Mechanism of the selective catalytic reduction of NO\textsubscript{x} by C\textsubscript{2}H\textsubscript{5}OH over Ag/Al\textsubscript{2}O\textsubscript{3}

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Abstract

The mechanism of the selective catalytic reduction (SCR) of NO\textsubscript{x} by C\textsubscript{2}H\textsubscript{5}OH over silver catalyst (Ag/Al\textsubscript{2}O\textsubscript{3}) was investigated using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Attention was focused on the formation and reactivity of novel enolic species on the Ag/Al\textsubscript{2}O\textsubscript{3} surface. DRIFTS spectra show that the surface enolic species, which was derived from partial oxidation of C\textsubscript{2}H\textsubscript{5}OH over Ag/Al\textsubscript{2}O\textsubscript{3} in the presence of excess oxygen, play a crucial role in the formation of isocyanate species (NCO) by reaction with NO + O\textsubscript{2} or NO\textsubscript{3}\textsuperscript{-} absorbed on the surface of Ag/Al\textsubscript{2}O\textsubscript{3}. 2,3-dihydrofuran was used as an enolic model compound in our DRIFTS study, and the results support our assignment. A novel mechanism of the SCR of NO\textsubscript{x} by C\textsubscript{2}H\textsubscript{5}OH is proposed based on the DRIFTS studies. The mechanistic differences between the SCR of NO\textsubscript{x} by C\textsubscript{2}H\textsubscript{5}OH and that by C\textsubscript{3}H\textsubscript{6} are discussed. The high reactivity of the enolic species results in high surface concentration of NCO and high efficiency of NO\textsubscript{x} reduction using C\textsubscript{2}H\textsubscript{5}OH as a reductant. The results of density functional theory (DFT) calculations are in good agreement with the DRIFTS spectra, and support our suggestions about the surface enolic species.

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Keywords: Selective catalytic reduction (SCR); NO\textsubscript{x}; In situ DRIFTS; Alumina supported silver; C\textsubscript{2}H\textsubscript{5}OH; Enolic species; Acetate; Density functional theory (DFT) calculations

1. Introduction

Alumina supported silver catalyst (Ag/Al\textsubscript{2}O\textsubscript{3}) has been studied as a promising catalyst due to its high activity for the selective catalytic reduction (SCR) of NO\subscript{x} by hydrocarbons and oxygenated hydrocarbons in the presence of excess oxygen [1–12]. In particular, C\textsubscript{2}H\textsubscript{5}OH is extremely effective for the SCR of NO\textsubscript{x} over Ag/Al\textsubscript{2}O\textsubscript{3} [1,5].

The adsorbed species on catalysts during the SCR of NO\textsubscript{x} have been observed by many researchers using IR spectroscopy, and several intermediates have been proposed to take part in the reduction of NO\textsubscript{x} such as NO\textsubscript{3}\textsuperscript{-} [4,8,12], CH\textsubscript{3}COO\textsuperscript{-} [9,12,13], R–NO\textsubscript{2} [7,9,13], R–ONO [7,9,13], and NCO [4,5,8,13,14]. IR spectra have shown that adsorbed nitrates (NO\textsubscript{3}\textsuperscript{-}) and acetate (CH\textsubscript{3}COO\textsuperscript{-}) were the predominant surface species during the SCR of NO\textsubscript{x} on Al\textsubscript{2}O\textsubscript{3} or Ag/Al\textsubscript{2}O\textsubscript{3} [8,12,15,16]. Based on our previous IR studies [4,5], isocyanate species (NCO) was detected respectively on Ag and Al sites by adsorption and reaction of NO + O\textsubscript{2} with C\textsubscript{2}H\textsubscript{5}OH or C\textsubscript{3}H\textsubscript{6} on Ag/Al\textsubscript{2}O\textsubscript{3} surface in a vacuum system. It was suggested that NCO species on the surface would be a crucial intermediate in the NO\textsubscript{x} reduction process over an Ag/Al\textsubscript{2}O\textsubscript{3} catalyst. Some organo-nitro and organo-nitrite compounds such as R–NO\textsubscript{2} and R–ONO have been observed as the precursors of NCO species [4,5]. Ukisu et al. [17,18] and Kameoka et al. [14,19] also reported that NCO species was a vital intermediate for the SCR of NO\textsubscript{x}, and suggested that the high productivity of NCO species resulted in a high efficiency of NO\textsubscript{x} reduction by C\textsubscript{2}H\textsubscript{5}OH or hydrocarbons. Recently, strongly adsorbed species such as nitrates and acetate were proposed to be key intermediates in the formation of organo-nitro and organo-nitrite compounds [12,13].

