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RESEARCH PAPER

Mechanistic Study of Selective Catalytic Reduction of NO$_x$ with C$_2$H$_5$OH and CH$_3$OCH$_3$ over Ag/Al$_2$O$_3$ by in Situ DRIFTS

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Abstract: Although C$_2$H$_5$OH and CH$_3$OCH$_3$ are isomeric compounds, C$_2$H$_5$OH is much more efficient for NO$_x$ reduction than CH$_3$OCH$_3$. In situ diffuse reflectance infrared Fourier transform spectroscopy was used to study the reaction mechanism. The enolic species derived from the partial oxidation of C$_2$H$_5$OH over Ag/Al$_2$O$_3$ plays a crucial role in the formation of –NCO species during the selective catalytic reduction (SCR) of NO$_x$ by C$_2$H$_5$OH. The high reactivity of the enolic species results in high surface concentration of –NCO species and high efficiency of NO$_x$ reduction when C$_2$H$_5$OH was used as the reductant. In the case of CH$_3$OCH$_3$, the formate species as the main intermediate has low activity for the formation of –NCO species, which results in the relatively low efficiency during the SCR of NO$_x$.

Key Words: silver; alumina; nitrogen oxide; selective catalytic reduction; ethanol; methyl ether; in situ diffuse reflectance infrared Fourier transform spectroscopy; enolic species; formate species; isocyanate species

Since the first discovery of the high activity of Cu-ZSM-5 in the selective catalytic reduction (SCR) of NO$_x$ by hydrocarbons [1], many studies have been carried out on this subject. Recently, Ag/Al$_2$O$_3$ has been investigated as a promising catalyst, which shows a relatively high activity for the SCR of NO$_x$ by hydrocarbons or oxygen-containing organic compounds in the presence of excess O$_2$ [2–8]. Previous work showed that the Ag/Al$_2$O$_3$-C$_2$H$_5$OH system has a very high activity for the SCR of NO$_x$ even in the presence of SO$_2$ and H$_2$O [4, 5].

It is well known that the reaction mechanism and the rate-determining step of the SCR of NO$_x$ depend on the type of the catalyst, the component of the reagent, the type of the reductant, and the reaction conditions. So far, researchers believed that the –NCO species acts as the key intermediates during the SCR of NO$_x$ [4, 5, 9–11]. Recently, He et al. [12] studied the mechanism of the SCR of NO$_x$ by C$_2$H$_5$OH over Ag/Al$_2$O$_3$ and proposed that a surface enolic species RCH=CH–O⁻, which is derived from the partial oxidation of C$_2$H$_5$OH, plays a crucial role in the formation of the –NCO species.

As C$_2$H$_5$OH and CH$_3$OCH$_3$ are isomeric compounds, it is of

great significance to establish if the SCR of NO$_x$ by CH$_3$OCH$_3$ follows the same mechanism as that of C$_2$H$_5$OH. To obtain further theoretical information with regard to the highly efficient catalyst-reductant system, it is important to investigate the different reaction mechanisms of the SCR of NO$_x$ for both cases. In this study, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to compare the different roles of C$_2$H$_5$OH and CH$_3$OCH$_3$ in the SCR of NO$_x$ over Ag/Al$_2$O$_3$. Emphasis was placed on studying the formation, the role, and the activity of the surface adsorbed species on the catalyst, which would provide a better understanding of the mechanism of the SCR of NO$_x$ for each case and help to design highly efficient systems for the SCR of NO$_x$.

1 Experimental

1.1 Preparation and activity test of the catalyst

The 4% Ag/Al$_2$O$_3$ catalyst was prepared by an impregnation method according to the literature [6]. The catalytic activity was measured in a fixed-bed reactor by passing a gaseous mixture of 0.08% NO, 0.1565% reductant, and 10% O$_2$ in

N_2 balance at a total flow rate of 2 L/min over 0.6 g catalyst ($W/F = 0.018$ (g·s)/ml, GHSV = 50000 h^{-1}). An aqueous C_2H_5OH solution was fed into the gas stream using a syringe pump and vaporized using a coiled heater at the inlet of the reactor. NO_x conversion was analyzed online using a chemiluminescence $NO/NO_2/NO_x$ analyzer (42C-HL, Thermo Environmental Instruments Inc.).

