# Disparate effects of $SO_2$ on the selective catalytic reduction of NO by $C_2H_5OH$ and IPA over $Ag/Al_2O_3$

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## Abstract

The selective catalytic reduction (SCR) of NO by $C_2H_5OH$ and IPA (isopropyl alcohol) over $Ag/Al_2O_3$ was studied in the presence of $SO_2$. The results showed that $C_2H_5OH$ performs much more effectively in the presence of $SO_2$ compared with IPA. In situ DRIFTS study did not show the formation of sulfate species on $Ag/Al_2O_3$, which might explain the high resistance of $Ag/Al_2O_3$ to $SO_2$ in the SCR of NO by $C_2H_5OH$. In addition, the deactivation mechanism for the case using IPA as a reductant was also proposed based on the IR spectra results.
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*Keywords:* In situ DRIFTS; Selective catalytic reduction; Sulfate species; Enolic species; Isocyanate species

## 1. Introduction

The SCR of NO by hydrocarbons or oxygen-containing organic compounds in the presence of oxygen over $Ag/Al_2O_3$ has attracted much attention as a potential technology to remove NO from diesel and lean-burning engine exhaust [1–9]. However, the activity of $Ag/Al_2O_3$ usually decreases in the presence of $SO_2$ especially at lower temperatures, and the deactivation effect of $SO_2$ is assigned to the formation of surface sulfate species on the catalyst [10,11]. From a practical point of view, the catalysts used for the SCR of NO should be resistant to inhibition by $SO_2$ and $H_2O$ in real exhaust gases [12–16]. Furthermore, the type of reductant is an important factor for the SCR of NO. Therefore, the development of more effective and inexpensive reductant in the presence of $SO_2$ is also required for practical use.

To get more evidence for the sulphur-tolerant catalyst/reductant, it is crucial to lay emphasis on investigating dif-

ferent mechanisms of the SCR of NO in the presence of $SO_2$. Since $C_2H_5OH$ and IPA display the similar reducing capabilities in most cases, in this paper, we chose both as model reductants for the SCR of NO in the presence of $SO_2$ to seek $SO_2$ resistance system for industry utilization. We used in situ DRIFTS method to study the effect of $SO_2$ on the formation of $NO_3^-$, acetate ($CH_3COO^-$), enolic species and isocyanate species (–NCO), which are the key intermediates in the SCR of NO by $C_2H_5OH$ or IPA. Through this study, we deduced the different mechanisms of the SCR of NO by these two reductants over $Ag/Al_2O_3$ in the presence of $SO_2$.

## 2. Experimental

### 2.1. Catalyst preparation

$Ag/Al_2O_3$ (5 wt%) catalyst was prepared by an impregnation method as following: $Al_2O_3$ powder (200 $m^2$/g) was dissolved in an appropriate amount of silver nitrate aqueous solution. The sample was dried at 393 K for 3 h and calcined at 873 K for 3 h in air.

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## 2.2. Activity measurements

The catalytic activity was measured in a fixed-bed reactor by passing a gaseous mixture of NO (800 ppm), reductant ($C_2H_5OH$ 1565 ppm, or IPA 1043 ppm), $SO_2$ (80 ppm), $O_2$ (10%) in $N_2$ balance at a total flow rate of 2000 mL/min over 0.6 g catalyst ($W/F = 0.018$ g s mL$^{-1}$, GHSV = ~50,000 h$^{-1}$). NO conversion was analyzed on-line by a chemiluminescence $NO/NO_2/NO$ analyzer (42C-hl, Thermo Electron). An aqueous $C_2H_5OH$ or IPA solution was supplied by a micro pump into the gas stream and vaporized by a coiled heater at the inlet of the reactor.

## 2.3. In situ DRIFTS procedure

In situ 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 catalyst was finely ground and placed in a ceramic crucible. Prior to each experiment, the catalyst was firstly heated in a flow of 10 vol% $O_2 + N_2$ for 60 min at 873 K, then cooled to the desired temperature, and a spectrum of the catalyst in the flow of $N_2 + O_2$ 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.

