Hydrogen promotes the selective catalytic reduction of NO\textsubscript{x} by ethanol over Ag/Al\textsubscript{2}O\textsubscript{3}

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Abstract

To understand the effect of H\textsubscript{2} on the selective catalytic reduction of NO\textsubscript{x} with C\textsubscript{2}H\textsubscript{5}OH over Ag/Al\textsubscript{2}O\textsubscript{3}, surface intermediates were examined using in situ DRIFTS spectra, and by-products were identified using GC–MS. Results showed that H\textsubscript{2} addition promoted the partial oxidation of C\textsubscript{2}H\textsubscript{5}OH to form enolic species, and enhanced the reaction of $\text{A NCO}$ with NO + O\textsubscript{2} at low temperature. We propose that the enhancement of the enolic species was the main contributor in accelerating NO\textsubscript{x} reduction under the presence of H\textsubscript{2} over Ag/Al\textsubscript{2}O\textsubscript{3} at low temperatures.

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1. Introduction

Ag/Al\textsubscript{2}O\textsubscript{3} is known as one of the most effective catalysts for the selective catalytic reduction (SCR) of NO\textsubscript{x} by reductants such as hydrocarbons and oxygenated organic compounds [1–4]. In particular, C\textsubscript{2}H\textsubscript{5}OH is extremely effective for NO\textsubscript{x} reduction over Ag/Al\textsubscript{2}O\textsubscript{3}, which displays high tolerances to water and SO\textsubscript{2} [1,4–6]. However, the activity of Ag/Al\textsubscript{2}O\textsubscript{3} for the SCR of NO\textsubscript{x} by C\textsubscript{2}H\textsubscript{5}OH in the low temperature range is still insufficient to be considered as a potential method for NO\textsubscript{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\textsubscript{x} reduction at temperatures below ca. 623 K using a series of lower alkanes (alk- enes) as reductants. Using in situ FTIR spectroscopy, it was discovered that the formation of some intermediates, such as acetate, nitrite, nitrate species, and isocyanate ($\text{A NCO}$), was promoted by the addition of H\textsubscript{2} over Ag/Al\textsubscript{2}O\textsubscript{3} surface in the SCR of NO\textsubscript{x} with several hydrocarbons [7–10]. However, the SCR of NO\textsubscript{x} by oxygenates in the presence of H\textsubscript{2} has not been reported.

Our previous studies proposed a possible reaction mechanism for the SCR of NO\textsubscript{x} by C\textsubscript{2}H\textsubscript{5}OH over Ag/Al\textsubscript{2}O\textsubscript{3} [11]. As an important intermediate, the novel enolic surface species originated from the partial oxidation of C\textsubscript{2}H\textsubscript{5}OH was identified on Ag/Al\textsubscript{2}O\textsubscript{3}. This species was highly reactive towards NO + O\textsubscript{2} to form the crucial intermediate $\text{A NCO}$ and related with the high efficiency of NO\textsubscript{x} reduction.

The present study aims at investigating the possible promotion effect of H\textsubscript{2} on the SCR of NO\textsubscript{x} by C\textsubscript{2}H\textsubscript{5}OH.

2. Experimental

2.1. Catalyst preparation

The alumina-supported silver catalyst (4% Ag/Al\textsubscript{2}O\textsubscript{3}) was prepared by an impregnation of $\gamma$-Al\textsubscript{2}O\textsubscript{3} powder...
2.2. Catalytic tests

The catalytic activity measurement over Ag/Al₂O₃ was carried out in a fixed-bed reactor connected to a temperature controller. A basic gas mixture consisting of 800 ppm NO, 1565 ppm C₂H₅OH, 10% O₂, and 10% H₂O in N₂ 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% H₂ to the basic gas mixture. NOₓ conversion was analyzed on-line by a chemiluminescence NO/NO₂/NOₓ 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/Al₂O₃ catalyst for in situ DRIFTS study was finely ground and placed into a ceramic crucible. Prior to recording each DRIFTS spectrum, Ag/Al₂O₃ catalyst was heated in situ in O₂+N₂ 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 H₂ on the catalytic activity

Figs. 1(a) and (b) show the NOₓ conversions for the C₂H₅OH-SCR of NOₓ without or with 1% H₂ over Ag/Al₂O₃ catalyst at various temperatures. The NOₓ conversion in the feed gas without H₂ 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 NOₓ was significantly enhanced by the addition of H₂, especially in the low temperature range of 423–523 K, as shown in Fig. 1(b). It is notable that H₂ addition increased NOₓ 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 H₂, the NOₓ conversion with H₂ was not significantly different from that without H₂ at temperatures higher than 623 K, indicating that H₂ is more efficient in increasing the NOₓ conversion at low temperatures than high temperatures. Figs. 1(c) and (d) show the C₂H₅OH conversion to CO₂ during the C₂H₅OH-SCR of NOₓ over Ag/Al₂O₃ catalyst. Compared with the case without H₂, the presence of H₂ also greatly promoted the oxidation of C₂H₅OH to CO₂.

