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Hydrogen promotes the selective catalytic reduction of NO_x by ethanol over Ag/Al_2O_3

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Abstract

To understand the effect of H_2 on the selective catalytic reduction of NO_x with C_2H_5OH over Ag/Al_2O_3, surface intermediates were examined using in situ DRIFTS spectra, and by-products were identified using GC–MS. Results showed that H_2 addition promoted the partial oxidation of C_2H_5OH to form enolic species, and enhanced the reaction of $-NCO$ with $NO + O_2$ at low temperature. We propose that the enhancement of the enolic species was the main contributor in accelerating NO_x reduction under the presence of H_2 over Ag/Al_2O_3 at low temperatures.

Keywords: Selective catalytic reduction; Ag/Al_2O_3; Enolic species; H_2; In situ DRIFTS; GC–MS

1. Introduction

Ag/Al_2O_3 is known as one of the most effective catalysts for the selective catalytic reduction (SCR) of NO_x by reductants such as hydrocarbons and oxygenated organic compounds [1–4]. In particular, C_2H_5OH is extremely effective for NO_x reduction over Ag/Al_2O_3, which displays high tolerances to water and SO_2 [1,4–6]. However, the activity of Ag/Al_2O_3 for the SCR of NO_x by C_2H_5OH in the low temperature range is still insufficient to be considered as a potential method for NO_x abatement from exhaust gases of diesel engines. Nevertheless, a recent report [7] indicated that the addition of hydrogen to the feed gas resulted in a remarkable improvement of the NO_x reduction at temperatures below ca. 623 K using a series of lower alkanes (alkenes) as reductants. Using in situ FTIR spectroscopy, it was discovered that the formation of some intermediates, such as acetate, nitrite, nitrate species, and isocyanate ($-NCO$), was promoted by the addition of H_2 over Ag/Al_2O_3 surface in the SCR of NO_x with several hydrocarbons [7–10]. However, the SCR of NO_x by oxygenates in the presence of H_2 has not been reported.

Our previous studies proposed a possible reaction mechanism for the SCR of NO_x by C_2H_5OH over Ag/Al_2O_3 [11]. As an important intermediate, the novel enolic surface species originated from the partial oxidation of C_2H_5OH was identified on Ag/Al_2O_3. This species was highly reactive towards $NO + O_2$ to form the crucial intermediate $-NCO$ and related with the high efficiency of NO_x reduction.

The present study aims at investigating the possible promotion effect of H_2 on the SCR of NO_x by C_2H_5OH.

2. Experimental

2.1. Catalyst preparation

The alumina-supported silver catalyst (4% Ag/Al_2O_3) was prepared by an impregnation of γ-Al_2O_3 powder

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(200 m^2/g) with an appropriate amount of silver nitrate aqueous solution. The sample was dried at 393 K overnight and calcined at 873 K for 3 h in air. The catalysts were then sieved into 20–40 meshes before use.

2.2. Catalytic tests

The catalytic activity measurement over Ag/Al_2O_3 was carried out in a fixed-bed reactor connected to a temperature controller. A basic gas mixture consisting of 800 ppm NO, 1565 ppm C_2H_5OH, 10% O_2, and 10% H_2O in N_2 was used in the activity tests. The total gas flow rate was 2000 mL/min over 0.6 g catalyst ($W/F = 0.018$ g s cm^{-3}, GHSV = ~50,000 h^{-1}). The effect of hydrogen was studied by adding 1% H_2 to the basic gas mixture. NO_x conversion was analyzed on-line by a chemiluminescene $NO/NO_2/NO_x$ analyzer (42C-HL, Thermo Electron).

2.3. Products analysis

The gas products were analyzed using gas chromatography (Agilent 6890N GC) coupled to a mass spectrometer (Agilent 5973N MS) with a capillary column HP-PLOT Q (Agilent 30 m × 0.32 mm, 20 μm film).

