

Study on Effect of SO₂ on the Selective Catalytic Reduction of NO_x with Propene over Ag/Al₂O₃ by in Situ DRIFTS

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Abstract: In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to investigate the effect of SO₂ on the selective catalytic reduction (SCR) of NO_x by C₃H₆ over an Ag/Al₂O₃ catalyst. The DRIFTS spectra showed an obvious blue shift in the band of sulfate species when its coverage over Ag/Al₂O₃ was increased. The sulfate species not only inhibited the formation of NO₃⁻, but also suppressed the reaction of the enolic species or acetate species with NO₃⁻ to form -NCO species. These behaviors are responsible for the deactivation of Ag/Al₂O₃ during the SCR of NO_x by C₃H₆ in the presence of SO₂.

Key Words: silver; alumina; nitrogen oxide; sulfur dioxide; propene; selective catalytic reduction; in situ diffuse reflectance infrared Fourier transform spectroscopy; sulfate species

It is well known that air pollution by nitrogen oxides (NO_x) emitted from mobile and stationary sources is a serious environmental problem because of the formation of acid rain and photochemical smog. Recently, Ag/Al₂O₃ has been found to be a promising catalyst for the selective catalytic reduction (SCR) of NO_x by ethanol even in the presence of SO₂ [1–5]. However, an ethanol feeding system is needed, which results in additional cost and limits its application. In addition, the use of ethanol results in emission of small amounts of unburned hydrocarbons in the exhaust gases. To overcome these problems, hydrocarbons were used as reductants for the SCR of NO_x over Ag/Al₂O₃ [6–9]. Previous studies have shown that Ag/Al₂O₃ is usually deactivated in the presence of SO₂ during the SCR of NO_x by C₃H₆ [1,7]. Since typical automobile exhausts contain small amounts of SO₂, the study of the effect of SO₂ on the SCR activity is very important for development of the catalyst and its application.

Up to now, the majority of investigations on the subject have focused on elucidating the effect of SO₂ on the SCR of NO_x, most of which deal with characterization of the sulfated catalyst and SO₂ poisoning mechanism. However, few fundamental studies have been published on the accumulation of the sulfate species on the catalyst and its influence on the key intermediates of the SCR of NO_x. We have proposed the

mechanism for the SCR of NO_x by C₃H₆ over Ag/Al₂O₃ [10]. It has been shown that the reaction starts with the formation of both adsorbed NO₃⁻ via NO oxidation by O₂ and enolic species (RCH=CH-O⁻) or acetate species (CH₃COO⁻) via partial oxidation of C₃H₆ over Ag/Al₂O₃. Then, the reaction between NO₃⁻ and the enolic or acetate species, directly or via organo-nitrogen compounds, leads to the formation of isocyanate species (-NCO). Subsequently, the -NCO species reacts with NO + O₂ to yield N₂. It was shown that the formation of the -NCO species is the rate-determining step.

In this paper, we report the effect of SO₂ on the formation of NO₃⁻, acetate species, enolic species, and isocyanate species, which are the key intermediates of the SCR of NO_x, by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). A deactivation mechanism of Ag/Al₂O₃ for the SCR of NO_x by C₃H₆ in the presence of SO₂ is proposed.

1 Experimental

1.1 Catalyst preparation and activity measurements

Catalyst 4% Ag/Al₂O₃ was prepared by an impregnation method described in our earlier papers [4,8]. The catalytic activity test was carried out in a fixed-bed quartz reactor (10

Received date: 2005-10-10.

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Foundation item: Supported by the National Natural Science Fund for Distinguished Young Scholars (20425722).

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mm i.d.). The feed contained 0.08% NO, 0.1714% C₃H₆, 0 or 0.008% SO₂, 10% O₂, and balance N₂. The total flow rate was 2 L/min, and GHSV was 50000 h⁻¹. NO_x concentration was analyzed online by a chemiluminescent NO/NO₂/NO_x analyzer (42C-HL, Thermo Electron).

