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Selective catalytic reduction of NO_x with C_3H_6 over an Ag/Al_2O_3 catalyst with a small quantity of noble metal

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Abstract

The selective catalytic reduction of NO_x with C_3H_6 (C_3H_6-SCR of NO_x) was carried out in the presence of water vapor over various trace noble metal (Pt, Au and Pd) co-impregnated with Ag/Al_2O_3 catalysts. The Ag–Pd (0.01%)/Al_2O_3 shows a higher NO_x conversion than Ag/Al_2O_3 does, especially at temperatures ranging from 300 to 500 °C. However, the additions of Au and Pt to Ag/Al_2O_3 only resulted in a decrease of activity for the C_3H_6-SCR of NO_x. In situ DRIFTS spectra suggests that the presence of trace Pd (0.01%) catalyzed the formation of an enolic species which was converted from C_3H_6, whereas the presence of Pt and Au did not show this effect. The surface enolic species is very active towards NO_2 and NO_3^-, resulting in the formation of an NCO species which is the key reaction intermediate in the selective catalytic reduction of NO_x.
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Keywords: Ag–Pd/Al_2O_3; Ag–Pt/Al_2O_3; Ag–Au/Al_2O_3; Enolic species; In situ DRIFTS; Catalytic reaction mechanism

1. Introduction

Since Iwamoto [1], Iwamoto et al. [2] and Held et al. [3] first reported that Cu-ZSM-5 is an effective catalyst for the SCR of NO by hydrocarbons in the presence of excess oxygen, the SCR of NO has received much attention as a potential technology for cleaning NO in various oxygen-rich exhausts of diesel, lean burn gasoline and gas engines. In recent studies [4–12], alumina-supported silver catalysts (denoted as Ag/Al_2O_3) which are relatively durable and inexpensive, are considered to be a candidate for practical use. However, NO_x conversion over Ag/Al_2O_3 is quite low at a temperature range of 300–400 °C, which is a major disadvantage considering that the temperature range is especially important for diesel engines exhaust. On the other hand, catalysts based on platinum group metals, such as well-known three-way catalysts, can eliminate NO_x, CO and unburned hydrocarbons altogether in the exhaust of gasoline engines which operate close to stoichiometric conditions. Unfortunately, those catalysts are almost all ineffective for

the selective catalytic reduction of NO_x in the presence of excess oxygen when the temperature is over 400 °C [13,14].

A general method used to improve catalytic performance is the modification of active sites by a dose of a second element. In this case, noble metal is one of the candidates because Obuchi et al. [13] have found that NO is reduced with C_3H_6 at lower temperatures over noble metal catalysts such as Pt/Al_2O_3 and Pd/Al_2O_3. With respect to Ag catalysts, we previously found that the C_3H_6-SCR of NO_x over the Ag/Al_2O_3 catalyst was effectively enhanced below 500 °C even in the presence of water vapor by the addition of trace Pd [15,16]. The positive effect of Pd was also reported by Masuda et al. [17] using Ag–Pd/mordenite. Seker et al. [18] showed a negative effect of Au on Ag/Al_2O_3 for NO_x reduction with C_3H_6. Previous studies [15,17,18] have shown that noble metals of more than 0.1 wt.% added to Ag/Al_2O_3 always resulted in a negative effect, but the mechanism of the additive effect has not been evaluated clearly.

In this paper, we elucidate the additive effect of noble metals (Pt, Au and Pd) at low concentrations (below 0.05 wt.%) on the C_3H_6-SCR of NO_x in the presence of water vapor using co-impregnated Ag–Pt/Al_2O_3, Ag–Au/Al_2O_3 and Ag–Pd/Al_2O_3 catalysts.

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2. Experimental

2.1. Catalyst preparation

The Ag/Al_2O_3 (Ag metal loading: 5 wt.%), $Ag–Pt/Al_2O_3$, $Ag–Pd/Al_2O_3$ and $Ag–Au/Al_2O_3$ catalysts were prepared by an impregnation method. The γ-Al_2O_3 powder (200 m² g⁻¹) was dissolved in an appropriate amount of aqueous solution of $AgNO_3$, followed by the small amount of H_2PtCl_6, $Pd(NO_3)_2$ or $H[AuCl_4]\cdot 4H_2O$, respectively. This was followed by evaporation to dryness in a rotary evaporator at 60 °C under reduced pressure. The resulting paste was dried at 120 °C overnight, and then calcined in air at 600 °C for 3 h. Before catalytic test, the catalysts were seived into 20–40 meshes.