On the basis of these findings, a possible mechanism for the SCR of NO\textsubscript{x} by C\textsubscript{2}H\textsubscript{5}OH over Ag/Al\textsubscript{2}O\textsubscript{3} was considered as similar to that of C\textsubscript{6}H\textsubscript{6}–approximately: NO + O\textsubscript{2} + C\textsubscript{2}H\textsubscript{5}OH → NO\textsubscript{3} (nitrate in particular) + C\textsubscript{2}H\textsubscript{5}OH (acetate in particular) → R–NO\textsubscript{2} + R–ONO → NCO + –CN + NO + O\textsubscript{2} → N\textsubscript{2} [13,20]. However, this mechanism does not sufficiently explain why C\textsubscript{2}H\textsubscript{5}OH has a higher efficiency for the SCR of NO\textsubscript{x} over Ag/Al\textsubscript{2}O\textsubscript{3} than hydrocarbons such as C\textsubscript{6}H\textsubscript{6}.

In this paper, the formation and dynamic performance of partial oxidation products of C\textsubscript{2}H\textsubscript{5}OH and C\textsubscript{3}H\textsubscript{6} over
Ag/Al₂O₃ were studied by an in situ DRIFTS method. The most significant observation is that enolic species, formed from the partial oxidation of C₂H₅OH and C₃H₆ over Ag/Al₂O₃, have high reactivity with NO + O₂ to form NCO. Finally, we propose a possible reaction scheme to explain the high efficiency of the NO₅ reduction by C₂H₅OH.

2. Experimental and theoretical

An Ag/Al₂O₃ catalyst (Ag loading is 5 wt.%) was prepared by an impregnation method described in our earlier paper[21]. The catalytic activity was measured in a fixed-bed reactor by passing a gaseous mixture of NO 800 ppm, reductant C₃H₆ 1714 ppm, or C₂H₅OH 1565 ppm, or CH₃CHO 1565 ppm, or CH₃COOH 1565 ppm, water vapor (10%), and O₂ (10%) in N₂ balance at a total flow rate of 4000 ml min⁻¹ (GHSV = 50,000 h⁻¹). NO₅ conversion was analyzed on-line by a chemiluminescence NO/NO₂/NOₓ analyzer (42C-hl, Thermo Environmental). An aqueous C₂H₅OH (or CH₃CHO, or CH₃COOH) solution was supplied with a micropump into the gas stream and vaporized by a coiled heater at the inlet of the reactor.

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 detector. The Ag/Al₂O₃ catalyst for the in situ DRIFTS studies was finely ground and placed into a ceramic crucible in the in situ chamber. Mass flow controllers and a sample temperature controller were used to simulate the real reaction conditions, which are the same as those in the catalytic activity test, such as mixture of gases, pressure, and sample temperature. Prior to recording each DRIFTS spectrum, the Ag/Al₂O₃ catalyst was heated in situ in (10%) O₂/N₂ flow at 873 K for 1 h, then cooled to the desired temperature for taking a reference spectrum. All spectra reported here were taken at a resolution of 4 cm⁻¹ for 100 scans.

Density functional theory (DFT) calculation was used to confirm the structure of surface enolic species on Ag/Al₂O₃ using the GAUSSIAN 98 suite of programs. The LANL2DZ basis set was employed to carry out the DFT-B3P86 (Becke’s three parameter function with a non-local correlation provided by the Perdew 86 expression) calculations. The calculated vibration frequencies and infrared intensity of the vibrational normal modes were picked up by the Hyperchem™ Version 6.0 package.