1.2 In situ DRIFTS analysis

In situ DRIFTS spectra were recorded on a NEXUS 670 FT-IR spectrometer equipped with a smart collector and an MCT/A detector cooled by liquid N_2. The catalyst (0.03 g) was finely ground and placed in a ceramic crucible. Prior to each experiment, the catalyst was heated to 873 K in a flow of 10% O_2/N_2 for 60 min and then cooled to the desired temperature. A spectrum of the catalyst in the flow of $N_2 + O_2$ 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 Comparison of the catalytic activity of Ag/Al$_2$O$_3$ during the SCR of NO$_x$ by C$_2$H$_5$OH and CH$_3$OCH$_3$

Fig. 1 compares the reduction of NO_x by C_2H_5OH and CH_3OCH_3 over the Ag/Al$_2$O$_3$ catalyst. When C_2H_5OH was used as the reductant, NO_x was reduced effectively within the whole temperature range, and the maximum NO_x conversion was 99.6% at 690 K. In contrast, there was a relatively low NO_x conversion using CH_3OCH_3 in the whole reaction temperature range, and the highest conversion of NO_x was only 22.5%. These results indicate that the NO_x conversion is
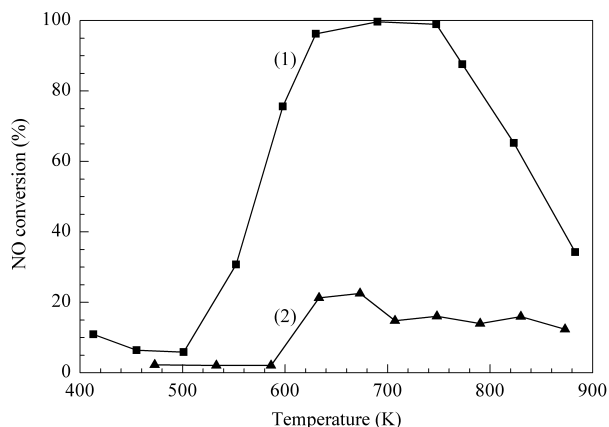

Fig. 1 Comparison of the catalytic activity of Ag/Al$_2$O$_3$ during the selective catalytic reduction (SCR) of NO$_x$ by C$_2$H$_5$OH (1) and CH$_3$OCH$_3$ (2) at various temperatures

(Reaction conditions: $\varphi(NO) = 0.08\%$, $\varphi(C_2H_5OH) = \varphi(CH_3OCH_3) = 0.1565\%$, $\varphi(O_2) = 10\%$, N_2 balance.)

strongly influenced by the structure of the reductants. It has been widely accepted that hydrocarbon activity in the SCR of NO_x increases with the number of carbon atoms and the degree of unsaturation [13]. Although C_2H_5OH and CH_3OCH_3 are isomeric compounds, CH_3OCH_3 is less effective compared with C_2H_5OH for the SCR of NO_x. This difference can be explained on the basis of different mechanisms for each case and it is described in the following sections.

2.2 In situ DRIFTS study of the SCR of NO$_x$ by C$_2$H$_5$OH and CH$_3$OCH$_3$ over Ag/Al$_2$O$_3$

The difference in behavior between C_2H_5OH and CH_3OCH_3 for the SCR of NO_x over Ag/Al$_2$O$_3$ was investigated using the in situ DRIFTS method. The in situ DRIFTS spectra of Ag/Al$_2$O$_3$ were recorded at various temperatures in a steady state after exposing Ag/Al$_2$O$_3$ to NO + O_2 + C_2H_5OH or to NO + O_2 + CH_3OCH_3. The reaction conditions are the same as those in the measurement of activity.