2.4. In situ diffuse reflectance infrared Fourier transform spectroscopy procedure

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded on a Nexus 670 (Thermo Nicolet) FT-IR, equipped with an in situ diffuse reflection chamber and a high sensitivity MCT/A detector cooled by liquid nitrogen. The Ag/Al_2O_3 catalyst for in situ DRIFTS study was finely ground and placed into a ceramic crucible. Prior to recording each DRIFTS spectrum, Ag/Al_2O_3 catalyst was heated in situ in $O_2 + N_2$ flow for 60 min at 573 and 873 K, respectively, then cooled to the desired temperature for taking the reference spectrum. 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. Effect of H_2 on the catalytic activity

Figs. 1(a) and (b) show the NO_x conversions for the C_2H_5OH-SCR of NO_x without or with 1% H_2 over Ag/Al_2O_3 catalyst at various temperatures. The NO_x conversion in the feed gas without H_2 was less than 20% at 473 K, but reached the maximum of 97% at 630 K, as shown in Fig. 1(a). Clearly, the reduction of NO_x was significantly enhanced by the addition of H_2, especially in the low temperature range of 423–523 K, as shown in Fig. 1(b). It is notable that H_2 addition increased NO_x conversion by ca. 85% at 473 K and up to 90% over a wide temperature range of 493–740 K. Compared with the case without H_2, the NO_x conversion with H_2 was not significantly different from that without H_2 at temperatures higher than 623 K, indicating that H_2 is more efficient in increasing the NO_x conversion at low temperatures than high temperatures. Figs. 1(c) and (d) show the C_2H_5OH conversion to CO_2 during the C_2H_5OH-SCR of NO_x over Ag/Al_2O_3 catalyst. Compared with the case without H_2, the presence of H_2 also greatly promoted the oxidation of C_2H_5OH to CO_2.

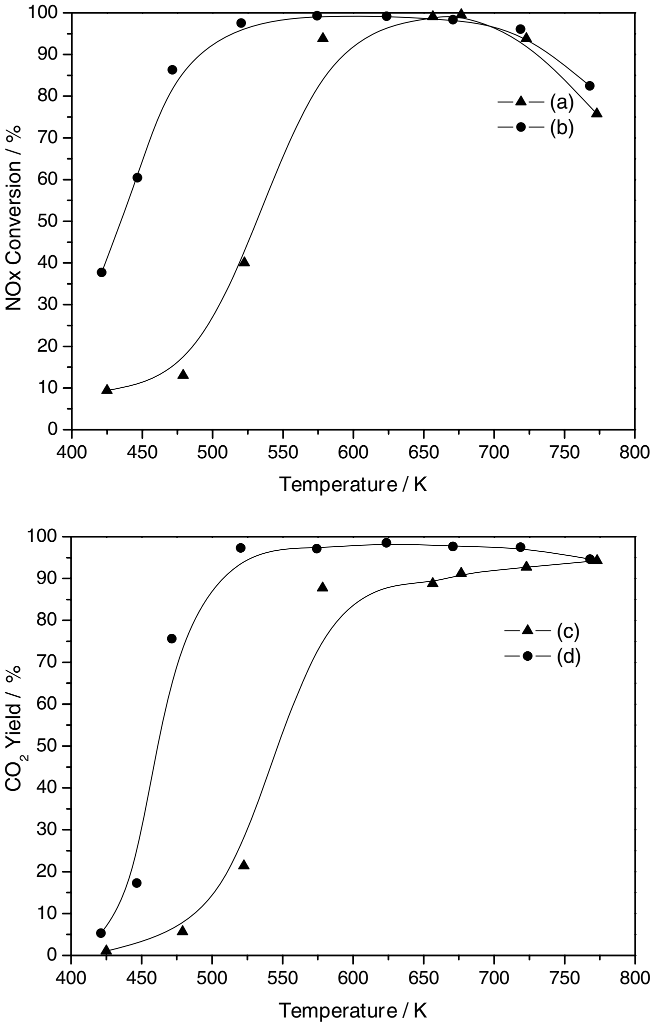


Fig. 1. NO_x conversion (a, b) and CO_2 yield (c, d) for the SCR of NO_x by C_2H_5OH over Ag/Al_2O_3 catalyst in the absence of H_2 (a, c) and presence of 1% H_2 (b, d). Reaction conditions: NO, 800 ppm; C_2H_5OH, 1565 ppm; O_2, 10%; H_2O, 10% in N_2 balance at total flow rate 2000 mL/min, GHSV = 50,000 h^{-1}.

