Effect of SO_2 on the performance of Ag-Pd/Al_2O_3 for the selective catalytic reduction of NOx with C_2H_5OH

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Abstract: The influence of SO_2 on the performance of Ag-Pd/Al_2O_3 for the selective catalytic reduction (SCR) of NOx with C_2H_5OH was investigated experimentally. The activity test results suggest that Ag-Pd/Al_2O_3 shows a small activity loss in the presence of SO_2 when using C_2H_5OH as a reductant. In situ DRIFTS spectra show that the activity loss originates from the formation of surface sulphate species on the Ag-Pd/Al_2O_3. The surface sulphate species formation inhibits the formation of nitrate, whereas hardly changes the partial oxidation of C_2H_5OH. Compared with the NOx reduction by C_3H_6, an obvious suppression of the surface sulphate species formation was observed by DRIFTS experiment when using C_2H_5OH as a reductant. This phenomenon reveals the better catalytic performance and strong SO_2 tolerance of Ag-Pd/Al_2O_3-C_2H_5OH system.

Keywords: sulphate; SCR; nitrate; enolic species; isocyanate; reaction mechanism

Introduction

The selective catalytic reduction(SCR) of NOx by hydrocarbons has attracted considerable interest as a method to control emissions from stationary sources and vehicles of which the engine operates under oxygen-rich conditions. Many effective catalysts such as various types of zeolites, metal oxides and noble metals have been found to catalyze the reaction. Among them, Ag-promoted alumina catalyst Ag/Al_2O_3 is one of the most active alumina-based catalysts for the NOx reduction with hydrocarbons (Miyadera, 1993; Bethke and Kung, 1997; Sumiya et al., 1998a, b; Meunier et al., 1999; Shimizu et al., 2000b; He and Yu, 2005). However, the low activity of Ag/Al_2O_3 at low temperatures is a major disadvantage. In order to increase the activity at low temperatures, we added trace noble metal to the Ag/Al_2O_3 catalyst, and found that 0.01 wt% Pd added to 5 wt% Ag/Al_2O_3 catalyst (denoted as Ag-Pd/Al_2O_3) greatly increased the NOx conversion during the SCR of NOx by C_3H_6 (He et al., 2003). While the addition of Pd results in an obvious loss of resistibility against SO_2, especially in the low temperature range (Wang et al., 2005). Thus, the SO_2 tolerance of the Ag-Pd/Al_2O_3 catalyst must be taken into account.

As SO_2 usually exists in diesel engine exhaust, the SO_2 tolerance of oxide and base metal catalysts has been widely investigated. An inhibition of the SCR of NOx by SO_2 was observed in essentially all cases, originating from the reaction among SO_2, O_2 and the catalyst surface to form thermodynamically stable sulphate phases under reaction conditions (Meunier and Ross, 2000). The formation of these sulphate species on Ag/Al_2O_3 reduces the surface concentration of strongly bound NOx, by decreasing both the number of adsorption site available to NOx and the oxidation activity of silver site (Burch et al., 1998; Meunier et al., 2000). It is demonstrated that silver sulphate performs well in NOx reduction, thus the formation of some aluminum sulphate phases might be responsible for the activity loss (Park and Boyer, 2005). Based on this prediction, it is reasonable that the SO_2 tolerance of Ag-Pd/Al_2O_3 can be enhanced by modifying the supporter to reduce the adsorption and accumulation of sulphate species, which was also supported by our recent experiments (Wang et al., 2005).

On the other hand, the inhibition extent of the SCR of NOx by SO_2 is dramatically dependent on the nature of the reductant. When using C_2H_5OH as reductant, only a slight decrease in catalytic activity took place over Ag/Al_2O_3 at the experimental temperatures (Sumiya et al., 1998a). As a result, using C_2H_5OH as a reductant may be an alternative to decrease the effect of SO_2 during the NOx reduction over Ag-Pd/Al_2O_3.

