

# Mechanism of the selective catalytic reduction of $\text{NO}_x$ by $\text{C}_2\text{H}_5\text{OH}$ over $\text{Ag}/\text{Al}_2\text{O}_3$

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## Abstract

The mechanism of the selective catalytic reduction (SCR) of  $\text{NO}_x$  by  $\text{C}_2\text{H}_5\text{OH}$  over silver catalyst ( $\text{Ag}/\text{Al}_2\text{O}_3$ ) 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  $\text{Ag}/\text{Al}_2\text{O}_3$  surface. DRIFTS spectra show that the surface enolic species, which was derived from partial oxidation of  $\text{C}_2\text{H}_5\text{OH}$  over  $\text{Ag}/\text{Al}_2\text{O}_3$  in the presence of excess oxygen, play a crucial role in the formation of isocyanate species (NCO) by reaction with  $\text{NO} + \text{O}_2$  or  $\text{NO}_3^-$  adsorbed on the surface of  $\text{Ag}/\text{Al}_2\text{O}_3$ . 2,3-dihydrofuran was used to an enolic model compound in our DRIFTS study, and the results support our assignment. A novel mechanism of the SCR of  $\text{NO}_x$  by  $\text{C}_2\text{H}_5\text{OH}$  is proposed based on the DRIFTS studies. The mechanistic differences between the SCR of  $\text{NO}_x$  by  $\text{C}_2\text{H}_5\text{OH}$  and that by  $\text{C}_3\text{H}_6$  are discussed. The high reactivity of the enolic species results in high surface concentration of NCO and high efficiency of  $\text{NO}_x$  reduction using  $\text{C}_2\text{H}_5\text{OH}$  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);  $\text{NO}_x$ ; In situ DRIFTS; Alumina supported silver;  $\text{C}_2\text{H}_5\text{OH}$ ; Enolic species; Acetate; Density functional theory (DFT) calculations

## 1. Introduction

Alumina supported silver catalyst ( $\text{Ag}/\text{Al}_2\text{O}_3$ ) has been studied as a promising catalyst due to its high activity for the selective catalytic reduction (SCR) of  $\text{NO}_x$  by hydrocarbons and oxygenated hydrocarbons in the presence of excess oxygen [1–12]. In particular,  $\text{C}_2\text{H}_5\text{OH}$  is extremely effective for the SCR of  $\text{NO}_x$  over  $\text{Ag}/\text{Al}_2\text{O}_3$  [1,5].

The adsorbed species on catalysts during the SCR of  $\text{NO}_x$  have been observed by many researchers using IR spectroscopy, and several intermediates have been proposed to take part in the reduction of  $\text{NO}_x$ , such as  $\text{NO}_3^-$  [4,8,12],  $\text{CH}_3\text{COO}^-$  [9,12,13],  $\text{R-NO}_2$  [7,9,13],  $\text{R-ONO}$  [7,9,13], and NCO [4,5,8,13,14]. IR spectra have shown that adsorbed nitrates ( $\text{NO}_3^-$ ) and acetate ( $\text{CH}_3\text{COO}^-$ ) were the predominant surface species during the SCR of  $\text{NO}_x$  on  $\text{Al}_2\text{O}_3$  or  $\text{Ag}/\text{Al}_2\text{O}_3$  [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  $\text{NO} + \text{O}_2 +$

$\text{C}_2\text{H}_5\text{OH}$  or  $\text{C}_3\text{H}_6$  on  $\text{Ag}/\text{Al}_2\text{O}_3$  surface in a vacuum system. It was suggested that NCO species on the surface would be a crucial intermediate in the  $\text{NO}_x$  reduction process over an  $\text{Ag}/\text{Al}_2\text{O}_3$  catalyst. Some organo-nitro and organo-nitrite compounds such as  $\text{R-NO}_2$  and  $\text{R-ONO}$  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  $\text{NO}_x$ , and suggested that the high productivity of NCO species resulted in a high efficiency of  $\text{NO}_x$  reduction by  $\text{C}_2\text{H}_5\text{OH}$  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  $\text{NO}_x$  by  $\text{C}_2\text{H}_5\text{OH}$  over  $\text{Ag}/\text{Al}_2\text{O}_3$  was considered as similar to that of  $\text{C}_3\text{H}_6$ , approximately,  $\text{NO} + \text{O}_2 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{NO}_x$  (nitrate in particular) +  $\text{C}_x\text{H}_y\text{O}_z$  (acetate in particular)  $\rightarrow \text{R-NO}_2 + \text{R-ONO} \rightarrow \text{-NCO} + \text{-CN} + \text{NO} + \text{O}_2 \rightarrow \text{N}_2$  [13,20]. However, this mechanism does not sufficiently explain why  $\text{C}_2\text{H}_5\text{OH}$  has a higher efficiency for the SCR of  $\text{NO}_x$  over  $\text{Ag}/\text{Al}_2\text{O}_3$  than hydrocarbons such as  $\text{C}_3\text{H}_6$ .

In this paper, the formation and dynamic performance of partial oxidation products of  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{C}_3\text{H}_6$  over

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Ag/Al<sub>2</sub>O<sub>3</sub> were studied by an in situ DRIFTS method. The most significant observation is that enolic species, formed from the partial oxidation of C<sub>2</sub>H<sub>5</sub>OH and C<sub>3</sub>H<sub>6</sub> over Ag/Al<sub>2</sub>O<sub>3</sub>, have high reactivity with NO + O<sub>2</sub> to form NCO. Finally, we propose a possible reaction scheme to explain the high efficiency of the NO<sub>x</sub> reduction by C<sub>2</sub>H<sub>5</sub>OH.

## 2. Experimental and theoretical

An Ag/Al<sub>2</sub>O<sub>3</sub> 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 C<sub>3</sub>H<sub>6</sub> 1714 ppm, or C<sub>2</sub>H<sub>5</sub>OH 1565 ppm, or CH<sub>3</sub>CHO 1565 ppm, or CH<sub>3</sub>COOH 1565 ppm, water vapor (10%), and O<sub>2</sub> (10%) in N<sub>2</sub> balance at a total flow rate of 4000 ml min<sup>-1</sup> (GHSV = 50,000 h<sup>-1</sup>). NO<sub>x</sub> conversion was analyzed on-line by a chemiluminescence NO/NO<sub>2</sub>/NO<sub>x</sub> analyzer (42C-hl, Thermo Environmental). An aqueous C<sub>2</sub>H<sub>5</sub>OH (or CH<sub>3</sub>CHO, or CH<sub>3</sub>COOH) 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/Al<sub>2</sub>O<sub>3</sub> 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/Al<sub>2</sub>O<sub>3</sub> catalyst was heated in situ in (10%) O<sub>2</sub>/N<sub>2</sub> 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<sup>-1</sup> for 100 scans.

Density functional theory (DFT) calculation was used to confirm the structure of surface enolic species on Ag/Al<sub>2</sub>O<sub>3</sub> 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<sup>TM</sup> Version 6.0 package.

## 3. Results

### 3.1. Reaction activity of various organic compounds for the SCR of NO<sub>x</sub> over Ag/Al<sub>2</sub>O<sub>3</sub>

Fig. 1 shows the reaction activity of various organic compounds for the SCR of NO<sub>x</sub> over Ag/Al<sub>2</sub>O<sub>3</sub>. When using C<sub>2</sub>H<sub>5</sub>OH as a reductant, the maximal conversion of NO<sub>x</sub> is

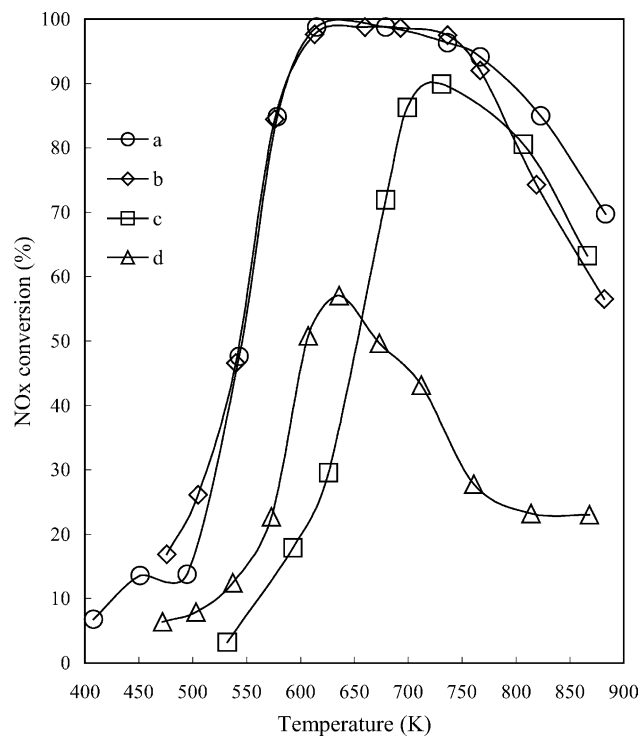


Fig. 1. Activity of Ag/Al<sub>2</sub>O<sub>3</sub> for the SCR of NO<sub>x</sub> by various reductants. Conditions: NO, 800 ppm; O<sub>2</sub>, 10%; H<sub>2</sub>O, 10% and reductants (a) C<sub>2</sub>H<sub>5</sub>OH, 1565 ppm, (b) CH<sub>3</sub>CHO, 1565 ppm, (c) C<sub>3</sub>H<sub>6</sub>, 1714 ppm, and (d) CH<sub>3</sub>COOH, 1565 ppm, N<sub>2</sub> balance, GHSV = 50,000 h<sup>-1</sup>.