3. Results

3.1. Reaction activity of various organic compounds for the SCR of NO₅ over Ag/Al₂O₃

Fig. 1 shows the reaction activity of various organic compounds for the SCR of NO₅ over Ag/Al₂O₃. When using C₃H₆OH as a reductant, the maximal conversion of NO₅ is up to 98.7%, and the average conversion of NO₅ is ca. 90% even in the wide temperature range of 578–883 K. In the case of CH₃CHO, it is worthwhile to note that the NO₅ conversion is nearly the same as that of C₂H₅OH at temperatures below 766 K. Compared with C₂H₅OH and CH₃CHO, there is a relatively lower NO₅ conversion by C₃H₆ in the whole reaction temperature range, especially in the low temperature range. However, when using CH₃COOH as a reductant with the same carbon atom concentration (ppm C), the highest conversion of NO₅ is only 58%. These results indicate that the NO₅ conversion is strongly influenced by the kind of reductant, and the order of the reaction activity is C₂H₅OH > CH₃CHO > C₃H₆OH > CH₃COOH. In other words, partially oxidized hydrocarbons such as C₂H₅OH and CH₃CHO are extremely efficient for the NO₅ reduction, while deep oxidation of hydrocarbons lowers NO₅ conversion.

3.2. Steady state in situ DRIFTS study of the SCR of NO₅ by C₂H₅OH over Ag/Al₂O₃

The difference of these reductants for the SCR of NO₅ over the Ag/Al₂O₃ was investigated using DRIFTS. Fig. 2 shows the in situ DRIFTS spectra of Ag/Al₂O₃ during the reaction of NO 800 ppm + C₂H₅OH 1565 ppm + O₂ (10%) at a temperature range of 473–823 K in steady states, together with a spectrum recorded at 473 K in a flow of NO 800 ppm + O₂ (10%). After an exposure of the Ag/Al₂O₃
Fig. 2. DRIFTS spectra of adsorbed species in the steady state over Ag/Al₂O₃ in the flow of NO + C₂H₅OH + O₂ at (a) 473 K, (b) 523 K, (c) 573 K, (d) 623 K, (e) 673 K, (f) 723 K, (g) 773 K, and (h) NO + O₂ for 120 min at 473 K. Conditions: NO, 800 ppm; C₂H₅OH, 1565 ppm; O₂, 10%.

to NO + O₂ for 120 min (spectrum i), strong peaks at 1583, 1302 cm⁻¹ and shoulders at 1612, 1560, and 1250 cm⁻¹ were observed, which were respectively assigned to univalent (1560, 1250 cm⁻¹), bidentate (1583, 1302 cm⁻¹), and bridging (1612 cm⁻¹) nitrates according to the literature [8,12].

During the NO + C₂H₅OH + O₂ reaction at various temperatures (473–823 K) in steady states over Ag/Al₂O₃ (spectra a–h), the peaks of nitrates mentioned above also appeared. We also detected strong peaks at 1572 and 1466 cm⁻¹. These peaks were attributed to νas (OCO), and νs (OCO) of adsorbed acetate respectively, because the frequencies of these peaks are in good agreement with those of CH₃COOH adsorbed on Ag/Al₂O₃ (this result not shown) and alumina [16,22]. More evidences of the assignment for these peaks will be discussed below.

In the region of 2300–2000 cm⁻¹, a strong peak at 2240 cm⁻¹ at 623 K (spectrum c) was observed and shifted to 2229 cm⁻¹ at 673 K (spectrum e) during the SCR of NOₓ over Ag/Al₂O₃, which was assigned to NCO bound to the Al site (2240 cm⁻¹) and Ag site (2229 cm⁻¹) [4,5,8,14,17,18]. In addition, another weak peak at 2154 cm⁻¹ was due to CN [4,23].

In the region of 3100–2800 cm⁻¹, peaks at 2972 and 2875 cm⁻¹ were assigned to νas (C–H) and νs (C–H) of –CH₃ [4,24], and the peak at 2935 cm⁻¹ was possibly due to νas (C–H) of methylene [24]. In addition, a very weak peak at 3020 cm⁻¹ was observed, which is characteristic of C–H stretching vibration model in C=CH group [24,25].
From a comparison of the intensity of each peak, it is considered that the acetate surface species is predominant within a high temperature range of 773–873 K, while at a low temperature range of 473–673 K, the enolic species and nitrates become dominant on the Ag/Al₂O₃ surface.