Fig. 2(a) shows the in situ DRIFTS spectra of the Ag/Al$_2$O$_3$ catalyst in a flow of NO + O_2 + C_2H_5OH. It can be seen that several peaks appeared in the region of 1700–1300 cm^{-1}. Based on the previous study [12, 14], the bands at 1585 and 1304 cm^{-1} are due to the adsorbed bidentate nitrate species (NO_3^-), and the peaks at 1579 and 1468 cm^{-1} are associated with the acetate species (CH_3COO^-), while the peaks at 1633, 1416, and 1336 cm^{-1} are assigned to the enolic species ($RCH=CH-O^-$), which was predominantly formed due to the partial oxidation of C_2H_5OH. Furthermore, a very strong peak appeared at 2233 cm^{-1}, which is assigned to the –NCO species. It has been widely accepted that –NCO species is the key intermediate in the SCR of NO_x over Ag/Al$_2$O$_3$, and its high productivity results in the high efficiency of NO_x reduction [9–12, 14]. As can be seen from Fig. 2(a), the intensities of nitrate species and enolic species decreased gradually with the increase in reaction temperature, while the intensity of –NCO species increased gradually with the reaction temperature. At 673 K, the intensity of –NCO species reached the maximum, indicating that the system underwent a quick and efficient reaction, which is in good agreement with the results of the activity study.

Fig. 2(b) represents the in situ DRIFTS spectra of the Ag/Al$_2$O$_3$ catalyst in a flow of NO + O_2 + CH_3OCH_3 in a steady state at various temperatures. Unlike the C_2H_5OH-containing system, when the Ag/Al$_2$O$_3$ catalyst was exposed to a NO + O_2 + CH_3OCH_3 mixture under the same experimental conditions, the peak due to the enolic species (around 1633 cm^{-1}) was not observed, whereas very strong peaks appeared at 1591 and 1379 cm^{-1}, which are assigned to $\nu_{as}(OCO)$ and $\nu_s(OCO)$ of formate species, respectively. In addition, the peaks at 1585 and 1304 cm^{-1} are attributed to the bidentate nitrate species, and the peak at 1562 cm^{-1} corresponds to the monodentate nitrate species, while the peaks at