2.2. Catalytic tests

The catalytic test was measured with a fixed-bed quartz flow reactor (10 mm i.d.) by passing a mixture of 800 ppm NO, 1714 ppm C_3H_6, and 10 vol.% O_2 in high pure N_2 at a rate of 4000 cm³ min⁻¹ over 1.2 g catalyst ($W/F = 0.018$ g s cm⁻³, SV: ~50 000 h⁻¹). About 10 vol.% H_2O vapor was supplied with a syringe pump and vaporized by a coiled heater set at the inlet of the reactor. Water was removed from the reactor effluent gas by passing a condenser instrument before reaching online analyzers. After reaching steady state, the effluent gas was analyzed by a chemiluminescence $NO/NO_2/NO_x$ analyzer (42C-HL, Thermo Environmental) for NO_x conversion analyses.

2.3. In situ diffuse reflectance infra-red fourier transform spectroscopy (DRIFTS) procedure

In situ DRIFTS spectra were recorded on a NEXUS 670 (Thermo Nicolet) FT-IR equipped with a smart collector and a MCT/A detector cooled by liquid N_2. The sample for studies (ca. 30 mg) was finely ground and placed in a ceramic crucible. Prior to each experiment, the catalyst was heated in the flow of 10 vol.% $O_2 + N_2$ for 60 min at 300 °C and for another 60 min at 600 °C, then cooled to desired temperature, and a spectrum of the catalyst in the flow of $N_2 + O_2$ serving as the background was recorded. All spectra were measured under real reaction conditions with a resolution of 4 cm⁻¹ and an accumulation of 100 scans.

3. Results and discussion

3.1. NO_x reduction over the co-impregnated Ag catalysts

The C_3H_6-SCR of NO_x was evaluated in a model exhaust gas over the $Ag–Pt/Al_2O_3$, $Ag–Au/Al_2O_3$ and $Ag–Pd/Al_2O_3$ catalysts, and compared with that over the Ag (5.0 wt.%)/Al_2O_3 catalyst.
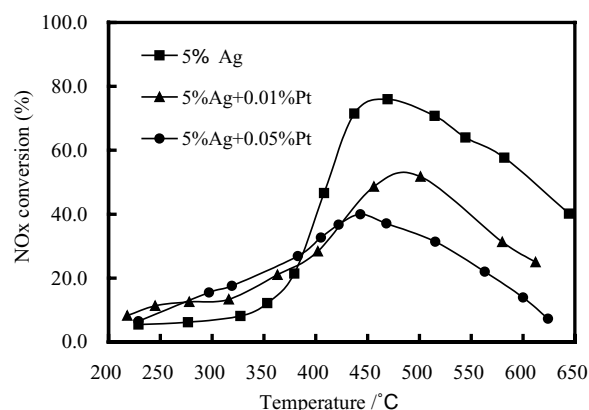

Fig. 1. The catalytic activity for NO_x reduction by C_3H_6 over Ag/Al_2O_3 and $Ag–Pt/Al_2O_3$ catalysts at various temperatures in the presence of water vapor. Reaction conditions: NO, 800 ppm; C_3H_6, 1714 ppm; O_2, 10 vol. %; water vapor, 10 vol. %; $W/F = 0.018$ g s cm⁻³ (GHSV: ~50000 h⁻¹); N_2 balance, total flow rate 4000 ml min⁻¹.

Fig. 1 shows the reduction of NO_x with C_3H_6 over the $Ag–Pt/Al_2O_3$ catalysts and Ag/Al_2O_3 catalyst. The Ag/Al_2O_3 catalyst exhibited high performance in the NO_x reduction, and the highest level of NO_x, 73%, was achieved at 470 °C. Addition of 0.01 wt.% Pt resulted in a little increase of NO_x reduction at 200–400 °C, while the NO_x reduction greatly decreased at 400–600 °C. NO_x reduction was further suppressed with an increase of Pt content.

Fig. 2 shows the reduction of NO_x over the $Ag–Au/Al_2O_3$ catalysts along with that over the Ag/Al_2O_3 catalyst. Addition of 0.01 wt.% of Au to the Ag/Al_2O_3 catalyst also led to the increase of NO_x reduction activity at 220–380 °C. However, when the Au content increased to 0.05 wt.%, NO_x reduction was greatly suppressed at 410–600 °C.