up to 98.7%, and the average conversion of NO<sub>x</sub> is ca. 90% even in the wide temperature range of 578–883 K. In the case of CH<sub>3</sub>CHO, it is worthwhile to note that the NO<sub>x</sub> conversion is nearly the same as that of C<sub>2</sub>H<sub>5</sub>OH at temperatures below 766 K. Compared with C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>CHO, there is a relatively lower NO<sub>x</sub> conversion by C<sub>3</sub>H<sub>6</sub> in the whole reaction temperature range, especially in the low temperature range. However, when using CH<sub>3</sub>COOH as a reductant with the same carbon atom concentration (ppm C), the highest conversion of NO<sub>x</sub> is only 58%. These results indicate that the NO<sub>x</sub> conversion is strongly influenced by the kind of reductant, and the order of the reaction activity is C<sub>2</sub>H<sub>5</sub>OH (CH<sub>3</sub>CHO) > C<sub>3</sub>H<sub>6</sub> > CH<sub>3</sub>COOH. In other words, partially oxidized hydrocarbons such as C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>CHO are extremely efficient for the NO<sub>x</sub> reduction, while deep oxidation of hydrocarbons lowers NO<sub>x</sub> conversion.

### 3.2. Steady state in situ DRIFTS study of the SCR of NO<sub>x</sub> by C<sub>2</sub>H<sub>5</sub>OH over Ag/Al<sub>2</sub>O<sub>3</sub>

The difference of these reductants for the SCR of NO<sub>x</sub> over the Ag/Al<sub>2</sub>O<sub>3</sub> was investigated using DRIFTS. Fig. 2 shows the in situ DRIFTS spectra of Ag/Al<sub>2</sub>O<sub>3</sub> during the reaction of NO 800 ppm + C<sub>2</sub>H<sub>5</sub>OH 1565 ppm + O<sub>2</sub> (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 + O<sub>2</sub> (10%). After an exposure of the Ag/Al<sub>2</sub>O<sub>3</sub>

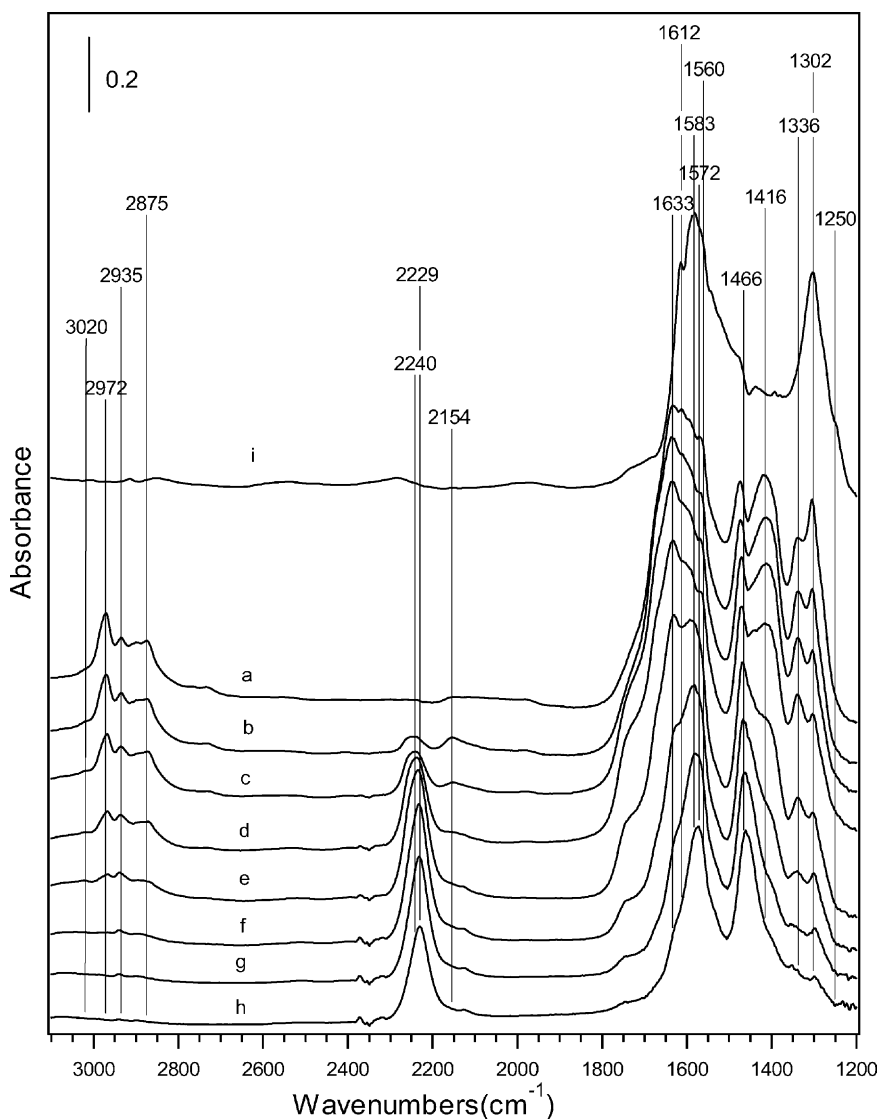


Fig. 2. DRIFTS spectra of adsorbed species in the steady state over Ag/Al<sub>2</sub>O<sub>3</sub> in the flow of NO + C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> at (a) 473 K, (b) 523 K, (c) 573 K, (d) 623 K, (e) 673 K, (f) 723 K, (g) 773 K, (h) 823 K, and (i) NO + O<sub>2</sub> for 120 min at 473 K. Conditions: NO, 800 ppm; C<sub>2</sub>H<sub>5</sub>OH, 1565 ppm; O<sub>2</sub>, 10%.

to NO + O<sub>2</sub> for 120 min (spectrum i), strong peaks at 1583, 1302 cm<sup>-1</sup> and shoulders at 1612, 1560, and 1250 cm<sup>-1</sup> were observed, which were respectively assigned to unidentate (1560, 1250 cm<sup>-1</sup>), bidentate (1583, 1302 cm<sup>-1</sup>), and bridging (1612 cm<sup>-1</sup>) nitrates according to the literature [8,12].

During the NO + C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> reaction at various temperatures (473–823 K) in steady states over Ag/Al<sub>2</sub>O<sub>3</sub> (spectra a–h), the peaks of nitrates mentioned above also appeared. We also detected strong peaks at 1572 and 1466 cm<sup>-1</sup>. These peaks were attributed to  $\nu_{\text{as}}(\text{OCO})$ , and  $\nu_{\text{s}}(\text{OCO})$  of adsorbed acetate respectively, because the frequencies of these peaks are in good agreement with those of CH<sub>3</sub>COOH adsorbed on Ag/Al<sub>2</sub>O<sub>3</sub> (this result not shown) and alumina [16,22]. It is interesting to note that, at low temperature region 473–673 K (spectra a–e), the peak at 1633 cm<sup>-1</sup> is predominant, accompanied by the appearance of strong peaks at 1416 and 1336 cm<sup>-1</sup>. The three peaks were also observed on

Ag/Al<sub>2</sub>O<sub>3</sub> during the oxidation of C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>CHO, and were attributed to a surface enolic species according to our earlier study [21]. More evidences of the assignment for these peaks will be discussed below.

In the region of 2300–2000 cm<sup>-1</sup>, a strong peak at 2240 cm<sup>-1</sup> at 623 K (spectrum c) was observed and shifted to 2229 cm<sup>-1</sup> at 673 K (spectrum e) during the SCR of NO<sub>x</sub> over Ag/Al<sub>2</sub>O<sub>3</sub>, which was assigned to NCO bound to the Al site (2240 cm<sup>-1</sup>) and Ag site (2229 cm<sup>-1</sup>) [4,5,8,14,17,18]. In addition, another weak peak at 2154 cm<sup>-1</sup> was due to CN [4,23].

In the region of 3100–2800 cm<sup>-1</sup>, peaks at 2972 and 2875 cm<sup>-1</sup> were assigned to  $\nu_{\text{as}}(\text{C-H})$  and  $\nu_{\text{s}}(\text{C-H})$  of -CH<sub>3</sub> [4,24], and the peak at 2935 cm<sup>-1</sup> was possibly due to  $\nu_{\text{as}}(\text{C-H})$  of methylene [24]. In addition, a very weak peak at 3020 cm<sup>-1</sup> was observed, which is the characteristic of C-H stretching vibration model in C=CH group [24,25].