1.2 DRIFTS analysis

In situ DRIFTS spectra were recorded on a Nicolet NEXUS 670 FT-IR instrument equipped with a smart collector and an MCT/A detector. A 0.03 g catalyst was placed in a ceramic crucible. Prior to each experiment, the catalyst was heated to 873 K in a flow of 10% O₂/N₂ for 60 min, and then cooled to a desired temperature. A spectrum of the catalyst in the flow of 10% O₂/N₂ was taken as the background. The overall gas flow rate was 300 ml/min. All the spectra were measured at a resolution of 4 cm⁻¹ with an accumulation of 100 scans.

2 Results and discussion

2.1 Effect of SO₂ on the catalytic activity of Ag/Al₂O₃

The effect of SO₂ addition on the SCR of NO over Ag/Al₂O₃ was monitored as a function of time on stream at 673 and 723 K. As indicated in Fig. 1, in the absence of SO₂, a steady-state NO conversion of 92.2% at 673 K was obtained in the first 2 h. Addition of 0.008% SO₂ to the feed, however, resulted in a significant decrease in NO conversion to a constant value of 12.6% in about 4 h. A similar decrease in the SCR activity occurred upon addition of 0.008% SO₂ to the feed gas at 723 K, but the activity decline stopped at 62.4% of NO conversion. These results demonstrate that SO₂ considerably deactivates the SCR activity of Ag/Al₂O₃ at these temperatures when C₃H₆ is used as a reductant. It is shown that

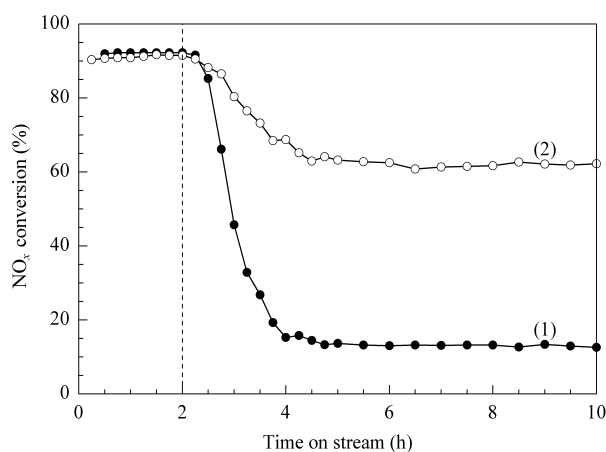


Fig. 1 Effect of SO₂ on the catalytic activity of Ag/Al₂O₃ at 673 K (1) and 723 K (2)
(Reaction conditions: 0.08% NO, 0.1714% C₃H₆, 0.008% SO₂, 10% O₂, N₂ as balance. SO₂ was introduced into the feed after reaction for 2 h.)

reaction temperature plays a very important role in NO reduction in the presence of SO₂. The lower the reaction temperature, the greater the negative effect of SO₂.

2.2 DRIFTS characterization

2.2.1 Formation of sulfate species over Ag/Al₂O₃

As no notable difference in XRD spectra (not shown) was found between the fresh and the sulfated Ag/Al₂O₃ samples, in situ DRIFTS was used to analyze the nature of the sulfate species on Ag/Al₂O₃.

Fig. 2 shows the DRIFTS spectra of the catalyst after exposing it to a flow of SO₂ + O₂ at different temperatures. Two weak bands appeared at 1346 and 1313 cm⁻¹ at 473 K after feeding SO₂ + O₂ for 30 min. On the basis of the previous literature [7], the band at 1346 cm⁻¹ was assigned to a surface sulfate species linked to Al sites, whereas the band at 1313 cm⁻¹ was attributed to similar surface sulfate species that are linked either solely or partly to Ag sites. At higher temperatures, a weak band at 1178 cm⁻¹ became visible, which could be assigned to a bulk-like sulfate species [11]. However, our study using in situ DRIFTS and density functional theory calculations has given new assignments for the two peaks, and the peaks at 1346 and 1178 cm⁻¹ were attributed to asymmetric and symmetric stretching vibrations of (OSO) in bidentate sulfate species on Ag/Al₂O₃, respectively. As shown in Fig. 2,