Fig. 3 shows the NO_x reduction activity of Ag/Al_2O_3 and $Ag–Pd/Al_2O_3$ catalysts at various temperatures. Both NO_x conversions increased with the increasing of reaction temperature and reached a maximum at 437 °C for Ag–Pd (0.01 wt.%)/Al_2O_3 and at 470 °C for Ag/Al_2O_3,
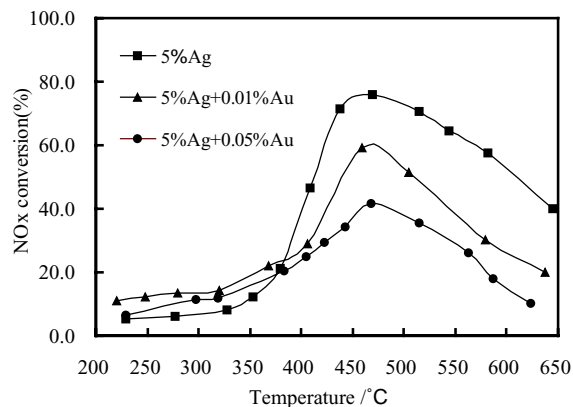

Fig. 2. The catalytic activity for NO_x reduction by C_3H_6 over Ag/Al_2O_3 and $Ag–Au/Al_2O_3$ catalysts at various temperatures in the presence of water vapor. Reaction conditions are the same as those shown in Fig. 1.
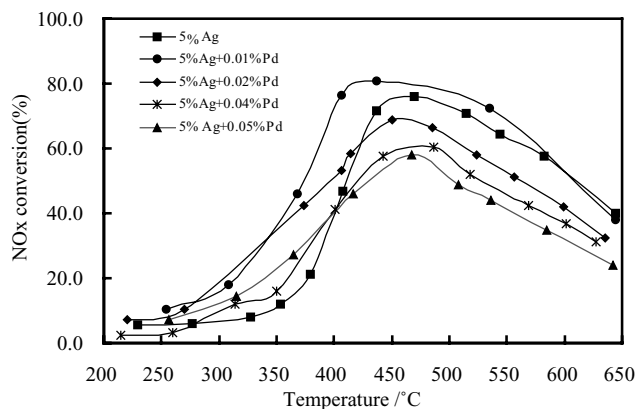
Fig. 3. The catalytic activity for NO_x reduction by C_3H_6 over Ag/Al_2O_3 and $Ag–Pd/Al_2O_3$ catalysts at various temperatures in the presence of water vapor. Reaction conditions are the same as those shown in Fig. 1.

and then decreased with the further increase of reaction temperatures. The highest NO_x conversion was 82% over $Ag–Pd/Al_2O_3$, which is higher than that of the 73% recorded over Ag/Al_2O_3. However, when Pd loading was increased to 0.02 wt.%, 0.04 and 0.05%, NO_x reduction was gradually suppressed at 420–600 °C. Obviously, a trace amount of Pd (0.01 wt.%) added to Ag/Al_2O_3 enhance the NO_x conversion in the presence of excess oxygen and water vapor, while the activity gradually decrease with increase of Pd addition into Ag/Al_2O_3.

These above results show that NO_x reduction over the Ag/Al_2O_3 catalyst is strongly affected by the addition of a small amount of Pt, Au or Pd. The activity of the Ag/Al_2O_3 catalyst for NO_x reduction increases in the presence of a very small amount of Pt, Au or Pd below 400 °C. In particular, the addition of 0.01 wt.% Pd effectively enhanced the NO_x

reduction at 300–500 °C and led to the extension of the temperature window for effective NO_x reduction.