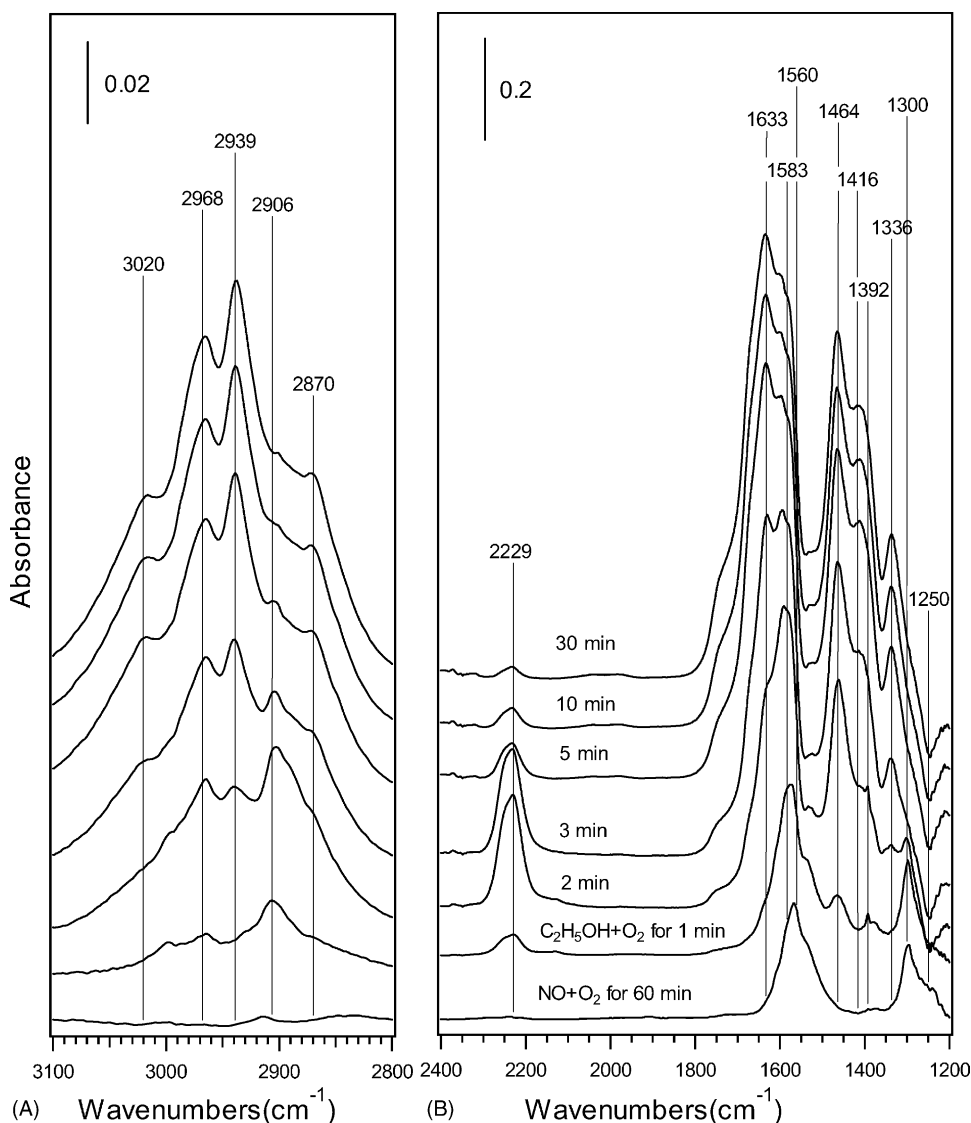


Fig. 3. Dynamic changes of in situ DRIFTS spectra over Ag/Al<sub>2</sub>O<sub>3</sub> as a function of time in a flow of C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> at 673 K. Before the measurement, the catalyst was pre-exposed to a flow of NO + O<sub>2</sub> for 60 min at 673 K. Conditions: NO, 800 ppm; C<sub>2</sub>H<sub>5</sub>OH, 1565 ppm; O<sub>2</sub>, 10%.

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/Al<sub>2</sub>O<sub>3</sub> surface.

### 3.3. Reactivity of adsorbed NO<sub>3</sub><sup>-</sup> over Ag/Al<sub>2</sub>O<sub>3</sub>

The reactivity of the nitrates toward C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> and C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> was studied by the transient response of DRIFTS method. Fig. 3A and B show the in situ DRIFTS spectra of Ag/Al<sub>2</sub>O<sub>3</sub> in a flow of C<sub>2</sub>H<sub>5</sub>OH 1565 ppm + O<sub>2</sub> (10%) after the catalyst was pre-exposed to a flow of NO 800 ppm + O<sub>2</sub> (10%) for 60 min at 673 K. Switching the fed gas from NO + O<sub>2</sub> to C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> led to a drastic decrease in the intensity of nitrate peaks (1250 and 1300 cm<sup>-1</sup>), and they disappeared completely after 3 min. Simultaneously,

the intensity of the peak at 2229 cm<sup>-1</sup> 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 C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> to form NCO.

The same set of experiments was also performed with C<sub>3</sub>H<sub>6</sub> 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<sup>-1</sup> dramatically slowed down, as did the increase rate of NCO peak, indicating that C<sub>3</sub>H<sub>6</sub> is not as active as C<sub>2</sub>H<sub>5</sub>OH for reaction with nitrate to form NCO.

### 3.4. Formation and reactivity of partial oxidation products of C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>CHO, and C<sub>3</sub>H<sub>6</sub> over Ag/Al<sub>2</sub>O<sub>3</sub>

Fig. 5 shows the in situ DRIFTS spectra of Ag/Al<sub>2</sub>O<sub>3</sub> at various temperatures in steady states in flowing

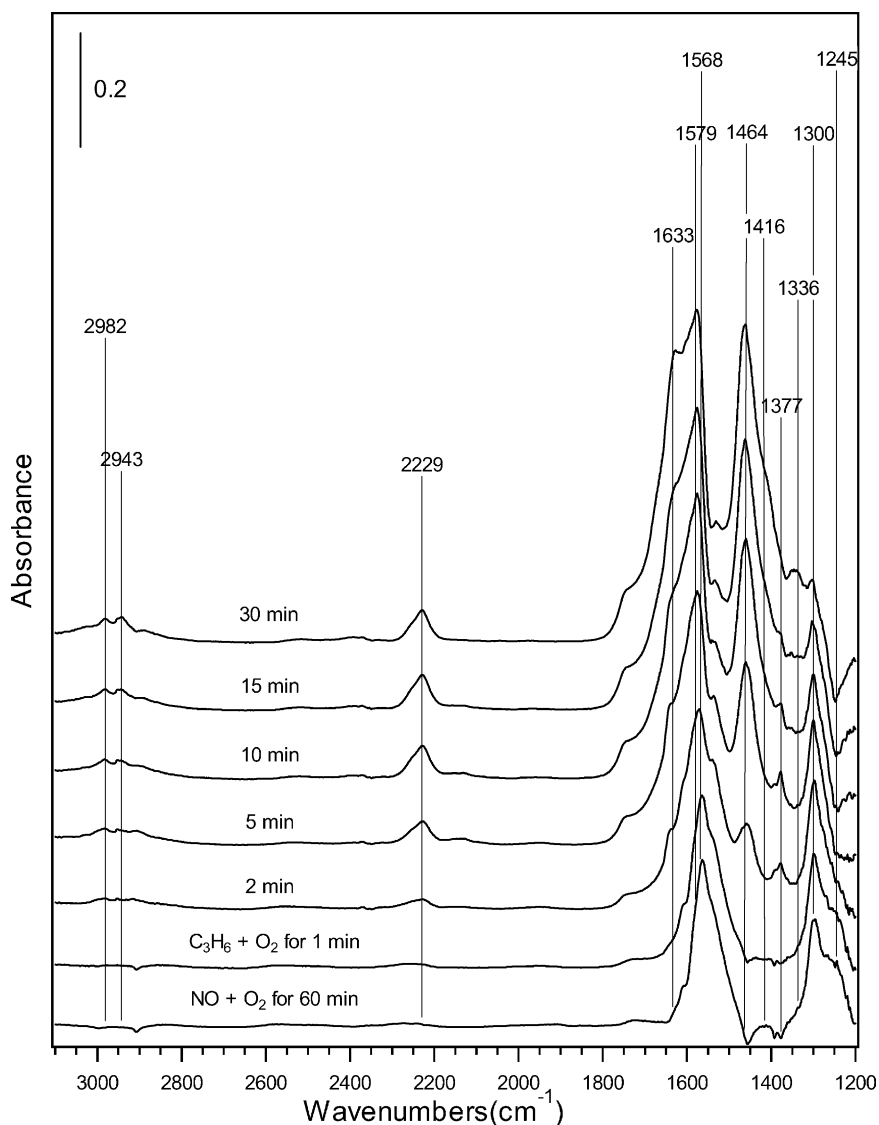


Fig. 4. Dynamic changes of in situ DRIFTS spectra over Ag/Al<sub>2</sub>O<sub>3</sub> as a function of time in a flow of C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> at 673 K. Before the measurement, the catalyst was pre-exposed to a flow of NO + O<sub>2</sub> for 60 min at 673 K. Conditions: NO, 800 ppm; C<sub>3</sub>H<sub>6</sub>, 1714 ppm; O<sub>2</sub>, 10%.