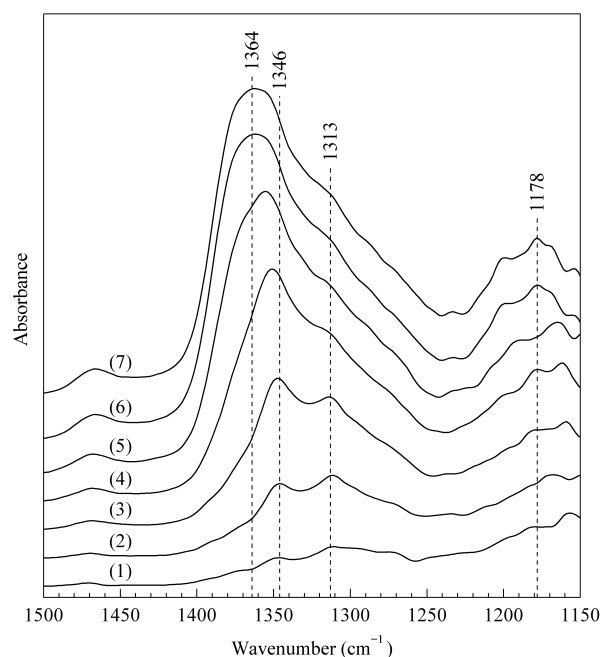


Fig. 2 DRIFTS spectra of Ag/Al₂O₃ in a flow of SO₂ + O₂ at various temperatures
(1) 473 K, (2) 523 K, (3) 573 K, (4) 623 K, (5) 673 K, (6) 723 K, (7) 773 K
(Reaction conditions: 0.008% SO₂, 10% O₂, N₂ as balance, reaction time 30 min.)

the band at 1346 cm^{-1} became predominant above 523 K, and its intensity increased with exposure time and reaction temperature, accompanied by the increase in intensity of another band at 1178 cm^{-1} . In addition, a band shift from 1346 to 1364 cm^{-1} of the sulfate species was observed and this might be caused by the accumulation of sulfate species by the reaction of $\text{SO}_2 + \text{O}_2$ with $\text{Ag}/\text{Al}_2\text{O}_3$.

Fig. 3 shows the DRIFTS spectra of $\text{Ag}/\text{Al}_2\text{O}_3$ as a function of exposure time in a flow of $\text{SO}_2 + \text{O}_2$ at 723 K. Similarly, the characteristic bands of the sulfate species mentioned above (Fig. 2) also appeared after feeding $\text{SO}_2 + \text{O}_2$ for 10 min, and the sulfate species band also underwent a blue shift (from 1346 to 1362 cm^{-1}) with increasing coverage of the surface sulfate species on $\text{Ag}/\text{Al}_2\text{O}_3$. Apparently, the blue shift resulted from the increasing coverage of surface sulfate species on $\text{Ag}/\text{Al}_2\text{O}_3$. In addition, the band at 1313 cm^{-1} , which was assignable to Ag_2SO_4 , showed little variation with the exposure time. This could be attributed to the low Ag loading (4%) of the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst, which allowed only a small amount of Ag_2SO_4 to be formed during the reaction of $\text{SO}_2 + \text{O}_2$ with $\text{Ag}/\text{Al}_2\text{O}_3$.