3.2. GC–MS analysis

GC–MS analyses of the gaseous products were performed between 423 and 623 K after steady state in the reaction of $NO + C_2H_5OH + O_2$ was reached in the absence or the presence of H_2, as shown in Figs. 2(a) and (b). The light gaseous molecules such as CO_2, N_2O, N_2, and CO were detected within 5 min retention time. The oxygen- and nitrogen-containing compounds were produced during the SCR of NO_x with C_2H_5OH accompanied with the main products N_2, CO_2 and H_2O. Therefore, it is possible to postulate a reaction pathway by following the origin of minor products even though their concentrations were very low in comparison with N_2, CO_2 and H_2O. In the absence of H_2, as shown in Fig. 2(a), a small amount of CH_3CHO was detected along with a large amount of unreacted C_2H_5OH, but no other nitrogen-containing compounds were observed at 423 K. The intensity of the CH_3CHO peak increased gradually from 423 to 523 K, and then decreased with further increasing temperature. Considering that the conversions of NO_x and C_2H_5OH were very low at both 423 and 473 K, as shown in Figs. 1(a) and (c), CH_3CHO likely originated from the partial oxidation of C_2H_5OH by molecular oxygen. At 523 K, where ca. 30% NO_x conversion was achieved (Fig. 1(a)), the production of CH_3CHO was maximized and CH_3NO_2 markedly appeared. At 573 K, CH_3CN appeared, accompanied with a disappearance of CH_3NO_2.

During the NO_x reduction by C_2H_5OH with the addition of H_2, CH_3CHO was produced significantly and the amount of CH_3CHO reached its maximum at 423 K, along with the appearance of CH_3NO_2 (Fig. 2(b)). These results were also reasonable if the NO_x and C_2H_5OH conversions in Figs. 1(b) and (d) were considered. At 473 K, the disappearance of C_2H_5OH and the traces of CH_3CHO and CH_3NO_2 under this condition suggested that the reaction proceeded efficiently. In comparison with Figs. 2(a) and (b), it is obvious that the presence of H_2 promoted the formation of oxygen-containing molecules (such as CH_3CHO) and nitrogen-containing molecules (such as CH_3NO_2) during the SCR of NO_x by C_2H_5OH even at a temperature as low as 423 K. On the other hand, the addition of H_2 improved the efficiency of NO_x reduction, and reduced the emission of CH_3CHO gas at temperatures above 473 K.

Based on the analysis of gaseous products, we surmise that the addition of H_2 significantly promoted the partial oxidation of C_2H_5OH to CH_3CHO. As we previously proposed, enolic surface species $(RCH{=}CH{-}O^-){-}M$ was formed when CH_3CHO adsorbed on the surface of Ag/Al_2O_3 [11,12]. The formation of enolic surface species could be attributed to the CH_3CHO isomerization between the gaseous phase and catalyst surface. The enolic species is related to the high efficiency of NO_x reduction by C_2H_5OH over Ag/Al_2O_3. Thereby, we studied the partial oxidation of C_2H_5OH on Ag/Al_2O_3 in the presence of H_2 and its effect on the SCR of NO_x using in situ DRIFTS.

3.3. FT-IR studies

3.3.1. Dynamic changes of in situ DRIFTS study of the partial oxidation of C_2H_5OH in the presence of H_2

The effect of hydrogen on the formation of oxygenated species was studied by in situ DRIFTS at 423 K. Fig. 3 shows the in situ DRIFTS spectra of Ag/Al_2O_3 in a flow of $C_2H_5OH + O_2$ and then $C_2H_5OH + O_2 + H_2$. After exposing Ag/Al_2O_3 to a flow of $C_2H_5OH + O_2$ for 30 min, the peaks at 1635, 1579, 1460, and 1392 cm^{-1} were detected. The strong bands at 1579 and 1460 cm^{-1} were attributed to $\nu_{as}(OCO)$ and $\nu_s(OCO)$ of adsorbed acetate,