three different gas mixtures: (A) C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub>, (B) CH<sub>3</sub>CHO + O<sub>2</sub> and (C) 2,3-dihydrofuran. For C<sub>2</sub>H<sub>5</sub>OH oxidation (Fig. 5A), two peaks at 1579 and 1466 cm<sup>-1</sup> were assigned to  $\nu_{\text{as}}(\text{OCO})$ , and  $\nu_{\text{as}}(\text{OCO})$  of acetate as the same as in Fig. 2. The peaks at 1633, 1416, and 1336 cm<sup>-1</sup> were assigned to a surface enolic species, which will be discussed below. Apparently, the enolic species are predominant during the oxidation of C<sub>2</sub>H<sub>5</sub>OH on the Ag/Al<sub>2</sub>O<sub>3</sub> 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 CH<sub>3</sub>CHO over Ag/Al<sub>2</sub>O<sub>3</sub> (Fig. 5B), the enolic species (peaks at 1633, 1412, and 1336 cm<sup>-1</sup>) were predominant within the whole temperature region. Heating the sample resulted in an increase in the intensity of acetate peaks (1579 and 1466 cm<sup>-1</sup>), 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  $\nu(\text{C}=\text{O})$  were observed at 1730 and 1759 cm<sup>-1</sup> [24] within the all temperature region, especially at low temperature region of 473–623 K, indicating that some CH<sub>3</sub>CHO molecules did not undergo partial oxidation to form enolic species and acetate.

2,3-dihydrofuran was used to a model compound to confirm the structure of surface enolic species. As shown in Fig. 5C, strong peak at 1630 cm<sup>-1</sup> was also observed, which similarly was accompanied by an appearance of peaks at 1423 and 1315 cm<sup>-1</sup>. This result strongly supports our assignment about the enolic species. The acetate peaks indicate that partial oxidation of 2,3-dihydrofuran occurred on Ag/Al<sub>2</sub>O<sub>3</sub> surface. In addition, peak at 1390 cm<sup>-1</sup> were observed and assigned to  $\delta(\text{C}-\text{H})$  [24].

The reactivity of the partial oxidation products of C<sub>2</sub>H<sub>5</sub>OH, formed during C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> reaction over Ag/Al<sub>2</sub>O<sub>3</sub> at 673 K, toward NO + O<sub>2</sub> 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/Al<sub>2</sub>O<sub>3</sub> in a flow of NO + O<sub>2</sub> 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 C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> for 60 min, very strong enolic species peaks at 1633, 1416, and 1336 cm<sup>-1</sup> and the acetate peaks (1579 and 1466 cm<sup>-1</sup>) were observed. Switching the fed gas to NO + O<sub>2</sub> 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<sup>-1</sup> formed, and its intensity promptly increased within 3 min, then decreased. However, the drastic decrease in acetate peak at 1464 cm<sup>-1</sup> 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/Al<sub>2</sub>O<sub>3</sub>, whereas the surface con-

centration of NCO was very low. Taking into account the high reactivity of nitrates toward C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub>, acetate is not highly reactive toward NO + O<sub>2</sub> to form NCO.

The same set of experiments was performed after exposing the catalyst to a flow of CH<sub>3</sub>CHO 1565 ppm + O<sub>2</sub> (10%), and similar changes were observed. As shown in Fig. 7A and B, after switching the fed gas to NO + O<sub>2</sub> 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 C<sub>3</sub>H<sub>6</sub> was evaluated in essentially the same manner as above. After the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was exposed to C<sub>3</sub>H<sub>6</sub> 1714 ppm + O<sub>2</sub> (10%) for 60 min, only a very weak shoulder at 1633 cm<sup>-1</sup> was observed (Fig. 8A). As shown in Fig. 8B, switching the

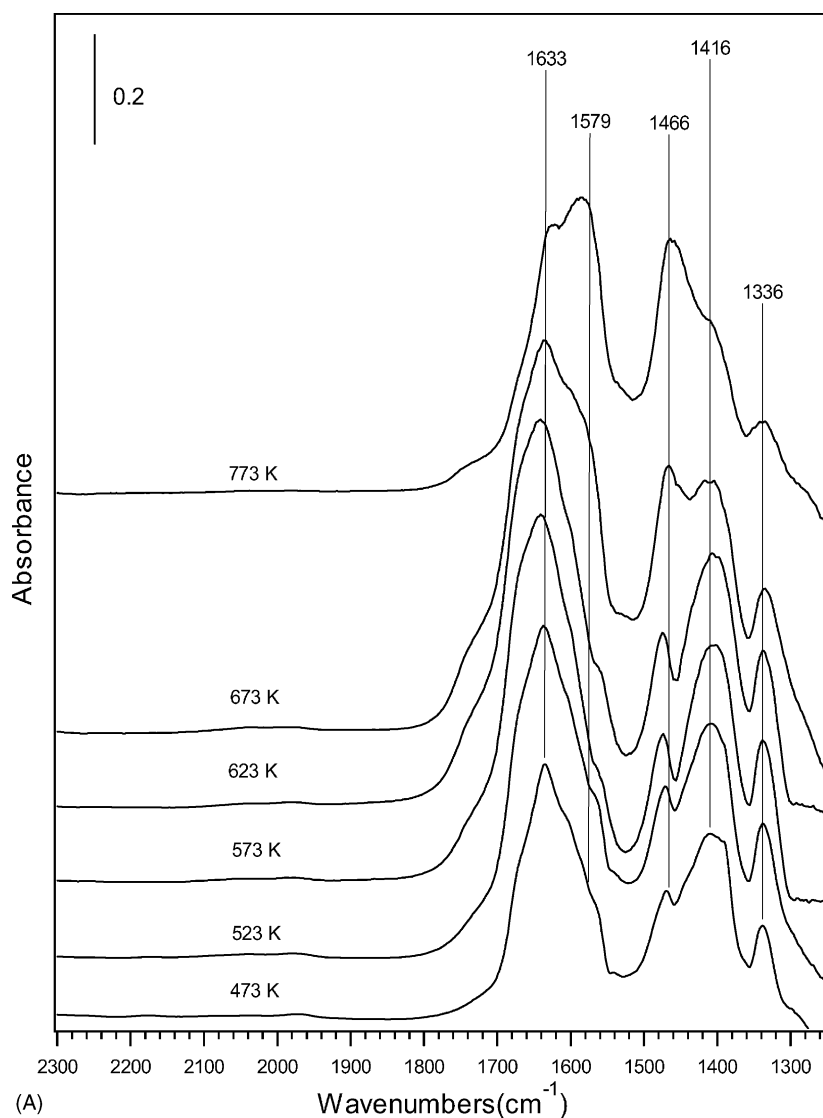


Fig. 5. In situ DRIFTS spectra over Ag/Al<sub>2</sub>O<sub>3</sub> in the steady states at different temperatures in a flow of (A) C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub>, (B) CH<sub>3</sub>CHO + O<sub>2</sub>, and (C) 2,3-dihydrofuran. Conditions: C<sub>2</sub>H<sub>5</sub>OH, 1565 ppm; CH<sub>3</sub>CHO, 1565 ppm; 2,3-dihydrofuran, 1565 ppm; O<sub>2</sub>, 10%.

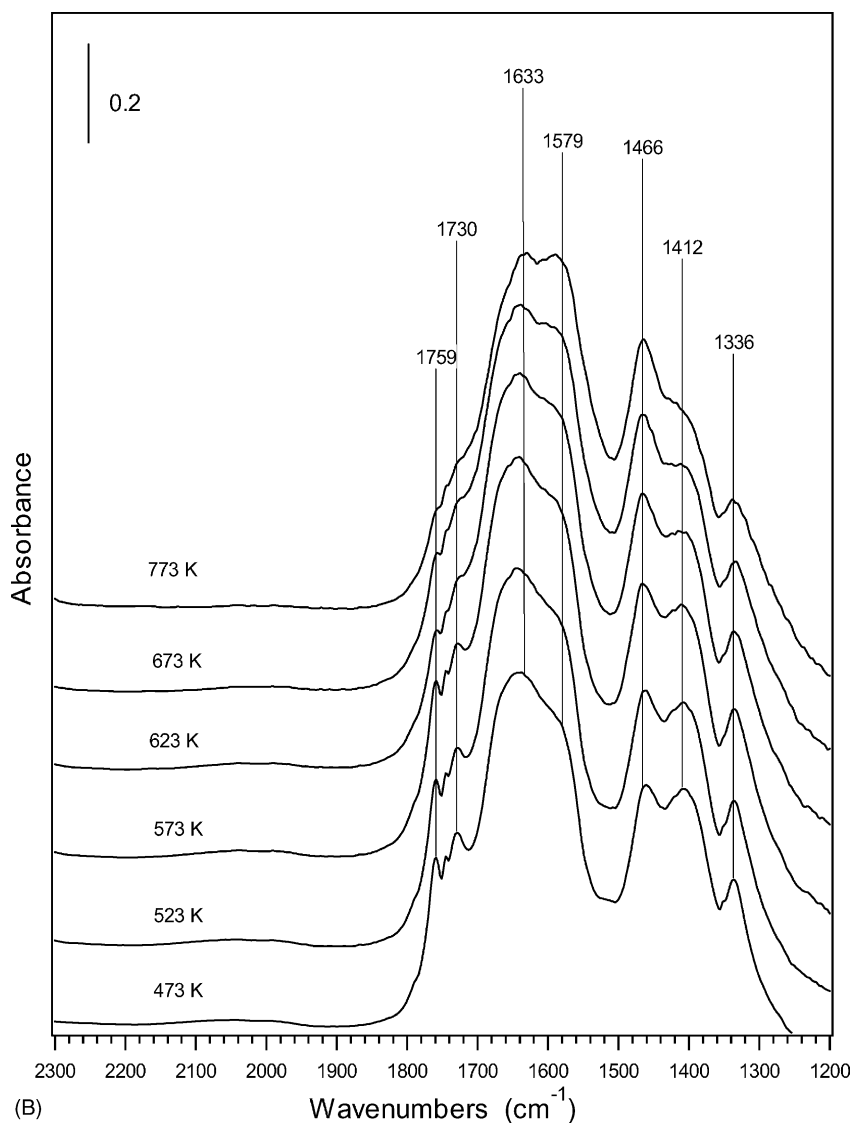


Fig. 5. (Continued).

