂O₃ during the SCR of NO by C₃H₆ and C₂H₅OH in our previous study [25,26], are attributed to enolic species, ν_{as} (RCH=C–O), ν_{s} (RCH=C–O) and δ (C–H), respectively. The bands at 1306 and 1593 cm⁻¹ are assigned to the unidentate (1306 cm⁻¹) and bidentate (1593 cm⁻¹) nitrates species



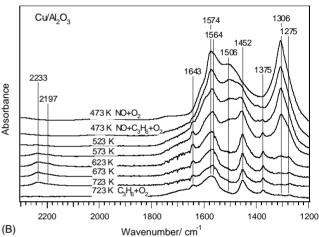


Fig. 4. In situ DRIFTS of the 4 wt.% Ag/Al₂O₃ catalyst (A) and the 10 wt.% Cu/Al₂O₃ catalyst (B) in a flow of 800 ppm NO + 1714 ppm C₃H₆ + 10.0 vol.% O₂/N₂ at various temperatures.

[5,8,17]. The peaks at 1570, 1466 and 1394 cm⁻¹ are assigned to υ_{as} (COO), υ_{s} (COO) and δ (–CH₃) of the adsorbed acetate [6,17–21], respectively. In addition, the weak bands, which could be observed at 2229 cm⁻¹, are assigned to -NCO species [4,5].

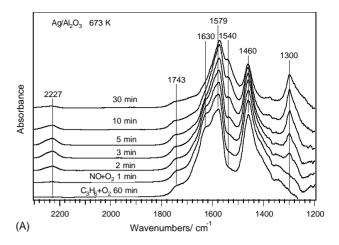
Fig. 4(B) shows the DRIFTS spectra of the $10\,\mathrm{wt.\%}$ Cu/Al₂O₃ catalyst in a flow of NO + C₃H₆ + O₂ at various temperatures (473–723 K) in a steady state, along with the spectrum recorded at 473 K in a flow of NO + O₂ and the spectrum recorded at 723 K in a flow of C₃H₆ + O₂. At 473 K, three strong bands at about 1574, 1506 and $1306\,\mathrm{cm^{-1}}$ were observed on the Cu/Al₂O₃ catalyst. These bands are in good agreement with the bands observed in the flow of NO + O₂, and are assigned to bidentate (1574 cm⁻¹) and unidentate (1506 and $1306\,\mathrm{cm^{-1}}$) nitrates on the Cu/Al₂O₃ [13,17,22,23], respectively. The bands at 1643, 1564, 1452, 1375 and 1275 cm⁻¹ at 723 K are consistent with the bands observed in the flow of C₃H₆ + O₂ at 723 K, so that these bands are the nitrogen-free species and are assigned to v (C=C) (1643 cm⁻¹), v_{as} (COO) (1564 cm⁻¹),

Table 2 Bands observed on Ag/Al_2O_3 and Cu/Al_2O_3 catalysts during DRIFTS experiments and the corresponding surface species and vibrations to which they were assigned

•	C		
Catalyst	Wavenumber (cm ⁻¹)	Species	Vibration
Ag/Al ₂ O ₃	1306 1593	NO ₃ ⁻ species	Unidentate NO ₃ ⁻ Bidentate NO ₃ ⁻
	1333	Enolic species	δ (C–H)
	1412 1630		$v_{\rm s}$ (RCH=C-O ⁻) $v_{\rm as}$ (RCH=C-O ⁻)
	1394	Acetate species	$\dot{\delta}$ (–CH ₃)
	1466		$v_{\rm s}~({\rm COO^-})$
	1570 2229	Isocyanate	υ _{as} (COO ⁻) -NCO
Cu/Al ₂ O ₃	1306, 1506 1574	NO ₃ ⁻ species	Unidentate NO ₃ ⁻ Bidentate NO ₃ ⁻
	1275	Carbonate species	Carbonate species
	1375	Acetate species	δ (–CH ₃)
	1452		$v_{\rm s}$ (COO)
	1564		$v_{\rm as}$ (COO)
	1643	C=C	<i>ὑ</i> (C=C)
	2197	Isocyanate	Cu-NCO
	2233		Al-NCO

