

Effect of SO₂ on the performance of Ag-Pd/Al₂O₃ for the selective catalytic reduction of NO_x with C₂H₅OH

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Abstract: The influence of SO₂ on the performance of Ag-Pd/Al₂O₃ for the selective catalytic reduction (SCR) of NO_x with C₂H₅OH was investigated experimentally. The activity test results suggest that Ag-Pd/Al₂O₃ shows a small activity loss in the presence of SO₂ when using C₂H₅OH as a reductant. *In situ* DRIFTS spectra show that the activity loss originates from the formation of surface sulphate species on the Ag-Pd/Al₂O₃. The surface sulphate species formation inhibits the formation of nitrate, whereas hardly changes the partial oxidation of C₂H₅OH. Compared with the NO_x reduction by C₃H₆, an obvious suppression of the surface sulphate species formation was observed by DRIFTS experiment when using C₂H₅OH as a reductant. This phenomenon reveals the better catalytic performance and strong SO₂ tolerance of Ag-Pd/Al₂O₃-C₂H₅OH system.

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

Introduction

The selective catalytic reduction (SCR) of NO_x 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/Al₂O₃ is one of the most active alumina-based catalysts for the NO_x 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/Al₂O₃ at low temperatures is a major disadvantage. In order to increase the activity at low temperatures, we added trace noble metal to the Ag/Al₂O₃ catalyst, and found that 0.01 wt% Pd added to 5 wt% Ag/Al₂O₃ catalyst (denoted as Ag-Pd/Al₂O₃) greatly increased the NO_x conversion during the SCR of NO_x by C₃H₆ (He *et al.*, 2003). While the addition of Pd results in an obvious loss of resistibility against SO₂, especially in the low temperature range (Wang *et al.*, 2005). Thus, the SO₂ tolerance of the Ag-Pd/Al₂O₃ catalyst must be taken into account.

As SO₂ usually exists in diesel engine exhaust, the SO₂ tolerance of oxide and base metal catalysts has been widely investigated. An inhibition of the SCR of NO_x by SO₂ was observed in essentially all cases, originating from the reaction among SO₂, O₂ 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/Al₂O₃ reduces the surface concentration of strongly bound NO_x, by decreasing both the

number of adsorption site available to NO_x and the oxidation activity of silver site (Burch *et al.*, 1998; Meunier *et al.*, 2000). It is demonstrated that silver sulphate performs well in NO_x 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 SO₂ tolerance of Ag-Pd/Al₂O₃ 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 NO_x by SO₂ is dramatically dependent on the nature of the reductant. When using C₂H₅OH as reductant, only a slight decrease in catalytic activity took place over Ag/Al₂O₃ at the experimental temperatures (Sumiya *et al.*, 1998a). As a result, using C₂H₅OH as a reductant may be an alternative to decrease the effect of SO₂ during the NO_x reduction over Ag-Pd/Al₂O₃.

Both the partial oxidation of reductant and the formation of nitrates are the important steps during the SCR of NO_x (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/Al₂O₃ upon sulfation (Meunier and Ross, 2000). The effect of SO₂ on the conversion of various hydrocarbons such as ethyl acetate, ethanol, propane and propene over Pt/Al₂O₃ and Pt/SiO₂ were investigated by Skoglundh *et al.* (2001). However, the suppression of SO₂ 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 SO₂ on the SCR of

NO_x by C₂H₅OH over Ag-Pd/Al₂O₃ and to evaluate the reaction mechanism. Considering that the inhibition extent of the SCR of NO_x by SO₂ is dramatically dependent on the nature of the reductant and the NO_x reduction starts with partial oxidation of reductant, particular attention was focused on the influence of SO₂ on the partial oxidation of C₂H₅OH as well as the formation of nitrates.

1 Experimental

1.1 Catalyst preparation

Ag-Pd/Al₂O₃ 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 C₂H₅OH/1714 ppm C₃H₆, 0 or 80 ppm SO₂, 10% O₂, 10 vol% H₂O and N₂ as a balance gas was fed to a 0.6 g catalyst at the rate of 2000 cm³/min (W/F=0.018 (g·s)/cm³, SV: ca.50000 h⁻¹). Water and C₂H₅OH 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/NO₂/NO_x analyzer (42C-HL, Thermo Electron USA) for NO_x 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 N₂. The fresh catalysts were pretreated in a flow of 10% O₂+N₂ for 30 min at 573 K and another 30 min at 873 K. The background spectrum was recorded in the flow of 10% O₂+N₂ 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/Al₂O₃