Both the partial oxidation of reductant and the formation of nitrates are the important steps during the SCR of NOx (Shimizu et al., 2000a; Satokawa et al., 2001; Burch et al., 2002; Corro et al., 2003; He et al., 2003, 2004; He and Yu, 2005; Yu et al., 2003, 2004; Wang et al., 2004). Meunier et al. reported that the oxidation of NO was suppressed over Ag/Al_2O_3 upon sulfation (Meunier and Ross, 2000). The effect of SO_2 on the conversion of various hydrocarbons such as ethyl acetate, ethanol, propane and propene over Pt/Al_2O_3 and Pt/SiO_2 were investigated by Skoglundh et al. (2001). However, the suppression of SO_2 on the partial oxidation of reductants and the formation of nitrates is still obscure. The aim of the present research was to study the effect of SO_2 on the SCR of

NOx by C_2H_5OH over $Ag-Pd/Al_2O_3$ and to evaluate the reaction mechanism. Considering that the inhibition extent of the SCR of NOx by SO_2 is dramatically dependent on the nature of the reductant and the NOx reduction starts with partial oxidation of reductant, particular attention was focused on the influence of SO_2 on the partial oxidation of C_2H_5OH as well as the formation of nitrates.

1 Experimental

1.1 Catalyst preparation

$Ag-Pd/Al_2O_3$ catalyst was prepared by an impregnation method described in our earlier paper (He et al., 2003; Wang et al., 2004).

1.2 Activity tests

The activity measurements were performed in a fixed-bed quartz flow reactor (10 mm i.d.) with a 0.6 g catalyst in the middle site. A gas mixture containing 800 ppm NO, 1565 ppm C_2H_5OH/1714 ppm C_3H_6, 0 or 80 ppm SO_2, 10% O_2, 10 vol% H_2O and N_2 as a balance gas was fed to a 0.6 g catalyst at the rate of 2000 cm^3/min (W/F=0.018 (g s)/cm^3, SV: ca.50000 h^{-1}). Water and C_2H_5OH were supplied with a syringe pump and vaporized by a coiled heater at the inlet of the reactor. Water in the effluent gas was removed by passing a condenser instrument before the effluent gas reaching the on-line analyzer. After the reaction reached steady state, the effluent gas was analyzed by a chemiluminescence $NO/NO_2/NOx$ analyzer (42C-HL, Thermo Electron USA) for NOx conversion analysis.

1.3 In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) procedure

In situ DRIFTS spectra were recorded on a NEXUS 670-FTIR spectrometer with a smart collector and a MCT/A detector cooled by liquid N_2. The fresh catalysts were pretreated in a flow of 10% O_2+N_2 for 30 min at 573 K and another 30 min at 873 K. The background spectrum was recorded in the flow of 10% O_2+N_2 at various temperatures. In the experiment, spectra were recorded by accumulating 100 scans at a spectral resolution of 4 cm^{-1}. The actual feed compositions used in each of the experiments reported in this paper are shown in the legends of the appropriate figures.

2 Results and discussion

2.1 Catalytic performance of $Ag-Pd/Al_2O_3$

The activity tests of $Ag-Pd/Al_2O_3$ for the SCR of NOx with C_2H_5OH and C_3H_6 were examined as shown in Fig.1. The results show that the NOx conversions over $Ag-Pd/Al_2O_3$ increased with the reaction temperature increasing and reached a maximum, and then decreased with further increasing of reaction temperature. When using C_2H_5OH as the reductant, the highest NOx conversion was 91% in the absence of

SO_2. When 80 ppm SO_2 was added into the feed gas, the $Ag-Pd/Al_2O_3$ still has a good performance for the reduction of NOx with C_2H_5OH, and the highest conversion was 80% at 677 K. However, when using C_3H_6 as the reductant, the NOx conversion drastically decreased, the highest value decreased from 81% at 710 K in the absence of SO_2 to 64% at 778 K in the presence of SO_2. Obviously, the rapid NOx conversion decrease in the presence of SO_2 occurred mainly at the higher temperatures (650—850 K) in $Ag-Pd/Al_2O_3$-C_2H_5OH system, whereas occurred mainly at the lower temperatures (550—750 K) in $Ag-Pd/Al_2O_3$-C_3H_6 system.
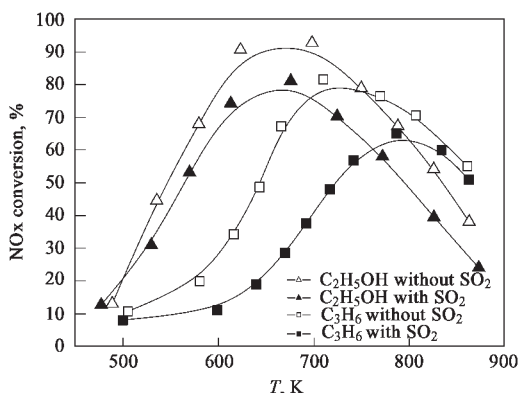

