

Novel Ag–Pd/Al₂O₃–SiO₂ for lean NO_x reduction by C₃H₆ with high tolerance of SO₂

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Abstract

Activity test and in situ DRIFTS experiments were carried out on the selective catalytic reduction of NO_x by propene over Ag (5 wt%)–Pd (0.01 wt%)/Al₂O₃ and Ag (5 wt%)–Pd (0.01 wt%)/Al₂O₃–SiO₂. The activity test results showed that the Ag–Pd/Al₂O₃–SiO₂ had a higher NO_x conversion than Ag–Pd/Al₂O₃ in the presence of SO₂. The in situ DRIFTS results showed the SO₂ poisoned Ag–Pd (0.01 wt%)/Al₂O₃ surface inhibited the formation of enolic species and NO₃[–], which are reactive intermediates to form –NCO species. However, the SO₂ poisoned Ag–Pd (0.01 wt%)/Al₂O₃–SiO₂ surface can hardly affect the formation of enolic species, NO₃[–] and –NCO species. The reaction mechanism of NO_x reduction and the effect of adding SiO₂ are discussed based on these results. © 2005 Elsevier B.V. All rights reserved.

Keywords: Selective catalytic reduction; Enolic species; In situ DRIFTS; Sulfate

1. Introduction

The selective catalytic reduction (SCR) of NO_x by hydrocarbons in the presence of excess O₂ can be applied to the removal of gaseous pollutants from diesel and lean-burn engines. Various types of zeolites [1], metal oxides and noble metals [2] have been found to catalyze the reaction. Ag/Al₂O₃ is one of the most active alumina-based catalysts for the NO_x reduction with hydrocarbons [3–5]. From a practical point of view, however, its activity is insufficient, especially under actual diesel exhaust gas conditions such as low temperature and the presence of SO₂ [6,7].

Our recent work [8] showed that the addition of 0.01 wt% Pd to 5 wt% Ag catalyst (Ag–Pd (0.01 wt%)/Al₂O₃) greatly increased the SCR of NO_x reaction activity especially at low temperatures. However, the NO_x

conversion over the catalyst decreased quickly in the presence of 80 ppm SO₂.

In this study, we prepared a novel Ag–Pd (0.01 wt%)/Al₂O₃–SiO₂ for the SCR of NO_x by C₃H₆ with high tolerance of SO₂. We made in situ DRIFTS observation of surface species on SO₂ poisoned Ag–Pd/Al₂O₃ and Ag–Pd/Al₂O₃–SiO₂ during the SCR of NO_x by C₃H₆, and attention was focused on the effect of silica additive on the formation of the key surface intermediate on SO₂ poisoned samples.

2. Experimental

2.1. Catalyst preparation

Ag–Pd/Al₂O₃ catalyst was prepared by an impregnation method described in our earlier paper [8]. Ag–Pd/Al₂O₃–SiO₂ was prepared by wet impregnation of silver nitrate and palladium nitrate onto the silica (50 m² g^{–1})

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and γ -alumina ($200 \text{ m}^2 \text{ g}^{-1}$). Prior to impregnation of the metals, 2 wt% silica and γ -alumina powders were finely grounded and then calcined in air at 773 K for 5 h. The $\text{Al}_2\text{O}_3\text{-SiO}_2$ was dissolved in an appropriate amount of aqueous solution of silver nitrate and palladium nitrate, followed by evaporation to dryness in a rotary evaporator at 333 K under reduced pressure. The resulting paste was dried at 393 K overnight, and then calcined in air at 873 K for 3 h. Before catalytic test, the catalysts were sieved into 20–40 meshes. The SO_2 poisoned samples were taken from the used catalyst that had been tested in the presence of 80 ppm SO_2 .

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 , 0 or 80 ppm SO_2 , and 10 vol% O_2 in highly purified N_2 at a rate of $2000 \text{ cm}^3 \text{ min}^{-1}$ over 0.6 g catalyst. ($W/F = 0.018 \text{ g s cm}^{-3}$, $SV: \sim 50,000 \text{ h}^{-1}$). 10 vol% water was supplied through a syringe pump and vaporized by a coiled heater at the inlet of the reactor. Water in the reactor effluent gas was removed by passing a condenser instrument before reaching the on-line analyzers. After the reaction had reached steady state, the effluent gas was analyzed by a chemiluminescence $\text{NO}/\text{NO}_2/\text{NO}_x$ analyzer (42C-HL, Thermo Environmental) for NO_x conversion analysis.