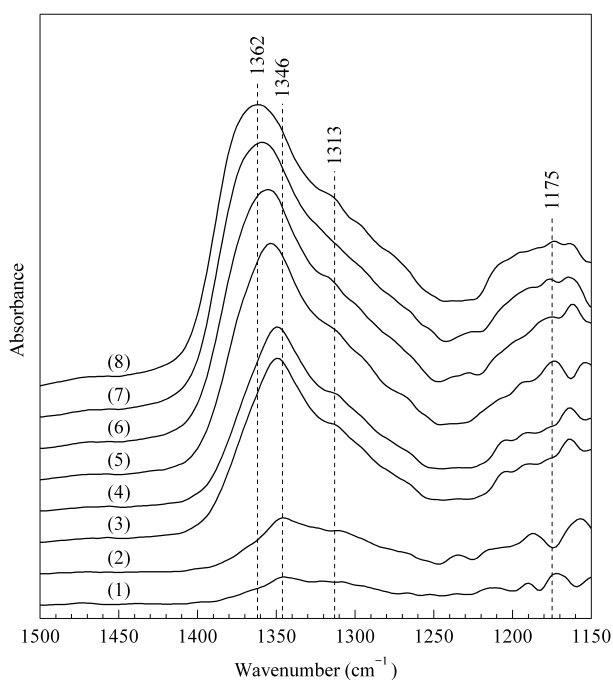


Fig. 3 Changes of DRIFTS spectra of $\text{Ag}/\text{Al}_2\text{O}_3$ with time in a flow of $\text{SO}_2 + \text{O}_2$ at 723 K
(1) 5 min, (2) 7 min, (3) 10 min, (4) 20 min, (5) 30 min,
(6) 40 min, (7) 50 min, (8) 60 min
(Reaction conditions: 0.008% SO_2 , 10% O_2 , N_2 as balance.)

2.2.2 Effect of SO_2 on SCR of NO_x by C_3H_6

The DRIFTS spectra of $\text{Ag}/\text{Al}_2\text{O}_3$ in the absence of SO_2 in a flow of $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$ at various temperatures (holding at each temperature for 30 min so as to get a steady reaction

state) are presented in Fig. 4(a). According to the previous studies [12,13], the bands at 1572 and 1464 cm^{-1} were assigned to the acetate species, the bands at 1302 , 1587 , and 1612 cm^{-1} were due to the adsorbed nitrates, the bands at 1392 and 1379 cm^{-1} were associated with $\delta(\text{C-H})$, and the band at 1639 cm^{-1} was assigned to the surface enolic species derived from the partial oxidation of C_3H_6 over $\text{Ag}/\text{Al}_2\text{O}_3$. In addition, the band at 2229 cm^{-1} was associated with the $-\text{NCO}$ species. It has been widely accepted that the enolic species reacts quickly with nitrates to give rise to $-\text{NCO}$ species, and the $-\text{NCO}$ species is a crucial intermediate during the SCR of NO_x over $\text{Ag}/\text{Al}_2\text{O}_3$, and its high productivity results in a high efficiency in NO_x reduction.