3.3. Reactivity of adsorbed NO₃⁻ over Ag/Al₂O₃

The reactivity of the nitrates toward C₂H₅OH + O₂ and C₃H₆ + O₂ was studied by the transient response of DRIFTS method. Fig. 3A and B show the in situ DRIFTS spectra of Ag/Al₂O₃ in a flow of C₂H₅OH 1565 ppm + O₂ (10%) after the catalyst was pre-exposed to a flow of NO 800 ppm + O₂ (10%) for 60 min at 673 K. Switching the fed gas from NO + O₂ to C₂H₅OH + O₂ led to a drastic decrease in the intensity of nitrate peaks (1250 and 1300 cm⁻¹), and they disappeared completely after 3 min. Simultaneously, the intensity of the peak at 2229 cm⁻¹ due to NCO sharply increased initially, reached a maximum after 3 min, and then decreased gradually. This indicates that the nitrates are highly active for reaction with C₂H₅OH + O₂ to form NCO.

The same set of experiments was also performed with C₃H₆ as a reductant, and the dynamic changes of DRIFTS spectra as a function of time are shown in Fig. 4. Compared with Fig. 3, the disappearance rate of nitrate peaks at 1245 and 1300 cm⁻¹ dramatically slowed down, as did the increase rate of NCO peak, indicating that C₃H₆ is not as active as C₂H₅OH for reaction with nitrate to form NCO.

3.4. Formation and reactivity of partial oxidation products of C₂H₅OH, CH₃CHO, and C₃H₆ over Ag/Al₂O₃

Fig. 5 shows the in situ DRIFTS spectra of Ag/Al₂O₃ at various temperatures in steady states in flowing
Fig. 4. Dynamic changes of in situ DRIFTS spectra over Ag/Al₂O₃ as a function of time in a flow of C₃H₆ + O₂ at 673 K. Before the measurement, the catalyst was pre-exposed to a flow of NO + O₂ for 60 min at 673 K. Conditions: NO, 800 ppm; C₃H₆, 1714 ppm; O₂, 10%.

Fig. 5A, 5B, and 5C show the in situ DRIFTS spectra for the oxidation of C₂H₅OH, CH₃CHO, and 2,3-dihydrofuran on Ag/Al₂O₃. The spectra show the presence of enolic species and acetate species. The enolic species are predominant during the low temperature range of 473–673 K, while the acetate species become dominant at high temperatures of 773–873 K.

Three different gas mixtures: (A) C₂H₅OH + O₂, (B) CH₃CHO + O₂, and (C) 2,3-dihydrofuran. For C₂H₅OH oxidation, two peaks at 1579 and 1466 cm⁻¹ were assigned to ν₂(OCO) and ν₃(OCO) of acetate as the same as in Fig. 2. The peaks at 1633, 1416, and 1336 cm⁻¹ were assigned to a surface enolic species, which will be discussed below. Apparently, the enolic species are predominant during the oxidation of C₂H₅OH on the Ag/Al₂O₃ surface within a low temperature range of 473–673 K. At a high temperature range of 773–873 K, however, the surface acetate species become dominant. During partial oxidation of CH₃CHO over Ag/Al₂O₃ (Fig. 5B), the enolic species (peaks at 1633, 1412, and 1336 cm⁻¹) were predominant within the whole temperature region. Heating the sample resulted in an increase in the intensity of acetate peaks (1579 and 1466 cm⁻¹), which was accompanied by a decrease in the intensity of the surface concentration of enolic species. Furthermore, it should be noted that peaks due to ν(C=O) were observed at 1730 and 1759 cm⁻¹ [24] within the all temperature region, indicating that some CH₃CHO molecules did not undergo partial oxidation to form enolic species and acetate.

2,3-dihydrofuran was used as a model compound to confirm the structure of surface enolic species. As shown in Fig. 5C, a strong peak at 1630 cm⁻¹ was also observed, which similarly was accompanied by an appearance of peaks at 1423 and 1315 cm⁻¹. This result strongly supports our assignment about the enolic species. The acetate peaks indicate that partial oxidation of 2,3-dihydrofuran occurred on Ag/Al₂O₃ surface. In addition, peak at 1390 cm⁻¹ was observed and assigned to δ(C–H) [24].