flowing gas to  $\text{NO} + \text{O}_2$  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  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{CH}_3\text{CHO}$ , and  $\text{C}_3\text{H}_6$  over  $\text{Ag}/\text{Al}_2\text{O}_3$  at 673 K, peaks at 1633, 1416, and  $1336\text{ cm}^{-1}$  were observed. Shimizu et al. [12] reported similar peaks at 1630, 1410, and  $1300\text{--}1336\text{ cm}^{-1}$  over  $\text{Ag}/\text{Al}_2\text{O}_3$  in flowing *n*-hexane +  $\text{NO} + \text{O}_2$  and assigned them to carbonate species. Turek et al. [26] reported that when  $\text{CO}_2$  chemisorbed on the surface of  $\gamma\text{-Al}_2\text{O}_3$ , the main adsorbed species were carbonates such as bicarbonates and free carbonates. We also studied the adsorption of  $\text{CO}_2$  on  $\text{Ag}/\text{Al}_2\text{O}_3$  at 673 K in flowing  $\text{CO}_2$ , but no peaks

at 1633, 1416,  $1336\text{ cm}^{-1}$  were observed even when the concentration of  $\text{CO}_2$  in the fed gas was as high as 8%. In addition, the peak at  $1633\text{ cm}^{-1}$  was assigned to the stretching vibration model of  $\text{C}=\text{O}$  in formyl species [27] or in aldehyde [28], and OH deformation of adsorbed water was observed at the same position [29].

The peak at  $1633\text{ cm}^{-1}$  can be associated with the frequency of double bond stretching vibration, such as  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{O})$ . In general, however, the stretching vibration frequencies of isolated  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  should be higher than  $1633\text{ cm}^{-1}$ . One evidence is that the IR spectra of syn-vinyl alcohol ( $\text{CH}_2=\text{CHOH}$ ) in gas phase, show strong peak between  $1644$  and  $1648\text{ cm}^{-1}$ , which is accompanied by two peaks at  $1409\text{--}1412$  and  $1300\text{--}1326\text{ cm}^{-1}$  [24,31–33]. The IR spectrum of adsorbed catechol on a  $\text{TiO}_2$  colloid also gives a similar peak at  $1620\text{ cm}^{-1}$  [25]. Their common characteristic is an enolic structure. We conjecture that in this study, an enolic structure  $(\text{CH}_2=\text{CH}-\text{O}^-)\text{-M}$  is formed when

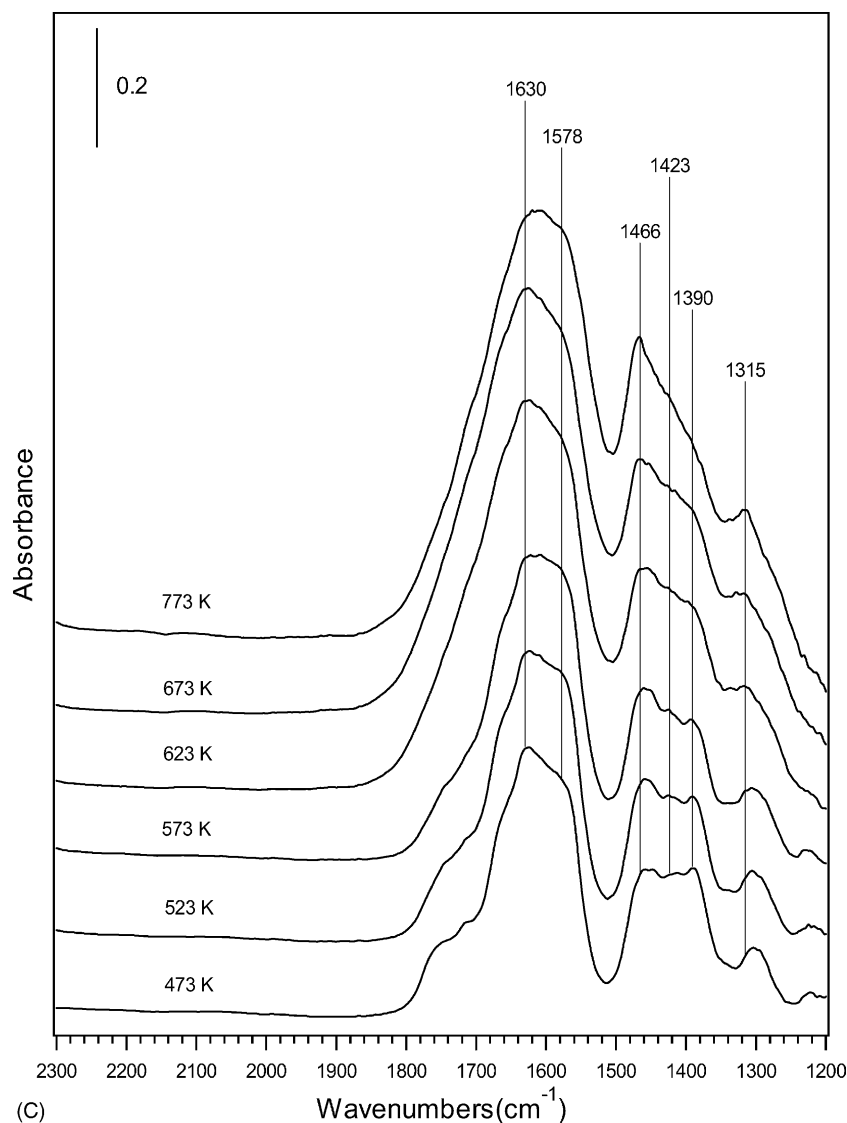


Fig. 5. (Continued).

$\text{CH}_3\text{CHO}$  adsorbs on the surface of  $\text{Ag}/\text{Al}_2\text{O}_3$ . The conjugation of  $\text{CH}_2=\text{CH}-\text{O}^-$  group may induce the stretching vibrational mode of  $\text{C}=\text{C}-\text{O}^-$  to shift to a frequency lower than  $\nu(\text{C}=\text{C})$  and higher than  $\nu(\text{C}-\text{O})$  [24,25]. The peaks between  $2872$  and  $3020\text{ cm}^{-1}$  in Fig. 6A also accord with the distribution of  $\nu(\text{C}-\text{H})$  for a  $\text{H}_2\text{C}=\text{CH}-$  group [24,25]. As a consequence, the peak at  $1633\text{ cm}^{-1}$  could be tentatively assigned to asymmetric stretching vibration mode of  $\text{CH}_2=\text{CH}-\text{O}^-$  group, and peaks at  $1416$  and  $1336\text{ cm}^{-1}$  could be tentatively attributed to symmetric stretching vibration mode of  $\text{CH}_2=\text{CH}-\text{O}^-$  and for a  $\text{C}-\text{H}$  deformation mode, respectively [24,30]. Furthermore, similar feature was observed on  $\text{Ag}/\text{Al}_2\text{O}_3$  in exposing to 2,3-dihydrofuran (in Fig. 5C), which has a  $\text{C}=\text{C}$  bonded with an oxygen structure. This result strongly supports our assignments about the surface enolic species. As shown in Fig. 5A and B, when  $\text{Ag}/\text{Al}_2\text{O}_3$  is exposed to  $\text{C}_2\text{H}_5\text{OH} + \text{O}_2$  and  $\text{CH}_3\text{CHO} + \text{O}_2$ , very strong peaks at  $1633$ ,  $1416$ , and  $1336\text{ cm}^{-1}$  are observed,

indicating that enolic species are the main surface species. However, these peaks are barely perceptible on  $\text{Ag}/\text{Al}_2\text{O}_3$  in the flow of  $\text{C}_3\text{H}_6 + \text{O}_2$  as shown in Fig. 8A, indicating a low surface concentration of  $\text{CH}_2=\text{CH}-\text{O}^-$  surface species.