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

In situ diffuse reflectance infra-red fourier transform spectroscopy (DRIFTS) spectra were recorded on a NEXUS 670-FTIR equipped with a smart collector and a MCT/A detector cooled by liquid N_2 . The samples for study (ca. 30 mg) were finely grounded and placed in a ceramic crucible. Prior to each experiment, the catalysts were heated in a flow of 10 vol% $\text{O}_2 + \text{N}_2$ for 60 min at 573 K and another 60 min at 873 K, then cooled to the desired temperature, and a spectrum of the catalyst in the flow of $\text{O}_2 + \text{N}_2$ 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. Influence of SO_2 on catalytic activity

The reduction of NO_x was evaluated in a model exhaust gas over the $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ and $\text{Ag-Pd}/\text{Al}_2\text{O}_3\text{-SiO}_2$ catalysts in the absence or presence of 80 ppm SO_2 as shown in Fig. 1. The results showed that the

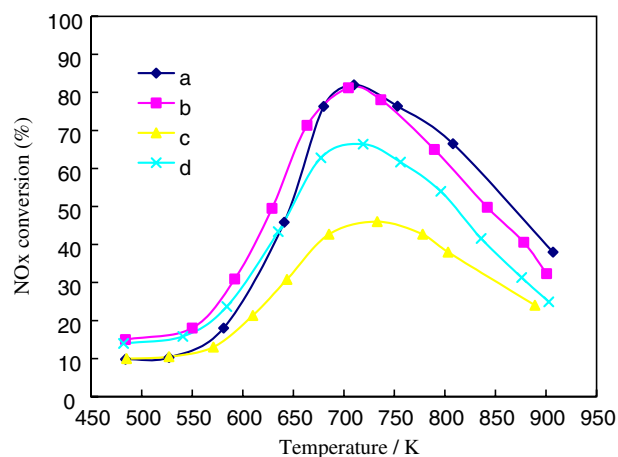


Fig. 1. The effect of SO_2 on the SCR of NO_x by C_3H_6 over $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ and $\text{Ag-Pd}/\text{Al}_2\text{O}_3\text{-SiO}_2$ as a function of temperature. Conditions: NO, 800 ppm; C_3H_6 , 1714 ppm; O_2 , 10 vol%; water vapor, 10 vol%; SO_2 , 0 or 80 ppm; $W/F = 0.018 \text{ g s cm}^{-3}$ (GHSV: $\sim 50,000 \text{ h}^{-1}$), N_2 balance. (a) $\text{Ag-Pd}/\text{Al}_2\text{O}_3$, without SO_2 . (b) $\text{Ag-Pd}/\text{Al}_2\text{O}_3\text{-SiO}_2$, without SO_2 . (c) $\text{Ag-Pd}/\text{Al}_2\text{O}_3$, 80 ppm SO_2 . (d) $\text{Ag-Pd}/\text{Al}_2\text{O}_3\text{-SiO}_2$, 80 ppm SO_2 .

NO_x conversions over $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ increased with the increasing of reaction temperature and reached a maximum at 710 K and then decreased with further increasing of reaction temperature, and the highest NO_x conversion was 82% in the absence of SO_2 . However, when 80 ppm SO_2 was added into the fed gas, the NO_x conversion over $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ rapidly decreased and the highest conversion was only 46% at 733 K. The conversion of NO_x over $\text{Ag-Pd}/\text{Al}_2\text{O}_3\text{-SiO}_2$ was similar to that of $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ in the absence of SO_2 . It was also noted that the highest NO_x conversion over $\text{Ag-Pd}/\text{Al}_2\text{O}_3\text{-SiO}_2$ in the presence of 80 ppm SO_2 was 67% at 720 K, which is higher than 46% of $\text{Ag-Pd}/\text{Al}_2\text{O}_3$. From the four curves in Fig. 1, the two catalysts almost take the same optimum temperature. It means that the activation energy and the function of active sites do not change by adding SiO_2 . In order to make clear the role of the addition of SiO_2 in $\text{Ag-Pd}/\text{Al}_2\text{O}_3\text{-SiO}_2$, the SCR of NO_x by C_3H_6 in the presence of SO_2 over the $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ and $\text{Ag-Pd}/\text{Al}_2\text{O}_3\text{-SiO}_2$ were studied by using the in situ DRIFTS.

