

# FTIR, TPD and DFT studies of intermediates on Ag/Al<sub>2</sub>O<sub>3</sub> during the selective catalytic reduction of NO by C<sub>2</sub>H<sub>5</sub>OH

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## Abstract

The intermediates on Ag/Al<sub>2</sub>O<sub>3</sub> during the C<sub>2</sub>H<sub>5</sub>OH-SCR of NO were studied using in situ DRIFTS, TPD, and DFT calculations. A ring structure enolic species was found on the surface of Ag/Al<sub>2</sub>O<sub>3</sub> during the C<sub>2</sub>H<sub>5</sub>OH-SCR of NO by in situ DRIFTS, and this finding was supported by DFT calculations. The adsorbed enolic species is more prone to react with NO + O<sub>2</sub> on Ag/Al<sub>2</sub>O<sub>3</sub> than acetate is, and plays a crucial role in the formation of NCO which is a key intermediate during the SCR of NO. TPD results suggest that the enolic species is derived from the aldol condensation reaction of a partial oxidation product of C<sub>2</sub>H<sub>5</sub>OH (such as CH<sub>3</sub>CHO) on the surface of Ag/Al<sub>2</sub>O<sub>3</sub>. The results of DFT calculations are in good agreement with the DRIFTS spectra, and support our conjecture that the enolic species has a ring structure.

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**Keywords:** Selective catalytic reduction of NO (SCR of NO); Enolic species; Ag/Al<sub>2</sub>O<sub>3</sub>; In situ DRIFTS; TPD; Density functional theory (DFT) calculations

## 1. Introduction

Selective catalytic reduction of NO by C<sub>2</sub>H<sub>5</sub>OH (C<sub>2</sub>H<sub>5</sub>OH-SCR of NO) on Ag/Al<sub>2</sub>O<sub>3</sub> has attracted much attention as a new de-NO<sub>x</sub> technology for diesel and lean burning engine exhaust [1–3]. Up to now, only a few studies have been devoted to an understanding of the mechanism of the C<sub>2</sub>H<sub>5</sub>OH-SCR of NO [2,4–6]. It has been suggested that the mechanism was similar to that of the C<sub>3</sub>H<sub>6</sub>-SCR of NO, which is approximately NO + O<sub>2</sub> + C<sub>2</sub>H<sub>5</sub>OH → NO<sub>x</sub> (such as nitrates) + C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> (such as acetate) → R-NO<sub>2</sub> + R-ONO → -NCO + -CN + NO + O<sub>2</sub> → N<sub>2</sub>. In particular, nitrates and acetate could be key intermediates in the formation of NCO [4,6]. However, this mechanism does not sufficiently explain the significant difference between the C<sub>3</sub>H<sub>6</sub>-SCR of NO and the C<sub>2</sub>H<sub>5</sub>OH-SCR of NO [1,2]. In our recent study [7], we proposed that an enolic species derived from the partial oxidation of C<sub>2</sub>H<sub>5</sub>OH over Ag/Al<sub>2</sub>O<sub>3</sub> plays a crucial role in NCO formation, which possibly explains such difference.

In this paper, in situ DRIFTS, TPD and density functional theory (DFT) calculations were used to study the mechanism of the C<sub>2</sub>H<sub>5</sub>OH-SCR of NO over Ag/Al<sub>2</sub>O<sub>3</sub>. The most significant observation is that a ring structure enolic species, formed from oxidation and condensation reactions of C<sub>2</sub>H<sub>5</sub>OH over Ag/Al<sub>2</sub>O<sub>3</sub>, has high reactivity with NO + O<sub>2</sub> to form NCO and plays a predominant role in the NO reduction process.

## 2. Experimental

An Ag/Al<sub>2</sub>O<sub>3</sub> (5 wt.%) catalyst was obtained by impregnation of γ-Al<sub>2</sub>O<sub>3</sub> powder (200 m<sup>2</sup>/g) with an appropriate amount of silver nitrate aqueous solution. The sample was dried at 393 K for 3 h and calcined at 873 K for 3 h in air.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded on a Nexus 670 (Thermo Nicolet) FTIR, equipped with an in situ diffuse reflection chamber and a high sensitivity MCT detector. An 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,

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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 gas mixtures were fed at a flow rate of 100 ml/min. All spectra were measured with a resolution of 4 cm<sup>-1</sup> and with an accumulation of 100 scans.