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 + C₂H₅OH + O₂ was reached in the absence or the presence of H₂, as shown in Figs. 2(a) and (b). The light gaseous molecules such as CO₂, N₂O, N₂, and CO were detected within 5 min retention time. The oxygen- and nitrogen-containing compounds were pro-
duced during the SCR of NO$_x$ with C$_2$H$_5$OH accompanied with the main products N$_2$, CO$_2$ and H$_2$O. 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$_2$O. In the absence of H$_2$, as shown in Fig. 2(a), a small amount of CH$_3$CHO was detected along with a large amount of unreacted C$_2$H$_5$OH, but no other nitrogen-containing compounds were observed at 423 K. The intensity of the CH$_3$CHO peak increased gradually from 423 to 523 K, and then decreased with further increasing temperature. Considering that the conversions of NO$_x$ and C$_2$H$_5$OH were very low at both 423 and 473 K, as shown in Figs. 1(a) and (c), CH$_3$CHO likely originated from the partial oxidation of C$_2$H$_5$OH by molecular oxygen. At 523 K, where ca. 30% NO$_x$ conversion was achieved (Fig. 1(a)), the production of CH$_3$CHO was maximized and CH$_3$NO$_2$ markedly appeared. At 573 K, CH$_3$CN appeared, accompanied with a disappearance of CH$_3$NO$_2$.

During the NO$_x$ reduction by C$_2$H$_5$OH with the addition of H$_2$, CH$_3$CHO was produced significantly and the amount of CH$_3$CHO reached its maximum at 423 K, along with the appearance of CH$_3$NO$_2$ (Fig. 2(b)). These results were also reasonable if the NO$_x$ and C$_2$H$_5$OH conversions in Figs. 1(b) and (d) were considered. At 473 K, the disappearance of C$_2$H$_5$OH and the traces of CH$_3$CHO and CH$_3$NO$_2$ 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$_3$CHO) and nitrogen-containing molecules (such as CH$_3$NO$_2$) during the SCR of NO$_x$ by C$_2$H$_5$OH 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$_3$CHO 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$_2$H$_5$OH to CH$_3$CHO. As we previously proposed, enolic surface species (RCH=CH−O−M) was formed when CH$_3$CHO adsorbed on the surface of Ag/Al$_2$O$_3$ [11,12]. The formation of enolic surface species could be attributed to the CH$_3$CHO isomerization between the gaseous phase and catalyst surface. The enolic species is related to the high efficiency of NO$_x$ reduction by C$_2$H$_5$OH over Ag/Al$_2$O$_3$. Thereby, we studied the partial oxidation of C$_2$H$_5$OH on Ag/Al$_2$O$_3$ 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$_2$H$_5$OH 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$_2$O$_3$ in a flow of C$_2$H$_5$OH + O$_2$ and then C$_2$H$_5$OH + O$_2$ + H$_2$. After exposing Ag/Al$_2$O$_3$ to a flow of C$_2$H$_5$OH + 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 $v_{as}$(OCO) and $v_{s}$(OCO) of adsorbed acetate,
respectively [13]. The peak at 1392 cm\(^{-1}\) was assigned to \(\delta(C-H)\) of adsorbed acetate [14]. Based on our previous studies [4,11,12], the weak peak at 1635 cm\(^{-1}\) could be assigned to \(v_{\text{as}}(\text{RCH}==\text{C}O)\) of a surface enolic structure, derived from the partial oxidation of \(\text{C}_2\text{H}_5\text{OH}\). The bands assignable to acetate were predominant at 423 K in the absence of \(\text{H}_2\). When \(\text{H}_2\) was added to the flow of \(\text{C}_2\text{H}_5\text{OH} + \text{O}_2\) at the same temperature, the bands due to adsorbed acetate (1579 and 1460 cm\(^{-1}\)) and \(\delta(C-H)\) (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 \(v_{\text{as}}(\text{RCH}==\text{C}O)\) and \(\delta(C-H)\) of the enolic species, respectively [4,11,12]. After flowing \(\text{H}_2\) 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 \(\text{H}_2\) might have promoted the partial oxidation of \(\text{C}_2\text{H}_5\text{OH}\), especially the formation of enolic species at 423 K.