1616 cm^{-1} is associated with bridge nitrate species [14]. The peak at 1392 cm^{-1} is associated with δ(C–H) of the formate species [12,14], while the very weak peak at 2239 cm^{-1} is due to the –NCO species. Although the formate species is the main surface species on Ag/Al$_2$O$_3$, it has low reactivity with NO$_3^-$ or NO + O$_2$ to form –NCO species, which may account for its relatively low efficiency for the SCR of NO$_x$. This result is in good agreement with that of the activity study.
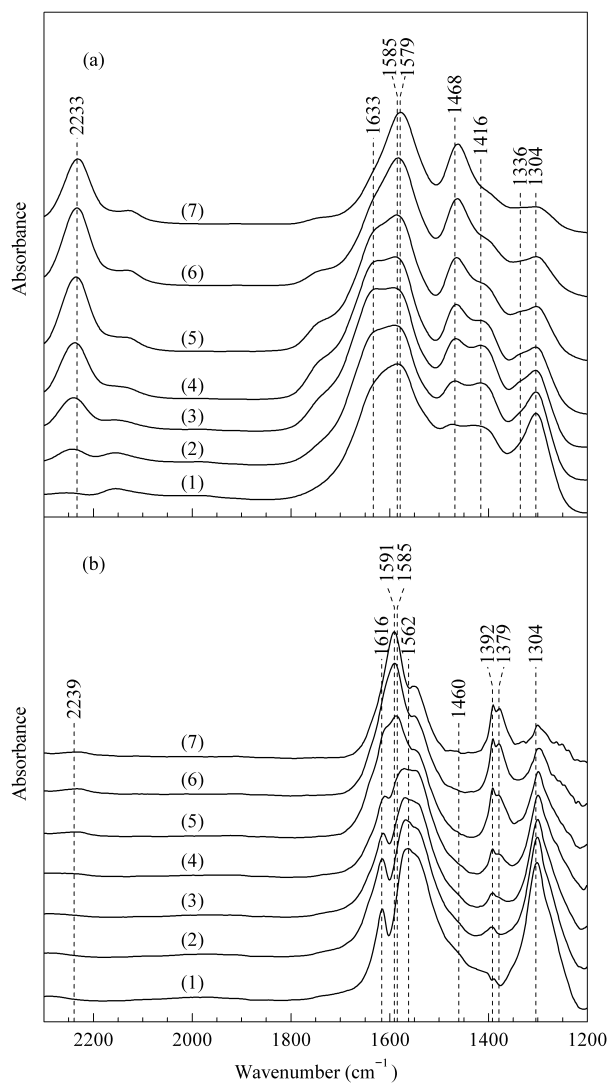
the surface adsorbed species formed on Ag/Al$_2$O$_3$ during the partial oxidation of C$_2$H$_5$OH or CH$_3$OCH$_3$. Fig. 3 shows the in situ DRIFTS spectra of Ag/Al$_2$O$_3$ at various temperatures in a steady state after exposing to the two reductants and O$_2$. As for C$_2$H$_5$OH, the peaks at 1633, 1416, and 1336 cm^{-1} are attributed to the enolic species, and the peaks at 1579 and 1466 cm^{-1} are assigned to the acetate species. In the case of CH$_3$OCH$_3$, the formate species (1595, 1379, and 1392 cm^{-1}) is predominant during its oxidative reaction. This comparative study shows that partial oxidation of CH$_3$OCH$_3$ is different from that of C$_2$H$_5$OH. It is concluded that the different partial oxidation reactions of C$_2$H$_5$OH and CH$_3$OCH$_3$ over Ag/Al$_2$O$_3$ results in the different mechanisms for the SCR of NO$_x$.

Fig. 2 In situ DRIFTS spectra of the adsorbed species over Ag/Al$_2$O$_3$ at different temperatures during the SCR of NO$_x$ by C$_2$H$_5$OH (a) and CH$_3$OCH$_3$ (b)

(1) 473 K, (2) 523 K, (3) 573 K, (4) 623 K,

(5) 673 K, (6) 723 K, (7) 773 K

(The reaction conditions are the same as in Fig. 1.)

2.3 In situ DRIFTS study of the partial oxidation of reductants over Ag/Al$_2$O$_3$

To elucidate the diverse effects of C$_2$H$_5$OH and CH$_3$OCH$_3$ in the SCR of NO$_x$, in situ DRIFTS was used to investigate

Fig. 3 In situ DRIFTS spectra of the adsorbed species over Ag/Al$_2$O$_3$ during the partial oxidation of C$_2$H$_5$OH (a) and CH$_3$OCH$_3$ (b) at different temperatures

(1) 473 K, (2) 523 K, (3) 573 K, (4) 623 K,

(5) 673 K, (6) 723 K, (7) 773 K

(Reaction conditions: φ(C$_2$H$_5$OH) = φ(CH$_3$OCH$_3$) = 0.1565%,

φ(O$_2$) = 10%, N$_2$ balance.)