Temperature-programmed desorption (TPD) was performed in a catalytic reactor. This reactor consisted of a 1.2 cm o.d. quartz tube with a 0.5 mm o.d. thermocouple placed in the center of a bed of 40–80 mesh catalyst particles (0.5 g). The thermocouple measured the temperature and provided feedback to the temperature programmer, which regulated heating of the electric furnace. An Agilent quadrupole mass spectrometer (5973N) detected products immediately downstream of the reactor as they were desorbed from the catalyst, and a computer allowed multiple signals and the thermocouple output to be recorded simultaneously. After being exposed to C<sub>2</sub>H<sub>5</sub>OH (1565 ppm) + O<sub>2</sub> (10%)/He for 60 min at 473 K, the catalyst was cooled to room temperature under an He flow (30 ml/min), followed by heating of the sample to 1023 K at a rate of 60 K/min. Then the desorbed products and temperatures were simultaneously recorded.

### 3. Results and discussion

#### 3.1. The formation of enolic species

Fig. 1 shows 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%) at a temperature range of 473–873 K in steady states. Exposure of this catalyst to the fed gas resulted in the appearance of five peaks (1633, 1579, 1471–1464, 1416, and 1336 cm<sup>-1</sup>). Peaks at 1579 and 1471–1464 cm<sup>-1</sup> were assigned to  $\nu_{\text{as}}(\text{OCO})$  and  $\nu_{\text{s}}(\text{OCO})$  of acetate, respectively [8–11]. According to our earlier study [7], peaks at 1633, 1416, and 1336 cm<sup>-1</sup> were assigned to an adsorbed enolic species. Apparently, the enolic species is 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 becomes dominant.

TPD spectra of Ag/Al<sub>2</sub>O<sub>3</sub> following exposure to C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub>/N<sub>2</sub> at 473 K for 60 min are shown in Fig. 2. Mass signals at 26, 27, 28, 31, 39, 41, 45, 46, 55, 56, 69 and 70 AMU were monitored during TPD to watch for gas-phase products from the enolic species, which is predominant on the Ag/Al<sub>2</sub>O<sub>3</sub> surface. The observed gas-phase products in Fig. 2a were C<sub>2</sub>H<sub>5</sub>OH (31, 45, 46 AMU), CO (28 AMU),

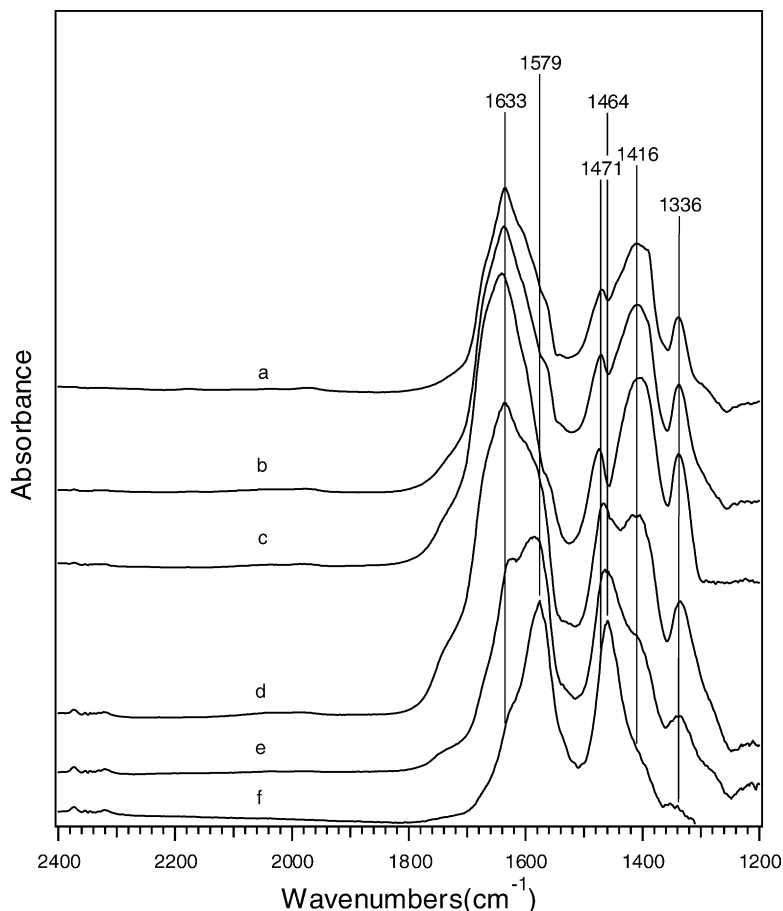
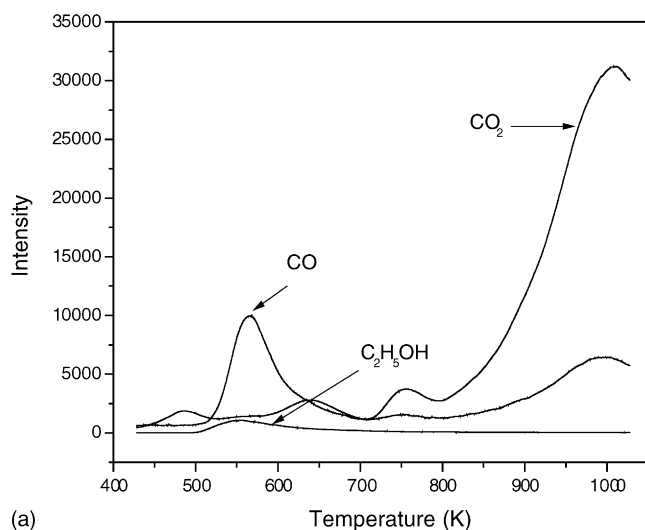
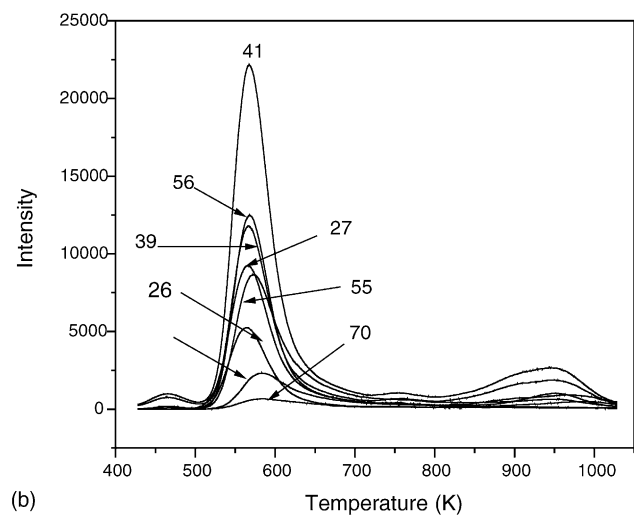