3.3.2. Dynamic changes of in situ DRIFTS study of the SCR of \(\text{NO}_x\) by \(\text{C}_2\text{H}_5\text{OH}\) in the presence of \(\text{H}_2\)

To elucidate the effect of \(\text{H}_2\) on the SCR of \(\text{NO}_x\), we investigated the reaction intermediates on the \(\text{Ag/Al}_2\text{O}_3\) at 473 K by DRIFTS. Fig. 4 shows the in situ DRIFTS spectra of \(\text{Ag/Al}_2\text{O}_3\) in a flow of \(\text{C}_2\text{H}_5\text{OH} + \text{NO} + \text{O}_2\) and then \(\text{C}_2\text{H}_5\text{OH} + \text{NO} + \text{O}_2 + \text{H}_2\). After pre-exposing the catalyst to a flow of \(\text{C}_2\text{H}_5\text{OH} + \text{NO} + \text{O}_2\) for 60 min, the strong bands at 1591 and 1304 cm\(^{-1}\) assigned to bidentate nitrates (\(\text{NO}_3^-\)) 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
a flow of C₂H₅OH + NO + O₂, the nitrates (1591 and 1304 cm⁻¹) appeared to dominate on Ag/Al₂O₃ at this temperature. After adding H₂ to the mixture of C₂H₅OH + NO + O₂, 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 H₂ facilitates the formation of enolic species during the NOₓ reduction by C₂H₅OH 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 H₂. According to our previous studies [4,11,12], the high reactivity between enolic species and NO₃⁻ is related with high efficiency of NOₓ reduction using C₂H₅OH 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 H₂.

To obtain further information on the effect of H₂ on the whole reaction, the reactions of −NCO with NO + O₂ with and without the addition of H₂ were further investigated by in situ DRIFTS. After pre-treating the sample in C₂H₅OH + NO + O₂ for 60 min at 523 K as shown in Figs. 5(a) and (b), the peak at 2233 cm⁻¹ for −NCO and the

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**Fig. 5.** Dynamic changes of in situ DRIFTS spectra of Ag/Al₂O₃ in a flow of NO + O₂ (a) and in a flow of NO + O₂ + H₂ (b) as a function of time at 523 K. Before the measurement, the catalyst was pre-exposed to a flow of C₂H₅OH + NO + O₂ for 60 min at 523 K. Conditions: NO, 800 ppm; C₂H₅OH, 1565 ppm; O₂, 10%; H₂, 1%.
peak at 2154 cm\(^{-1}\) for \(-\text{CN}\) were observed [13,15]. As seen in Fig. 5(a), when C\(_2\)H\(_5\)OH flow was interrupted, continual monitoring of the adsorbed species in the flow of NO + O\(_2\) revealed that \(-\text{NCO}\) and \(-\text{CN}\) 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 \(-\text{NCO}\) bands decreased and completely disappeared in 20 min, indicating a strong reactivity of the adsorbed \(-\text{NCO}\) 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 \(-\text{NCO}\), and this new peak may be due to a deformation mode of adsorbed NH\(_x\) [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\(_x\) species [18]. Based on the results above, the consumption of \(-\text{NCO}\) species may be related with rapid hydrolysis of \(-\text{NCO}\) species in the flow of NO + O\(_2\) + H\(_2\), resulting in the formation of NH\(_x\) species. In addition, the intensity of enolic species (1633 cm\(^{-1}\) decreased in NO + O\(_2\) + H\(_2\) after \(-\text{NCO}\) 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\(_2\)H\(_5\)OH 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\(_2\)H\(_5\)OH over Ag/Al\(_2\)O\(_3\). The reaction between the nitrates and enolic species (and/or acetate) then leads to the formation of \(-\text{NCO}\), 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\(_2\)H\(_5\)OH in the presence of H\(_2\). As shown in Scheme 1, the presence of H\(_2\) first promotes the partial oxidation of C\(_2\)H\(_5\)OH 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 \(-\text{NCO}\) was observed (Fig. 5(b)), possibly because the hydrolysis of \(-\text{NCO}\) by hydroxyl groups formed in the flow of NO + O\(_2\) + H\(_2\) resulted in the formation of NH\(_x\) species. In fact, the \(-\text{NCO}\) hydrolysis products (NH\(_x\) and NH\(_3\)) were observed by in situ DRIFTS spectra in this experiment (Fig. 5(b)). The resulting NH\(_x\) species are known to be highly active towards NO\(_x\) reduction when using NH\(_3\) as a reductant over Ag/Al\(_2\)O\(_3\) in the presence of H\(_2\) [19]. Therefore, the formation of NH\(_x\) 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\(_2\)O for \(-\text{NCO}\) hydrolysis, the particularity of the Ag/Al\(_2\)O\(_3\) catalyst may also play an important role.

### 4. Conclusion

The selective catalytic reduction of NO\(_x\) with ethanol over Ag/Al\(_2\)O\(_3\) was promoted by the addition of H\(_2\) to the mixture of C\(_2\)H\(_5\)OH + 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 \(-\text{NCO}\).

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### References


Scheme 1. The possible effect of H\(_2\) on the SCR of NO\(_x\) by C\(_2\)H\(_5\)OH over Ag/Al\(_2\)O\(_3\).