3.2. In situ steady state DRIFTS of the NO_x reduction over co-impregnated Ag catalysts

To directly investigate the effect of noble metals added into Ag/Al_2O_3 under real catalytic reaction conditions, we carried out experiments using in situ DRIFTS. Conditions for in situ DRIFTS were the same as those shown in Fig. 1, except that flow rate decreased to 300 ml min^{-1}. All in situ DRIFTS spectra were recorded in a steady state at various temperatures of 473, 523, 573, 623, 673, 723, and 773 K. After an exposure of the catalyst to $NO+C_3H_6+O_2$ mixture gas for 60 min at 473 K, as shown in Fig. 4, many IR peaks appeared in the region between 1700 and 1300 cm^{-1}. According to the previous literatures [8,19,20], the bands at 1304, 1556, and 1610 cm^{-1} were attributed to bidentate, monodentate, and bridge nitrates, respectively. The bands at 1394 and 1377 cm^{-1} were attributed to $\delta(–CH_3)$ and $\delta(–CH_2)$ of adsorbed acetate [16,21]. The peaks at 1572 and 1466 cm^{-1} were assigned to $\nu_{as}(COO)$ and $\nu_s(COO)$ of the adsorbed acetate [19–24]. When we increased the reaction temperature, as shown in Fig. 4, the band at 1633 cm^{-1} first increased gradually, and then decreased gradually, while weak bands at 2229 and 2146 cm^{-1} could be observed at 523 K. A band at 2229 cm^{-1} was assigned to an isocyanate (–NCO) species, which is a key intermediate species reported by many researchers [9,11,12,14]. The band at 2146 cm^{-1} was assigned to a –CN surface species [8,25]. When temperature was increased to 723 K, the peak at 2229 cm^{-1} reached the strongest intensity. Meanwhile, the peaks at 1633 and 1304 cm^{-1} disappeared gradually. The bands at 1466 and 1572 cm^{-1} were still very strong. From these results we can
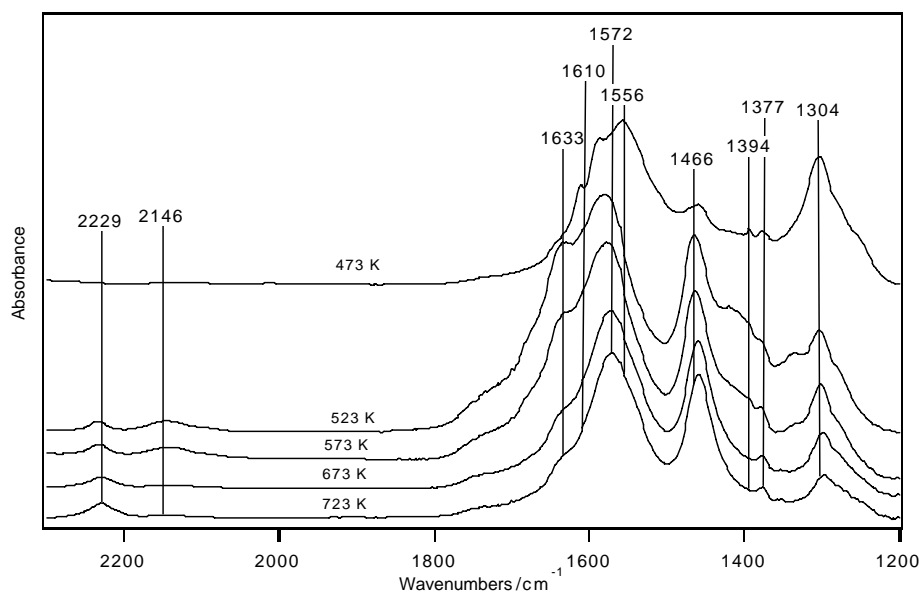

Fig. 4. In situ DRIFTS spectra of 4% Ag/Al_2O_3 in a steady state at various temperatures in a flow of $C_3H_6 + O_2 + NO$. Feed: the composition is the same as those shown Fig. 1, except that flow rate is 300 ml min^{-1}.

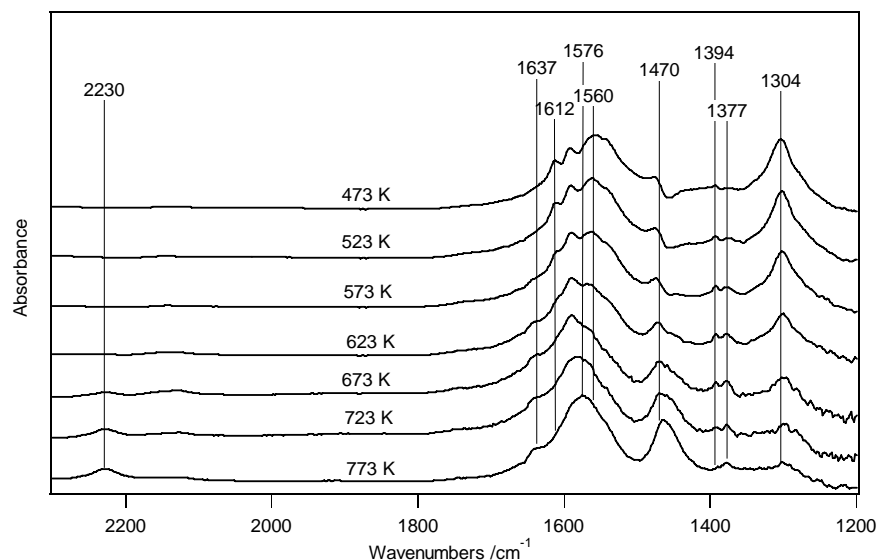Fig. 5. In situ DRIFTS spectra of Ag–Pt(0.01 wt.%)/Al$_2$O$_3$ in a steady state at various temperatures in a flow of C$_3$H$_6$ + O$_2$ + NO. Feed is the same as those shown in Fig. 4.

speculate that the species at 1633 cm^{-1} is very active towards NO$_3^{-1}$ to form key intermediate –NCO, while the activity of acetate is relatively weak. Yu et al. [26] also drew similar results.