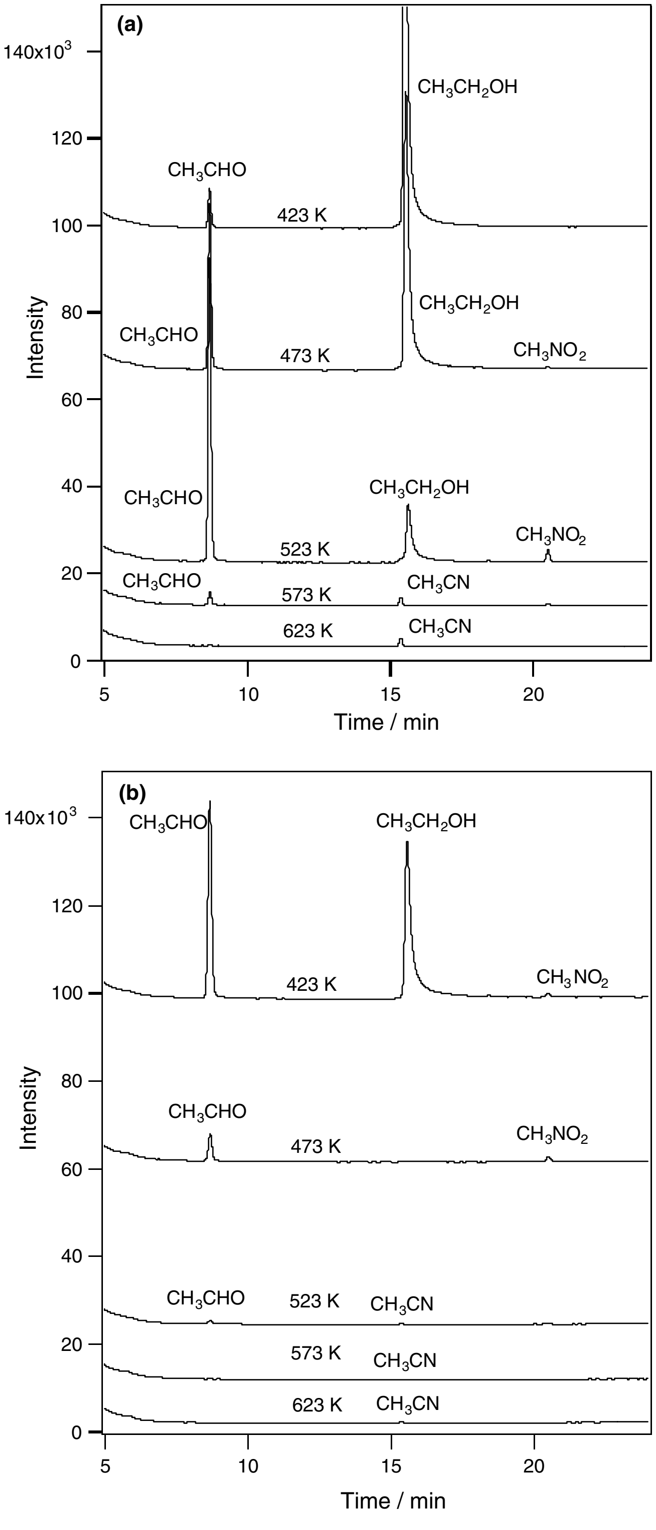


Fig. 2. GC–MS chromatogram of gaseous products of $C_2H_5OH + NO + O_2$ reaction in the absence of H_2 (a) and presence of 1% H_2 (b) at various temperatures over Ag/Al_2O_3 catalyst. Reaction conditions: NO, 800 ppm; C_2H_5OH, 1565 ppm; O_2, 10%; H_2O, 10% in N_2 balance at total flow rate 2000 mL/min, GHSV = 50,000 h^{-1}.

