

Conformational Analysis of Sulfate Species on Ag/Al₂O₃ by Means of Theoretical and Experimental Vibration Spectra

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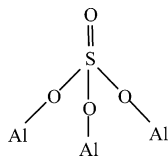
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The formation and configuration of sulfate species on Ag/Al₂O₃ were studied by means of in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and density functional theory (DFT) calculations. The comparison between theoretical and experimental vibration spectra enable us to draw the following conclusions: Bidentate sulfate species rather than tridentate sulfate species are the predominant surface species on Ag/Al₂O₃. Moreover, both bidentate and tridentate sulfate species may coexist on the catalyst surface at a lower coverage. The accumulation of surface sulfate species could well explain the blue shift of the sulfate species in IR spectra. In addition, the in situ DRIFTS could distinguish between the sulfate species that linked to Al site and Ag site, which was well supported by temperature-programmed desorption (TPD) results.

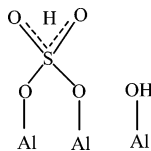
1. Introduction

Sulfur-containing compounds that exist as trace impurities in fuels are readily oxidized to SO₂ during combustion. Exhaust SO₂ is a significant poison for the catalyst used for exhaust gas treatment, since it can react further to form sulfate species, and the accumulation of the sulfate species on the catalyst can lead to a significant degradation in catalyst performance.^{1–5} So far, Ag/Al₂O₃ has been considered to be a promising catalyst due to its relatively high activity for the selective catalytic reduction (SCR) of NO_x by hydrocarbons.^{3–8} However, the NO_x conversion over this catalyst decreased in the presence of SO₂ when using hydrocarbons as reductants.^{3–5} As a result, a better understanding of the interaction of SO₂ with Ag/Al₂O₃ is especially important.

Up to now, although a majority of investigations have been focused on elucidating the interaction mechanism between γ -Al₂O₃ and SO₂, there is still a limited understanding about the formation and configuration of the sulfate species over Ag/Al₂O₃.^{9–14} Saur et al.¹⁵ established the structure of the tridentate sulfate species in anhydrous form on Al₂O₃ through isotopic study, as shown in the following structure



This kind of sulfate species can be hydrated to another structure



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Dunn et al.¹⁶ have adopted the tridentate sulfate species structure in their IR and Ramam study of the interactions between surface vanadate and sulfate species on various metal oxide catalysts. Riemer¹⁷ also has supported this kind of surface sulfate species structure. However, the interaction between SO₂ and Al₂O₃ is very complicated, depending on the nature of the adsorption sites. To determine more conclusively the structure of the sulfate species requires more knowledge of the mechanism of the sulfate species bonding to different coordinated surface aluminum atoms, the classification of structures that satisfy valence requirements, and the calculation of vibrational frequencies for the proposed structures.

The aim of this study was to analyze in more detail the formation and structure of the sulfate species on Ag/Al₂O₃, using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), density functional theory (DFT) calculations, and temperature programmed desorption (TPD) methods, in order to get a better understanding of the nature of sulfate species adsorbed on Ag/Al₂O₃.

2. Experimental Section

Ag/Al₂O₃ (5 wt %) was prepared by an impregnation method described in our previous works.^{8,18} Pure γ -Al₂O₃ was also dried at 393 K for 3 h and calcined at 873 K for 3 h in air for a parallel experiment. SO₂-poisoned samples were prepared by exposing the corresponding fresh samples to a gas stream composed of 80 ppm SO₂ + 10% O₂ in N₂ balance at 673 K for 10 h.

In situ DRIFTS spectra were recorded on a NEXUS 670-FTIR equipped with a smart collector and a MCT/A detector cooled by liquid N₂. The catalyst was finely ground and placed in a ceramic crucible. Prior to each experiment, the catalyst was first heated in a flow of 10 vol % O₂ + N₂ for 60 min at 873 K, then cooled to the desired temperature, and a spectrum of the catalyst in the flow of N₂ + O₂ serving as the background was recorded. All gas mixtures were fed at a flow rate of 300 mL/min. All spectra were measured with a resolution of 4 cm⁻¹ and with an accumulation of 100 scans.