Fig. 5 shows the IR spectra of Ag–Pt (0.01%)/Al$_2$O$_3$ catalyst in the flow of NO + C$_3$H$_6$ + O$_2$ in the steady state at various temperatures. Based on a comparison of Figs. 4 and 5, the bands at 1304, 1560 and 1612 cm^{-1} were similarly assigned to bands of adsorbed nitrates. The bands at 1576 and 1470 cm^{-1} were similarly assigned to ν_{as}(COO) and ν_s(COO) of the adsorbed acetate. The bands at 1394 and 1377 cm^{-1} were similarly assigned to δ(–CH$_3$) and δ(–CH$_2$) of adsorbed acetate. The principle difference between Figs. 4 and 5 is the peak on the Ag–Pt/Al$_2$O$_3$ catalyst at 1633 cm^{-1} which had almost disappeared, as well as the decreasing peak at 2231 cm^{-1} that was assigned to the band of a –NCO

in Fig. 4. This species is the key intermediate in the reaction and the intensity of this peak decides reaction rate. Fig. 6 shows the IR spectra of the Ag–Au (0.01%)/Al$_2$O$_3$ catalyst in the flow of NO + C$_3$H$_6$ + O$_2$ in the steady state at various temperatures. The results are quite similar to those shown in Fig. 5. These results are in good agreement with activity tests.

Fig. 7 shows the IR spectra of the Ag–Pd (0.01%)/Al$_2$O$_3$ catalyst in the flow of NO + C$_3$H$_6$ + O$_2$ in the steady state at various temperatures. Based on the comparison between Figs. 7 and 4, the bands at 1300, 1580, and 1614 cm^{-1} which were assigned to adsorbed nitrate could also be observed in Fig. 7. The bands at 1572, 1460 (1460–1475), 1377, and 1394 cm^{-1} were similarly assigned to ν_{as}(COO), ν_s(COO), δ(–CH$_3$), and δ(–CH$_2$) species of the adsorbed acetate, respectively. The biggest difference is the intensity
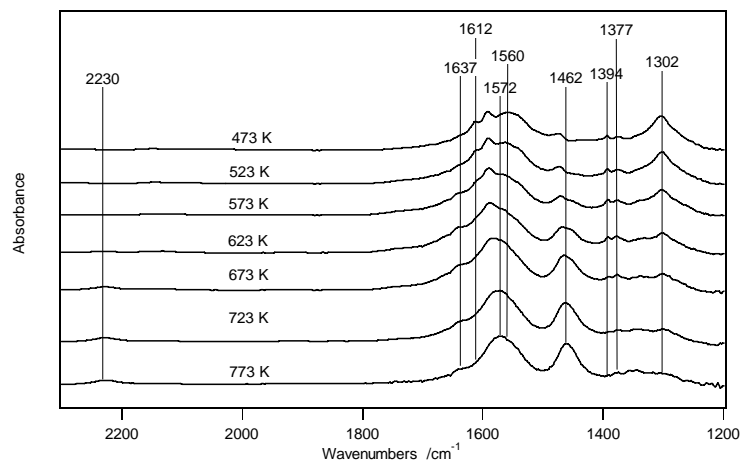

Fig. 6. In situ DRIFTS spectra of Ag–Au(0.01 wt.%)/Al$_2$O$_3$ in a steady state at various temperatures in a flow of C$_3$H$_6$ + O$_2$ + NO. Feed is the same as those shown in Fig. 4.
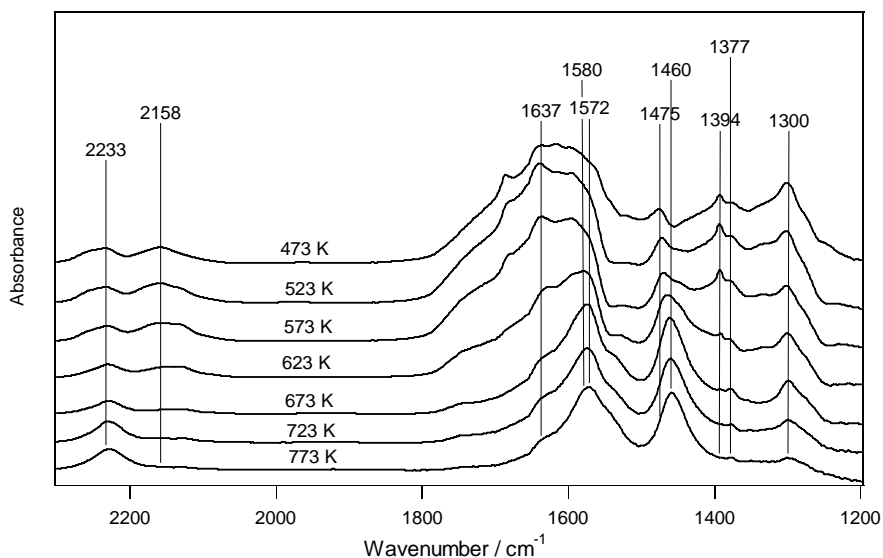
Fig. 7. In situ DRIFTS spectra of Ag–Pd(0.01 wt.%)/Al$_2$O$_3$ in a steady state at various temperatures in a flow of C$_3$H$_6$ + O$_2$ + NO. Feed is the same as those shown in Fig. 4.