respectively [13]. The peak at 1392 cm^{-1} was assigned to δ(C—H) of adsorbed acetate [14]. Based on our previous studies [4,11,12], the weak peak at 1635 cm^{-1} could be assigned to ν_{as}(RCH═C—O) of a surface enolic structure, derived from the partial oxidation of C_2H_5OH. The bands assignable to acetate were predominant at 423 K in the absence of H_2. When H_2 was added to the flow of $C_2H_5OH + O_2$ at the same temperature, the bands due to adsorbed acetate (1579 and 1460 cm^{-1}) and δ(C—H) (1392 cm^{-1}) were similarly observed. However, it should be noted that the peak at 1635 cm^{-1} (attributed to enolic species) intensified gradually as a function of time, accompanied by the appearance of the peaks at 1417 and 1336 cm^{-1}. The bands at 1417 and 1336 cm^{-1} were attributed to ν_s(RCH═C—O) and δ(C—H) of the enolic species, respectively [4,11,12]. After flowing H_2 for 30 min, the peak at 1635 cm^{-1} achieved its maximum intensity, indicating that enolic species became the predominant surface species. On the basis of these observations, it is suggested that the presence of H_2 might have promoted the partial oxidation of C_2H_5OH, especially the formation of enolic species at 423 K.

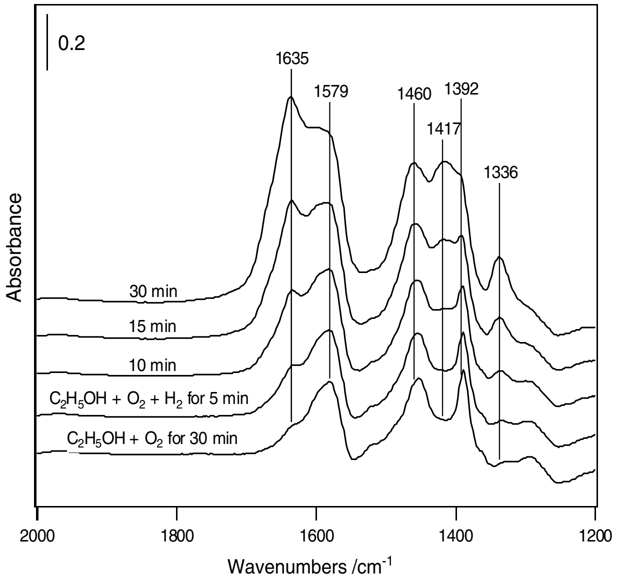


Fig. 3. Dynamic changes of in situ DRIFTS spectra of Ag/Al_2O_3 as a function of time in a flow of $C_2H_5OH + O_2 + H_2$ at 423 K. Before the measurement, the catalyst was pre-exposed to a flow of $C_2H_5OH + O_2$ for 30 min at 423 K. Conditions: C_2H_5OH, 1565 ppm; O_2, 10%; H_2, 1%.

3.3.2. Dynamic changes of in situ DRIFTS study of the SCR of NO_x by C_2H_5OH in the presence of H_2

To elucidate the effect of H_2 on the SCR of NO_x, we investigated the reaction intermediates on the Ag/Al_2O_3 at 473 K by DRIFTS. Fig. 4 shows the in situ DRIFTS spectra of Ag/Al_2O_3 in a flow of $C_2H_5OH + NO + O_2$ and then $C_2H_5OH + NO + O_2 + H_2$. After pre-exposing the catalyst to a flow of $C_2H_5OH + NO + O_2$ for 60 min, the strong bands at 1591 and 1304 cm^{-1} assigned to bidentate nitrates (NO_3^-) and the bands at 1576 and 1466 cm^{-1} assigned to acetate were observed [13,14]. In addition, the band at 1633 cm^{-1} which is associated with enolic species appeared. By examining the intensity of each peak under