The activity tests of Ag-Pd/Al₂O₃ for the SCR of NO_x with C₂H₅OH and C₃H₆ were examined as shown in Fig.1. The results show that the NO_x conversions over Ag-Pd/Al₂O₃ increased with the reaction temperature increasing and reached a maximum, and then decreased with further increasing of reaction temperature. When using C₂H₅OH as the reductant, the highest NO_x conversion was 91% in the absence of

SO₂. When 80 ppm SO₂ was added into the feed gas, the Ag-Pd/Al₂O₃ still has a good performance for the reduction of NO_x with C₂H₅OH, and the highest conversion was 80% at 677 K. However, when using C₃H₆ as the reductant, the NO_x conversion drastically decreased, the highest value decreased from 81% at 710 K in the absence of SO₂ to 64% at 778 K in the presence of SO₂. Obviously, the rapid NO_x conversion decrease in the presence of SO₂ occurred mainly at the higher temperatures (650—850 K) in Ag-Pd/Al₂O₃-C₂H₅OH system, whereas occurred mainly at the lower temperatures (550—750 K) in Ag-Pd/Al₂O₃-C₃H₆ system.

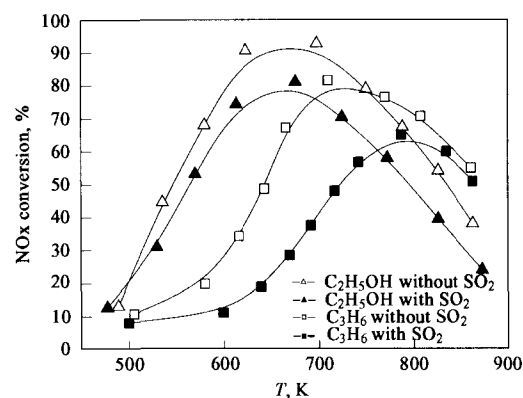


Fig.1 Catalytic activity for the SCR of NO_x by C₂H₅OH/C₃H₆ over Ag-Pd/Al₂O₃ catalysts at various temperatures
Conditions: NO 800 ppm, C₂H₅OH 1565 ppm/C₃H₆ 1714 ppm, O₂ 10%, water vapor 10 vol%, SO₂ 0 or 80 ppm, W/F = 0.018 (g·s)/cm³ (GHSV: ca. 50000 h⁻¹), N₂ balance

2.2 DRIFTS studies

2.2.1 Formation of sulphate on Ag-Pd/Al₂O₃

In order to investigate the behavior of SO₂ on the surface of Ag-Pd/Al₂O₃, DRIFTS experiment in the flow of SO₂+O₂ was carried out (Fig.2). After SO₂ 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/Al₂O₃ during the SCR of NO_x with C₂H₅OH in the presence or absence of SO₂

Fig.3a and b show the *in situ* DRIFTS spectra of Ag-Pd/Al₂O₃ catalyst during the reaction of C₂H₅OH+NO+O₂+SO₂ (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)

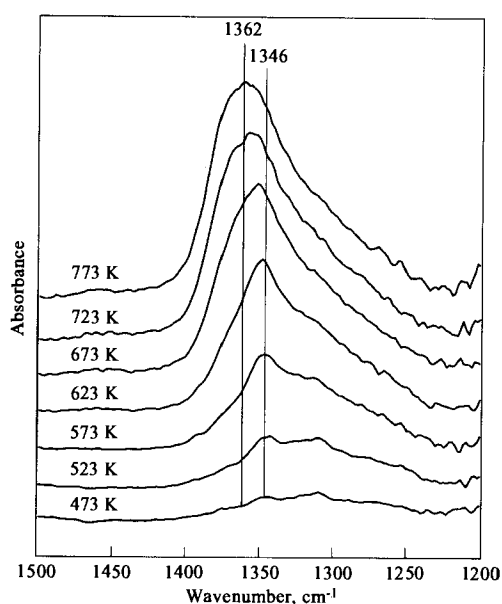


Fig.2 *In situ* steady state DRIFTS spectra of Ag-Pd/Al₂O₃ at various temperatures in a flow of SO₂ + O₂
 Conditions: SO₂ 80 ppm, O₂ 10%, N₂ balance

appeared on the Ag-Pd/Al₂O₃ surface in the presence of SO₂ 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 SO₂ on the reaction of C₂H₅OH/C₃H₆ + O₂ 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 C₂H₅OH/C₃H₆+O₂+SO₂ at 673 K. In Fig.4a, after the catalyst was exposed to C₂H₅OH+O₂ 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 SO₂, the bands of enolic species at 1635 and 1414 cm⁻¹ became relatively weak to those