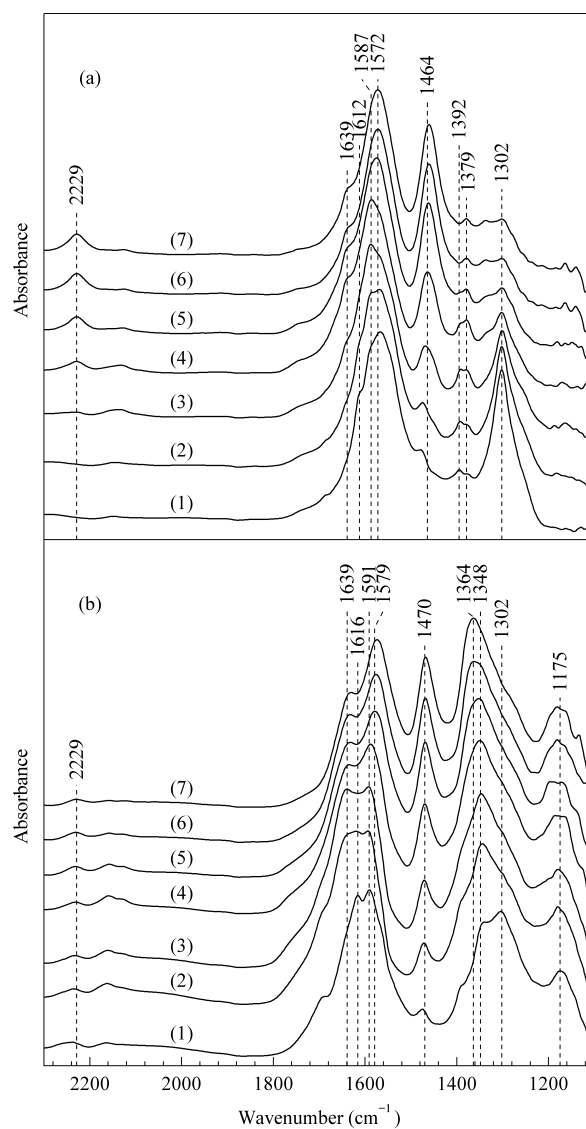


Fig. 4 DRIFTS spectra of $\text{Ag}/\text{Al}_2\text{O}_3$ under different conditions
(a) In the absence of SO_2 , (b) In the presence of 0.008% SO_2
(1) 473 K, (2) 523 K, (3) 573 K, (4) 623 K,
(5) 673 K, (6) 723 K, (7) 773 K
(Reaction conditions: 0.08% NO , 0.1714% C_3H_6 ,
10% O_2 , N_2 as balance.)

Fig. 4(b) shows the DRIFTS spectra of Ag/Al₂O₃ in a flow of NO + C₃H₆ + O₂ with 0.008% SO₂ at different temperatures for 30 min. Compared with Fig. 4(a), there was a new broad band at 1348 cm⁻¹, its intensity increased with the exposure time, and its position shifted gradually to 1364 cm⁻¹. The band at 1175 cm⁻¹ also increased with the exposure time. Meanwhile, the intensities of the nitrate band at 1302 cm⁻¹ and the -NCO band at 2229 cm⁻¹ also decreased promptly in the presence of SO₂ in the feed, while other bands showed little changes. Apparently, the sulfate species inhibited the formation of NO₃⁻ and consequently reduced its reaction with the enolic species or acetate species to form -NCO species, which led to a corresponding decrease in the SCR activity.

To further investigate the effect of SO₂ on Ag/Al₂O₃ in the flow of NO + C₃H₆ + O₂, an additional in situ DRIFTS experiment was conducted at 723 K. The reaction was initially carried out in a flow of NO + C₃H₆ + O₂ to a steady state and maintained for a total of 60 min, then 0.008% SO₂ was introduced into the feed. The bottom two spectra in Fig. 5 were obtained under a SO₂-free flow and the other spectra were obtained in the presence of 0.008% SO₂ with different reaction time. It can be seen that a new band appeared at 1342 cm⁻¹ upon introduction of SO₂. It shifted to 1362 cm⁻¹ and its

intensity increased gradually with increasing time on stream. A band at 1178 cm⁻¹ showed a similar trend. These behaviors were consistent with those in Fig. 4(b). On the contrary, the nitrate band at 1300 cm⁻¹ and -NCO species band at 2229 cm⁻¹ decreased promptly with increasing time on stream, whereas other bands remained almost unchanged. These results suggested that the formation of sulfate species on Ag/Al₂O₃ not only inhibited the formation of NO₃⁻, but also suppressed the reactions of enolic species or acetate species with NO₃⁻ to form -NCO species. This should be responsible for the poor activity of Ag/Al₂O₃ for the SCR of NO_x by C₃H₆ in the presence of SO₂.

2.2.3 Effect of SO₂ on partial oxidation of C₃H₆

To elucidate the effect of SO₂ on the SCR of NO_x by C₃H₆ over Ag/Al₂O₃ in more detail, we investigated the effect of SO₂ on the partial oxidation of C₃H₆ over the catalyst. The results are shown in Fig. 6. After exposing Ag/Al₂O₃ to C₃H₆ + O₂ for 60 min at 723 K, very strong acetate bands (1579 and 1466 cm⁻¹) and enolic species bands (1633, 1412, and 1336 cm⁻¹) appeared. The addition of 0.008% SO₂ in the feed for 30 min resulted in the appearance of a new surface sulfate spe-