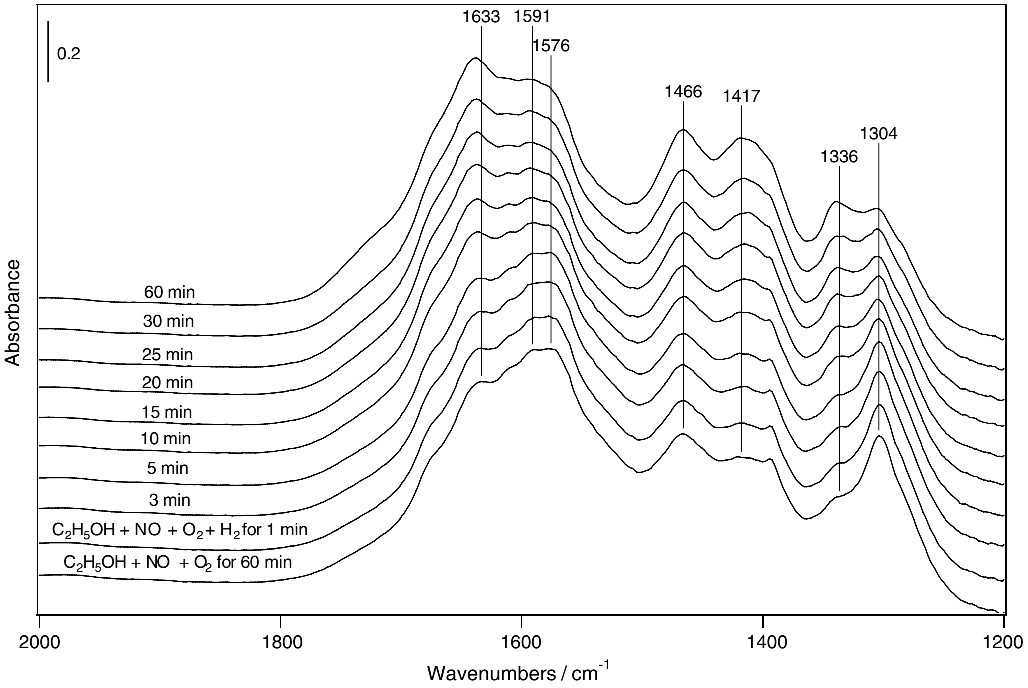


Fig. 4. Dynamic changes of in situ DRIFTS spectra of Ag/Al_2O_3 as a function of time in a flow of $C_2H_5OH + NO + O_2 + H_2$ at 473 K. Before the measurement, the catalyst was pre-exposed to a flow of $C_2H_5OH + NO + O_2$ for 60 min at 473 K. Conditions: NO, 800 ppm; C_2H_5OH, 1565 ppm; O_2, 10%; H_2, 1%.

a flow of $C_2H_5OH + NO + O_2$, the nitrates (1591 and 1304 cm^{-1}) appeared to dominate on Ag/Al_2O_3 at this temperature. After adding H_2 to the mixture of $C_2H_5OH + NO + O_2$, the bands of adsorbed bidentate nitrate (1591 and 1304 cm^{-1}) and acetate (1576 and 1466 cm^{-1}) were still visible at the same temperature. The surface concentration of the enolic species (1633, 1417 and 1336 cm^{-1}) increased significantly with time, and the peaks associated with this species became the most intense among all absorbed species peaks in 20 min. This result strongly suggests that the presence of H_2 facilitates the formation of enolic species during the NO_x reduction by C_2H_5OH even at very low temperature. Another obvious difference was that the bands for surface bidentate nitrates (1591 and 1304 cm^{-1}) clearly decreased with time, indicating low steady state nitrate coverage in the presence of H_2. According to our previous studies [4,11,12], the high reactivity between enolic species and NO_3^- is related with high efficiency of NO_x reduction using C_2H_5OH as a reductant. Considering the relatively high surface concentration of enolic species and its high reactivity towards nitrates, it is also reasonable that the intensity of nitrates decreases in the presence of H_2.

To obtain further information on the effect of H_2 on the whole reaction, the reactions of —NCO with $NO + O_2$ with and without the addition of H_2 were further investigated by in situ DRIFTS. After pre-treating the sample in $C_2H_5OH + NO + O_2$ for 60 min at 523 K as shown in Figs. 5(a) and (b), the peak at 2233 cm^{-1} for —NCO and the