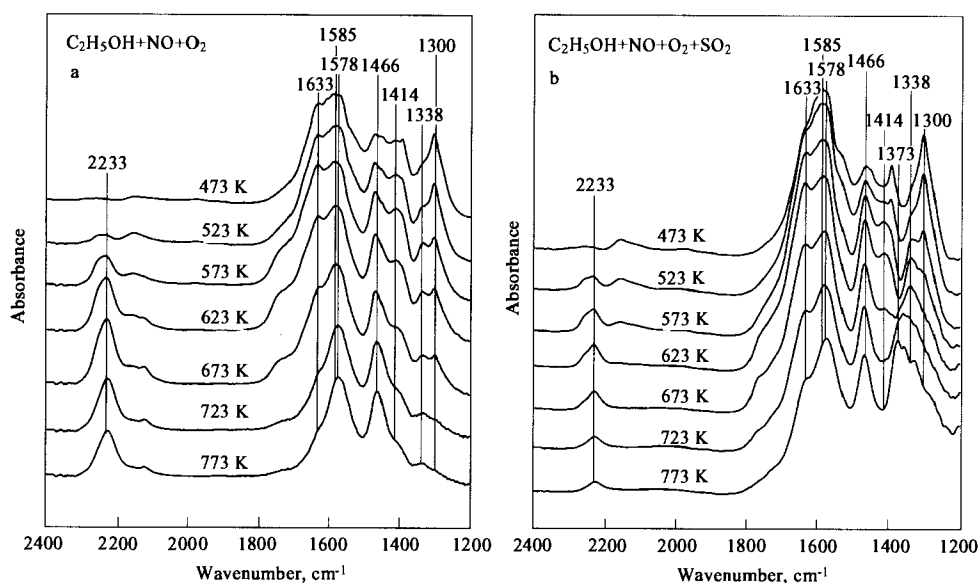


Fig.3 *In situ* steady state DRIFTS of Ag-Pd/Al₂O₃ at various temperatures in a flow of C₂H₅OH + O₂ + NO + SO₂ (0 or 80 ppm)
 Conditions: NO 800 ppm, C₂H₅OH 1565 ppm, O₂ 10%, N₂ balance

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 SO₂. In Fig.4b, when SO₂ was introduced, the bands of enolic species and acetate species did not change obviously. The above results indicate the effect of SO₂ on the partial oxidation of C₂H₅OH and C₃H₆ was weak. As described above, the inhibition extent of the

SCR of NO_x by SO₂ is dramatically dependent on the nature of reductants, however, our results show that the presence of SO₂ hardly affected partial oxidation of different reductants such as C₂H₅OH and C₃H₆.

2.2.4 Influence of SO₂ on the reaction of NO+O₂ on Ag-Pd/Al₂O₃ catalyst

The influence of SO₂ on NO+O₂ adsorption on Ag-Pd/Al₂O₃ was investigated by DRIFTS as shown in Fig.5. After the catalyst was exposed to NO+O₂ for 30 min at 673 K, strong bands assignable to bidentate (1583 and 1300 cm⁻¹) and unidentate (1556 and 1250

