

FTIR, TPD and DFT studies of intermediates on Ag/Al₂O₃ during the selective catalytic reduction of NO by C₂H₅OH

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Abstract

The intermediates on Ag/Al₂O₃ during the C₂H₅OH-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/Al₂O₃ during the C₂H₅OH-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 + O₂ on Ag/Al₂O₃ 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 C₂H₅OH (such as CH₃CHO) on the surface of Ag/Al₂O₃. 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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1. Introduction

Selective catalytic reduction of NO by C₂H₅OH (C₂H₅OH-SCR of NO) on Ag/Al₂O₃ has attracted much attention as a new de-NO_x 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 C₂H₅OH-SCR of NO [2,4–6]. It has been suggested that the mechanism was similar to that of the C₃H₆-SCR of NO, which is approximately NO + O₂ + C₂H₅OH → NO_x (such as nitrates) + C_xH_yO_z (such as acetate) → R-NO₂ + R-ONO → -NCO + -CN + NO + O₂ → N₂. 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 C₃H₆-SCR of NO and the C₂H₅OH-SCR of NO [1,2]. In our recent study [7], we proposed that an enolic species derived from the partial oxidation of C₂H₅OH over Ag/Al₂O₃ 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 C₂H₅OH-SCR of NO over Ag/Al₂O₃. The most significant observation is that a ring structure enolic species, formed from oxidation and condensation reactions of C₂H₅OH over Ag/Al₂O₃, has high reactivity with NO + O₂ to form NCO and plays a predominant role in the NO reduction process.

2. Experimental

An Ag/Al₂O₃ (5 wt.%) catalyst was obtained by impregnation of γ-Al₂O₃ powder (200 m²/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/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,

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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 gas mixtures were fed at a flow rate of 100 ml/min. All spectra were measured with a resolution of 4 cm⁻¹ 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 C₂H₅OH (1565 ppm) + O₂ (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/Al₂O₃ in a flow of C₂H₅OH (1565 ppm) + O₂ (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⁻¹). Peaks at 1579 and 1471–1464 cm⁻¹ 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⁻¹ were assigned to an adsorbed enolic species. Apparently, the enolic species is 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 becomes dominant.

TPD spectra of Ag/Al₂O₃ following exposure to C₂H₅OH + O₂/N₂ 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/Al₂O₃ surface. The observed gas-phase products in Fig. 2a were C₂H₅OH (31, 45, 46 AMU), CO (28 AMU),