Fig.1 Catalytic activity for the SCR of NOx by C_2H_5OH/C_3H_6 over $Ag-Pd/Al_2O_3$ catalysts at various temperatures
Conditions: NO 800 ppm, C_2H_5OH 1565 ppm/C_3H_6 1714 ppm, O_2 10%, water vapor 10 vol%, SO_2 0 or 80 ppm, W/F = 0.018 (g s)/cm^3 (GHSV: ca. 50000 h^{-1}), N_2 balance

2.2 DRIFTS studies

2.2.1 Formation of sulphate on $Ag-Pd/Al_2O_3$

In order to investigate the behavior of SO_2 on the surface of $Ag-Pd/Al_2O_3$, DRIFTS experiment in the flow of SO_2+O_2 was carried out (Fig.2). After SO_2 was exposed to the catalyst, the band assignable to surface sulphate (1346 cm^{-1}) (Khodayari and Odenbrand, 2001; Watson and Ozkan, 2003 ; Lou and Gorte, 2004) appeared. The band intensity increased with the experiment continuing, and shifted to high frequency. This may be due to the accumulation of sulphate on the surface, which is also in accordance with the results of Datta et al. (1985) and Waqif et al. (1991).

2.2.2 Comparison of in situ DRIFTS spectra on $Ag-Pd/Al_2O_3$ during the SCR of NOx with C_2H_5OH in the presence or absence of SO_2

Fig.3a and b show the in situ DRIFTS spectra of $Ag-Pd/Al_2O_3$ catalyst during the reaction of $C_2H_5OH+NO+O_2+SO_2$ (0 or 80 ppm) with a temperature range of 473—773 K. In the two figures, bands of acetate (1466 and 1578 cm^{-1}), nitrates (1300 and 1585 cm^{-1}) (He et al., 2003; Wang et al., 2004), enolic species $RHC{=}CH{-}O{-}M$ (1338, 1414, 1633 cm^{-1}) (Yu et al., 2003, 2004) and $-NCO$ (2233 cm^{-1}) can be observed. Sulphate species (1338—1373 cm^{-1})
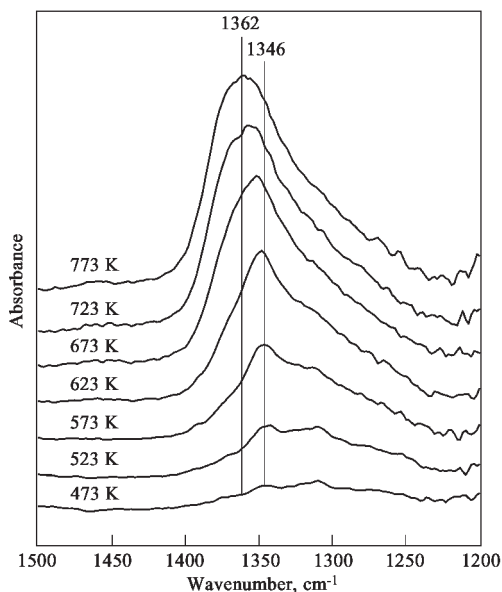
Fig.2 In situ steady state DRIFTS spectra of Ag-Pd/Al₂O₃ at various temperatures in a flow of $SO_2 + O_2$
Conditions: SO_2 80 ppm, O_2 10%, N_2 balance

appeared on the Ag-Pd/Al₂O₃ surface in the presence of SO_2 when the temperature was above 573 K (Fig. 3b). The sulphate peak intensity increased with the experiment continuing. According to the results of activity tests, it is reasonable that the activity loss originates from the formation of sulphate and the effect mainly occurs at higher temperatures (>573 K). In the same experimental condition, no sulphate was detected on the Ag/Al₂O₃ surface (Wu et al., 2006). This is possibly due to the addition of Pd enhancing the formation of sulphate .