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



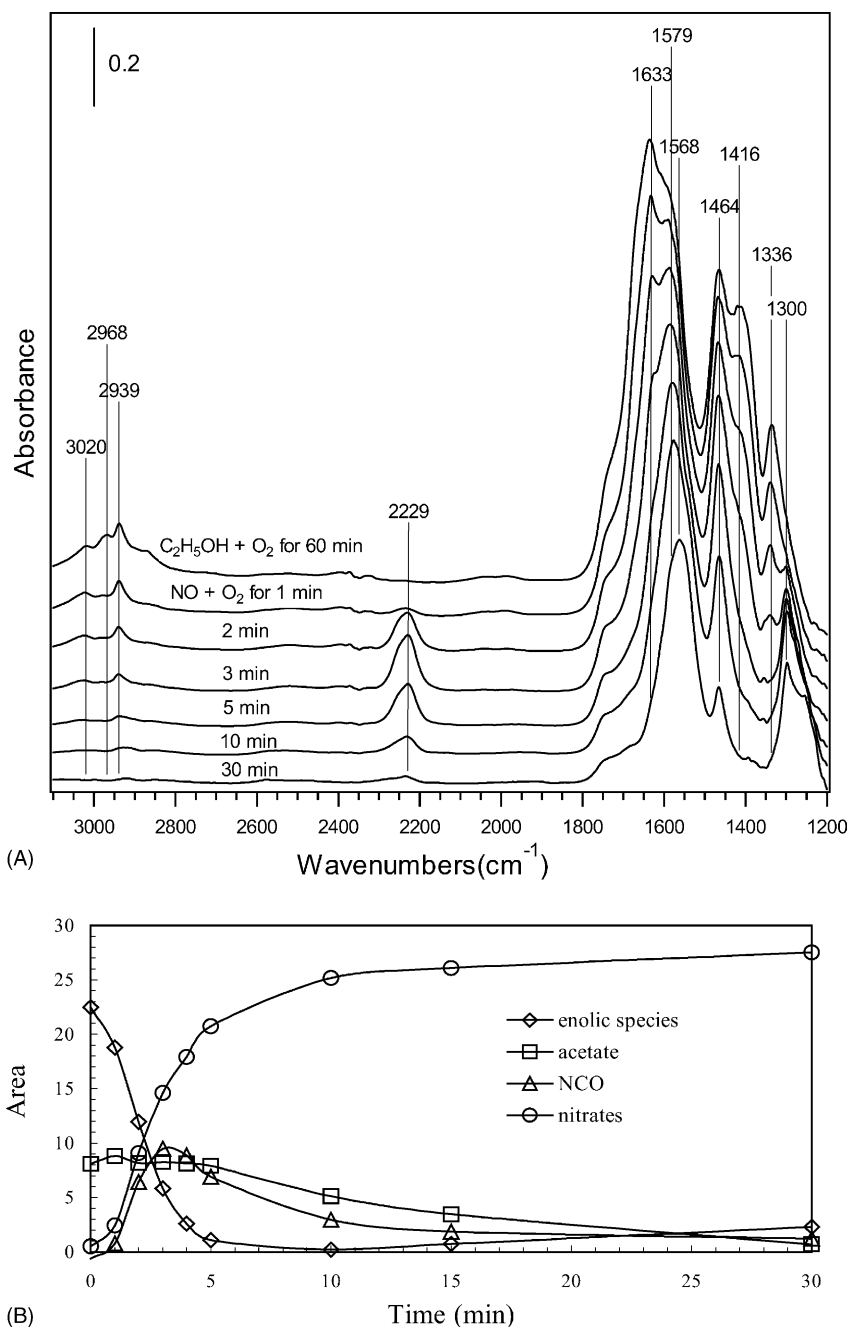


Fig. 6. (A) Dynamic changes of in situ DRIFTS spectra over  $\text{Ag}/\text{Al}_2\text{O}_3$  as a function of time in a flow of  $\text{NO} + \text{O}_2$  at 673 K. Before the measurement, the catalyst was pre-exposed to a flow of  $\text{C}_2\text{H}_5\text{OH} + \text{O}_2$  for 60 min at 673 K. Conditions:  $\text{NO}$ , 800 ppm;  $\text{C}_2\text{H}_5\text{OH}$ , 1565 ppm;  $\text{O}_2$ , 10%. (B) Time dependence of the integrated areas of the peak in the range of  $2160\text{--}2305\text{ cm}^{-1}$  ( $\Delta$ , NCO),  $1612\text{--}1711\text{ cm}^{-1}$  ( $\diamond$ , enolic species),  $1439\text{--}1508\text{ cm}^{-1}$  ( $\square$ , acetate) and  $1209\text{--}1321\text{ cm}^{-1}$  ( $\circ$ , nitrates).

Summarizing the above discussion, the formation of the surface enolic species over  $\text{Ag}/\text{Al}_2\text{O}_3$  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  $\text{Ag}/\text{Al}_2\text{O}_3$  are shown in Fig. 9A and B. In this model, the enolic species

( $\text{CH}_2=\text{CH}-\text{O}^-$ ) bond with silver atom, and the optimized distance between the oxygen and silver atom is  $2.072\text{ \AA}$ . 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  $1645\text{ cm}^{-1}$  with a relatively high infrared intensity of  $61\text{ km mol}^{-1}$ , which is  $12\text{ cm}^{-1}$  higher than the experimental harmonic frequency ( $1633\text{ cm}^{-1}$ ). Compared to the experimental value, the calculated symmetric

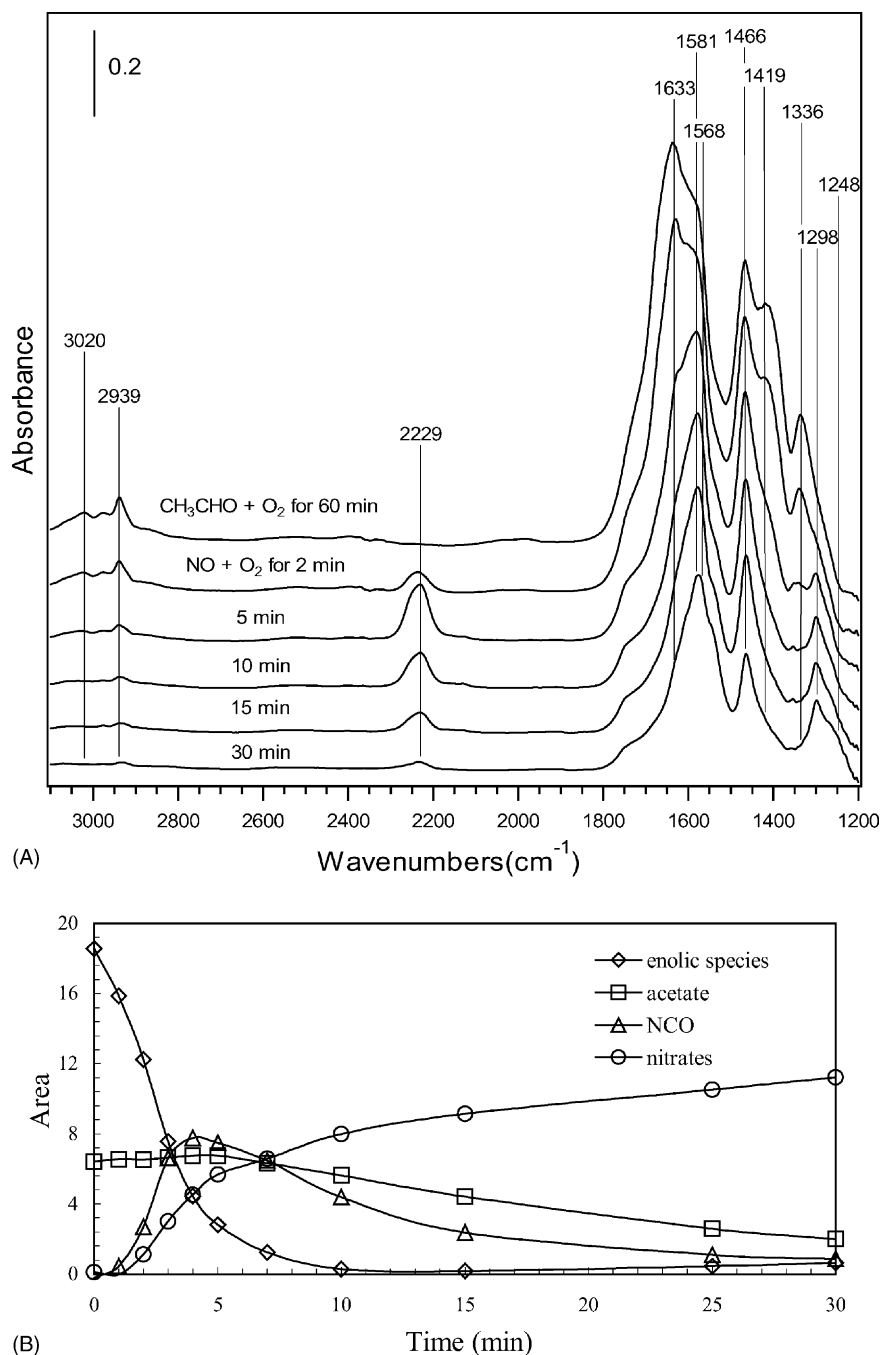
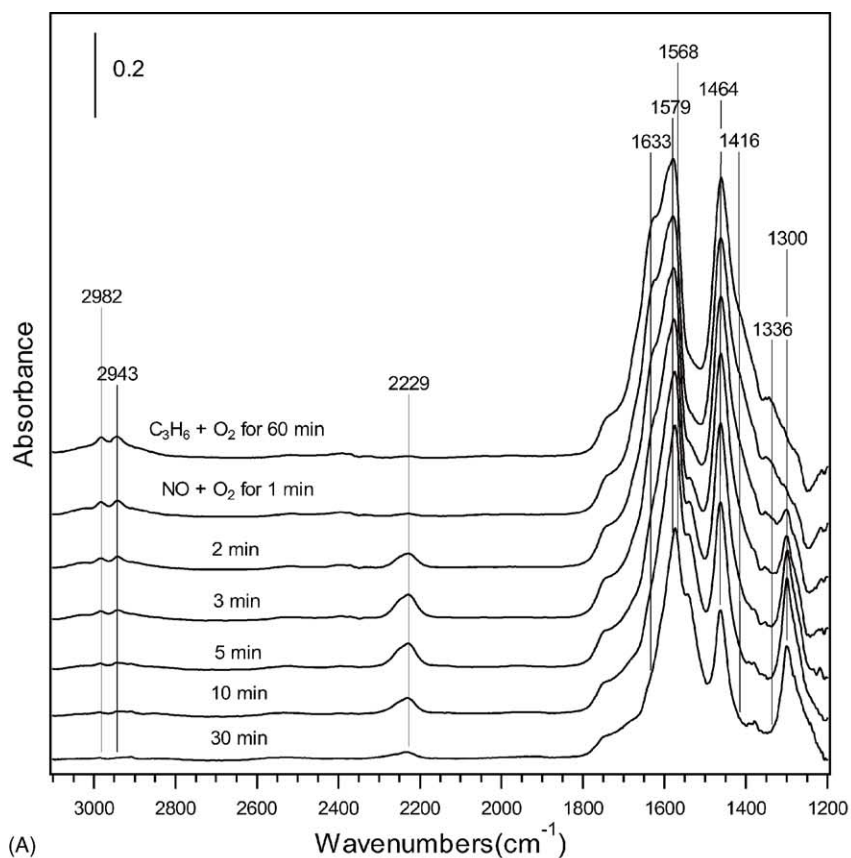