3.2. FT-IR studies

3.2.1. In situ steady state DRIFTS over SO_2 poisoned $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ and $\text{Ag-Pd}/\text{Al}_2\text{O}_3\text{-SiO}_2$

Fig. 2(a) shows the in situ DRIFTS spectra of SO_2 poisoned $\text{Ag-Pd}/\text{Al}_2\text{O}_3$ catalyst during the reaction of $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ in the steady state with a temperature range of 473–773 K. Based on our previous studies [8,9], the peaks at 1473, 1572, and 1587 cm^{-1} are associated with adsorbed acetates ($1473, 1572 \text{ cm}^{-1}$) and NO_3^- (1587 cm^{-1}). A negative peak at 1394 cm^{-1} is the evi-

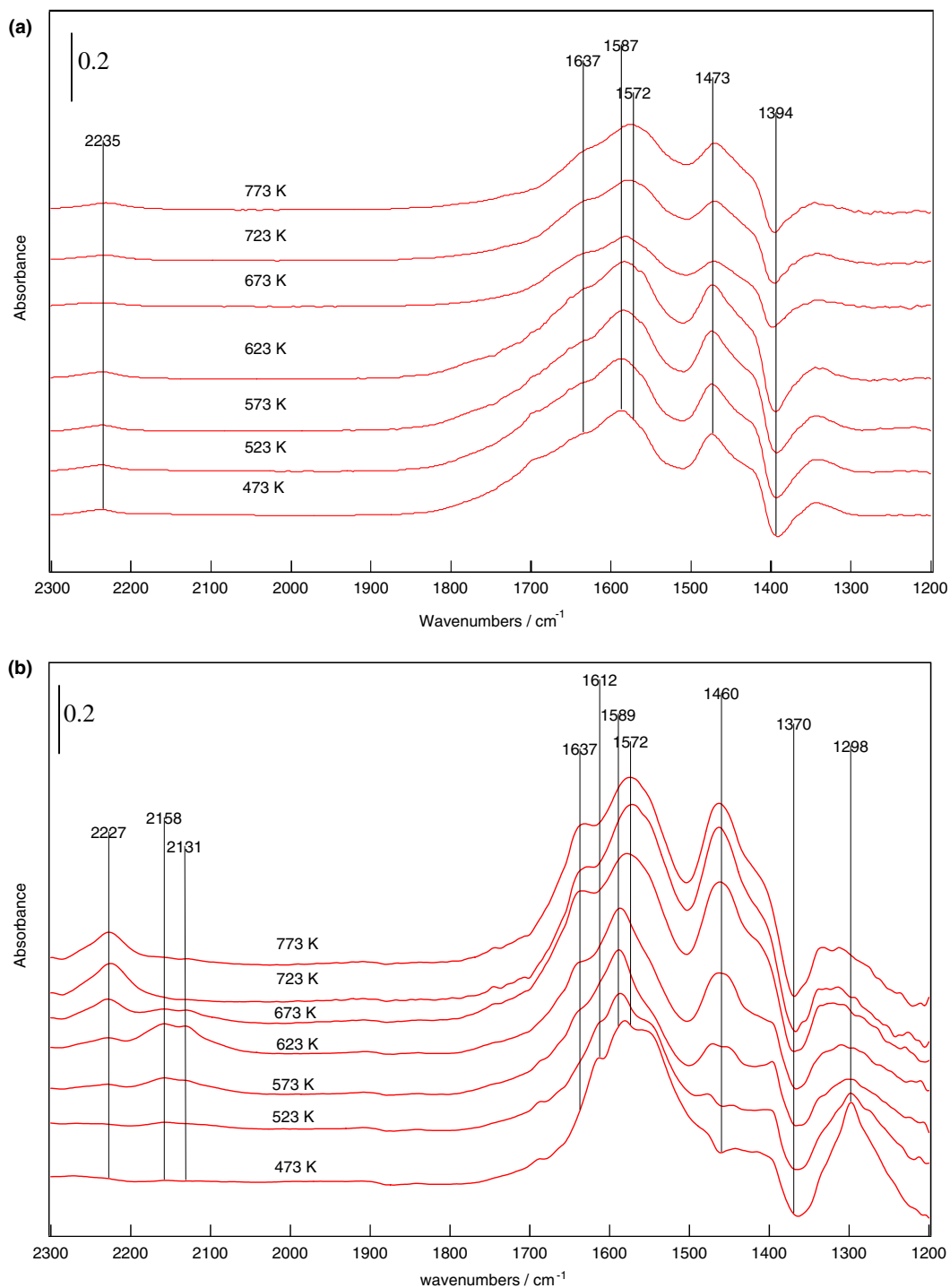


Fig. 2. (a) In situ steady state DRIFTS spectra of SO₂ poisoned Ag-Pd/Al₂O₃ at various temperatures in a flow of C₃H₆ + O₂ + NO. Conditions: NO, 800 ppm; C₃H₆, 1714 ppm; O₂, 10 vol%; N₂ balance. (b) In situ steady state DRIFTS spectra of SO₂ poisoned Ag-Pd/Al₂O₃-SiO₂ at various temperatures in a flow of C₃H₆ + O₂ + NO. Conditions: NO, 800 ppm; C₃H₆, 1714 ppm; O₂, 10 vol%; N₂ balance.