of peak at 1637 cm^{-1} on the Ag–Pd/Al$_2$O$_3$ catalyst. According to our previous work [16,26,27], the peak at 1637 cm^{-1} in Fig. 7 can be assigned to a surface enolic structure (H$_2$C=CH–O–M$^+$) which derived from the partial oxidation of C$_3$H$_6$. The conjugation of a H$_2$C=CH–O$^-$ group may induce the vibrational mode of C–C–O to shift to a frequency which is lower than ν(C=C) and higher than ν(C–O) [25]. With increasing temperature, the bands of nitrate (1300 cm^{-1}) and enolic species (1637 cm^{-1}) decreased promptly, while the –NCO band (2233 cm^{-1}) and –CN

band (2158 cm^{-1}) [16] progressively appeared. This indicates that the enolic surface species is very active towards nitrate to form an –NCO species. As a result, Ag–Pd/Al$_2$O$_3$ has a higher –NCO surface concentration than Ag/Al$_2$O$_3$ during the SCR of NO by C$_3$H$_6$. This result is in very good agreement with Ag/Al$_2$O$_3$ and Ag–Pd/Al$_2$O$_3$ activity tests.

Fig. 8 shows the IR spectra of Ag–Pd (0.02%)/Al$_2$O$_3$ catalyst in the flow of NO + C$_3$H$_6$ + O$_2$ in the steady state at various temperatures. Comparing with Fig. 7, Fig. 8 shows the relative low surface concentration of enolic (1639 cm^{-1})
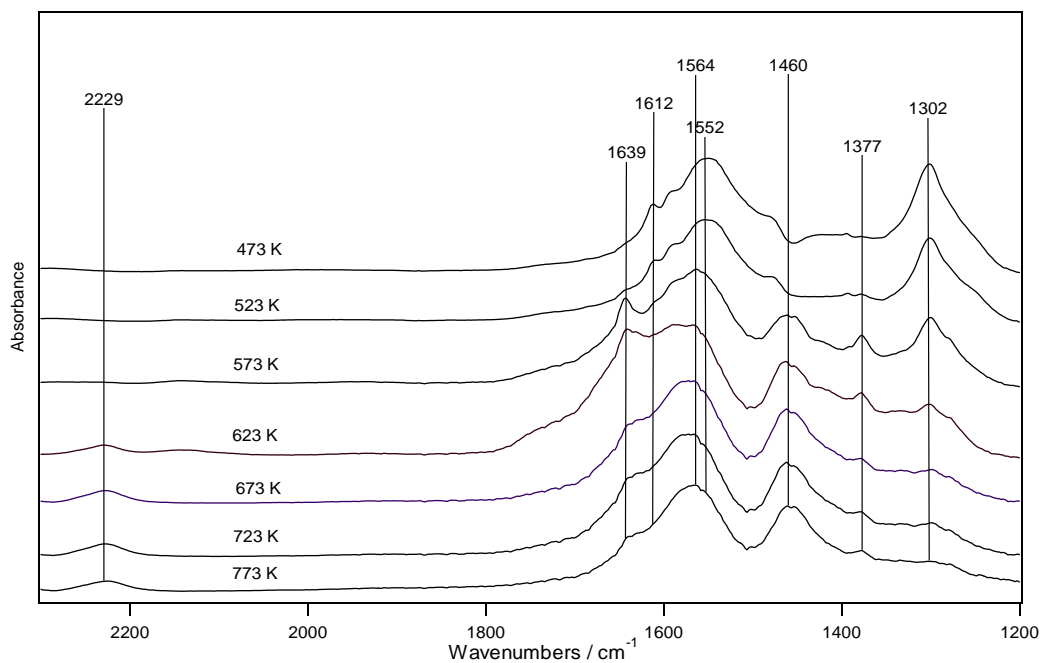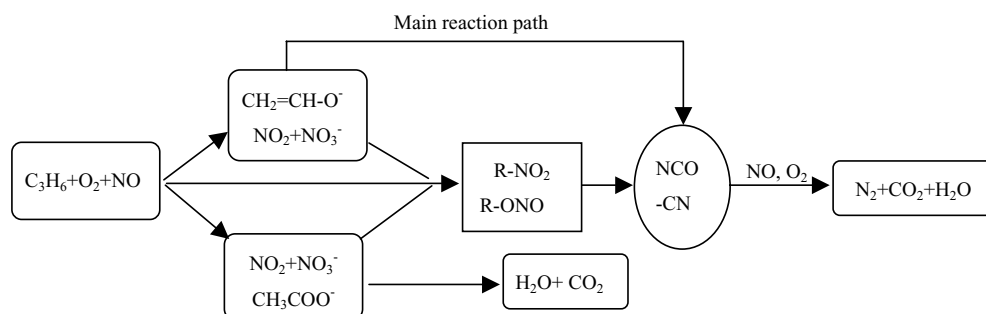