 υ_{s} (COO) (1452 cm⁻¹), δ (–CH₃) (1375 cm⁻¹) and carbonate species (1275 cm⁻¹), respectively [13,17,22,23]. Weak bands at 2233 and 2197 cm⁻¹ are assigned to Al-NCO (2233 cm⁻¹) and Cu-NCO (2197 cm⁻¹), respectively [13,22]. From above assignments, it is shown that the nitrate species was a dominant ad-species at low temperature, while the acetate species was a dominant ad-species at high temperature during the SCR of NO by C₃H₆ over the Cu/Al₂O₃. The IR bands and their proposed assignments in Fig. 4(A) and (B) are summarized in Table 2.

Up to now, it has been widely accepted that -NCO species, which can react with NO, O_2 or NO + O_2 to produce N_2 , is one of the important intermediates, and organo-nitro compounds -C_xH_yNO_z (such as R-ONO and R-NO₂) are the precursor of -NCO species [4,5,8,14,24]. However, we did not find any clear feature in our DRIFTS which can be assigned to R-ONO and R-NO2. As shown in Fig. 4(A), surface enolic species (1633, 1412 and 1333 cm⁻¹), acetate species (1466 and $1570 \,\mathrm{cm}^{-1}$) and nitrates species (1593 and 1306 cm⁻¹) co-existed on the 4 wt.% Ag/Al₂O₃ catalyst at 473 K, because next reaction among acetate, enolic species and nitrates species had not occured yet. With increasing the reaction temperature, the intensity of acetate, enolic and nitrates species gradually decreased and almost disappeared at 723 K, accompanying the formation of -NCO species. However, as shown in Fig. 4(B), hardly any enolic species was observed on the Cu/Al₂O₃ catalyst besides a little amount of acetate species (1452 and $564 \,\mathrm{cm}^{-1}$), and $\mathrm{NO_3}^-$ (1574 and 306 cm⁻¹) became the dominant species on the catalyst surface at 473 K. It was shown that C₃H₆ can only be partially oxidized into an acetate species on the Cu/Al₂O₃ catalyst. With increasing the reaction temperature, nitrates species gradually decreased and almost disappeared at 623 K, and



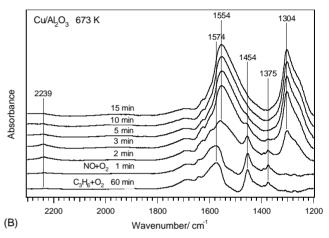


Fig. 5. Dynamic changes of in situ DRIFTS spectra of the 4 wt.% Ag/Al_2O_3 catalyst (A) and the 10 wt.% Cu/Al_2O_3 catalyst (B) as a function of time in a flow of 800 ppm NO + 10.0 vol.% O_2/N_2 at 673 K. Before the measurement, the catalysts were pre-exposed to a flow of 1714 ppm $C_3H_6+10.0$ vol.% O_2/N_2 for 60 min at 673 K.

the acetate species gradually became the dominant species on the catalyst surface. In the following section, we performed the transient reaction to investigate the reactivity of enolic and acetate species towards nitrate species.

3.3. In situ transient DRIFTS

The reactivity of partial oxidized C_3H_6 species on the Ag/Al_2O_3 and the Cu/Al_2O_3 catalysts towards $NO + O_2$ was studied at 673 K which is close to T_{max} for both catalysts. Fig. 5(A) and (B) shows the changes in the DRIFTS spectra as a function of time in a flow of $NO + O_2$ after the Ag/Al_2O_3 and the Cu/Al_2O_3 catalysts were exposed to a flow of $C_3H_6 + O_2$ for 60 min. The bands due to surface acetate (1579 and $1460\,\mathrm{cm}^{-1}$), surface carbonyl (1743 cm⁻¹) and enolic species (1630 cm⁻¹) were observed on the Ag/Al_2O_3 in the flow of $C_3H_6 + O_2$ (Fig. 5(A)). The intensity of enolic and acetate bands at 1630, 1579 and $1460\,\mathrm{cm}^{-1}$ gradually dropped by exposing the Ag/Al_2O_3 to the flow of $NO + O_2$. Simultaneously, the bands at

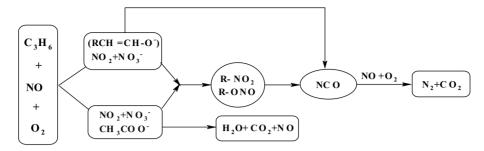


Fig. 6. Reaction scheme of the SCR of NO by C₃H₆ over Ag/Al₂O₃ and Cu/Al₂O₃ catalysts.