dence of surface sulfate because we used SO₂ poisoned Ag-Pd/Al₂O₃ catalyst as the background. The peak at 1637 cm⁻¹ could be associated with a surface enolic structure (H₂C=CH-O-M) species, which is due to the partial oxidation of C₃H₆ [8,10]. The peak at 2235 cm⁻¹ can be assigned to -NCO surface species

[8,11]. Fig. 2(b) shows the in situ DRIFTS spectra of SO₂ poisoned Ag-Pd/Al₂O₃-SiO₂ catalyst, and the reaction conditions were the same as those shown in Fig. 2(a). The bands in Fig. 2(b) could be similarly assigned to adsorbed acetate (1460, 1572 cm⁻¹), bidentate nitrate (1298, 1589 cm⁻¹) and bridging nitrate (1612 cm⁻¹)

[8,11–13]. However, there are noticeable differences between Fig. 2(a) and (b); that is, we observed higher surface concentrations of NO_3^- , enolic species, $-\text{NCO}$ and $-\text{CN}$ (2131 cm^{-1}) [14] on SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$ catalyst than that on SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3$ catalyst. From Fig. 2(b), we can also observe that the

$-\text{NCO}$ peak appears at temperature higher than 623 K and the NO_x conversion starts to increase from 623 K in Fig. 1. It is well known that there is a correlation between the high efficiency of NO_x reduction by hydrocarbons and the high productivity of a surface $-\text{NCO}$ [2,8,9,13]. In other words, the formation of $-\text{NCO}$ and