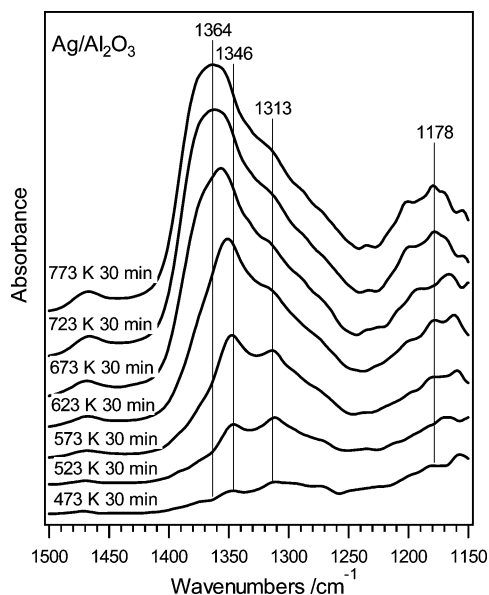


Figure 1. In situ DRIFTS spectra of adsorbed sulfate species on Ag/Al₂O₃ in a flow of SO₂ + O₂ at various temperatures. Conditions: SO₂ 80 ppm, O₂ 10%.

TPD experiment of the SO₂-poisoned Ag/Al₂O₃ was performed by a HIDEN analytical instrument, equipped with a QMS sampling system (HPR 20). In a typical measurement, 200 mg of SO₂-poisoned Ag/Al₂O₃ was placed in the tubular reactor in which the feed to the reactor can be switched by using solenoid valves controlled by a computer. The carrier gas was kept at a flow rate of 30 mL of He/min while the temperature was increased at a temperature ramp rate of 30 deg K/min, and the effluent composition can be monitored continuously by using a quadrupole mass spectrometer.

3. Theoretical Section

DFT calculations were performed to estimate the structure of surface sulfate species formed on Ag/Al₂O₃. The Gaussian 98 program¹⁹ running on an OPTIPLEX (TM) GX260SD with an Interl (R) Pentium (R) 4, 2.26G Hz Processor and 512 MB RAM was performed to optimize the structures and calculate the vibrational wavenumbers for the calculated models (shown in Figures 7 and 10), and the 3-21G* basis set was employed to carry out the DFT-B3PW91 (Becke's three-parameter functional with the nonlocal correlation provided by the Perdew 91 expression) calculations. The vibrational frequencies and intensities for the calculated models by the Gaussian 98 program were analyzed by the Gaussview 2.1 program package.

4. Results and Discussion

4.1. In Situ DRIFTS Analysis of Adsorbed Sulfate Species on Ag/Al₂O₃. Figure 1 shows the in situ DRIFTS spectra of Ag/Al₂O₃ at various temperatures in a flow of SO₂ + O₂ for a total of 210 min. Two weak bands appeared at 1346 and 1313 cm⁻¹ after exposing the catalyst to SO₂ + O₂ for 30 min at 473 K, and the band at 1346 cm⁻¹ became predominant with increasing exposure time and temperature. The band at 1346 cm⁻¹ is assigned to a surface sulfate species linked to the Al site according to literature,^{20–22} while the band at 1313 cm⁻¹ was likely a similar surface sulfate species that linked either solely or partly to the Ag site.³ At higher temperatures, a weak band at 1178 cm⁻¹ was also visible. At present, its assignment is not evident, but it obviously arises from the sulfuration of γ -Al₂O₃ since it is also present on the pure γ -Al₂O₃. In addition,

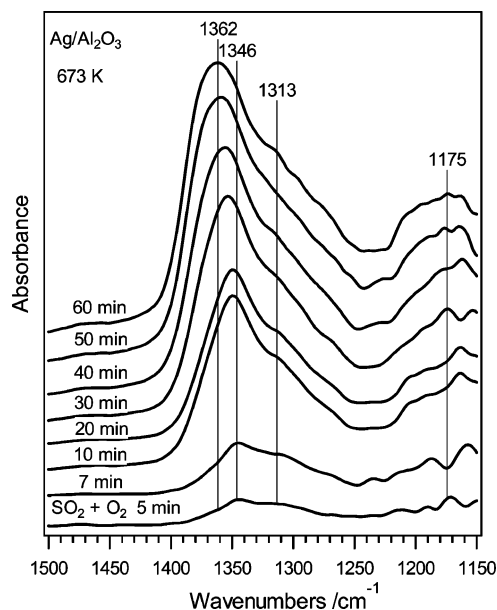


Figure 2. In situ DRIFTS spectra of adsorbed sulfate species on Ag/Al₂O₃ in a flow of SO₂ + O₂ at 673 K. Conditions: SO₂ 80 ppm, O₂ 10%.

a noticeable fact was a distinct shift of the sulfate band from 1346 to 1364 cm⁻¹, which may be caused by the accumulation of sulfate species by the reaction of SO₂ + O₂ with Ag/Al₂O₃.