2.2.3 Influence of SO_2 on the reaction of $C_2H_5OH/C_3H_6 + O_2$ on the Ag-Pd/Al₂O₃ catalyst

Figs.4a and b show the dynamic changes of in situ DRIFTS spectra of the adsorbed species on Ag-Pd/Al₂O₃ in the flow of $C_2H_5OH/C_3H_6+O_2+SO_2$ at 673 K. In Fig.4a, after the catalyst was exposed to $C_2H_5OH+O_2$ for 30 min, bands of acetate (1578 and 1466 cm⁻¹) and enolic species (1635, 1414 and 1338 cm⁻¹) appeared on the surface of the catalyst. After the introduction of SO_2, the bands of enolic species at 1635 and 1414 cm⁻¹ became relatively weak to those
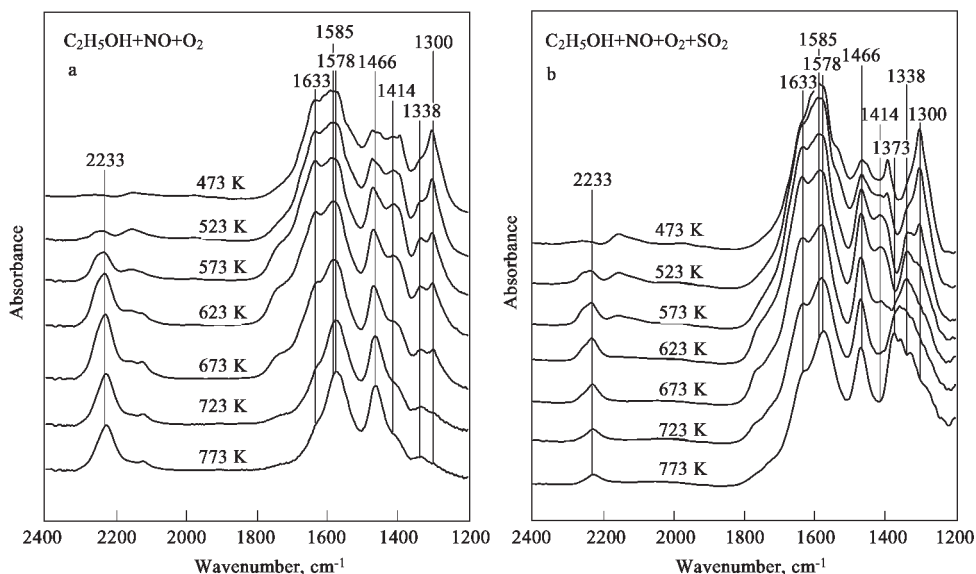

Fig.3 In situ steady state DRIFTS of Ag-Pd/Al₂O₃ at various temperatures in a flow of $C_2H_5OH + O_2 + NO + SO_2$ (0 or 80 ppm)
Conditions: NO 800 ppm, C_2H_5OH 1565 ppm, O_2 10%, N_2 balance

of acetate species at 1578 and 1466 cm⁻¹. The feature of 1338 cm⁻¹ changed because the band of surface sulphate also appears at this site. However, the peaks intensity of enolic species was still very strong even after 100 min which indicates the amount of enolic species on the surface dropped slightly in the presence of SO_2. In Fig.4b, when SO_2 was introduced, the bands of enolic species and acetate species did not change obviously. The above results indicate the effect of SO_2 on the partial oxidation of C_2H_5OH and C_3H_6 was weak. As described above, the inhibition extent of the

SCR of NOx by SO_2 is dramatically dependent on the nature of reductants, however, our results show that the presence of SO_2 hardly affected partial oxidation of different reductants such as C_2H_5OH and C_3H_6.