Fig. 7. (A) Dynamic changes of in situ DRIFTS spectra over  $\text{Ag}/\text{Al}_2\text{O}_3$  as a function of time in a flow of  $\text{NO} + \text{O}_2$  at 673 K. Before the measurement, the catalyst was pre-exposed to a flow of  $\text{CH}_3\text{CHO} + \text{O}_2$  for 60 min at 673 K. Conditions:  $\text{NO}$ , 800 ppm;  $\text{CH}_3\text{CHO}$ , 1565 ppm;  $\text{O}_2$ , 10%. (B) Time dependence of the integrated areas of the peak in the range of  $2160\text{--}2305\text{ cm}^{-1}$  ( $\Delta$ , NCO),  $1612\text{--}1711\text{ cm}^{-1}$  ( $\diamond$ , enolic species),  $1439\text{--}1508\text{ cm}^{-1}$  ( $\square$ , acetate), and  $1209\text{--}1321\text{ cm}^{-1}$  ( $\circ$ , nitrates).

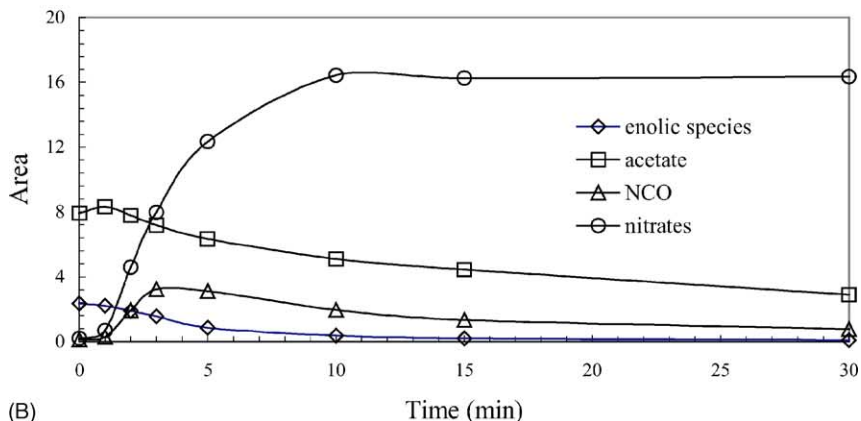
stretching vibrational mode of this species varied within less than  $13\text{ cm}^{-1}$  ( $1429\text{ cm}^{-1}$  against  $1416\text{ cm}^{-1}$ ). The calculated C–H deformation vibration mode ( $1328\text{ cm}^{-1}$ ) was  $8\text{ cm}^{-1}$  lower than the experimental one ( $1336\text{ cm}^{-1}$ ). On the basis of this result, we conclude that there is excellent agreement between the calculational vibration spectrum and the experimental spectrum, supporting our assignment about the structure of surface enolic species.

#### 4.3. Reactivity of enolic species and acetate

Many research groups have studied the formation and reactivity of acetate during  $\text{NO} + \text{C}_3\text{H}_6 + \text{O}_2$  reaction on oxide catalysts and metal supported catalysts such as  $\text{Al}_2\text{O}_3$  [15,16], and  $\text{Ag}/\text{Al}_2\text{O}_3$  [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



(A)



(B)

Fig. 8. (A) Dynamic changes of in situ DRIFTS spectra over Ag/Al<sub>2</sub>O<sub>3</sub> as a function of time in a flow of NO + O<sub>2</sub> at 673 K. Before the measurement, the catalyst was pre-exposed to a flow of C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> for 60 min at 673 K. Conditions: NO, 800 ppm; C<sub>3</sub>H<sub>6</sub>, 1714 ppm; O<sub>2</sub>, 10%. (B) Time dependence of the integrated areas of the peak in the range of 2160–2305 cm<sup>-1</sup> (Δ, NCO), 1612–1711 cm<sup>-1</sup> (◇, enolic species), 1439–1508 cm<sup>-1</sup> (□, acetate), and 1209–1321 cm<sup>-1</sup> (○, nitrates).

toward NO + O<sub>2</sub>. In the case of the SCR of NO<sub>x</sub> by C<sub>2</sub>H<sub>5</sub>OH over Ag/Al<sub>2</sub>O<sub>3</sub>, Kameoka et al. [8] proposed that more acetate and less nitrates were observed in comparison with the SCR of NO<sub>x</sub> by C<sub>3</sub>H<sub>6</sub>, which probably explains why NCO is more easily observed when using C<sub>2</sub>H<sub>5</sub>OH as a reductant. If the acetate really plays a crucial role in NCO formation during the SCR of NO<sub>x</sub> by C<sub>2</sub>H<sub>5</sub>OH, it should be active for the reaction with NO + O<sub>2</sub>. However, as shown in Fig. 6, the enolic species have much higher reactivity than acetate on Ag/Al<sub>2</sub>O<sub>3</sub> towards NO + O<sub>2</sub> to form NCO species. Actu-

ally, the acetate did not react with NO + O<sub>2</sub> until the enolic species had nearly disappeared on the Ag/Al<sub>2</sub>O<sub>3</sub> surface. This means that enolic species, instead of acetate, play a crucial role in the NO<sub>x</sub> reduction by C<sub>2</sub>H<sub>5</sub>OH.

As mentioned above, exposure the sample to C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> for 3 min leads to the complete disappearance of nitrate peaks at 1300 and 1250 cm<sup>-1</sup> (Fig. 3B), indicating that adsorbed nitrates are highly active in their reaction with C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> to form NCO. However, Fig. 6 shows that after switching the fed gas to NO + O<sub>2</sub> for 30 min, strong nitrate

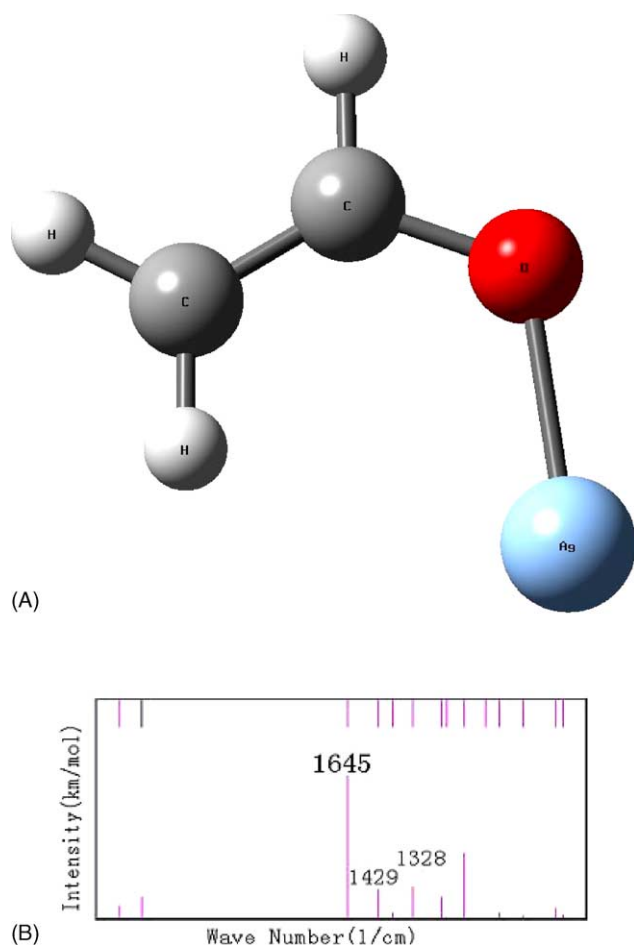
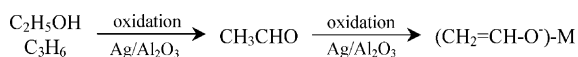