Figure 2 illustrates the in situ DRIFTS spectra of the Ag/Al₂O₃ as a function of the exposing time to SO₂ + O₂ at 673 K. Similarly, the characteristic bands of sulfate species mentioned in Figure 1 also appeared in Figure 2, and the sulfate species band also underwent an obvious blue shift along with the increasing coverage of surface sulfate species on Ag/Al₂O₃ (1346–1362 cm⁻¹). As a result, it is the coverage of surface sulfate species rather than sample temperature that plays a crucial role in the blue shift for IR spectra.

For a comparison, pure γ -Al₂O₃ was also submitted to the same experiment, and the in situ DRIFTS spectra of γ -Al₂O₃ obtained in a flow of SO₂ + O₂ at various temperatures are shown in Figure 3. Similarly, a dominant band near 1346 cm⁻¹ and a weak band at 1176 cm⁻¹ were also observed in the spectra of γ -Al₂O₃ at temperatures above 573 K, indicating that the sulfate species mostly occurred on γ -Al₂O₃. However, the band at 1313 cm⁻¹ was not visible, suggesting that this band related with sulfate species at the Ag site. No other major change in the characteristic bands was found between Ag/Al₂O₃ and γ -Al₂O₃ (Figures 1 and 3). Furthermore, the band at 1346 shifting to 1369 cm⁻¹ arising from the accumulation of surface sulfate species was also in good agreement with what has been found in Figures 1 and 2.

To identify these surface sulfate species formed on the Ag site, experiments were conducted through thermal treatment of SO₂-treated Ag/Al₂O₃. Figure 4 shows a series of in situ DRIFTS spectra obtained with the SO₂-treated Ag/Al₂O₃ (6 wt %) at 673 K for a total of 150 min, and with the same sample subsequently undergoing thermal treatment at elevated temperatures. In Figure 4, two bands at ca. 1348 and 1313 cm⁻¹ could be observed on SO₂-treated Ag/Al₂O₃ at 673 K. After thermal treatment above 773 K, the band at 1313 cm⁻¹ gradually decreased and finally disappeared at 973 K, whereas the band at 1360 cm⁻¹ (1348 cm⁻¹ shifted to 1360 cm⁻¹) was hardly affected. The results indicate that the less thermal stable sulfate species at 1313 cm⁻¹ is linked to the Ag site, while the more thermal stable sulfate species appearing at 1360 cm⁻¹ is linked

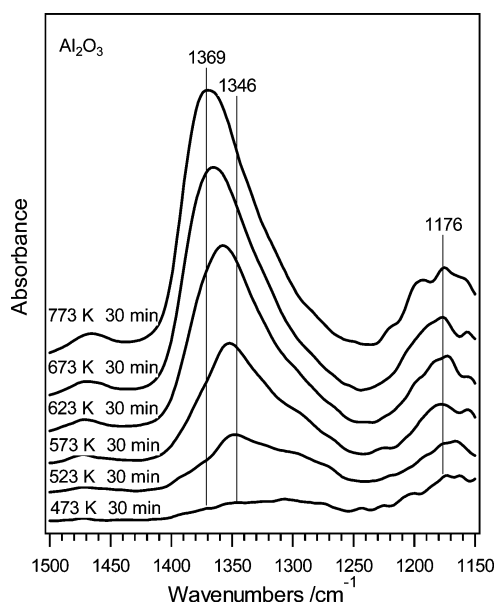


Figure 3. In situ DRIFTS spectra of adsorbed sulfate species on pure γ - Al_2O_3 in a flow of $\text{SO}_2 + \text{O}_2$ at various temperatures. Conditions: SO_2 80 ppm, O_2 10%.

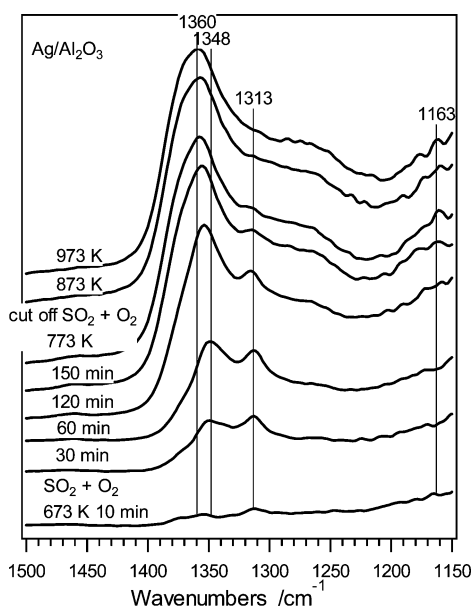


Figure 4. In situ DRIFTS spectra of SO_2 -treated $\text{Ag}/\text{Al}_2\text{O}_3$ (6 wt %) at 673 K for a total of 150 min and its thermal treatment at elevated temperatures.