Fig. 1. The in situ DRIFTS spectra of adsorbed species in steady states on Ag/Al<sub>2</sub>O<sub>3</sub> in a flow of 1565 ppm C<sub>2</sub>H<sub>5</sub>OH + 10% O<sub>2</sub>/N<sub>2</sub> at (a) 473 K, (b) 523 K, (c) 573 K, (d) 673 K, (e) 773 K, and (f) 873 K.



(a)



(b)

Fig. 2. TPD spectra of adsorbed species on Ag/Al<sub>2</sub>O<sub>3</sub> after exposure to 1565 ppm C<sub>2</sub>H<sub>5</sub>OH + 10% O<sub>2</sub>/He for 60 min at 473 K. TPD conditions: He flow (30 ml/min) with heating to 973 K at a rate of 60 K/min after cooling to room temperature in a He flow.

and CO<sub>2</sub> (44 AMU). A very weak C<sub>2</sub>H<sub>5</sub>OH peak and strong peaks due to CO and CO<sub>2</sub> indicate the occurrence of partial oxidation of C<sub>2</sub>H<sub>5</sub>OH, for under this reaction system, it is widely accepted that the two products are derived from the

decomposition and/or oxidation of oxygen-containing hydrocarbons (C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>) [12,13]. As shown in Fig. 2b, peaks corresponding to C<sub>3</sub>H<sub>6</sub> (41 and 39 AMU), C<sub>3</sub>H<sub>4</sub>O (56, 55, 27, 26 AMU) and C<sub>4</sub>H<sub>6</sub>O (70, 69, 41, 39 AMU) were also observed at the same temperature, which could be related to the decomposition of the surface enolic species. This result indicates that a condensation reaction would occur synchronously during the partial oxidation of C<sub>2</sub>H<sub>5</sub>OH over Ag/Al<sub>2</sub>O<sub>3</sub>, which leads to chain growth of desorption products. The condensation reactions of aldehydes, as well as of ketones, are widely used in organic synthesis and are commonly catalyzed by zeolites, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> [14–16]. The TPD results shown in Fig. 2 are in good agreement with our DRIFTS results, namely the enolic species is predominant on the surface of Ag/Al<sub>2</sub>O<sub>3</sub>.