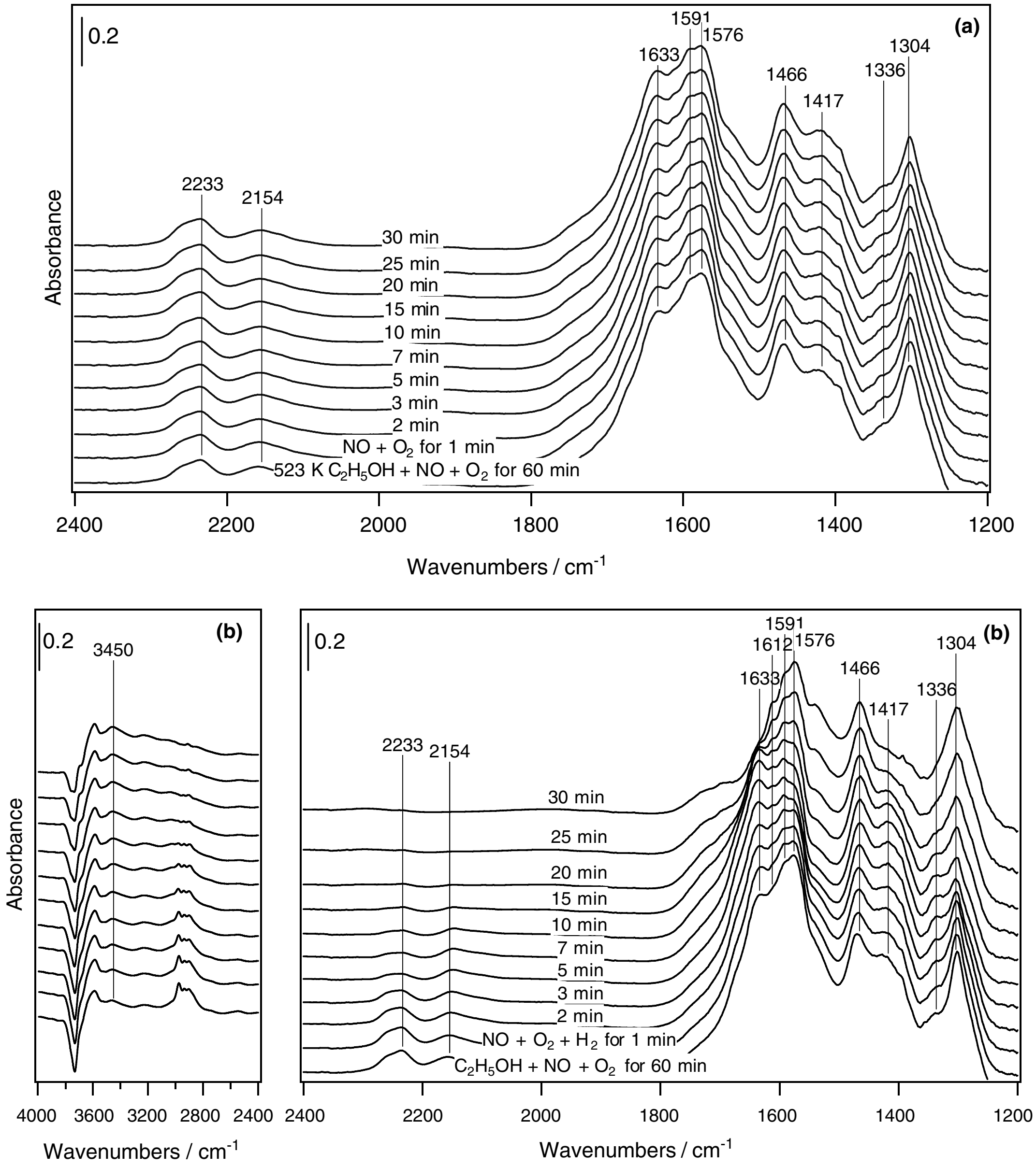
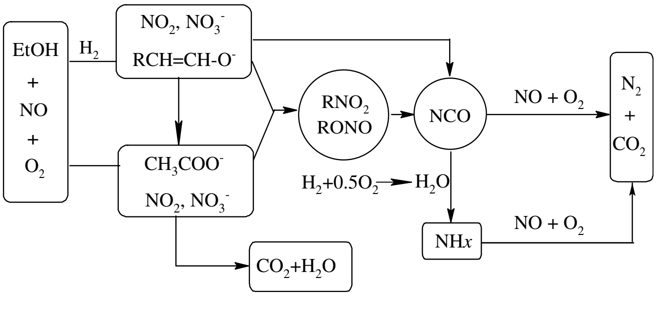