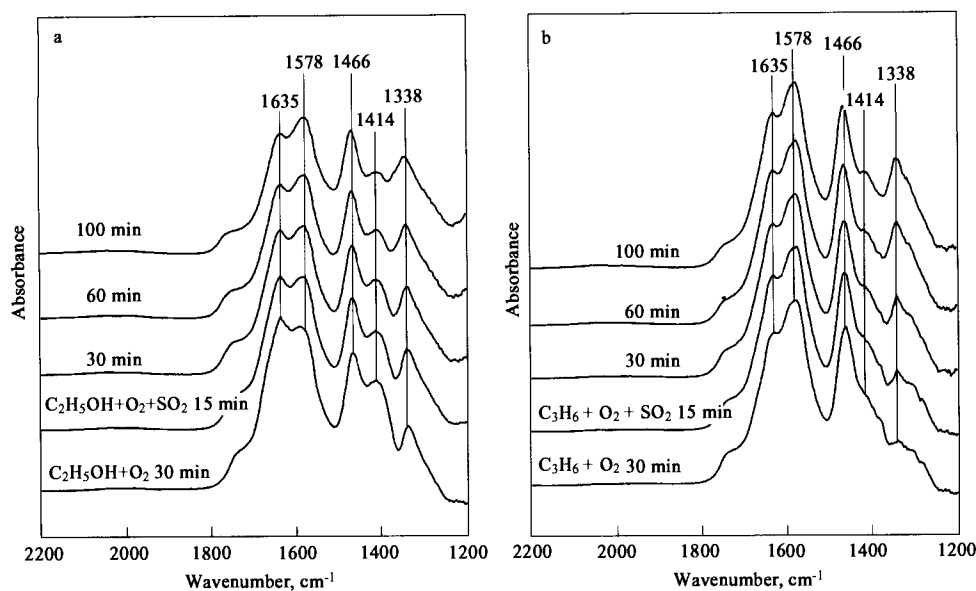


Fig.4 Dynamic changes of *in situ* DRIFTS spectra of Ag-Pd/Al₂O₃ as a function of time in a flow of C₂H₅OH/C₃H₆+SO₂+O₂ at 673 K (before the measurement, the catalyst was pre-exposed to a flow of C₂H₅OH/C₃H₆+O₂ for 30 min at 673 K)

a. C₂H₅OH partial oxidation; b. C₃H₆ partial oxidation; conditions: SO₂ 80 ppm, C₂H₅OH 1565 ppm/C₃H₆ 1714 ppm, O₂ 10%, N₂ balance

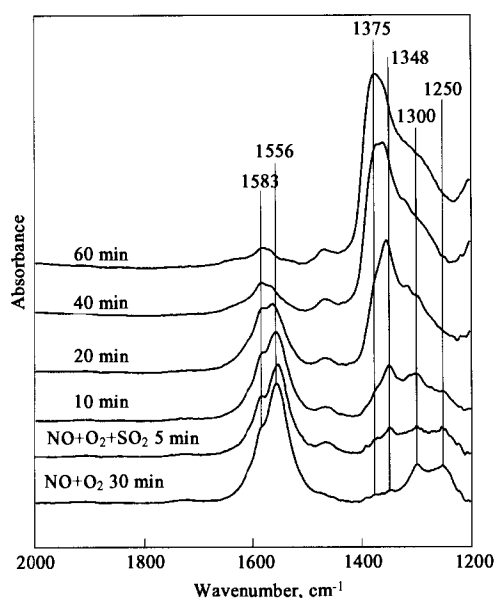


Fig.5 Dynamic changes of *in situ* DRIFTS spectra of Ag-Pd/Al₂O₃ as a function of time in a flow of NO + SO₂ + O₂ at 673 K (before the measurement, the catalyst was pre-exposed to a flow of NO + O₂ for 30 min at 673 K)

Conditions: SO₂ 80 ppm, NO 800 ppm, O₂ 10%, N₂ balance

cm⁻¹) nitrates formed (Kameoka *et al.*, 2000; Shimizu *et al.*, 2001). When 80 ppm SO₂ 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 NO_x reduction (Shimizu *et al.*, 1999, 2001; Kameoka *et al.*, 2000). Since reaction of NO+O₂ takes

place on basic surface sites of Ag-Pd/Al₂O₃, 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/Al₂O₃ during the SCR of NO_x with C₂H₅OH or C₃H₆ in the presence of SO₂

Figs.6a and b show the *in situ* DRIFTS spectra of Ag-Pd/Al₂O₃ in the presence or absence of 80 ppm SO₂ after the catalyst was pre-exposed to a flow of NO+C₂H₅OH/C₃H₆+O₂ for 30 min at 673 K. In the two figures, introducing SO₂ 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 SO₂ 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+C₂H₅OH+O₂ than in NO+C₃H₆+O₂. After switching the feed gas from NO+C₂H₅OH+O₂+SO₂ to NO+C₂H₅OH+O₂, bands of —NCO, enolic species and acetate did not change.

The above results show that the effect of gas phase SO₂ on the SCR of NO_x with C₂H₅OH 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 NO_x is. Since

more sulphate appeared on the catalyst surface in the presence of C₃H₆ than C₂H₅OH, the NO_x conversion decreased more seriously when C₃H₆ as the reductant than C₂H₅OH.