2.4 Reactivity of the surface adsorbed species over Ag/Al$_2$O$_3$

To obtain further information with regard to the reactivity of the surface adsorbed species during the SCR of NO$_x$ over Ag/Al$_2$O$_3$, in situ DRIFTS was used to evaluate the dynamic performance of these surface adsorbed species. Fig. 4 shows the dynamic changes of in situ DRIFTS spectra of the two reductants and O$_2$ over Ag/Al$_2$O$_3$ as a function of time in a flow of NO + O$_2$ at 673 K. When the catalyst was exposed to C$_2$H$_5$OH + O$_2$ for 60 min (Fig. 4(a)), very strong peaks corresponding to enolic species appeared at 1633, 1416, and 1338
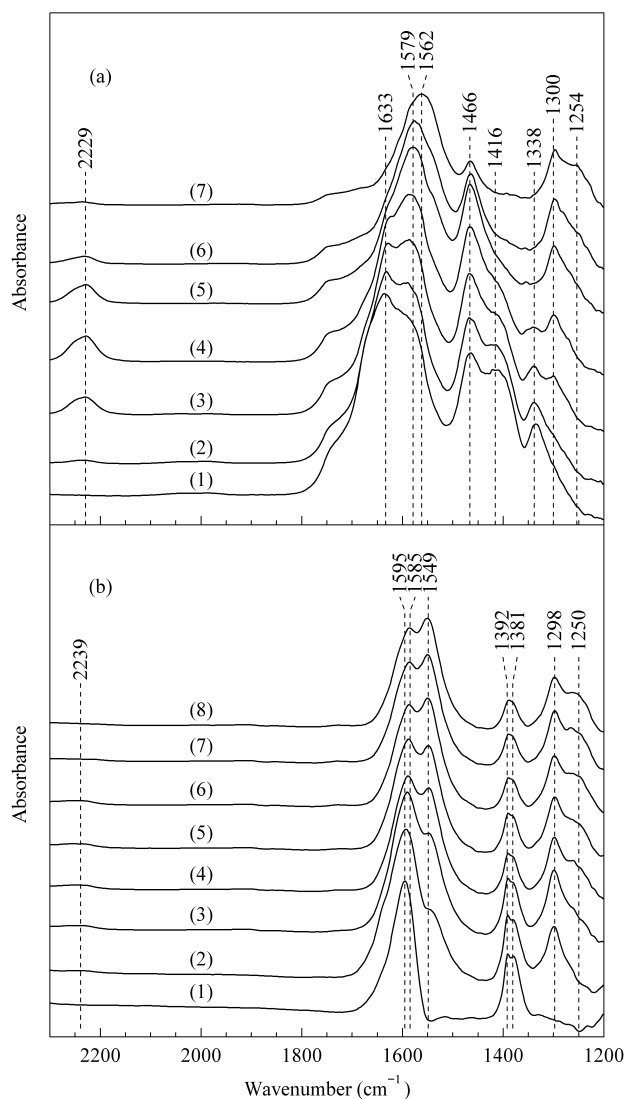

Fig. 4 In situ DRIFTS spectra of the adsorbed species over Ag/Al$_2$O$_3$ during the reaction of the partial oxidation products of C$_2$H$_5$OH (a) and CH$_3$OCH$_3$ (b) with NO + O$_2$ at 673 K
(a) (1) C$_2$H$_5$OH + O$_2$ for 60 min, (2)–(7) NO + O$_2$ for 1 min, 2 min, 3 min, 5 min, 10 min, and 30 min;
(b) (1) CH$_3$OCH$_3$ + O$_2$ for 60 min, (2)–(8) NO + O$_2$ for 1 min, 3 min, 5 min, 10 min, 20 min, 30 min, and 60 min
(The reaction conditions are the same as in Fig. 1.)

cm^{-1}, and the peaks corresponding to acetate species were also observed at 1579 and 1466 cm^{-1}. Switching the feed gas to a flow of NO + O$_2$ resulted in a sharp decrease in the intensity of the enolic species. Meanwhile, a new –NCO peak appeared at 2229 cm^{-1}, and its intensity initially increased and then decreased. When the enolic species was completely consumed, a large amount of nitrates and acetate species became the dominant surface species on Ag/Al$_2$O$_3$, while the surface concentration of –NCO was very low. This result indicates that the enolic species effectively react toward NO + O$_2$ to form –NCO species compared with the acetate species. As a result, it is the enolic species rather than the acetate species that plays a crucial role in the formation of –NCO by the reaction with NO + O$_2$.