The reactivity of the partial oxidation products of C₂H₅OH, formed during C₂H₅OH + O₂ reaction over Ag/Al₂O₃ at 673 K, toward NO + O₂ was evaluated by the
transient response of DRIFTS method. Fig. 6A shows the
dynamic changes of in situ DRIFTS spectra of adsorbed
species on Ag/Al₂O₃ in a flow of NO + O₂ at 673 K. The
integrated areas of these peaks in Fig. 6A were displayed
as a function of time in Fig. 6B. After the catalyst was
exposed to C₂H₅OH + O₂ for 60 min, very strong enolic
species peaks at 1633, 1416, and 1336 cm⁻¹ and the acetate
peaks (1579 and 1464 cm⁻¹) were observed. Switching the
fed gas to NO + O₂ resulted in a sharp decrease of the
intensity of peaks due to enolic species, and then quickly
disappeared after 5 min. Simultaneously, a new NCO peak
at 2229 cm⁻¹ formed, and its intensity promptly increased
within 3 min, then decreased. However, the drastic decrease
in acetate peak at 1464 cm⁻¹ did not occur until the peaks
due to enolic species had disappeared nearly. Meanwhile, it
was worthwhile to note that large amounts of nitrates and
acetate coexisted on Ag/Al₂O₃, whereas the surface con-
centration of NCO was very low. Taking into account the
high reactivity of nitrates toward C₂H₅OH + O₂, acetate is
not highly reactive toward NO + O₂ to form NCO.

The same set of experiments was performed after expos-
ing the catalyst to a flow of CH₃CHO 1565 ppm + O₂ (10%),
and similar changes were observed. As shown in Fig. 7A
and B, after switching the fed gas to NO + O₂ within 10 min,
the sharp decrease in the intensity of enolic species peaks
was accompanied by a drastic increase in that of NCO peak.
After disappearance of the peaks due to enolic species, the
intensity of acetate peaks decreased slowly, and a relatively
weak NCO peak was observed.

The reactivity of the partial oxidation products of C₃H₆
was evaluated in essentially the same manner as above. After
the Ag/Al₂O₃ catalyst was exposed to C₃H₆ 1714 ppm + O₂
(10%) for 60 min, only a very weak shoulder at 1633 cm⁻¹
was observed (Fig. 8A). As shown in Fig. 8B, switching the

![Graph](image-url)
flowing gas to NO + O2 resulted in similar changes of the enolic species, NCO, acetate, and nitrates.

4. Discussion

4.1. Formation of enolic species

During the partial oxidation of C2H5OH, CH3CHO, and C3H6 over Ag/Al2O3 at 673 K, peaks at 1633, 1416, and 1336 cm⁻¹ were observed. Shimizu et al. [12] reported similar peaks at 1630, 1410, and 1300–1336 cm⁻¹ over Ag/Al2O3 in flowing n-hexane + NO + O2 and assigned them to carbonate species. Turek et al. [26] reported that when CO2 chemisorbed on the surface of γ-Al2O3, the main adsorbed species were carbonates such as bicarbonates and free carbonates. We also studied the adsorption of CO2 on Ag/Al2O3 at 673 K in flowing CO2, but no peaks at 1633, 1416, 1336 cm⁻¹ were observed even when the concentration of CO2 in the fed gas was as high as 8%. In addition, the peak at 1633 cm⁻¹ was assigned to the stretching vibration model of C=O in formyl species [27] or in aldehyde [28], and OH deformation of adsorbed water was observed at the same position [29].