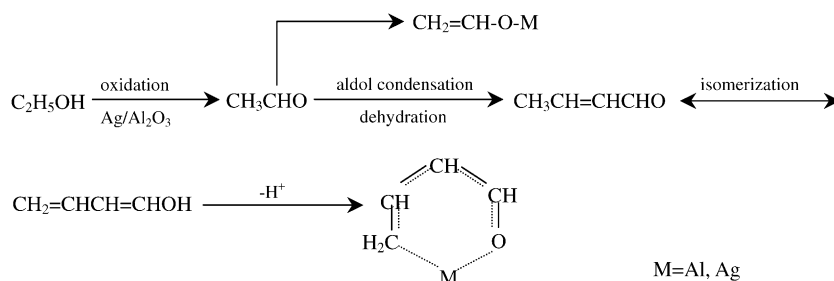
On the basis of our previous work [7] and the results of DRIFTS and TPD studies, a surface reaction mechanism was proposed for the formation of enolic species as shown in Scheme 1.

### 3.2. Density functional theory calculations

Density functional theory (DFT) calculations were used to confirm the structure of adsorbed 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.

The molecular structure and the optimized geometries of the calculational model for the adsorbed enolic species on Ag/Al<sub>2</sub>O<sub>3</sub> are shown in Fig. 3a and b. The optimized distance between the oxygen atom in CH<sub>2</sub>=CH-CH=CHO<sup>-</sup> and the aluminum atom in the Ag-Al cluster was 1.77 Å, while the optimized bond length for the Ag-Al bond in the Ag-Al cluster was 2.66 Å.

As shown in Fig. 4, the calculated FTIR spectrum is of reasonable similarity to the corresponding experimental one (see Fig. 1). The asymmetric stretching vibration mode of the enolic species was calculated at 1654 cm<sup>-1</sup> with a relatively high infrared intensity of 61 kJ/mol, which is 21 cm<sup>-1</sup> higher than the experimental harmonic frequency



Scheme 1. The formation of an adsorbed enolic species on Ag/Al<sub>2</sub>O<sub>3</sub>.

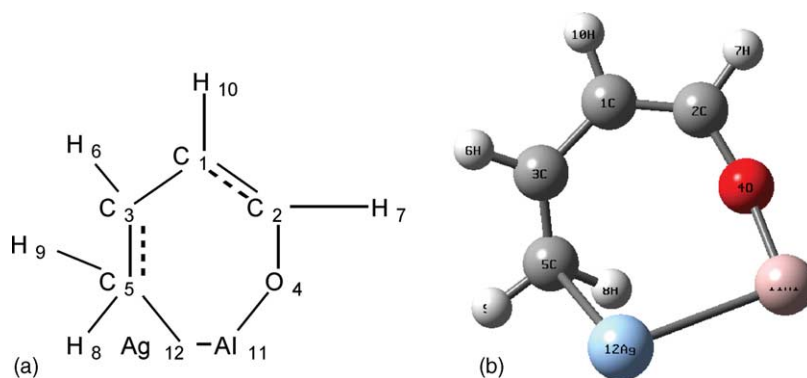


Fig. 3. The molecular structure and the optimized geometries of the calculational model for the absorbed enolic species on Ag/Al<sub>2</sub>O<sub>3</sub>.

(1633 cm<sup>-1</sup>). Compared to the experimental value, the calculated symmetric stretching vibrational mode of this species varied within less than 15 cm<sup>-1</sup> (1416 cm<sup>-1</sup> against 1431 cm<sup>-1</sup>). The calculated C–H deformation vibration mode (1345 cm<sup>-1</sup>) was 9 cm<sup>-1</sup> higher than the experimental one (1336 cm<sup>-1</sup>). Through the analysis of the vibration mode and the vibration frequency, we concluded that there is excellent agreement between the calculational vibration spectrum and the experimental one. Actually, 32 models of adsorbed species were calculated, however, only enolic species' DFT calculations are in good agreement with the experimental value.