2227 cm $^{-1}$ (-NCO), 1540 and 1300 cm $^{-1}$ (nitrate) appeared, but the intensity of -NCO increased within 5 min and then decreased. After the Ag/Al₂O₃ catalyst surface reached a steady state in the flow of NO + O₂ with time up to 30 min, it is found that the enolic band at $1630 \, \mathrm{cm}^{-1}$ disappeared completely, but the acetate (1579 and $1460 \, \mathrm{cm}^{-1}$) and the nitrate (1540 and $1300 \, \mathrm{cm}^{-1}$) coexisted, and the acetate species was still the dominant species on the surface. This suggests that the enolic species participated in the NO reduction via -NCO species, and that the enolic species is a more active intermediate towards NO + O₂ than the acetate on the Ag/Al₂O₃.

The enolic band at 1630 cm⁻¹ was not observed in the DRIFTS spectra when the Cu/Al₂O₃ catalyst was exposed to the flow of $C_3H_6 + O_2$ for 60 min, and only acetate bands were observed at 1574, 1454 and 1375 cm⁻¹ (Fig. 5(B)). After the flowing gas was switched to $NO + O_2$, the intensity of acetate bands steeply dropped and completely disappeared in 5 min. Meanwhile, the nitrate species (1554 and 1304 cm⁻¹) was quickly formed, and became the dominant species on the Cu/Al_2O_3 surface. The band of -NCO (2239 cm⁻¹) also appeared, but it was very weak. Comparing Fig. 5(A) with Fig. 5(B), it is clear that the acetate species on the Cu/Al₂O₃ catalyst is more reactive towards $NO + O_2$ than that on the Ag/Al₂O₃ catalyst, but the surface concentration of -NCO produced on the Cu/Al₂O₃ catalyst was much lower than that on the Ag/Al₂O₃ catalyst. This result suggests that the reaction between NO_x and acetate species on the Cu/Al₂O₃ catalyst did not selectively produce -NCO, but yielded CO₂. According to the analysis above, it is concluded that the C₃H₆ can be directly oxidized into acetate, and the enolic species cannot steadily exist because of the high oxidation activity of the Cu/Al₂O₃ catalyst, which is a reasonable explanation why the Cu/Al₂O₃ has a lower selectivity for NO reduction than the Ag/Al₂O₃.

Fig. 6 gives a simplified reaction scheme for the SCR of NO by C_3H_6 over Cu/Al_2O_3 and Ag/Al_2O_3 catalysts. The main route over Ag/Al_2O_3 catalyst is summarized as follows: NO + C_3H_6 + O_2 \rightarrow CH_3COO^- + RCH=CH–O $^-$ + NO $_2$ (NO $_3^-$) \rightarrow (R–NO $_2$ + R–ONO) \rightarrow NCO + NO + O_2 \rightarrow N $_2$ + CO $_2$. On the other hand, the main route over Cu/Al_2O_3 catalyst is summarized as follows: NO + C_3H_6 + O_2 \rightarrow NO $_2$ (NO $_3^-$) + CH $_3$ COO $^ \rightarrow$ H $_2$ O + CO $_2$ + NO.

4. Conclusions

Both Ag/Al_2O_3 and Cu/Al_2O_3 catalysts showed their highest catalytic activity for the SCR of NO with the highest Ag or Cu loading before the presence of Ag and Cu metal oxide phases on γ - Al_2O_3 . Ag/Al_2O_3 has a higher activity for the SCR of NO by C_3H_6 than Cu/Al_2O_3 . However, Cu/Al_2O_3 has a higher activity for C_3H_6 combustion than Ag/Al_2O_3 . C_3H_6 can be partially oxidized into enolic species and acetate species on the Ag/Al_2O_3 , and the enolic species is a more reactive intermediate for the formation of NCO species via the reaction with $NO + O_2$ than acetate species. However, the C_3H_6 can only be partially oxidized into acetate species and then CO_2 on the Cu/Al_2O_3 catalyst. This is the main reason why the activity of the Cu/Al_2O_3 catalyst for NO reduction is much lower than that of the Ag/Al_2O_3 catalyst.