The same experiment was carried out by exposing the catalyst to a flow of CH$_3$OCH$_3$ + O$_2$. As shown in Fig. 4(b), the peaks of the formate species (1595, 1392, and 1381 cm^{-1}) were very strong after Ag/Al$_2$O$_3$ was exposed to CH$_3$OCH$_3$ + O$_2$ at 673 K, and switching the feed gas to NO + O$_2$ resulted in a decrease in the intensity of the formate species. Simultaneously, a very weak –NCO peak (2239 cm^{-1}) was observed. The results suggest that the formate species is the main intermediate in the formation of –NCO species during the SCR of NO$_x$ by CH$_3$OCH$_3$ over Ag/Al$_2$O$_3$. This comparative study shows that enolic species has much higher reactivity toward NO + O$_2$ to form –NCO species compared with the formate species over Ag/Al$_2$O$_3$.

Fig. 5 shows the dynamic changes of in situ DRIFTS spectra of NO + O$_2$ over Ag/Al$_2$O$_3$ in a flow of the two reductants and O$_2$ at 673 K, respectively. Exposing the Ag/Al$_2$O$_3$ catalyst to a flow of NO + O$_2$ resulted in the formation of four peaks (1254, 1566, 1298, and 1589 cm^{-1}). As shown in Fig. 5(a), the peaks at 1254 and 1566 cm^{-1} are assigned to the monodentate nitrate species, and the peaks at 1298 and 1589 cm^{-1} are associated with the bidentate nitrate species. Switching the feed gas from NO + O$_2$ to C$_2$H$_5$OH + O$_2$ led to a drastic decrease in the peak intensity of the monodentate nitrate species. In contrast, the intensity of the bidentate nitrate species slowly decreased, suggesting that monodentate nitrate species has a higher reactivity than bidentate nitrate species. Meanwhile, a new –NCO peak appeared at 2229 cm^{-1}, and its intensity increased and then decreased with the time. This indicates that the nitrate species is highly active to react with C$_2$H$_5$OH + O$_2$ to form –NCO species. On the other hand, when the nitrate species was completely consumed, a large amount of enolic species and acetate species became the dominant surface species over Ag/Al$_2$O$_3$.

The same experiment was also carried out using CH$_3$OCH$_3$ as the reductant, and the dynamic changes of in situ DRIFTS spectra as a function of time in a flow of CH$_3$OCH$_3$ + O$_2$ are presented in Fig. 5(b). After the feed gas was switched from NO + O$_2$ to CH$_3$OCH$_3$ + O$_2$, a large amount of nitrate species and formate species still remained on the Ag/Al$_2$O$_3$ catalyst,

indicating that the nitrate species has a low reactivity toward $CH_3OCH_3 + O_2$ to form –NCO species. This result again confirms that C_2H_5OH has a higher reactivity than CH_3OCH_3 during the SCR of NO_x over Ag/Al_2O_3.