### 3.3. The reactivity of enolic species

The reactivity of the enolic species toward NO + O<sub>2</sub> was evaluated by the in situ DRIFTS method. As shown in Fig. 5, after Ag/Al<sub>2</sub>O<sub>3</sub> was exposed to C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub>/N<sub>2</sub> for 60 min (curve a), very strong peaks due to the absorbed enolic species (1633, 1416, and 1336 cm<sup>-1</sup>), and acetate peaks (1579 and 1464 cm<sup>-1</sup>) were observed. Switching the fed gas to NO + O<sub>2</sub> resulted in a sharp decrease in the intensity of enolic species peaks accompanied by a corresponding increase in the intensity of a new NCO peak at 2229 cm<sup>-1</sup> [2,3,17], indicating that the enolic species is important to the formation of NCO. It was widely accepted that the NCO species could be a crucial intermediate in the SCR-NO<sub>x</sub> over

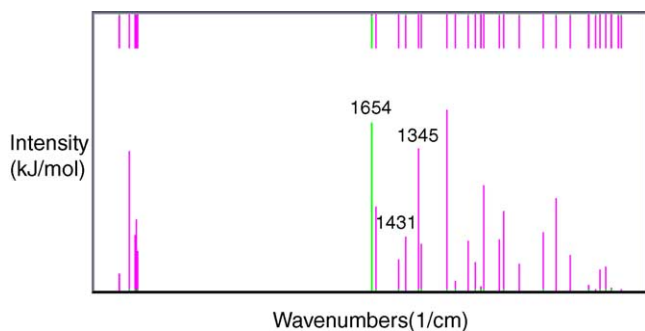
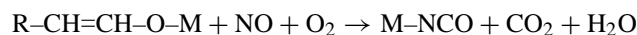


Fig. 4. The calculational FTIR spectrum of the absorbed enolic species on Ag/Al<sub>2</sub>O<sub>3</sub>.

Ag/Al<sub>2</sub>O<sub>3</sub>, and its high productivity would result in high efficiency of NO<sub>x</sub> reduction by C<sub>2</sub>H<sub>5</sub>OH or hydrocarbons [5,18–20]. Since the enolic species plays an important role in NCO formation, this species must also be another crucial intermediate in the C<sub>2</sub>H<sub>5</sub>OH-SCR of NO. The reaction of the enolic species with NO + O<sub>2</sub> is proposed as



Recently, it was proposed that strongly adsorbed acetate was a key intermediate in the formation of NCO [4,6,21]. However, Fig. 5 shows that a drastic decrease of acetate (peak

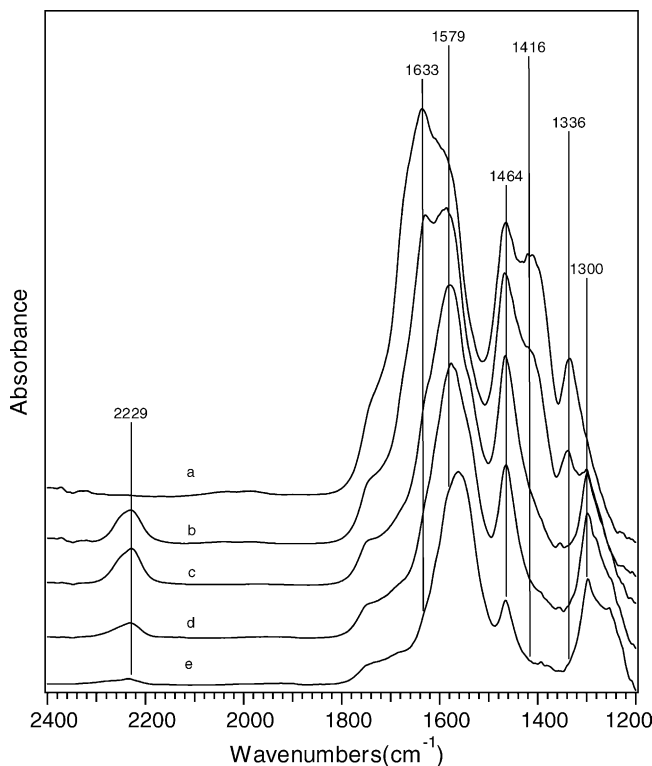


Fig. 5. The dynamic changes of in situ DRIFTS spectra on Ag/Al<sub>2</sub>O<sub>3</sub> as a function of time in a flow of NO + O<sub>2</sub> at 673 K. Before measurement, the catalyst was pre-exposed to a flow of 1565 ppm C<sub>2</sub>H<sub>5</sub>OH + 10% O<sub>2</sub>/N<sub>2</sub> for 60 min at 673 K (a), in a flow of 800 ppm NO + 10% O<sub>2</sub>/N<sub>2</sub> (b) 1 min, (c) 5 min, (d) 10 min, and (e) 30 min.