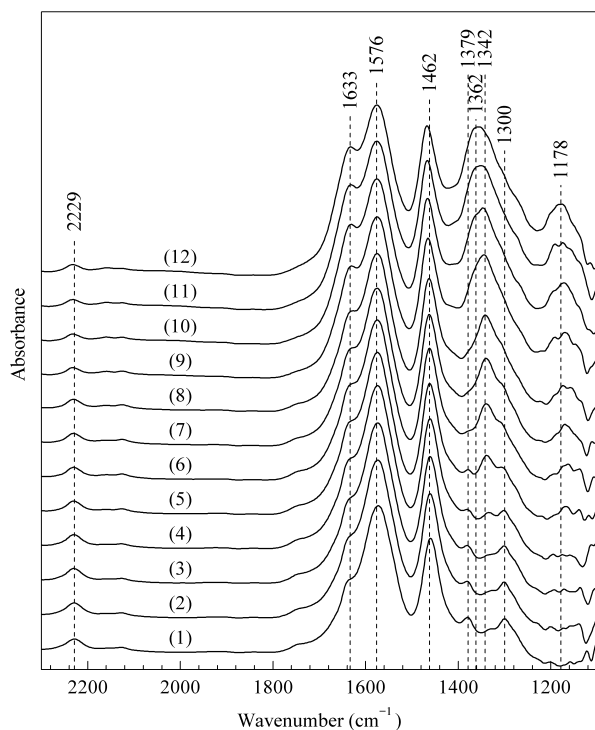


Fig. 5 DRIFTS spectra of Ag/Al₂O₃ in a flow of NO + C₃H₆ + O₂ before and after adding 0.008% SO₂ at 723 K

(1) No SO₂ for 30 min; (2) No SO₂ for 60 min;
(3)–(12) Adding SO₂ for 5 min, 10 min, 15 min, 20 min, 25 min, 30 min, 60 min, 90 min, 120 min, and 150 min, respectively
(Reaction conditions: 0.08% NO, 0.1714% C₃H₆, 10% O₂, N₂ as balance.)

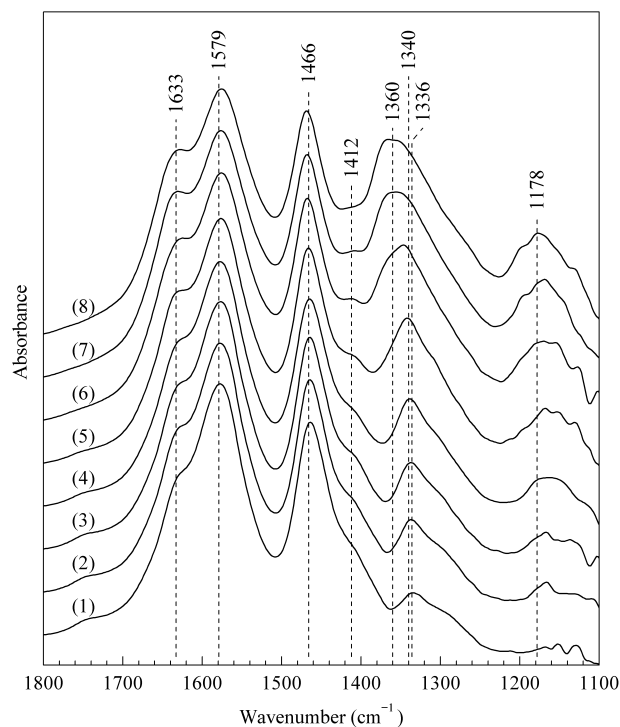


Fig. 6 DRIFTS spectra of Ag/Al₂O₃ in a flow of C₃H₆ + O₂ before and after adding 0.008% SO₂ at 723 K

(1) No SO₂ for 60 min; (2)–(8) Adding SO₂ for 3 min, 5 min, 10 min, 30 min, 60 min, 90 min, and 120 min, respectively
(Reaction conditions: 0.1714% C₃H₆, 10% O₂, N₂ as balance.)

cies band at 1340 cm^{-1} . It shifted to 1360 cm^{-1} and its intensity increased sharply. The band at 1178 cm^{-1} also appeared upon the introduction of SO_2 and increased with increasing time on stream. The bands at 1633 , 1579 , and 1466 cm^{-1} , however, remained almost unchanged, indicating that SO_2 had no apparent effect on the formation of the enolic species and acetate species.