Fig. 8. In situ DRIFTS spectra of Ag–Pd(0.02 wt.%)/Al$_2$O$_3$ in a steady state at various temperatures in a flow of C$_3$H$_6$ + O$_2$ + NO. Feed is the same as those shown in Fig. 4.

Main reaction path

$C_3H_6+O_2+NO$ →

$CH_2=CH-O^-$
$NO_2+NO_3^-$

$NO_2+NO_3^-$
CH_3COO^-

→ R-NO$_2$
R-ONO

→ NCO
-CN

→ NO, O$_2$ → $N_2+CO_2+H_2O$

→ H$_2$O+ CO$_2$

Scheme 1. The proposed reaction mechanism of the SCR-NO$_x$ by C$_3$H$_6$ over Pd promoted Ag/Al$_2$O$_3$.

and NCO species (2229 cm^{-1}). The main species on the catalyst surface are nitrates (1552 and 1302 cm^{-1}) at low temperature ranging from 473 to 573 K and acetate (1564 and 1460 cm^{-1}) at temperatures ranging from 623 to 773 K. Similar results can be achieved over Pd (0.04 and 0.05%) (figures are not shown here). Our activity test results also show that C$_3$H$_6$ light off curve monotonously shift to low temperature with increasing of Pd loading (figures are not shown here). From these results, we can draw the conclusion that the addition of trace amounts of Pd is very sensitive to Ag/Al$_2$O$_3$ catalyst for the SCR of NO$_x$ reaction. The oxidation ability of the catalyst increases with increasing Pd addition into an Ag/Al$_2$O$_3$; much of C$_3$H$_6$ was directly converted into CO$_2$ instead of enolic surface species which can react with NO$_3^-$ to form –NCO species [27]. These above results are in very good agreements with activity results shown in Fig. 3.

3.3. Reaction mechanism on Ag–Pd/Al$_2$O$_3$

The reaction mechanism of the SCR of NO$_x$ by C$_3$H$_6$ over Ag/Al$_2$O$_3$ has been proposed with R–ONO, R–NO$_2$ and –NCO as the key intermediates [8,10,22]. Several intermediates have been proposed to take part in the reduction of NO$_x$, such as inorganic NO$_3^-$ [8,9] and organic CH$_3$COO$^-$ [9,21]. IR spectra have shown that adsorbed nitrates (NO$_3^-$) and acetate (CH$_3$COO$^-$) could react to form organic compound such as R–NO$_2$ [11,12], R–ONO [8,11,12], and –NCO [8,9] during the SCR of NO$_x$ on Al$_2$O$_3$ or Ag/Al$_2$O$_3$ [9,21,22]. Burch et al. [14] proposed a similar reaction mechanism to all oxide catalysts in a review. They described the mechanism approximately as: NO + O$_2$ + C$_3$H$_6$ → NO$_x$ + C$_x$H$_y$O$_z$ → R–NO$_2$ + R–ONO → R–NCO + R–CN + NO + O$_2$ → N$_2$. However, this mechanism cannot sufficiently explain why Pd promoted Ag/Al$_2$O$_3$ has a higher efficiency for the SCR of NO$_x$ over Ag/Al$_2$O$_3$ at low temperatures. Our in situ DRIFTS in Fig. 7 shows that an enolic species is the main intermediate which is derived from partial oxidation of C$_3$H$_6$ at low temperatures and the reaction mechanism is dramatically altered with the addition of a trace quantity of Pd to Ag/Al$_2$O$_3$ (Scheme 1). In the case of Ag–Pd (0.01%)/Al$_2$O$_3$, the band at 1637 cm^{-1} is the main peak at low temperatures. The results indicate that the presence of Pd catalyzes the formation of an eno-

lic species, which is very active towards NO$_2$ and NO$_3^-$ to form –NCO and –CN, and subsequently into N$_2$.

Much additional knowledge will be required before a reliable reaction mechanism can be described. Further studies are underway in order to test some of the hypotheses made in this paper.