The peak at 1633 cm⁻¹ can be associated with the frequency of double bond stretching vibration, such as ν(C=C) and ν(C=O). In general, however, the stretching vibration frequencies of isolated C=C and C=O should be higher than 1633 cm⁻¹. One evidence is that the IR spectra of syn-vinyl alcohol (CH2=CHOH) in gas phase, show strong peak between 1644 and 1648 cm⁻¹, which is accompanied by two peaks at 1409–1412 and 1300–1326 cm⁻¹ [24,31–33]. The IR spectrum of adsorbed catechol on a TiO2 colloid also gives a similar peak at 1620 cm⁻¹ [25]. Their common characteristic is an enolic structure. We conjecture that in this study, an enolic structure (CH2=CH–O⁻)•–M is formed when
CH$_3$CHO adsorbs on the surface of Ag/Al$_2$O$_3$. The conjugation of CH$_2$=CH–O$^-$ group may induce the stretching vibrational mode of C=C–O$^-$ to shift to a frequency lower than $\nu$(C=C) and higher than $\nu$(C–O) [24,25]. The peaks between 2872 and 3020 cm$^{-1}$ in Fig. 6A also accord with the distribution of $\nu$(C–H) for a H$_2$C=CH– group [24,25]. As a consequence, the peak at 1633 cm$^{-1}$ could be tentatively assigned to asymmetric stretching vibration mode of CH$_2$=CH–O$^-$ group, and peaks at 1416 and 1336 cm$^{-1}$ could be tentatively attributed to symmetric stretching vibration mode of CH$_2$=CH–O$^-$ and for a C–H deformation mode, respectively [24,30]. Furthermore, similar feature was observed on Ag/Al$_2$O$_3$ in exposing to 2,3-dihydrofuran (in Fig. 5C), which has a C=C bonded with an oxygen structure. This result strongly supports our assignments about the surface enolic species. As shown in Fig. 5A and B, when Ag/Al$_2$O$_3$ is exposed to C$_2$H$_5$OH + O$_2$ and CH$_3$CHO + O$_2$, very strong peaks at 1633, 1416, and 1336 cm$^{-1}$ are observed, indicating that enolic species are the main surface species. However, these peaks are barely perceptible on Ag/Al$_2$O$_3$ in the flow of C$_3$H$_6$ + O$_2$ as shown in Fig. 8A, indicating a low surface concentration of CH$_2$=CH–O$^-$ surface species.

As shown in Fig. 2, during NO + C$_2$H$_5$OH + O$_2$ reaction at low temperature region 473–673 K, peak at 1633 cm$^{-1}$ was predominant as well, together with strong peaks at 1416 and 1336 cm$^{-1}$, indicating that the enolic species are the dominant surface species during the SCR of NO$_x$ by C$_2$H$_5$OH over Ag/Al$_2$O$_3$ at the low temperature region. Chatik et al. [20] observed a similar peak at 1635 cm$^{-1}$ during NO + C$_2$H$_5$OH + O$_2$ over Ag/Al$_2$O$_3$, and assigned it to adsorbed organic nitrogen-containing compound. However, in a flow of C$_2$H$_5$OH + O$_2$ in Fig. 5A, the peak at 1633 cm$^{-1}$ is absolutely the main peak, which strongly suggests that this peak is due to free-nitrogen species on Ag/Al$_2$O$_3$. 

![Graph showing absorbance vs. wavenumbers](image)
Summarizing the above discussion, the formation of the surface enolic species over Ag/Al₂O₃ can be proposed as shown in Scheme 1.

4.2. Density functional theory calculations

The simulation molecular structure model and FTIR spectrum of the surface enolic species on Ag/Al₂O₃ are shown in Fig. 9A and B. In this model, the enolic species (CH₂=CH–O⁻) bond with silver atom, and the optimized distance between the oxygen and silver atom is 2.072 Å. Apparently, the calculated FTIR spectrum is of reasonable similarity to the corresponding experimental result. The asymmetric stretching vibration mode of the enolic species was calculated at 1645 cm⁻¹ with a relatively high infrared intensity of 61 km mol⁻¹, which is 12 cm⁻¹ higher than the experimental harmonic frequency (1633 cm⁻¹). Compared to the experimental value, the calculated symmetric
Fig. 7. (A) Dynamic changes of in situ DRIFTS spectra over Ag/Al₂O₃ as a function of time in a flow of NO + O₂ at 673 K. Before the measurement, the catalyst was pre-exposed to a flow of CH₃CHO + O₂ for 60 min at 673 K. Conditions: NO, 800 ppm; CH₃CHO, 1565 ppm; O₂, 10%. (B) Time dependence of the integrated areas of the peak in the range of 2160–2305 cm⁻¹ (△, NCO), 1612–1711 cm⁻¹ (H17003, enolic species), 1439–1508 cm⁻¹ (H17040, acetate), and 1209–1321 cm⁻¹ (H17034, nitrates).