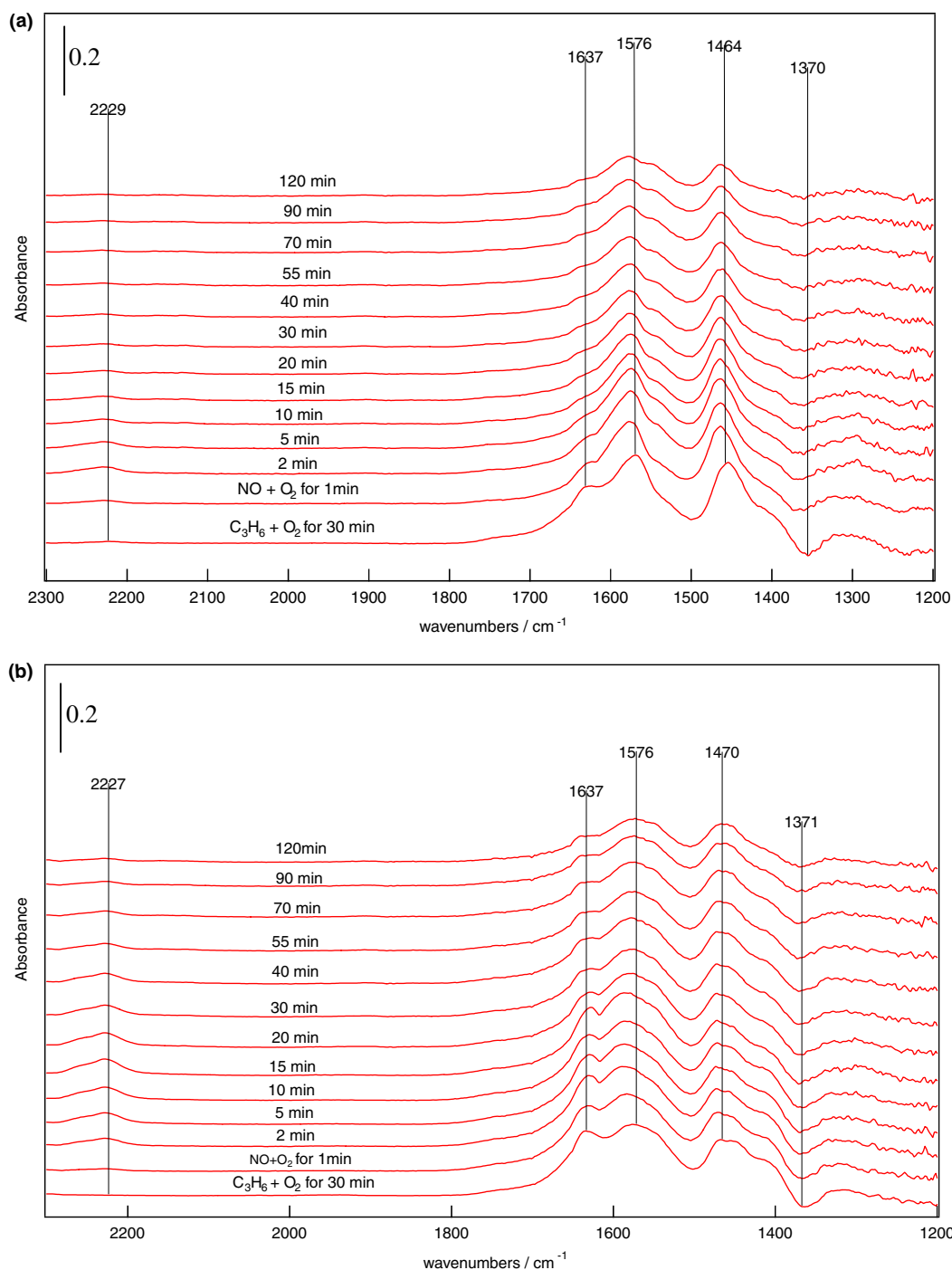


Fig. 3. (a) Dynamic changes of in situ DRIFTS spectra over $\text{Ag-Pd/Al}_2\text{O}_3$ as a function of time in a flow of $\text{NO} + \text{O}_2$ at 673 K. Before the measurement, the catalyst was pre-exposed to a flow of $\text{C}_3\text{H}_6 + \text{O}_2$ for 30 min at 673 K. Conditions: NO , 800 ppm; C_3H_6 , 1714 ppm; O_2 , 10 vol%; N_2 balance. (b) Dynamic changes of in situ DRIFTS spectra over $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$ as a function of time in a flow of $\text{NO} + \text{O}_2$ at 673 K. Before the measurement, the catalyst was pre-exposed to a flow of $\text{C}_3\text{H}_6 + \text{O}_2$ for 30 min at 673 K. Conditions: NO , 800 ppm; C_3H_6 , 1714 ppm; O_2 , 10 vol%; N_2 balance.

–CN species is the rate-determining step in the SCR of NO_x by propene. The adding SiO_2 results in the high surface concentrations of NO_3^- , enolic species and –NCO on the SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$ catalyst, and then the high activity of NO_x reduction.

From a comparison of three kinds of surface species (NO_3^- , enolic species, –NCO) on SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3$ and $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$, it is considered that the sulfate species formed on $\text{Ag-Pd/Al}_2\text{O}_3$ surface inhibits the formation of enolic species and NO_3^- , which can react with each other to form –NCO and –CN species. However, the sulfate species formed on $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$ surface hardly inhibits the formation of enolic and NO_3^- species. Therefore, $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$ is better than $\text{Ag-Pd/Al}_2\text{O}_3$ for the SCR of NO_x by propene.