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 NO_x (Tanaka *et al.*, 1994; Burch *et al.*, 1998; Chafik *et al.*, 1998; Kameoka *et al.*, 2000), a

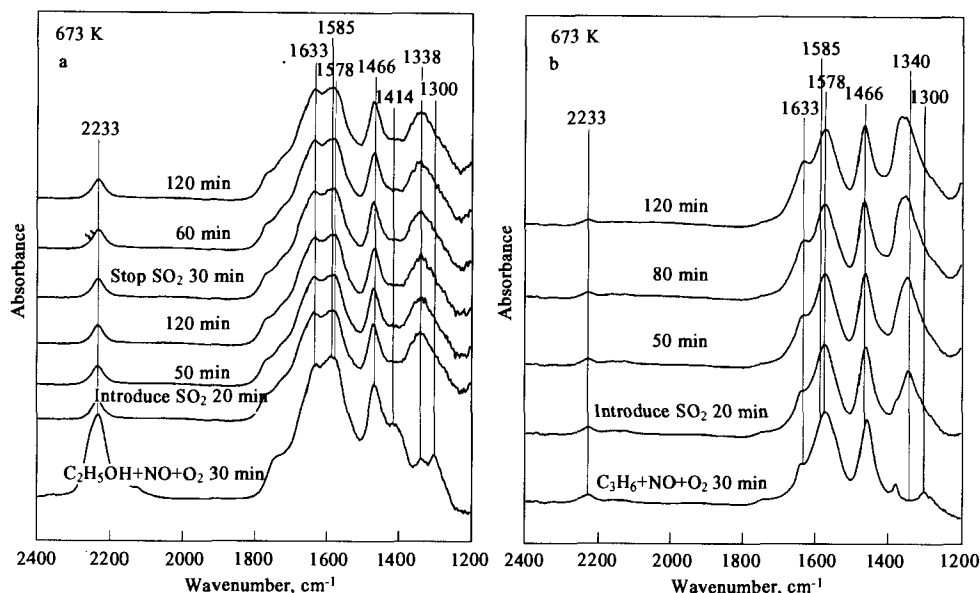
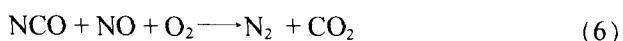
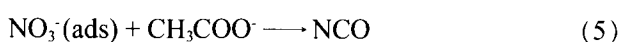
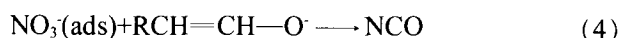
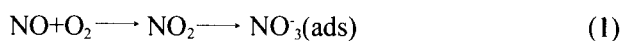


Fig.6 Dynamic changes of *in situ* DRIFTS spectra of Ag-Pd/Al₂O₃ as a function of time in the presence or absence of 80 ppm SO₂ at 673 K during the SCR of NO_x with C₂H₅OH or C₃H₆. Conditions: a. C₂H₅OH 1565 ppm, O₂ 10%, NO 800 ppm, N₂ balance; b. C₃H₆ 1714 ppm, O₂ 10%, NO 800 ppm, N₂ balance

simplified reaction scheme for the NO_x reduction by C₂H₅OH/C₃H₆ is shown below.

The main partial oxidation product of C₂H₅OH and C₃H₆ 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 NO_x. When SO₂ is fed into the



system of C₂H₅OH+NO+O₂, the partial oxidation of C₂H₅OH was not obviously affected and a large amount of enolic species exists on the catalyst surface. Compared with C₂H₅OH, when SO₂ is fed into the

system of C₃H₆ + NO + O₂, 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/Al₂O₃-C₂H₅OH system shows a better catalytic performance and strong SO₂ tolerance.

3 Conclusions

The presence of 80 ppm SO₂ induced a slight loss in activity of Ag-Pd/Al₂O₃ for the SCR of NO_x with C₂H₅OH. The maximum of NO_x conversion decreased from 91% to 80% in the presence of SO₂. The formation of surface sulphate on Ag-Pd/Al₂O₃ was observed by DRIFTS and we presume that Pd site catalyses the SO₂ oxidation and sulphate formation. The *in situ* DRIFTS results indicated the partial oxidation of C₂H₅OH was hardly affected by the surface sulphate, whereas the formation of nitrates was inhibited. Compared with the NO_x reduction by C₃H₆, no obvious suppression effect of the surface sulphate species was observed when using C₂H₅OH as a reductant. These suggest that the proper reductant is beneficial to promote the SO₂ durability of the catalyst in the SCR of NO_x.

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