4.3. Reactivity of enolic species and acetate

Many research groups have studied the formation and reactivity of acetate during NO + C₃H₆ + O₂ reaction on oxide catalysts and metal supported catalysts such as Al₂O₃ [15,16], and Ag/Al₂O₃ [13], and have suggested that the acetate, as a dominant adsorbed species at high temperatures, plays a crucial role in the formation of NCO by reaction.
Fig. 8. (A) Dynamic changes of in situ DRIFTS spectra over Ag/Al₂O₃ as a function of time in a flow of NO + O₂ at 673 K. Before the measurement, the catalyst was pre-exposed to a flow of C₃H₆ + O₂ for 60 min at 673 K. Conditions: NO, 800 ppm; C₃H₆, 1714 ppm; O₂, 10%. (B) Time dependence of the integrated areas of the peak in the range of 2160–2305 cm⁻¹ (△, NCO), 1612–1711 cm⁻¹ (□, enolic species), 1439–1508 cm⁻¹ (○, acetate), and 1209–1321 cm⁻¹ (●, nitrates).

Fig. 8. (A) Dynamic changes of in situ DRIFTS spectra over Ag/Al₂O₃ as a function of time in a flow of NO + O₂ at 673 K. Before the measurement, the catalyst was pre-exposed to a flow of C₃H₆ + O₂ for 60 min at 673 K. Conditions: NO, 800 ppm; C₃H₆, 1714 ppm; O₂, 10%. (B) Time dependence of the integrated areas of the peak in the range of 2160–2305 cm⁻¹ (△, NCO), 1612–1711 cm⁻¹ (□, enolic species), 1439–1508 cm⁻¹ (○, acetate), and 1209–1321 cm⁻¹ (●, nitrates).

toward NO + O₂. In the case of the SCR of NOₓ by C₂H₅OH over Ag/Al₂O₃, Kameoka et al. [8] proposed that more acetate and less nitrates were observed in comparison with the SCR of NOₓ by C₃H₆, which probably explains why NCO is more easily observed when using C₂H₅OH as a reductant. If the acetate really plays a crucial role in NCO formation during the SCR of NOₓ by C₂H₅OH, it should be active for the reaction with NO + O₂. However, as shown in Fig. 6, the enolic species have much higher reactivity than acetate on Ag/Al₂O₃ towards NO + O₂ to form NCO species. Actually, the acetate did not react with NO + O₂ until the enolic species had nearly disappeared on the Ag/Al₂O₃ surface. This means that enolic species, instead of acetate, play a crucial role in the NOₓ reduction by C₂H₅OH.

As mentioned above, exposure the sample to C₂H₅OH + O₂ for 3 min leads to the complete disappearance of nitrate peaks at 1300 and 1250 cm⁻¹ (Fig. 3B), indicating that adsorbed nitrates are highly active in their reaction with C₂H₅OH + O₂ to form NCO. However, Fig. 6 shows that after switching the fed gas to NO + O₂ for 30 min, strong nitrate
and acetate peaks coexisted on the surface of Ag/Al₂O₃, whereas the NCO peak was very weak, which also reveals that acetate is not highly active in its reaction with nitrates to form NCO.

Shimizu et al. [16] have reported that the main adsorption species of CH₃COOH on Al₂O₃ was acetate. We have studied the adsorption of CH₃COOH over Ag/Al₂O₃ and obtained a similar result. As shown in Fig. 1, when using CH₃COOH as a reductant, the highest conversion of NOₓ was only 58%. However, when using the same concentration of C₂H₅OH as a reductant, conversion of NOₓ was up to 98.7%. Fig. 5 shows that there are only two kinds of partial oxidation products of C₂H₅OH: acetate and adsorbed enolic species, which is additional evidence in favor of our suggestion that enolic species are quite active in their reaction with NOₓ to form NCO during the SCR of NOₓ by C₂H₅OH.

Scheme 1. The formation of enolic species over Ag/Al₂O₃ from C₂H₅OH, CH₃CHO and C₂H₆.