to the Al site. In addition, comparing Figures 2 and 4, it should be noted that the intensity of surface sulfate species (appearing at 1313 cm^{-1}) on SO_2 -treated $\text{Ag}/\text{Al}_2\text{O}_3$ (6 wt %) was stronger than that of SO_2 -treated $\text{Ag}/\text{Al}_2\text{O}_3$ (5 wt %), thus it is reasonable to deduce that the band at 1313 cm^{-1} was related to sulfate species formed on the Ag site. This is also well supported by the following TPD results.

As discussed above, in situ DRIFTS analysis of the formation of surface sulfate species on $\text{Ag}/\text{Al}_2\text{O}_3$ and γ - Al_2O_3 presented similar bands and blue shifts in IR spectra, suggesting that there is a strong interaction between SO_2 and the γ - Al_2O_3 surface, thus sulfate species was mostly present on the γ - Al_2O_3 support. This can be explained by the basicity of the support, which makes it easier to adsorb acidic SO_2 molecules on the alkaline surface, as demonstrated in other literature.^{9,14}

4.2. Conformational Analysis of Adsorbed Sulfate Species over Al_2O_3 by DFT Calculations. It has been shown that

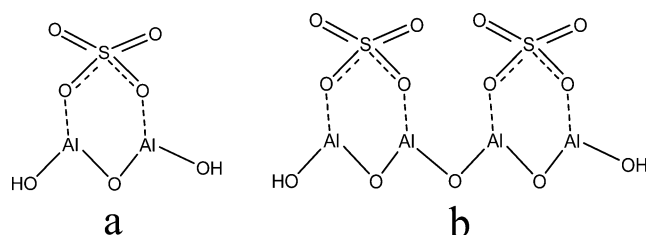


Figure 5. Calculated models for the bidentate sulfate species formed on Al_2O_3 .

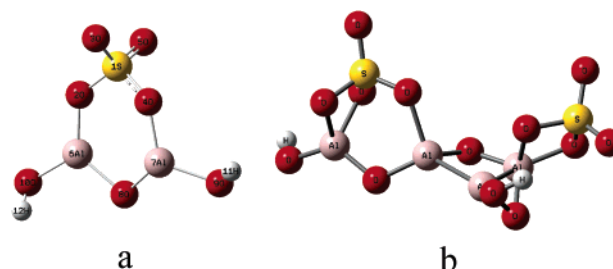


Figure 6. Optimized configuration of calculational models for the bidentate sulfate species formed on Al_2O_3 .

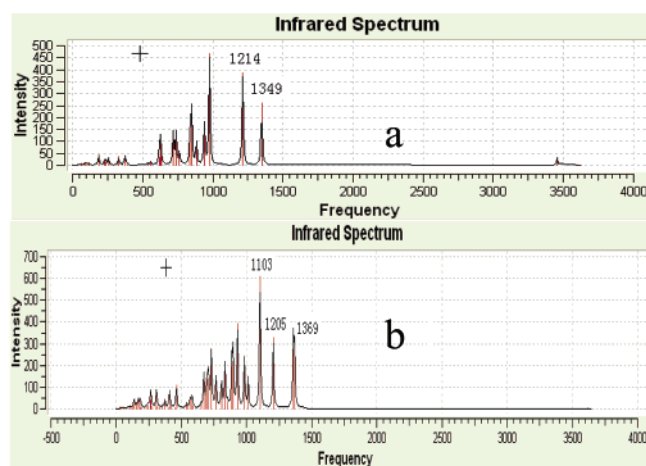


Figure 7. Calculated vibrational IR spectra for the bidentate sulfate species formed on Al_2O_3 .

sulfate species were mostly formed on γ - Al_2O_3 support, and for this reason, we designed two kinds of calculated models on Al_2O_3 (bidentate and tridentate sulfate species) to obtain a better analysis of the nature of the sulfate species and to explain the phenomenon of the blue shift for the in situ DRIFTS spectra.