2.2.4 Effect of SO_2 on oxidation of NO

To obtain further information, the effect of SO_2 on the oxidation of NO was also studied by DRIFTS, and the results are shown in Fig. 7. The exposure of the catalyst to a flow of $\text{NO} + \text{O}_2$ at 723 K for 60 min resulted in five bands at 1614 , 1585 , 1560 , 1298 , and 1254 cm^{-1} , which were all assignable to adsorbed nitrate species. The introduction of 0.008% SO_2 in the

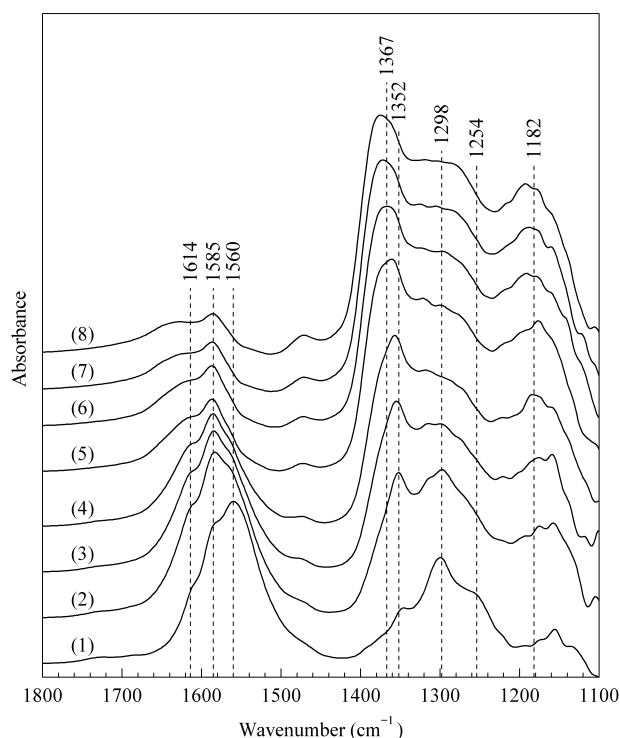


Fig. 7 DRIFTS spectra of $\text{Ag}/\text{Al}_2\text{O}_3$ in a flow of $\text{NO} + \text{O}_2$ before and after adding 0.008% SO_2 at 723 K
(1) No SO_2 for 60 min ; (2)–(8) Adding SO_2 for 5 min , 10 min , 15 min , 30 min , 40 min , 60 min , and 90 min , respectively (Reaction conditions: 0.08% NO , 10% O_2 , N_2 as balance.)

feed resulted in the appearance of a new band at 1352 cm^{-1} . It was assignable to surface sulfate species, it shifted to 1367 cm^{-1} , and its intensity increased with the exposure time, together with another band beginning to appear at 1182 cm^{-1} . On the other hand, clear decreases were observed for the bands at 1298 , 1254 , and 1560 cm^{-1} . In contrast, the intensity of the bands at 1585 and 1614 cm^{-1} slightly increased initially and then decreased with time on stream. This again confirmed the inhibiting effect of SO_2 on the formation of NO_3^- , as presented earlier in Figs. 4(b) and 5.

3 Conclusions

In situ DRIFTS spectra reveal the formation of sulfate species on the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst and show that the sulfate species band underwent an obvious blue shift with the increase in the sulfate species concentration. The sulfate species formed on $\text{Ag}/\text{Al}_2\text{O}_3$ not only inhibits the formation of NO_3^- , but also suppresses the reaction between the enolic species or acetate species and NO_3^- to form $-\text{NCO}$ species. This should be the main reason for the deactivation of $\text{Ag}/\text{Al}_2\text{O}_3$ during the SCR of NO_x by C_3H_6 in the presence of SO_2 .

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