We already know that there is a correlation between the high efficiency of NOₓ reduction by C₂H₅OH and the high productivity of a surface NCO over Ag/Al₂O₃ [5,14,19]. Since enolic species are active in their reaction with NO + O₂ to form NCO, and are the predominant surface species during the C₂H₅OH + O₂ and the C₂H₅OH + NO + O₂ reaction, it is reasonable to expect and obtain a high concentration of surface NCO and high efficiency of NOₓ reduction by C₂H₅OH.

In comparison with C₂H₅OH, the same enolic species were obtained during partial oxidation of CH₃CHO. The results of TPO experiments of C₂H₅OH over Ag/Al₂O₃ [34] indicated that CH₃CHO was the main product of partial oxidation of C₂H₅OH. As described above, CH₃CHO is produced from partial oxidation of C₂H₅OH over Ag/Al₂O₃, so using CH₃CHO or C₂H₅OH as reductant has the same efficiency for the SCR of NOₓ. Our results in Fig. 1 show that NOₓ conversions by C₂H₅OH and CH₃CHO are nearly the same at temperatures below 766 K, which is in good agreement with the suggestion based on our DRIFTS studies. In addition, NOₓ conversion by CH₃CHO is relatively lower than that by C₂H₅OH at temperatures above 766 K. It is possible that non-selective oxidation reaction of CH₃CHO in gas phase may occur easily above 766 K, which induces a smaller amount of CH₃CHO to participate in the selective reduction of NOₓ.

In the case of partial oxidation of C₂H₆, a small amount of enolic species was formed, accompanied by large amounts of acetate on Ag/Al₂O₃. Therefore, it is reasonable that the efficiency of C₂H₆ for NOₓ reduction is much lower than that of C₂H₅OH and CH₃CHO, which has been tested by our results in Fig. 1.

4.4. Mechanism of the SCR of NOₓ by C₂H₅OH over Ag/Al₂O₃

On the basis of the results in this work together with the mechanism suggested for the SCR of NOₓ by C₂H₆, we propose a simplified reaction scheme for the NOₓ reduction by C₂H₅OH. As shown in Scheme 2, the reaction starts with the formation of both adsorbed nitrates via the NO oxidation by O₂ and enolic species and acetate via the partial oxidation of C₂H₅OH over Ag/Al₂O₃. The reaction between the two kinds of adsorbed species then leads to the formation of NCO directly, or via organo-nitrogen compounds (such as R–ONO and R–NO₂), which is widely accepted in the study of the SCR of NOₓ [4,8,13,20,35]. Subsequently, NCO reacts with NO + O₂ and nitrates to yield N₂. It should be pointed out that the acetate formed by the reaction of C₂H₅OH + O₂ also reacts toward NO + O₂ to produce NCO. However, the relatively low activity of acetate toward NO + O₂ results in this parallel reaction not playing an important role in the formation of NCO.

Obviously, the DRIFTS results for the SCR of NOₓ by C₂H₅OH are quite different from previous studies for the SCR of NOₓ by C₂H₆. It is worthwhile to point out that this
difference may be induced by sample preparation such as dilution with KBr. We find that DRIFTS spectra are quite different at the same conditions with or without KBr in Ag/Al₂O₃. Our previous work used samples with KBr [4,5], and this work used samples without KBr. The detailed discussion is expected in the next paper.

5. Conclusions

Enolic species, as important intermediate, are formed on Ag/Al₂O₃ during the SCR of NOₓ by C₂H₅OH. Both enolic species and acetate are formed over Ag/Al₂O₃ during the partial oxidation of C₂H₅OH or CH₃CHO over Ag/Al₂O₃. Peaks at 1633, 1416, 1336 cm⁻¹ are assigned to surface enolic species, which are in good agreement with results of DFT calculations. The enolic species have higher reactivity with NO + O₂ on Ag/Al₂O₃ than acetate species have. The enolic species are the main surface species during the partial oxidation of C₂H₅OH or CH₃CHO over Ag/Al₂O₃. As a result, high surface concentration of NCO and high efficiency of NOₓ reduction are obtained when using C₂H₅OH or CH₃CHO as a reductant during the SCR of NOₓ. In contrast, acetate is the main surface species over Ag/Al₂O₃ during the partial oxidation of C₃H₆. This relates to a lower NCO concentration over Ag/Al₂O₃ as well as a relatively lower NOₓ conversion when using C₃H₆ as a reductant.

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