2.2.4 Influence of SO_2 on the reaction of $NO+O_2$ on Ag-Pd/Al₂O₃ catalyst

The influence of SO_2 on $NO+O_2$ adsorption on Ag-Pd/Al₂O₃ was investigated by DRIFTS as shown in Fig.5. After the catalyst was exposed to $NO+O_2$ for 30 min at 673 K, strong bands assignable to bidentate (1583 and 1300 cm⁻¹) and unidentate (1556 and 1250
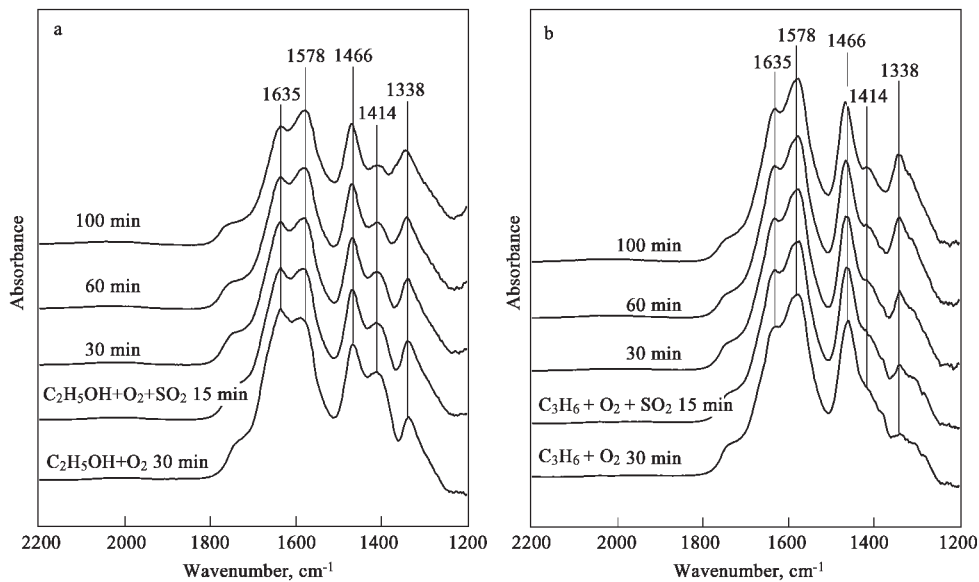
Fig.4 Dynamic changes of in situ DRIFTS spectra of Ag-Pd/Al$_2$O$_3$ as a function of time in a flow of C$_2$H$_5$OH/C$_3$H$_6$+SO$_2$+O$_2$ at 673 K (before the measurement, the catalyst was pre-exposed to a flow of C$_2$H$_5$OH/C$_3$H$_6$+O$_2$ for 30 min at 673 K)

a. C$_2$H$_5$OH partial oxidation; b. C$_3$H$_6$ partial oxidation; conditions: SO$_2$ 80 ppm, C$_2$H$_5$OH 1565 ppm/C$_3$H$_6$ 1714 ppm, O$_2$ 10%, N$_2$ balance
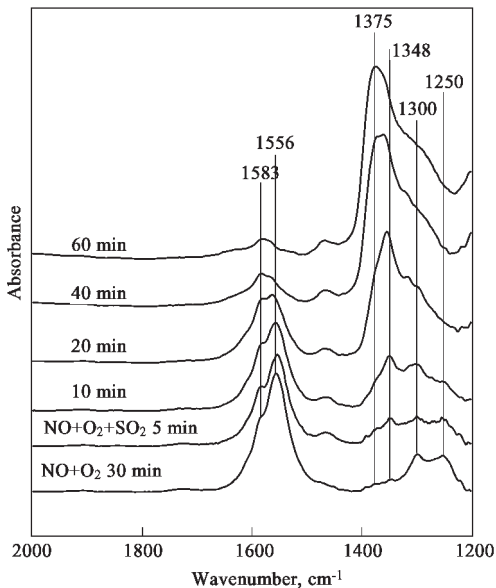

Fig.5 Dynamic changes of in situ DRIFTS spectra of Ag-Pd/Al$_2$O$_3$ as a function of time in a flow of NO + SO$_2$ + O$_2$ at 673 K (before the measurement, the catalyst was pre-exposed to a flow of NO + O$_2$ for 30 min at 673 K)