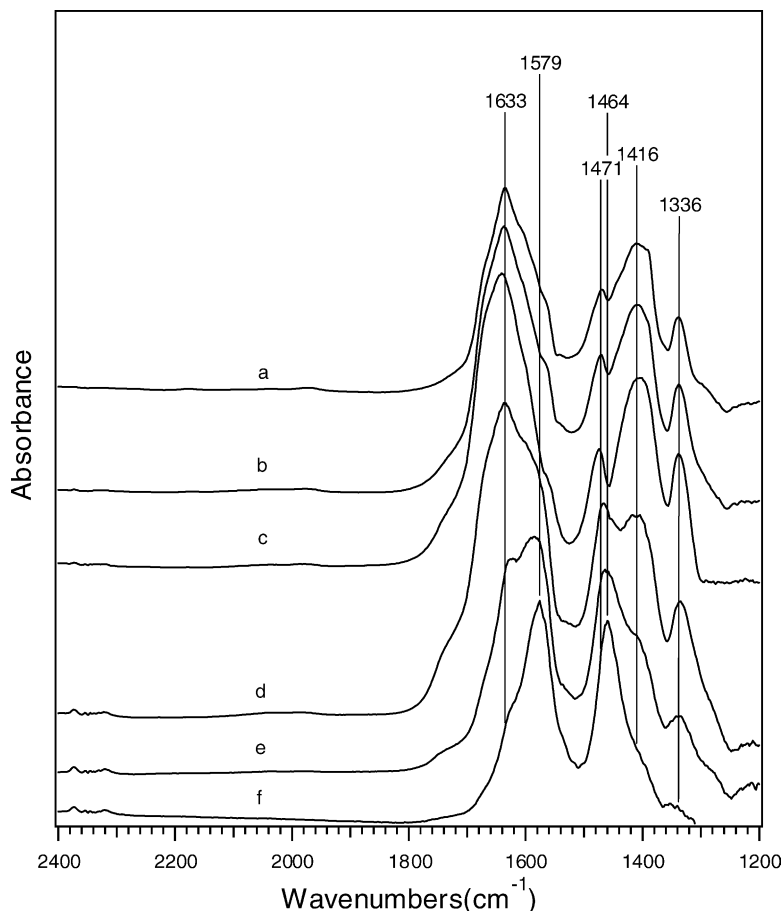
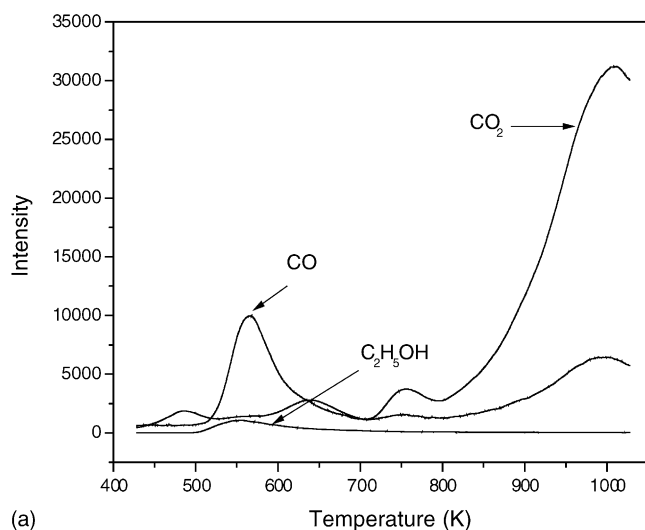
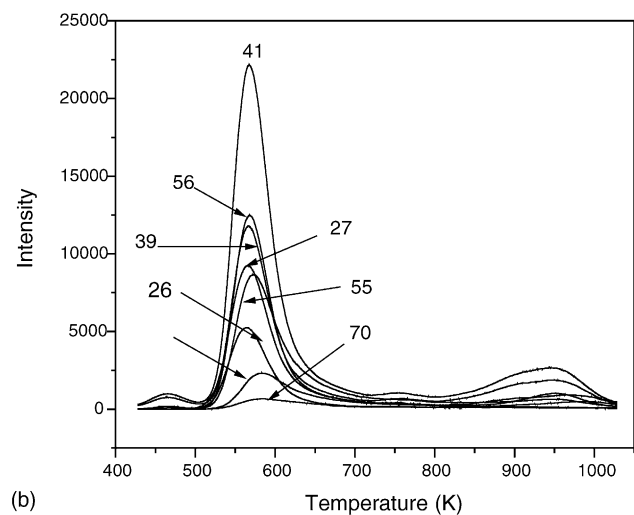


Fig. 1. The in situ DRIFTS spectra of adsorbed species in steady states on Ag/Al₂O₃ in a flow of 1565 ppm C₂H₅OH + 10% O₂/N₂ at (a) 473 K, (b) 523 K, (c) 573 K, (d) 673 K, (e) 773 K, and (f) 873 K.



(a)



(b)

Fig. 2. TPD spectra of adsorbed species on Ag/Al₂O₃ after exposure to 1565 ppm C₂H₅OH + 10% O₂/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 CO₂ (44 AMU). A very weak C₂H₅OH peak and strong peaks due to CO and CO₂ indicate the occurrence of partial oxidation of C₂H₅OH, 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_xH_yO_z) [12,13]. As shown in Fig. 2b, peaks corresponding to C₃H₆ (41 and 39 AMU), C₃H₄O (56, 55, 27, 26 AMU) and C₄H₆O (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 C₂H₅OH over Ag/Al₂O₃, 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, Al₂O₃, and TiO₂ [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/Al₂O₃.

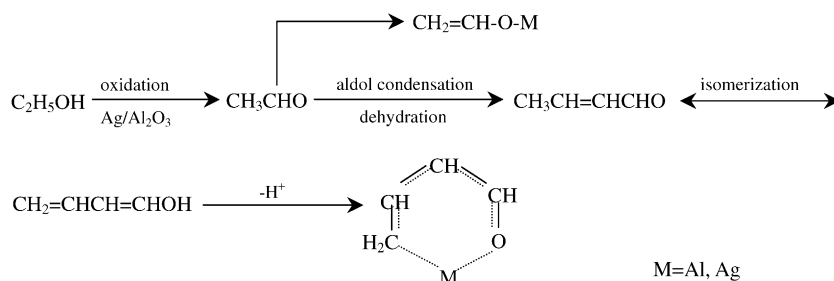
On the basis of our previous work [7] and the results of DRIFTS and TPD studies, a surface reaction mechanism was proposed for the formation of enolic species as shown in Scheme 1.

3.2. Density functional theory calculations

Density functional theory (DFT) calculations were used to confirm the structure of adsorbed enolic species on Ag/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 HyperchemTM Version 6.0 package.