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References

- M. Iwamoto, in: Proceedings of the Symposium on catalytic Technology for the Removal of nitrogen oxides, Catal. Soc. Jpn (1990) 19;
 - M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u, N. Mizuno, Appl. Catal. 69 (1991) L15.
- [2] W. Held, A. Koenig, T. Richiter, L. Puppe, SAE Paper, 1990 p. 900496.
- [3] T. Miyadera, Appl. Catal. B 2 (1993) 199.
- [4] S. Sumiya, M. Saito, H. He, Q.C. Feng, N. Takezawa, K. Yoshida, Catal. Lett. 50 (1998) 87.
- [5] S. Sumiya, H. He, A. Abe, N. Takezawa, K. Yoshida, J. Chem. Soc., Faraday Trans. 94 (1998) 2217.
- [6] F.C. Meunier, V. Zuzaniuk, J.P. Breen, M. Olsson, J.R.H. Ross, Catal. Today 59 (2000) 287.
- [7] K. Shimizu, J. Shibata, H. Yoshida, A. Satsuma, T. Hattori, Appl. Catal. B 30 (2001) 151.

- [8] S. Kameoka, Y. Ukisu, T. Miyadera, Phys. Chem. Chem. Phys. 2 (2000) 367.
- [9] M. Haneda, Y. Kintaichi, M. Inaba, H. Hamada, Appl. Surf. Sci. 121/122 (1997) 391.
- [10] K.A. Bethke, M.C. Kung, B. Yang, M. Shah, D. Alt, C. Li, H.H. Kung, Catal. Today 26 (1995) 169.
- [11] K. Shimizu, H. Maeshima, A. Satsuma, T. Hattori, Appl. Catal. B 18 (1998) 163.
- [12] T.W. Kim, M.W. Song, H.L. Koh, K.L. Kim, Appl. Catal. A 210 (2001) 35.
- [13] K. Shimizu, H. Kawabata, H. Maeshima, A. Satsuma, T. Hattori, J. Phys. Chem. B 104 (2000) 2885.
- [14] R. Burch, J.P. Breen, F.C. Meunier, Appl. Catal. B 39 (2002) 283.
- [15] H. Hamada, Y. Kintaichi, M. Inaba, M. Tabata, T. Yoshinari, H. Tsuchida, Catal. Today 29 (1996) 53.
- [16] N. Okazaki, S. Tsuda, Y. Shiina, A. Tada, Chem. Lett. 27 (1998)

- [17] K. Shimizu, H. Kawabata, A. Satsuma, T. Hattori, Appl. Catal. B 19 (1998) L87.
- [18] K. Shimizu, A. Satsuma, T. Hattori, Appl. Catal. B 25 (2000) 239.
- [19] F.C. Meunier, J.P. Breen, V. Zuzaniuk, M. Olsson, J.R.H. Ross, J. Catal. 187 (1999) 493.
- [20] K. Shimizu, H. Kawabata, A. Satsuma, T. Hattori, J. Phys. Chem. B 103 (1999) 5240.
- [21] A. Martínez-Arias, M. Fernández-García, A. Iglesias-Juez, J.A. Anderson, J.C. Conesa, J. Soria, Appl. Catal. B 28 (2000) 29.
- [22] J. Shibata, K. Shimizu, A. Satsuma, T. Hattori, Appl. Catal. B 37 (2002) 197.
- [23] K. Shimizu, H. Kawabata, A. Satsuma, T. Hattori, J. Phys. Chem. B 103 (1999) 1542.
- [24] T. Tanaka, T. Okuhara, M. Misono, Appl. Catal. B 4 (1994) L1.
- [25] H. He, J. Wang, Q.C. Feng, Y. Yu, K. Yoshida, Appl. Catal. B 46 (2003) 365.
- [26] Y. Yu, H. He, Q.C. Feng, J. Phys. Chem. B 107 (2003) 13090.