Conditions: SO$_2$ 80 ppm, NO 800 ppm, O$_2$ 10%, N$_2$ balance

cm^{-1}) nitrates formed (Kameoka et al., 2000; Shimizu et al., 2001). When 80 ppm SO$_2$ was introduced into the feed gas, the band of surface sulphate (1348—1375 cm^{-1}) appeared in 10 min and became strong with the exposure time increasing. Simultaneously, bands of nitrates became weak, and nearly disappeared at 60 min. Nitrate adspecies formed on the catalyst surface is known to play an important role in NOx reduction (Shimizu et al., 1999, 2001; Kameoka et al., 2000). Since reaction of NO+O$_2$ takes

place on basic surface sites of Ag-Pd/Al$_2$O$_3$, sulphate surface species would affect the formation of nitrate on the catalyst surface (Haneda et al., 2001). Therefore, it can be concluded that surface sulphate occupies some active sites, subsequently causes a decrease in the number of sites available for the nitrate species formation, and hence the amount of adsorbed nitrate species.

2.2.5 Dynamic changes of in situ DRIFTS spectra of Ag-Pd/Al$_2$O$_3$ during the SCR of NOx with C$_2$H$_5$OH or C$_3$H$_6$ in the presence of SO$_2$

Figs.6a and b show the in situ DRIFTS spectra of Ag-Pd/Al$_2$O$_3$ in the presence or absence of 80 ppm SO$_2$ after the catalyst was pre-exposed to a flow of NO+C$_2$H$_5$OH/C$_3$H$_6$+O$_2$ for 30 min at 673 K. In the two figures, introducing SO$_2$ to the reaction gas did not lead to obvious decrease in the intensity of enolic and acetate species, whereas led to an observable decrease in the intensity of —NCO and nitrate species (1578 and 1300 cm^{-1}), and nitrate disappeared completely after 20 min. According to the previous result, the formation of nitrate was suppressed once sulphate appeared on the catalyst surface. Subsequently, the formation of —NCO was suppressed. Comparison with the two figures, the sulphate peak increasing was quicker in Fig.6b than Fig.6a. After introducing SO$_2$ for 120 min, the intensity of sulphate band was stronger than that of acetate and became the strongest peak in Fig.6b, whereas it was still weaker than that of acetate in Fig.6a. This means the formation of sulphate is slower in the system of NO+C$_2$H$_5$OH+O$_2$ than in NO+C$_3$H$_6$+O$_2$. After switching the feed gas from NO+C$_2$H$_5$OH+O$_2$+SO$_2$ to NO+C$_2$H$_5$OH+O$_2$, bands of —NCO, enolic species and acetate did not change

The above results show that the effect of gas phase SO_2 on the SCR of NOx with C_2H_5OH was negligible and the sulphate species occupies the same adsorption sites as nitrates and —NCO, once the sulphate appeared on the catalyst surface, the formation of nitrates and —NCO will be inhibited and the suppression is irreversible. The results of Fig.5, Figs.6a and b show that the more the amount of sulphate is on the surface, the greater suppression of sulphate on the formation of nitrate and the SCR of NOx is. Since

more sulphate appeared on the catalyst surface in the presence of C_3H_6 than C_2H_5OH, the NOx conversion decreased more seriously when C_3H_6 as the reductant than C_2H_5OH.