The molecular structure and the optimized geometries of the calculational model for the adsorbed enolic species on Ag/Al₂O₃ are shown in Fig. 3a and b. The optimized distance between the oxygen atom in CH₂=CH–CH=CHO[−] 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^{−1} with a relatively high infrared intensity of 61 kJ/mol, which is 21 cm^{−1} higher than the experimental harmonic frequency



Scheme 1. The formation of an adsorbed enolic species on Ag/Al₂O₃.

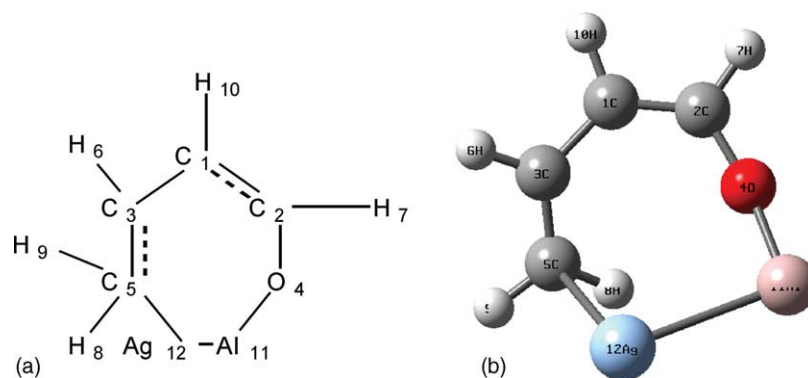


Fig. 3. The molecular structure and the optimized geometries of the calculational model for the absorbed enolic species on Ag/Al₂O₃.

(1633 cm⁻¹). Compared to the experimental value, the calculated symmetric stretching vibrational mode of this species varied within less than 15 cm⁻¹ (1416 cm⁻¹ against 1431 cm⁻¹). The calculated C–H deformation vibration mode (1345 cm⁻¹) was 9 cm⁻¹ higher than the experimental one (1336 cm⁻¹). 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 + O₂ was evaluated by the in situ DRIFTS method. As shown in Fig. 5, after Ag/Al₂O₃ was exposed to C₂H₅OH + O₂/N₂ for 60 min (curve a), very strong peaks due to the absorbed enolic species (1633, 1416, and 1336 cm⁻¹), and acetate peaks (1579 and 1464 cm⁻¹) were observed. Switching the fed gas to NO + O₂ 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⁻¹ [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_x over

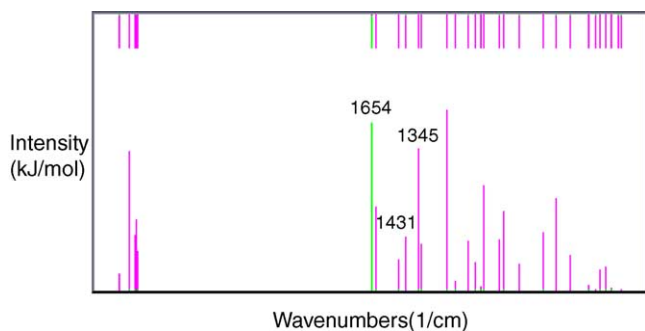
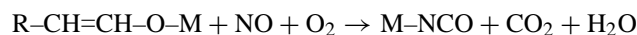


Fig. 4. The calculational FTIR spectrum of the absorbed enolic species on Ag/Al₂O₃.

Ag/Al₂O₃, and its high productivity would result in high efficiency of NO_x reduction by C₂H₅OH 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 C₂H₅OH-SCR of NO. The reaction of the enolic species with NO + O₂ 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