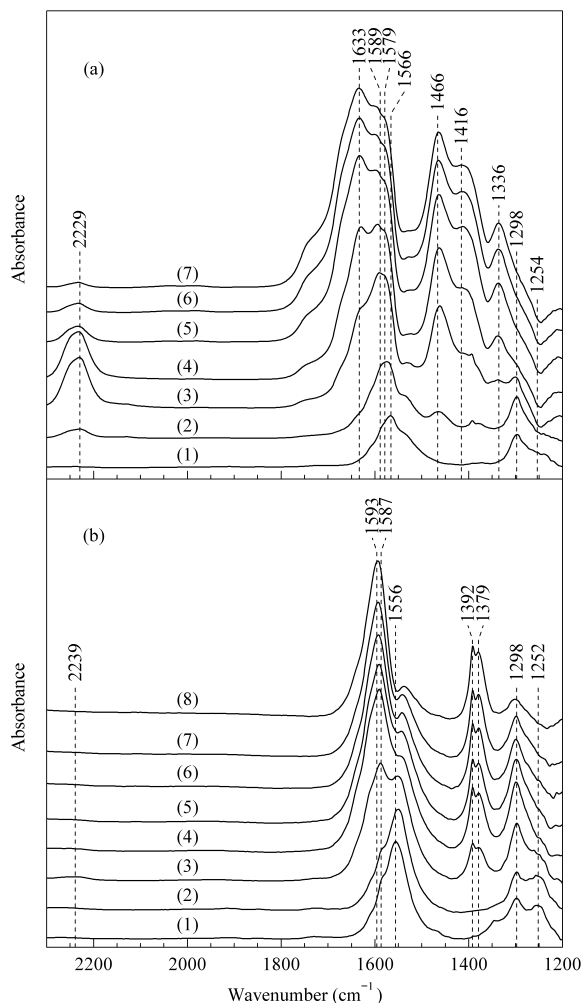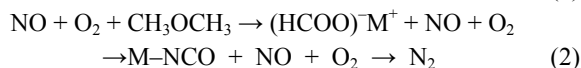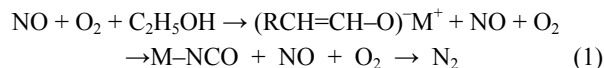**Fig. 5** In situ DRIFTS spectra of the adsorbed species on Ag/Al_2O_3 during the reaction of $NO+O_2$ with the partial oxidation products of C_2H_5OH (a) and CH_3OCH_3 (b) at 673 K

(a) (1) $NO + O_2$ for 60 min; (2)–(7) $C_2H_5OH + O_2$ for 1 min, 2 min, 3 min, 5 min, 10 min, and 30 min;

(b) (1) $NO + O_2$ for 60 min; (2)–(8) $CH_3OCH_3 + O_2$ for 1 min, 2 min, 3 min, 5 min, 10 min, 30 min, and 60 min

(The reaction conditions are the same as in Fig. 1.)

The above dynamic studies by in situ DRIFTS show that during the SCR of NO_x with CH_3OCH_3 over Ag/Al_2O_3, formate species and nitrate species are the main intermediates. In the case of C_2H_5OH, enolic species and nitrate species are the key intermediates. These results suggest that the SCR of NO_x over Ag/Al_2O_3 by C_2H_5OH and CH_3OCH_3 follows different mechanisms, namely:

$$NO + O_2 + C_2H_5OH \rightarrow (RCH{=}CH{-}O)^- M^+ + NO + O_2$$
$$\rightarrow M{-}NCO + NO + O_2 \rightarrow N_2 \qquad (1)$$
$$NO + O_2 + CH_3OCH_3 \rightarrow (HCOO)^- M^+ + NO + O_2$$
$$\rightarrow M{-}NCO + NO + O_2 \rightarrow N_2 \qquad (2)$$

The enolic species and nitrate species formed from partial oxidation and adsorption of NO and C_2H_5OH over the catalyst, respectively, have a high reactivity to react with each other to form –NCO species, thus resulting in high NO_x reduction by C_2H_5OH. However, formate species and nitrate species formed from partial oxidation and adsorption of NO and CH_3OCH_3 over the catalyst have a low reactivity to react with each other to form –NCO species, and this results in the poor reduction of NO_x by CH_3OCH_3 over Ag/Al_2O_3.

3 Conclusions

The SCR of NO_x over Ag/Al_2O_3 by C_2H_5OH and CH_3OCH_3 follows different reaction mechanisms. As the enolic species from C_2H_5OH has much higher reactivity toward $NO + O_2$ to form –NCO species (a major intermediate of the SCR of NO_x with high activity) compared with the formate species from CH_3OCH_3 over Ag/Al_2O_3, C_2H_5OH is more effective than CH_3OCH_3 for the NO_x reduction over Ag/Al_2O_3.

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