Fig. 5. Dynamic changes of in situ DRIFTS spectra of Ag/Al_2O_3 in a flow of $NO + O_2$ (a) and in a flow of $NO + O_2 + H_2$ (b) as a function of time at 523 K. Before the measurement, the catalyst was pre-exposed to a flow of $C_2H_5OH + NO + O_2$ for 60 min at 523 K. Conditions: NO, 800 ppm; C_2H_5OH, 1565 ppm; O_2, 10%; H_2, 1%.

peak at 2154 cm^{-1} for —CN were observed [13,15]. As seen in Fig. 5(a), when C_2H_5OH flow was interrupted, continual monitoring of the adsorbed species in the flow of $NO + O_2$ revealed that —NCO and —CN did not react with $NO + O_2$ in 30 min at 523 K. However, as shown in Fig. 5(b), the intensity of the adsorbed —NCO bands decreased and completely disappeared in 20 min, indicating a strong reactivity of the adsorbed —NCO species in the flow of $NO + O_2 + H_2$ at this temperature. It is noticeable that a new peak at 1612 cm^{-1} in Fig. 5(b) gradually showed up accompanied with the disappearance of —NCO, and this new peak may be due to a deformation mode of adsorbed NHx [16,17]. At the same time, a weak peak was also observed at 3450 cm^{-1}, which may be assigned to the stretching vibration mode of NH species [18]. Based on the results above, the consumption of —NCO species may be related with rapid hydrolysis of —NCO species in the flow of $NO + O_2 + H_2$, resulting in the formation of NHx species. In addition, the intensity of enolic species (1633 cm^{-1}) decreased in $NO + O_2 + H_2$ after —NCO disappeared, indicating that the enolic species was also reactive in $NO + O_2 + H_2$.

3.4. Mechanism analysis

In the absence of H_2, the SCR of NO_x by C_2H_5OH starts with the formation of both adsorbed nitrates via NO oxidation by O_2 and enolic and acetate species via the partial oxidation of C_2H_5OH over Ag/Al_2O_3. The reaction between the nitrates and enolic species (and/or acetate) then leads to the formation of —NCO, which reacts with $NO + O_2$ and nitrates to yield N_2 [4,11,12]. Combining the results of this experiment with the mechanism proposed above, we summarize a simplified reaction scheme for the NO_x reduction by C_2H_5OH in the presence of H_2. As shown in Scheme 1, the presence of H_2 first promotes the partial oxidation of C_2H_5OH to enolic species. Because the high reactivity of enolic species with nitrates is related with the high efficiency of NO_x reduction, the addition of H_2 improves the reaction activity. On the other hand, when H_2 was added to the $NO + O_2$ feed gas, a rapid consumption of —NCO was observed (Fig. 5(b)), possibly because the hydrolysis of —NCO by hydroxyl groups formed in the flow of $NO + O_2 + H_2$ resulted in the formation of NHx species. In fact, the —NCO hydrolysis products (NHx and NH_3) were observed by in situ DRIFTS spectra in this experiment (Fig. 5(b)). The resulting NHx species are known to be highly active towards NO_x reduction when using NH_3 as a reductant over Ag/Al_2O_3 in the presence of H_2 [19]. Therefore, the formation of NHx species may be another reason that the addition of H_2 improves the reaction activity. While the influence of H_2 may not be exactly the same as the influence of OH/H_2O for —NCO hydrolysis, the particularity of the Ag/Al_2O_3 catalyst may also play an important role.



Scheme 1. The possible effect of H_2 on the SCR of NO_x by C_2H_5OH over Ag/Al_2O_3.

4. Conclusion

The selective catalytic reduction of NO_x with ethanol over Ag/Al_2O_3 was promoted by the addition of H_2 to the mixture of $C_2H_5OH + NO + O_2$ at low temperatures. Based on the experimental results, we propose that the addition of H_2 improves NO_x reduction by promoting the formation of the enolic species and enhancing the reactivity of —NCO.

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