## 3. Results and discussion

### 3.1. Reaction activity of $C_2H_5OH$ and IPA for the SCR of NO over Ag/Al$_2$O$_3$ in the presence of $SO_2$

The effect of $SO_2$ addition to the feed gas mixture on the SCR activity over Ag/Al$_2$O$_3$ was monitored as a function of time on stream at 673 and 723 K, which corresponded to the temperatures for high NO conversions with $C_2H_5OH$ and IPA. As indicated in Fig. 1, in the absence of $SO_2$, a steady state NO conversion of 96.2% at 673 K was achieved in the first 2 h when using IPA as a reductant. Addition of 80 ppm $SO_2$ to the feed gas dramatically decreased NO conversion from 96.2 to 13.2% in another 2 h. Subsequently, a stable NO conversion was obtained for more than 6 h. A similar decrease in the SCR activity occurred upon addition of 80 ppm $SO_2$ to the feed gas at 723 K for IPA, but the activity decline stopped at 34.2% of NO conversion. This indicates that $SO_2$ greatly deactivates the SCR activity of Ag/Al$_2$O$_3$ when using IPA as a reductant, especially at low temperatures. In the case of $C_2H_5OH$, the NO conversion was observed to increase slightly at short times and then pass a maximum to reach a stable level. The final NO conversion seemed to be slightly influenced by $SO_2$. Such significant difference indicates that the reaction mechanism of the SCR of NO by $C_2H_5OH$ in the presence of $SO_2$ over Ag/Al$_2$O$_3$ is different from that of using IPA as a reductant.
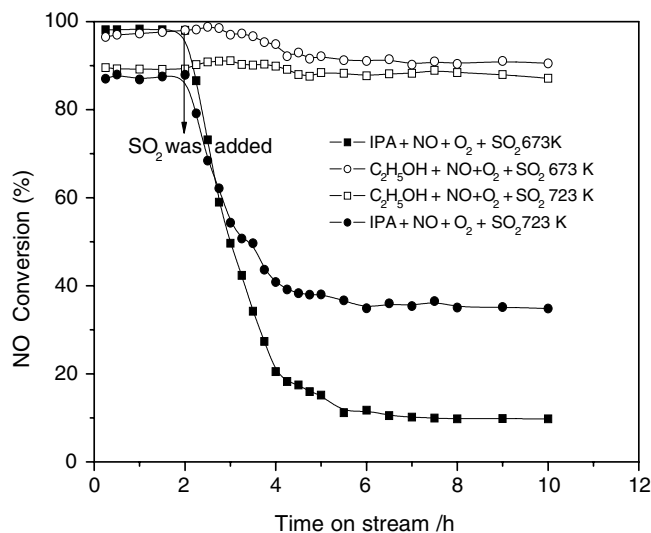


Fig. 1. Catalytic activity for NO reduction by $C_2H_5OH$ and IPA over Ag/Al$_2$O$_3$ in the presence of $SO_2$ at 673 and 723 K. Conditions: NO 800 ppm, $C_2H_5OH$ 1565 ppm or IPA 1043 ppm, $O_2$ 10%, $SO_2$ 80 ppm, $W/F = 0.018$ g s mL$^{-1}$ (GHSV = ~50,000 h$^{-1}$), $N_2$ balance, total flow rate: 2000 mL/min.