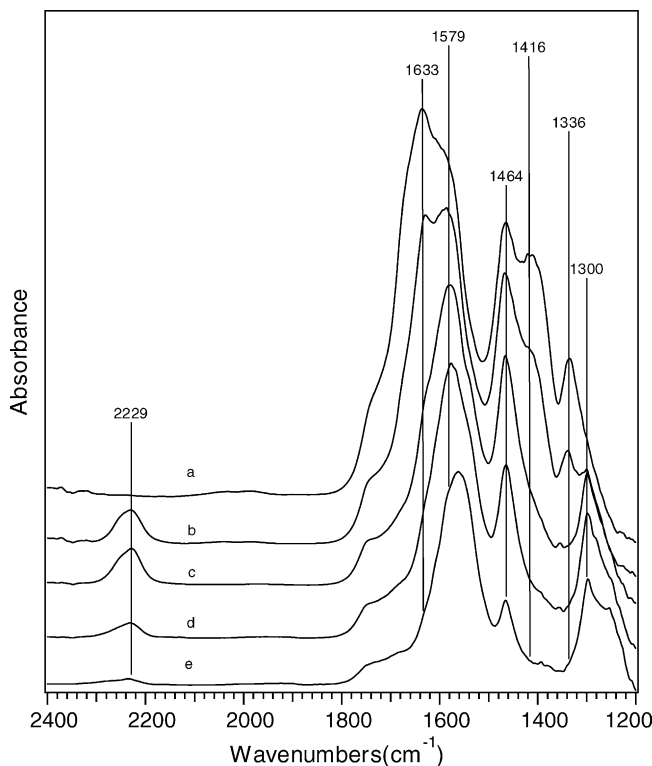


Fig. 5. The dynamic changes of in situ DRIFTS spectra on Ag/Al₂O₃ as a function of time in a flow of NO + O₂ at 673 K. Before measurement, the catalyst was pre-exposed to a flow of 1565 ppm C₂H₅OH + 10% O₂/N₂ for 60 min at 673 K (a), in a flow of 800 ppm NO + 10% O₂/N₂ (b) 1 min, (c) 5 min, (d) 10 min, and (e) 30 min.

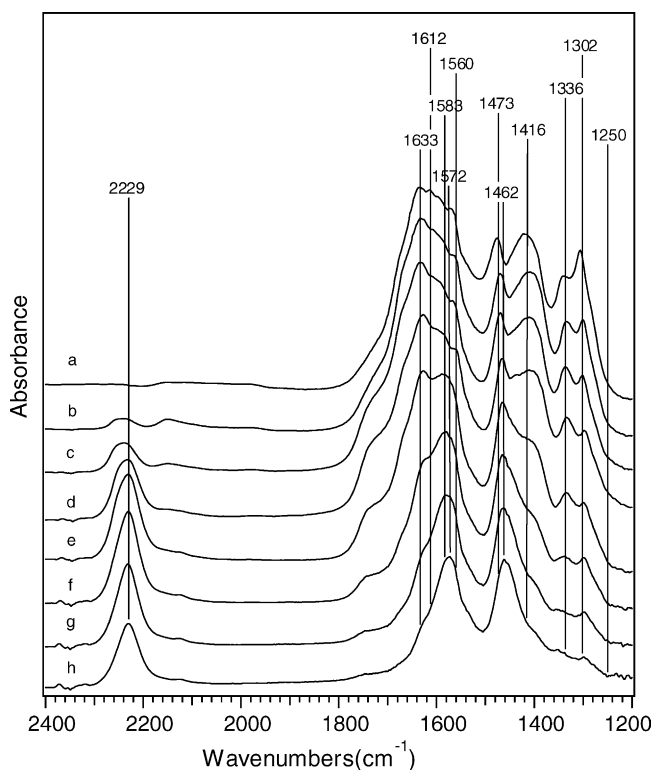


Fig. 6. The in situ DRIFTS spectra of adsorbed species in steady states over Ag/Al₂O₃ in a flow of 800 ppm NO + 1565 ppm C₂H₅OH + 10% O₂/N₂ at (a) 473 K, (b) 523 K, (c) 573 K, (d) 623 K, (e) 673 K, (f) 723 K, (g) 773 K, and (h) 823 K.

at 1464 cm⁻¹) 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 C₂H₅OH-SCR of NO.

During the NO + C₂H₅OH + O₂/N₂ reaction over Ag/Al₂O₃ at various temperatures (473–823 K) in steady states (Fig. 6), surface species such as the enolic species (1633, 1416, and 1336 cm⁻¹), acetate (1572 and 1473–1462 cm⁻¹), and NCO (2229 cm⁻¹) were found. In addition, strong peaks at 1583, 1302 cm⁻¹ and shoulders at 1612, 1560 and 1250 cm⁻¹ were also observed, and they were respectively assigned to unidentate (1560, 1250 cm⁻¹), bidentate (1583, 1302 cm⁻¹), and bridging (1612 cm⁻¹) nitrates according to the literature [3,21]. Kameoka et al. [3] reported that these nitrates were highly active in their reaction with C₂H₅OH + O₂/N₂ 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 C₂H₅OH-SCR of NO over Ag/Al₂O₃.

4. Conclusions

In conclusion, a novel surface enolic species has been found on an Ag/Al₂O₃ surface during the C₂H₅OH-SCR of NO. The enolic species, with a stable ring structure, is derived from the partial oxidation and aldol condensation reactions of C₂H₅OH (CH₃CHO). It has a higher reactivity with NO + O₂ than acetate does and plays a crucial role in NCO formation, which can clearly explain the high efficiency of C₂H₅OH for the SCR of NO over Ag/Al₂O₃.

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