Fig. 9. (A) Molecular structure of the calculational model for the surface enolic species on Ag/Al<sub>2</sub>O<sub>3</sub>, and (B) calculational FTIR spectrum of the surface enolic species on Ag/Al<sub>2</sub>O<sub>3</sub>.

and acetate peaks coexisted on the surface of Ag/Al<sub>2</sub>O<sub>3</sub>, 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 CH<sub>3</sub>COOH on Al<sub>2</sub>O<sub>3</sub> was acetate. We have studied the adsorption of CH<sub>3</sub>COOH over Ag/Al<sub>2</sub>O<sub>3</sub> and obtained a similar result. As shown in Fig. 1, when using CH<sub>3</sub>COOH as a reductant, the highest conversion of NO<sub>x</sub> was only 58%. However, when using the same concentration of C<sub>2</sub>H<sub>5</sub>OH as a reductant, conversion of NO<sub>x</sub> was up to 98.7%. Fig. 5 shows that there are only two kinds of partial oxidation products of C<sub>2</sub>H<sub>5</sub>OH: acetate and adsorbed enolic species, which is additional evidence in favor of our suggestion that enolic species are quite active in their reaction with NO + O<sub>2</sub> to form NCO during the SCR of NO<sub>x</sub> by C<sub>2</sub>H<sub>5</sub>OH.



Scheme 1. The formation of enolic species over Ag/Al<sub>2</sub>O<sub>3</sub> from C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>CHO and C<sub>3</sub>H<sub>6</sub>.

We already know that there is a correlation between the high efficiency of NO<sub>x</sub> reduction by C<sub>2</sub>H<sub>5</sub>OH and the high productivity of a surface NCO over Ag/Al<sub>2</sub>O<sub>3</sub> [5,14,19]. Since enolic species are active in their reaction with NO + O<sub>2</sub> to form NCO, and are the predominant surface species during the C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> and the C<sub>2</sub>H<sub>5</sub>OH + NO + O<sub>2</sub> reaction, it is reasonable to expect and obtain a high concentration of surface NCO and high efficiency of NO<sub>x</sub> reduction by C<sub>2</sub>H<sub>5</sub>OH.

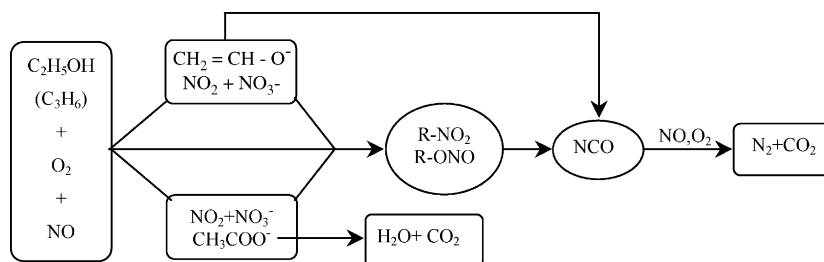
In comparison with C<sub>2</sub>H<sub>5</sub>OH, the same enolic species were obtained during partial oxidation of CH<sub>3</sub>CHO. The results of TPO experiments of C<sub>2</sub>H<sub>5</sub>OH over Ag/Al<sub>2</sub>O<sub>3</sub> [34] indicated that CH<sub>3</sub>CHO was the main product of partial oxidation of C<sub>2</sub>H<sub>5</sub>OH. As described above, CH<sub>3</sub>CHO is produced from partial oxidation of C<sub>2</sub>H<sub>5</sub>OH over Ag/Al<sub>2</sub>O<sub>3</sub>, so using CH<sub>3</sub>CHO or C<sub>2</sub>H<sub>5</sub>OH as reductant has the same efficiency for the SCR of NO<sub>x</sub>. Our results in Fig. 1 show that NO<sub>x</sub> conversions by C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>CHO are nearly the same at temperatures below 766 K, which is in good agreement with the suggestion based on our DRIFTS studies. In addition, NO<sub>x</sub> conversion by CH<sub>3</sub>CHO is relatively lower than that by C<sub>2</sub>H<sub>5</sub>OH at temperatures above 766 K. It is possible that non-selective oxidation reaction of CH<sub>3</sub>CHO in gas phase may occur easily above 766 K, which induces a smaller amount of CH<sub>3</sub>CHO to participate in the selective reduction of NO<sub>x</sub>.

In the case of partial oxidation of C<sub>3</sub>H<sub>6</sub>, a small amount of enolic species was formed, accompanied by large amounts of acetate on Ag/Al<sub>2</sub>O<sub>3</sub>. Therefore, it is reasonable that the efficiency of C<sub>3</sub>H<sub>6</sub> for NO<sub>x</sub> reduction is much lower than that of C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>CHO, which has been tested by our results in Fig. 1.

#### 4.4. Mechanism of the SCR of NO<sub>x</sub> by C<sub>2</sub>H<sub>5</sub>OH over Ag/Al<sub>2</sub>O<sub>3</sub>

On the basis of the results in this work together with the mechanism suggested for the SCR of NO<sub>x</sub> by C<sub>3</sub>H<sub>6</sub>, we propose a simplified reaction scheme for the NO<sub>x</sub> reduction by C<sub>2</sub>H<sub>5</sub>OH. As shown in Scheme 2, the reaction starts with the formation of both adsorbed nitrates via the NO oxidation by O<sub>2</sub> and enolic species and acetate via the partial oxidation of C<sub>2</sub>H<sub>5</sub>OH over Ag/Al<sub>2</sub>O<sub>3</sub>. 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-NO<sub>2</sub>), which is widely accepted in the study of the SCR of NO<sub>x</sub> [4,8,13,20,35]. Subsequently, NCO reacts with NO + O<sub>2</sub> and nitrates to yield N<sub>2</sub>. It should be pointed out that the acetate formed by the reaction of C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> also reacts toward NO + O<sub>2</sub> to produce NCO. However, the relatively low activity of acetate toward NO + O<sub>2</sub> results in this parallel reaction not playing an important role in the formation of NCO.

Obviously, the DRIFTS results for the SCR of NO<sub>x</sub> by C<sub>2</sub>H<sub>5</sub>OH are quite different from previous studies for the SCR of NO<sub>x</sub> by C<sub>3</sub>H<sub>6</sub>. It is worthwhile to point out that this



Scheme 2. The possible mechanism of the SCR of  $\text{NO}_x$  by  $\text{C}_2\text{H}_5\text{OH}$  ( $\text{C}_3\text{H}_6$ ) over  $\text{Ag}/\text{Al}_2\text{O}_3$ .

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  $\text{Ag}/\text{Al}_2\text{O}_3$ . 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  $\text{Ag}/\text{Al}_2\text{O}_3$  during the SCR of  $\text{NO}_x$  by  $\text{C}_2\text{H}_5\text{OH}$ . Both enolic species and acetate are formed over  $\text{Ag}/\text{Al}_2\text{O}_3$  during the partial oxidation of  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{CH}_3\text{CHO}$  or  $\text{C}_3\text{H}_6$  over  $\text{Ag}/\text{Al}_2\text{O}_3$ . Peaks at 1633, 1416,  $1336\text{ cm}^{-1}$  are assigned to surface enolic species, which are in good agreement with results of DFT calculations. The enolic species have higher reactivity with  $\text{NO} + \text{O}_2$  on  $\text{Ag}/\text{Al}_2\text{O}_3$  than acetate species have. The enolic species are the main surface species during the partial oxidation of  $\text{C}_2\text{H}_5\text{OH}$  or  $\text{CH}_3\text{CHO}$  over  $\text{Ag}/\text{Al}_2\text{O}_3$ . As a result, high surface concentration of NCO and high efficiency of  $\text{NO}_x$  reduction are obtained when using  $\text{C}_2\text{H}_5\text{OH}$  or  $\text{CH}_3\text{CHO}$  as a reductant during the SCR of  $\text{NO}_x$ . In contrast, acetate is the main surface species over  $\text{Ag}/\text{Al}_2\text{O}_3$  during the partial oxidation of  $\text{C}_3\text{H}_6$ . This relates to a lower NCO concentration over  $\text{Ag}/\text{Al}_2\text{O}_3$  as well as a relatively lower  $\text{NO}_x$  conversion when using  $\text{C}_3\text{H}_6$  as a reductant.

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