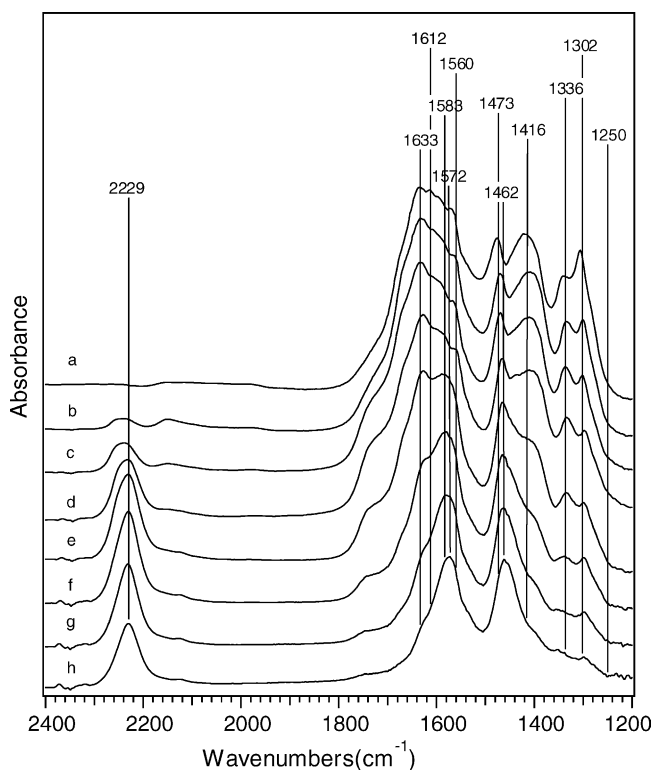


Fig. 6. The in situ DRIFTS spectra of adsorbed species in steady states over Ag/Al<sub>2</sub>O<sub>3</sub> in a flow of 800 ppm NO + 1565 ppm C<sub>2</sub>H<sub>5</sub>OH + 10% O<sub>2</sub>/N<sub>2</sub> at (a) 473 K, (b) 523 K, (c) 573 K, (d) 623 K, (e) 673 K, (f) 723 K, (g) 773 K, and (h) 823 K.

at 1464 cm<sup>-1</sup>) occurs after exhausting of the surface enolic species (curve d) accompanied by a very low surface concentration of NCO. This result strongly suggests that the enolic species plays a crucial role in the NCO formation and therefore in the C<sub>2</sub>H<sub>5</sub>OH-SCR of NO.

During the NO + C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub>/N<sub>2</sub> reaction over Ag/Al<sub>2</sub>O<sub>3</sub> at various temperatures (473–823 K) in steady states (Fig. 6), surface species such as the enolic species (1633, 1416, and 1336 cm<sup>-1</sup>), acetate (1572 and 1473–1462 cm<sup>-1</sup>), and NCO (2229 cm<sup>-1</sup>) were found. In addition, strong peaks at 1583, 1302 cm<sup>-1</sup> and shoulders at 1612, 1560 and 1250 cm<sup>-1</sup> were also observed, and they 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 [3,21]. Kameoka et al. [3] reported that these nitrates were highly active in their reaction with C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub>/N<sub>2</sub> to form NCO. From a comparison of the intensity of each peak, the enolic species and nitrates are predominant at 473 K. Heating the sample results in a decrease in the intensity of these two types of species peaks accompanied by a sharp increase in the intensity of the NCO peak. At 723 K, the NCO peak reached a maximum, while the peaks of enolic species and nitrates became very weak. Heating the sample in sequential increments to 823 K, the enolic species and nitrate peaks were barely perceptible and acetate became the predominant sur-

face species. These results strongly suggest that the enolic species and nitrates are key intermediates in the formation of NCO during the C<sub>2</sub>H<sub>5</sub>OH-SCR of NO over Ag/Al<sub>2</sub>O<sub>3</sub>.

#### 4. Conclusions

In conclusion, a novel surface enolic species has been found on an Ag/Al<sub>2</sub>O<sub>3</sub> surface during the C<sub>2</sub>H<sub>5</sub>OH-SCR of NO. The enolic species, with a stable ring structure, is derived from the partial oxidation and aldol condensation reactions of C<sub>2</sub>H<sub>5</sub>OH (CH<sub>3</sub>CHO). It has a higher reactivity with NO + O<sub>2</sub> than acetate does and plays a crucial role in NCO formation, which can clearly explain the high efficiency of C<sub>2</sub>H<sub>5</sub>OH for the SCR of NO over Ag/Al<sub>2</sub>O<sub>3</sub>.

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