4. Conclusion

According to investigate the effect of the addition of different noble metals into Ag/Al$_2$O$_3$, we have developed a novel Ag–Pd (0.01%)/Al$_2$O$_3$ catalyst for NO$_x$ reduction by C$_3$H$_6$ under lean burning conditions. Catalytic tests over Ag–Pd/Al$_2$O$_3$ and contrastive Ag/Al$_2$O$_3$ showed that loading trace amounts of Pd on Ag/Al$_2$O$_3$ leads to a significant improvement of NO$_x$ conversion during the SCR of NO by C$_3$H$_6$, especially at low reaction temperatures. However, the trace addition of Au or Pt into Ag/Al$_2$O$_3$ have negative effect on the SCR of NO$_x$ by C$_3$H$_6$. In situ DRIFTS results suggest that Pd addition catalyzes the partial oxidation of C$_3$H$_6$ into a surface enolic species, and the surface enolic species is quite reactive towards NO$_3^-$ to form a surface NCO species. Based on these results, a new reaction mechanism was proposed with enolic species and NCO species as the key reaction intermediates.

References

[1] M. Iwamoto, in: Proceedings of the Symposium on Catalytic Technology for the Removal of Nitrogen Oxides, Catal. Soc. Jpn. (1990) 19.
[2] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u, N. Mizuno, Appl. Catal. 69 (1991) L15.

[3] W. Held, A. Köenig, T. Richiter, L. Puppe, SAE Paper 900496, 1990.

[4] T. Miyadera, Appl. Catal. B 2 (1993) 199.

[5] K.A. Bethke, H.H. Kung, J. Catal. 172 (1997) 93.

[6] K. Shimizu, H. Maeshuma, A. Satsuma, T. Hattori, Appl. Catal. B 18 (1998) 163.

[7] S. Sumiya, M. Saito, H. He, Q-C. Feng, N. Takezawa, Catal. Lett. 50 (1998) 87.

[8] S. Sumiya, H. He, A. Abe, N. Takezawa, K.J. Yoshida, J. Chem. Soc. Faraday Trans. 94 (1998) 2217.

[9] S. Kameoka, Y. Ukisu, T. Miyadera, Phys. Chem. Chem. Phys. 2 (2000) 367.

[10] F.C. Meunier, V. Zuzaniuk, J.P. Breen, M. Olsson, J.R.H. Ross, Catal. Today 59 (2000) 287.

[11] F.C. Meunier, J.P. Breen, V. Zuzaniuk, M. Olsson, J.R.H. Ross, J. Catal. 187 (1999) 493.

[12] K. Shimizu, A. Satsuma, T. Hattori, Appl. Catal. B 25 (2000) 239.

[13] A. Obuchi, A. Ohi, M. Nakamura, A. Ogata, K. Mizuno, H. Ohuchi, Appl. Catal. B 2 (1993) 71.

[14] R. Burch, J.P. Breen, F.C. Meaner, Appl. Catal. B 39 (2002) 283.

[15] H. He, N. Irite, K. Onai, K. Yoshida, in: Proceedings of the 69th Annual Meeting of Chem. Soc. Jpn., A314.

[16] H. He, J. Wang, Q.C. Feng, Y.B. Yu, K. Yoshida, Appl. Catal. B 46 (2003) 365.

[17] K. Masuda, K. Shinoda, T. Kato, K. Tsujimura, Appl. Catal. B 15 (1998) 29.

[18] E. Seker, J. Cavataio, E. Gulari, P. Lorpongpaiboon, S. Osuwan, Appl. Catal. A 183 (1999) 121.

[19] M. Haneda, Y. Kintaichi, M. Inaba, H. Hamada, Appl. Surf. Sci. 121/122 (1997) 391.

[20] T. Tanaka, T. Okuhara, M. Misono, Appl. Catal. B 4 (1994) L1.

[21] K. Shimizu, J. Shibata, H. Yoshida, A. Satsuma, T. Hattori, Appl. Catal. B 30 (2001) 151.

[22] K. Shimizu, H. Kawabata, A. Satuma, T. Hattori, Appl. Catal. B 19 (1998) L87.

[23] K. Shimizu, A. Satsuma, T. Hattori, Appl. Catal. B 25 (2000) 239.

[24] K. Shimizu, H. Kawabata, H. Maeshima, A. Satuma, T. Hattori, J. Phys. Chem. B 104 (2000) 2885.

[25] Standard IR Spectra, Sadtler Research Labs.

[26] Y.B. Yu, H. He, Q.C. Feng, J. Phys. Chem. B 107 (2003) 13090.

[27] Y.B. Yu, H. He, Q.C. Feng, H.W. Gao, X. Yang, Appl. Catal. B 49 (2004) 159.