### 3.2. Effect of $SO_2$ on Ag/Al$_2$O$_3$ for the SCR of NO by $C_2H_5OH$ or IPA with in situ DRIFTS spectra

The in situ DRIFTS spectra of Ag/Al$_2$O$_3$ were recorded at various temperatures in steady states after exposing to $C_2H_5OH + NO + O_2$ or to IPA + NO + O$_2$. As shown in both Figs. 2A and 2B, the very strong peak appeared at 2233 cm$^{-1}$ is associated with the –NCO species, as observed in other NO/O$_2$/hydrocarbons systems [7,17]. It has been widely accepted that –NCO species is a crucial intermediate in the SCR of NO over Ag/Al$_2$O$_3$, and its high productivity results in a high efficiency of NO reduction. The peaks at 1633, 1416 and 1336 cm$^{-1}$ are assigned to the surface enolic species derived from the partial oxidation of $C_2H_5OH$ or IPA over Ag/Al$_2$O$_3$ (1633, 1412 and 1338 cm$^{-1}$ for IPA)
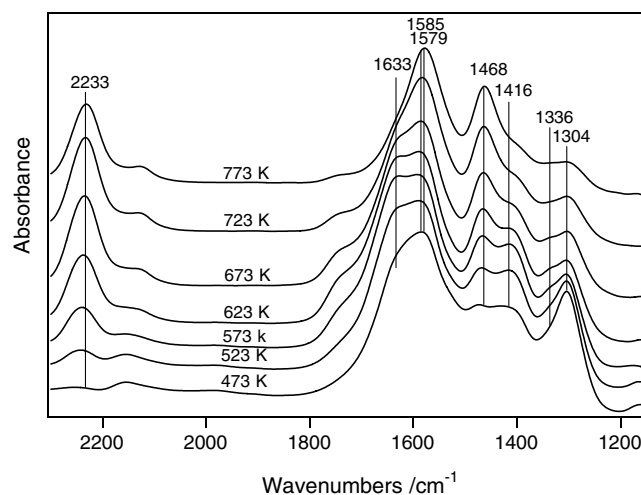


Fig. 2A. In situ DRIFTS spectra of adsorbed species on Ag/Al$_2$O$_3$ in steady state at various temperatures in a flow of $C_2H_5OH + O_2 + NO$. Conditions: NO 800 ppm, $C_2H_5OH$ 1565 ppm, $O_2$ 10%.
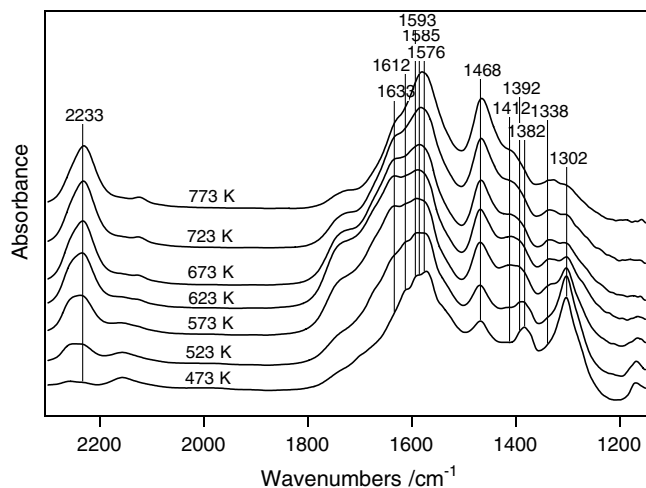
Fig. 2B. In situ DRIFTS spectra of adsorbed species on Ag/Al$_2$O$_3$ in steady state at various temperatures in a flow of IPA + O$_2$ + NO. Conditions: NO 800 ppm, IPA 1043 ppm, O$_2$ 10%.

[18,19]. The enolic species has been proved to play a crucial role in the –NCO species formation during the SCR of NO by C$_2$H$_5$OH or IPA. In addition, the peaks at 1579 (1576 for IPA) and 1468 cm$^{-1}$ are assigned to the acetate species, the peaks at 1585 and 1304 cm$^{-1}$ (1302 for IPA) are due to the adsorbed nitrates [7,19], and the peak at 1392 cm$^{-1}$ in Fig. 2B can be associated with $\delta$(C–H) [18,20]. We cannot observe the obvious difference between the two figures (Figs. 2A and 2B), which is in a good agreement with the Ag/Al$_2$O$_3$ activities for the SCR of NO with C$_2$H$_5$OH or IPA [19].