3.2.2. Dynamic changes of in situ DRIFTS of the NO_x reduction over SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3$ and $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$

The reactivity of the surface enolic species towards $\text{NO} + \text{O}_2$ over SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3$ and $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$ was studied by the transient response of DRIFTS method. Fig. 3(a) and (b) show the in situ DRIFTS spectra of the SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3$ and $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$ in a flow of $\text{NO} + \text{O}_2$ after the catalysts were pre-exposed to a flow of $\text{C}_3\text{H}_6 + \text{O}_2$ for 30 min at 673 K. As can be seen from Fig. 3(a), there were two kinds of species, enolic species (1637 cm^{-1}) and acetate ($1464, 1576\text{ cm}^{-1}$) on the SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3$ after pre-exposing to a flow of $\text{C}_3\text{H}_6 + \text{O}_2$ for 30 min at 673 K. Switching the fed gas from $\text{C}_3\text{H}_6 + \text{O}_2$ to $\text{NO} + \text{O}_2$ led to a slow decrease in the intensity of enolic peaks (1637 cm^{-1}) in 10 min. Simultaneously, the intensity of the –NCO peak (2229 cm^{-1}) slowly increased initially, reached a maximum after 10 min, and then decreased gradually. The similar phenomenon was also observed over the SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$ as shown in Fig. 3(b). More enolic species are formed on the SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$ catalyst compared to that on poisoned $\text{Ag-Pd/Al}_2\text{O}_3$ catalyst by exposing to a flow of $\text{C}_3\text{H}_6 + \text{O}_2$ at 673 K. We found that the peak intensity ratio of enolic species (integrating from 1798 to 1606 cm^{-1}) to acetate species (integrating from 1504 to

1401 cm^{-1}) of the bottom curve is 0.76 in Fig. 3(a), and it is 1.18 in Fig. 3(b). In other words, the formation of enolic species on the SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$ is easier than that on the SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3$ during the $\text{C}_3\text{H}_6 + \text{O}_2$ reaction. The relative high surface concentrations of enolic species and –NCO result in the high activity of SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$.

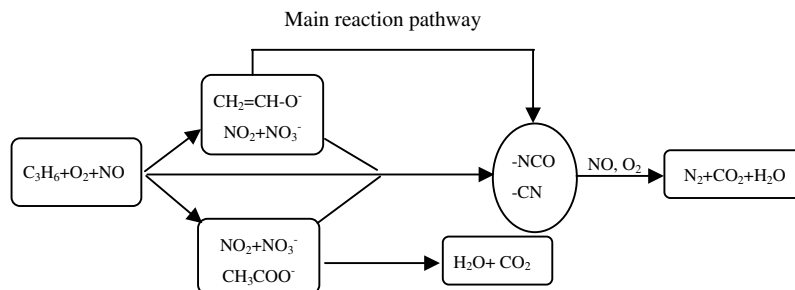
He and coworkers [8] drew a reaction mechanism for the SCR of NO_x by propene over Pd promoted $\text{Ag/Al}_2\text{O}_3$ as shown in Scheme 1. The results obtained in this experiment also support the above mechanism. The adding SiO_2 to $\text{Ag-Pd/Al}_2\text{O}_3$ does not change the activation energy and the function of active sites, but does increase the number of working active sites, which results in high surface concentration of enolic species and –NCO. Based on the above experimental results and discussion, the –NCO formation reaction between the surface enolic species and NO_3^- is considered as the rate determining step in this mechanism.

4. Conclusion

Our work shows that $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$ catalyst is a better catalyst than $\text{Ag-Pd/Al}_2\text{O}_3$ for the SCR of NO_x by C_3H_6 in the presence of SO_2 . The SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3$ surface inhibits the formation of enolic species and NO_3^- . The surface enolic species and NO_3^- can react with each other to form –NCO species, which is the rate determining step. However, the SO_2 poisoned $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$ surface hardly inhibits the formation of enolic and NO_3^- species. Therefore, the addition of SiO_2 into $\text{Ag-Pd/Al}_2\text{O}_3$ promotes the SCR of NO_x by C_3H_6 in the presence of SO_2 . Further studies on surface sulfate on $\text{Ag-Pd/Al}_2\text{O}_3\text{-SiO}_2$ and $\text{Ag-Pd/Al}_2\text{O}_3$ catalysts are in progress and the details are expected in the next paper.

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Scheme 1. Reaction mechanism of SCR- NO_x by C_3H_6 over Pd promoted $\text{Ag/Al}_2\text{O}_3$.

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