According to our previous work (Sumiya et al., 1998b; He et al., 2003, 2004; He and Yu, 2005; Yu et al., 2004; Wang et al., 2004, 2005) and the results in this work together with the mechanism suggested for the SCR of NOx (Tanaka et al., 1994; Burch et al., 1998; Chafik et al., 1998; Kameoka et al., 2000), a
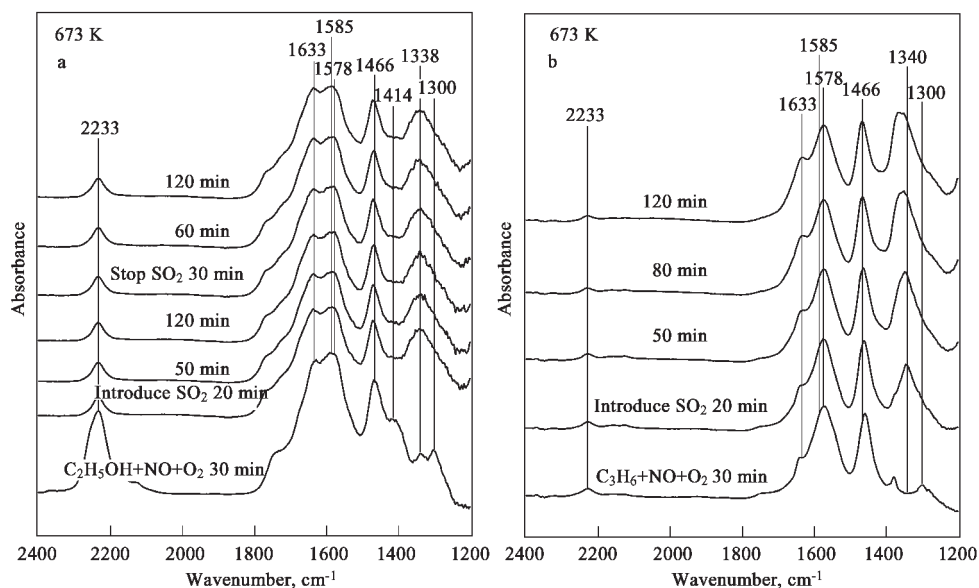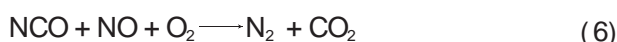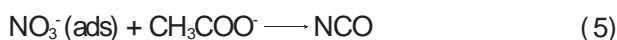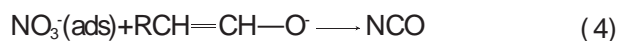

Fig.6　Dynamic changes of in situ DRIFTS spectra of Ag-Pd/Al_2O_3 as a function of time in the presence or absence of 80 ppm SO_2 at 673 K during the SCR of NOx with C_2H_5OH or C_3H_6
Conditions: a. C_2H_5OH 1565 ppm, O_2 10%, NO 800 ppm, N_2 balance; b. C_3H_6 1714 ppm, O_2 10%, NO 800 ppm, N_2 balance

simplified reaction scheme for the NOx reduction by C_2H_5OH/C_3H_6 is shown below.

The main partial oxidation product of C_2H_5OH and C_3H_6 is enolic and acetate, respectively. According to our previous results (Yu et al., 2004; Wu et al., 2005), enolic species has much higher reactivity than acetate in the SCR of NOx. When SO_2 is fed into the

$$NO + O_2 \longrightarrow NO_2 \longrightarrow NO_3^-(ads) \qquad (1)$$

$$C_2H_5OH/C_3H_6 + O_2 \Big\langle \begin{array}{l} RCH\!=\!CH\!-\!O^- \quad (2) \\[2mm] CH_3COO^- \quad\quad\quad (3) \end{array}$$

$$NO_3^-(ads) + RCH\!=\!CH\!-\!O^- \longrightarrow NCO \qquad (4)$$

$$NO_3^-(ads) + CH_3COO^- \longrightarrow NCO \qquad (5)$$

$$NCO + NO + O_2 \longrightarrow N_2 + CO_2 \qquad (6)$$

system of $C_2H_5OH + NO + O_2$, the partial oxidation of C_2H_5OH was not obviously affected and a large amount of enolic species exists on the catalyst surface. Compared with C_2H_5OH, when SO_2 is fed into the

system of C_3H_6 + NO + O_2, the amount of enolic species on the catalyst surface is relatively small and the amount of sulphate is relatively large. As a consequence, Ag-Pd/Al_2O_3-C_2H_5OH system shows a better catalytic performance and strong SO_2 tolerance.

3 Conclusions

The presence of 80 ppm SO_2 induced a slight loss in activity of Ag-Pd/Al_2O_3 for the SCR of NOx with C_2H_5OH. The maximum of NOx conversion decreased from 91% to 80% in the presence of SO_2. The formation of surface sulphate on Ag-Pd/Al_2O_3 was observed by DRIFTS and we presume that Pd site catalyses the SO_2 oxidation and sulphate formation. The in situ DRIFTS results indicated the partial oxidation of C_2H_5OH was hardly affected by the surface sulphate, whereas the formation of nitrates was inhibited. Compared with the NOx reduction by C_3H_6, no obvious suppression effect of the surface sulphate species was observed when using C_2H_5OH as a reductant. These suggest that the proper reductant is beneficial to promote the SO_2 durability of the catalyst in the SCR of NOx.

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