Figs. 3A and 3B show the spectra of Ag/Al$_2$O$_3$ in the presence of 80 ppm SO$_2$ in the flow of NO + C$_2$H$_5$OH + O$_2$ or NO + IPA + O$_2$ at different temperatures, respectively. Comparing Figs. 2A with 3A, no obvious difference was observed between the two figures, that is, there was no sulfate species formed on Ag/Al$_2$O$_3$. Therefore, we can conclude that co-existing SO$_2$ hardly affects the NO reduc-
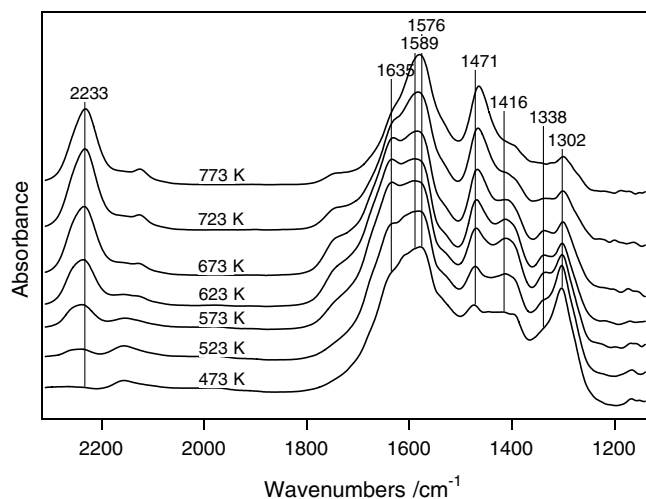


Fig. 3A. In situ DRIFTS spectra of adsorbed species on Ag/Al$_2$O$_3$ at various temperatures in a flow of C$_2$H$_5$OH + O$_2$ + NO + SO$_2$. Conditions: NO 800 ppm, C$_2$H$_5$OH 1565 ppm, SO$_2$ 80 ppm, O$_2$ 10%.
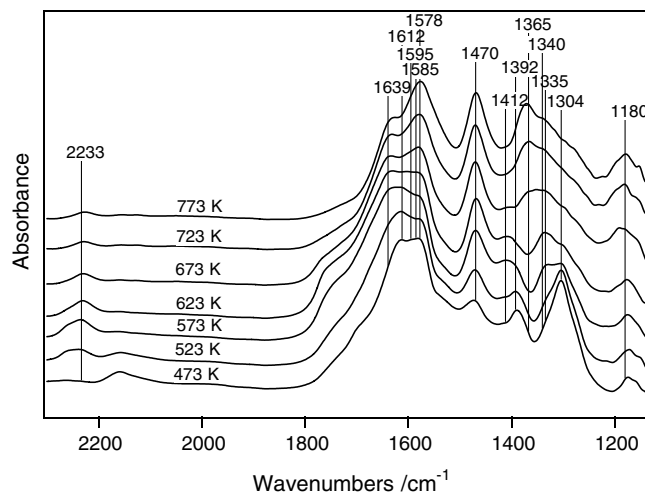


Fig. 3B. In situ DRIFTS spectra of adsorbed species on Ag/Al$_2$O$_3$ at various temperatures in a flow of IPA + O$_2$ + NO + SO$_2$. Conditions: NO 800 ppm, IPA 1043 ppm, SO$_2$ 80 ppm, O$_2$ 10%.