The chemical structures of the calculated models for bidentate sulfate species on Al_2O_3 are shown in Figure 5. Model a was adopted to simulate the lower coverage state, while model b was adopted for the simulation of the higher coverage state. The optimized structures and the simulated spectra for bidentate sulfate species are presented in Figures 6 and 7, respectively. As can be seen from Figure 7a, the $\nu_{\text{as}}(\text{OSO})$ vibration frequency of model a was calculated at 1349 cm^{-1} with 260 km/mol intensity, which was close to the experimental value of 1346 cm^{-1} with strong adsorption, and the $\nu_{\text{s}}(\text{OSO})$ vibration frequency of model a was calculated at 1214 cm^{-1} with 386 km/mol intensity, which was 36 cm^{-1} higher than the experimental value of 1178 cm^{-1} (Figure 1). As evidenced in Figure 7b, the $\nu_{\text{as}}(\text{OSO})$ vibration frequency of model b was calculated at 1369 cm^{-1} with 273 km/mol intensity, which was very close to the experimental value of 1364 cm^{-1} , while the $\nu_{\text{s}}(\text{OSO})$ vibration frequency of model b was calculated at 1205 cm^{-1} with 327 km/mol intensity, which was 27 cm^{-1} higher than the

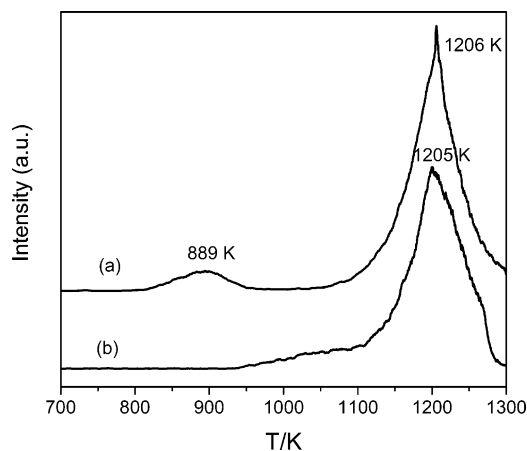


Figure 12. TPD spectra of SO_2 of $\text{Ag}/\text{Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ poisoned by 80 ppm SO_2 for 10 h at 673 K: (a) SO_2 -poisoned $\text{Ag}/\text{Al}_2\text{O}_3$ and (b) SO_2 -poisoned $\gamma\text{-Al}_2\text{O}_3$.

4.3. TPD Analysis for SO_2 -Poisoned $\text{Ag}/\text{Al}_2\text{O}_3$. To obtain insights into the nature of the species formed on the SO_2 -poisoned $\text{Ag}/\text{Al}_2\text{O}_3$, we also examined TPD curves for $\text{Ag}/\text{Al}_2\text{O}_3$ after exposure to 80 ppm SO_2 in 10% O_2 at 673 K for 10 h, by monitoring SO_2 (m/e 64) and O_2 (m/e 32) signals. For comparison, the TPD pattern of $\gamma\text{-Al}_2\text{O}_3$ poisoned by 80 ppm SO_2 under the same conditions was also recorded. As shown in Figure 12, SO_2 desorbed in two peaks for SO_2 -poisoned $\text{Ag}/\text{Al}_2\text{O}_3$, centered at 889 and 1206 K, respectively (spectrum a). In contrast with SO_2 -poisoned $\text{Ag}/\text{Al}_2\text{O}_3$, the TPD spectrum of SO_2 -poisoned $\gamma\text{-Al}_2\text{O}_3$ only showed a peak centered at about 1205 K (spectrum b). Both of these desorption peaks at 889 and 1206 K are associated with two different kinds of surface sulfate species decomposition on $\text{Ag}/\text{Al}_2\text{O}_3$. According to the previous literature, $\text{Al}_2(\text{SO}_4)_3$ formed through the treatment of alumina with SO_2 , and it decomposed to yield alumina oxide at 1073–1193 K.²³ Therefore, the high-temperature peak centered around 1206 K should be derived from the thermally stable sulfate compounds formed on the Al site, while the low-temperature peak should be attributed to SO_2 decomposed from the sulfate species formed on the Ag site. The TPD results provide clear evidence for the formation of sulfate species by the reaction of $\text{Ag}/\text{Al}_2\text{O}_3$ with SO_2 .

5. Conclusions

The exact structure of the sulfate species formed on $\text{Ag}/\text{Al}_2\text{O}_3$ was established based on the in situ DRIFTS spectra and TPD and DFT calculations. The experimental results revealed the

formation of sulfate species on Ag and Al_2O_3 sites, and showed that the IR band underwent an obvious blue shift along with the increase of sulfate species surface concentration. The calculated results show that the models of bidentate sulfate species are the reasonable models for investigating the configuration of the sulfate species formed on Al_2O_3 . Also, both bidentate and tridentate sulfate species might coexist on the catalyst surface at a lower coverage. The accumulation of surface sulfate species could well explain the phenomenon of the blue shift in IR spectra.

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References and Notes

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