tion by C$_2$H$_5$OH over Ag/Al$_2$O$_3$. This might explain the high efficiency of NO reduction by C$_2$H$_5$OH over Ag/Al$_2$O$_3$ in the presence of SO$_2$, as confirmed by other experiments [4]. Comparing Figs. 2B with 3B, a most significant difference between the two figures was that a new broad peak appeared at 1340 cm$^{-1}$ in Fig. 3B. Its intensity increased with the exposure time while its position shifted to 1365 cm$^{-1}$, accompanied by another peak at 1180 cm$^{-1}$ growing in intensity. According to the previous studies [21,22], the peak at 1340 cm$^{-1}$ could be observed and assigned to a surface sulfate species, while the peak at 1180 cm$^{-1}$ could be assigned to a bulk sulfate species. However, our study using in situ DRIFTS and density functional theory (DFT) calculations has given new assignments for the two peaks, and the peaks at 1340 and 1180 cm$^{-1}$ were attributed to asymmetric and symmetric stretching vibrations of (OSO) in bidentate sulfate species on Ag/Al$_2$O$_3$, respectively. The second difference between Figs. 2B and 3B was that the intensity of the nitrates peak at 1304 cm$^{-1}$ decreased promptly when the feed gas contains 80 ppm SO$_2$. The third difference was that the –NCO peak (2233 cm$^{-1}$) also decreased dramatically in intensity. However, other peaks took little influence in intensity by the presence of SO$_2$. Apparently, the presence of sulfate species blocked the formation of NO$_3^-$, which can react easily with enolic species to form –NCO species. This led to the corresponding decrease in the SCR activity.

To further investigate the effect of SO$_2$ on Ag/Al$_2$O$_3$ in the flow of NO + C$_2$H$_5$OH + O$_2$ or NO + IPA + O$_2$, we also performed the in situ DRIFTS experiments as follows: when the reaction reaching a steady state at 60 min, 80 ppm SO$_2$ was introduced into the feed gas at 673 K. The first two spectra in Figs. 4A and 4B were taken under SO$_2$-free flow and other spectra were taken in the presence of 80 ppm SO$_2$ at different time. Once again, we could not observe the presence of the sulfate species on Ag/Al$_2$O$_3$ in Fig. 4A, indicating NO reduction by C$_2$H$_5$OH is not

apparently affected by introducing $SO_2$ into the feed gas. In contrast, in the case with IPA as a reductant in Fig. 4B, a new sulfate species peak also appeared at 1342 cm$^{-1}$, with its intensity increased gradually and shifted to 1358 cm$^{-1}$, along with another increasing peak appeared at 1178 cm$^{-1}$, likewise the spectra in Fig. 3B. At the same time, both –NCO species peak (2233 cm$^{-1}$) and nitrates peak (1300 cm$^{-1}$) decreased promptly in intensity with the exposure time. The results again suggest that the formation of sulfates species on $Ag/Al_2O_3$ not only inhibited the formation of $NO_3^-$, but also suppressed the reaction of enolic species with $NO_3^-$ to form –NCO species. This should be responsible for the poor reduction of NO by IPA over $Ag/Al_2O_3$ in the presence of $SO_2$.
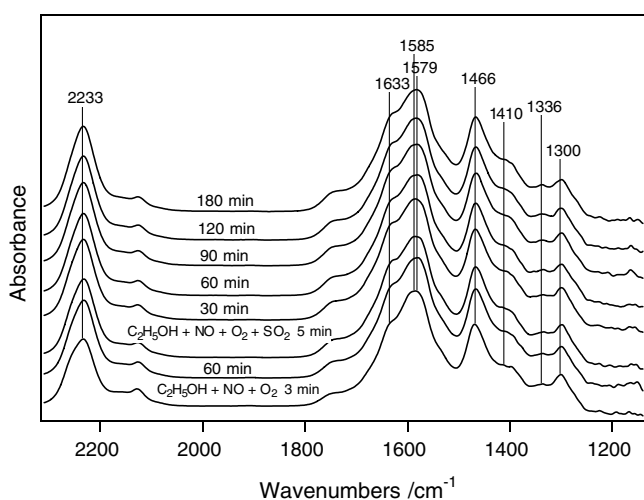


Fig. 4A. Changes of in situ DRIFTS spectra of adsorbed species on Ag/Al$_2$O$_3$ at 673 K in a flow of C$_2$H$_5$OH + O$_2$ + NO + SO$_2$. Before the measurement, the catalyst was pre-exposed to a flow of C$_2$H$_5$OH + O$_2$ + NO for 60 min at 673 K. Conditions: NO 800 ppm, C$_2$H$_5$OH 1565 ppm, SO$_2$ 80 ppm, O$_2$ 10%.
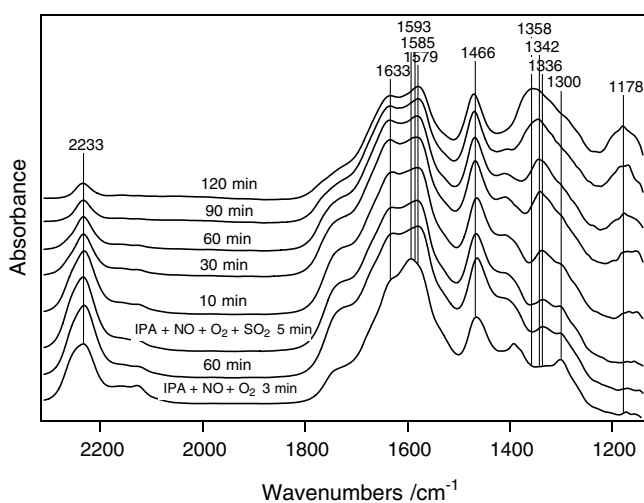


Fig. 4B. Changes of in situ DRIFTS spectra of adsorbed species on Ag/Al$_2$O$_3$ at 673 K in a flow of IPA + O$_2$ + NO + SO$_2$. Before the measurement, the catalyst was pre-exposed to a flow of IPA + O$_2$ + NO for 60 min at 673 K. Conditions: NO 800 ppm, IPA 1043 ppm, SO$_2$ 80 ppm, O$_2$ 10%.

### 3.3. Mechanism analysis

We have proposed a novel mechanism of the SCR of NO by $C_2H_5OH$ or IPA over $Ag/Al_2O_3$ [19]. It was shown that the enolic species, which are the main surface species during the partial oxidation of $C_2H_5OH$ or IPA in the presence of oxygen, play a crucial role in the formation of –NCO species by reacting with NO + $O_2$ or $NO_3^-$ on $Ag/Al_2O_3$. The formation of –NCO species is the rate-determining step in the SCR of NO by $C_2H_5OH$ or IPA over $Ag/Al_2O_3$. As can be seen from the in situ DRIFTS spectra (Fig. 4B), adding 80 ppm $SO_2$ to the feed gas strongly inhibited the –NCO formation in the case of IPA, whereas $C_2H_5OH$ took little influence (Fig. 4A). This was likely due to different kinds of enolic species formed from the partial oxidation of $C_2H_5OH$ or IPA on $Ag/Al_2O_3$. If the same enolic species were obtained during the partial oxidation of $C_2H_5OH$ or IPA, significant difference in IR spectra between Figs. 3A and 3B (Figs. 4A and 4B) should not be expected. We assumed that the enolic species formed from the partial oxidation of $C_2H_5OH$ contains two or four carbon atoms with high $SO_2$ tolerance [18], while the enolic species derived from the partial oxidation of IPA contains three carbon atoms, which could not inhibit the formation of surface sulfate species on $Ag/Al_2O_3$.

## 4. Conclusions

The SCR activity of NO reduction by IPA is significantly suppressed upon exposure of $Ag/Al_2O_3$ to 80 ppm $SO_2$. In situ DRIFTS spectra indicated that the presence of sulfate species on $Ag/Al_2O_3$ not only inhibits the formation of $NO_3^-$, but also suppresses the reaction between enolic species and $NO_3^-$ to form –NCO species, which could account for the deactivation in the SCR of NO by IPA in the presence of $SO_2$. In contrast, $C_2H_5OH$-SCR of $NO_x$ system has a high $SO_2$ tolerance under the same experimental conditions. In situ DRIFTS spectra did not apparently show the formation of sulfate species on $Ag/Al_2O_3$ in the case of $C_2H_5OH$. This probably explains the reason why $C_2H_5OH$ is a more effective reductant than IPA in the SCR of NO over $Ag/Al_2O_3$ in the presence of $SO_2$.

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