

# Novel Enolic Surface Species Formed during Partial Oxidation of CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>5</sub>OH, and C<sub>3</sub>H<sub>6</sub> on Ag/Al<sub>2</sub>O<sub>3</sub>: An in Situ DRIFTS Study

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In situ DRIFTS was used to investigate the formation and reactivity of surface species on Ag/Al<sub>2</sub>O<sub>3</sub> during partial oxidation of CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>5</sub>OH, and C<sub>3</sub>H<sub>6</sub>. The exposure of Ag/Al<sub>2</sub>O<sub>3</sub> to CH<sub>3</sub>CHO/C<sub>2</sub>H<sub>5</sub>OH/C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> in a steady state leads to the formation of two kinds of partial oxidation products: acetate and a novel enolic surface species. Peaks at 1633, 1416, and 1336 cm<sup>-1</sup> are assigned to an adsorbed enolic species. 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 selective catalytic reduction of NO.

## Introduction

Alumina-supported silver catalyst (Ag/Al<sub>2</sub>O<sub>3</sub>) has been widely studied as a promising catalyst due to its relatively high activity for the selective catalytic reduction (SCR) of NO by hydrocarbons (HC), and a possible mechanism for the SCR of NO on Ag/Al<sub>2</sub>O<sub>3</sub> has been proposed.<sup>1–17</sup> By means of infrared spectroscopy, several adsorbed species on Ag/Al<sub>2</sub>O<sub>3</sub> surface, such as NO<sub>3</sub><sup>-</sup>,<sup>3–9,11</sup> CH<sub>3</sub>COO<sup>-</sup>,<sup>6–9</sup> R-NO<sub>2</sub>,<sup>3,8,9,15</sup> R-ONO,<sup>3,8,9,15</sup> and NCO,<sup>3–9,11,15</sup> have been observed during the SCR of NO by organic reductants. Burch et al.<sup>16</sup> and Chafik et al.<sup>17</sup> suggested that the mechanism of the SCR of NO by ethanol was similar to that of the SCR of NO by C<sub>3</sub>H<sub>6</sub>, that is, NO + O<sub>2</sub> + HC → R-NO<sub>2</sub> + R-ONO → NCO + NO + O<sub>2</sub> → N<sub>2</sub>. However, this mechanism did not sufficiently elucidate a significant difference for the SCR of NO by C<sub>2</sub>H<sub>5</sub>OH or by C<sub>3</sub>H<sub>6</sub> over Ag/Al<sub>2</sub>O<sub>3</sub>.<sup>1,4,15</sup>

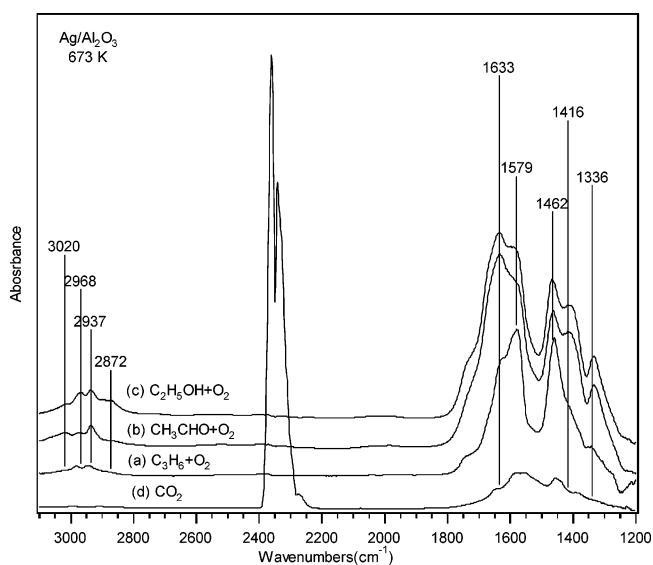
In this study, we report a novel enolic species formed during the partial oxidation of CH<sub>3</sub>CHO, C<sub>2</sub>H<sub>5</sub>OH, and C<sub>3</sub>H<sub>6</sub> on Ag/Al<sub>2</sub>O<sub>3</sub>. On the basis of this finding, a possible reaction scheme is established to explain the different roles of C<sub>2</sub>H<sub>5</sub>OH and C<sub>3</sub>H<sub>6</sub> as reductants for the SCR of NO.

## Experimental Section

Ag/Al<sub>2</sub>O<sub>3</sub> catalyst (Ag loading is 5.0 wt %) was prepared by an impregnation method described in our earlier paper.<sup>15</sup> In situ DRIFTS spectra were recorded by a NEXUS 670-FTIR equipped with a liquid N<sub>2</sub> cooled MCT detector. The sample for this study was finely ground and placed in a ceramic crucible in an in situ chamber.

Prior to each experiment, the catalyst was heated in 10% O<sub>2</sub>/N<sub>2</sub> for 30 min at 873 K, and then cooled to 673 K in 10% O<sub>2</sub>/N<sub>2</sub>, and a spectrum of Ag/Al<sub>2</sub>O<sub>3</sub> serving as the background was recorded in 10% O<sub>2</sub>/N<sub>2</sub> at 673 K. 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> with an accumulation of 100 scans.

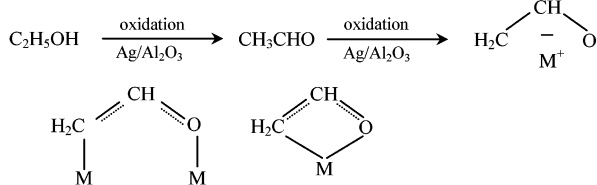
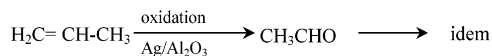
Catalyst pretreated as mentioned above was exposed to C<sub>2</sub>H<sub>5</sub>OH/CH<sub>3</sub>CHO/C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> (C<sub>2</sub>H<sub>5</sub>OH 1565 ppm, CH<sub>3</sub>CHO 1636 ppm, C<sub>3</sub>H<sub>6</sub> 1714 ppm, O<sub>2</sub> 10%, and balanced by N<sub>2</sub>) for 60 min at 673 K, then spectra were recorded. Subsequently, the fed gas was switched to NO + O<sub>2</sub> (NO 800 ppm, O<sub>2</sub> 10%, and balanced by N<sub>2</sub>). Then in situ DRIFTS were recorded as a function of time.



**Figure 1.** In situ DRIFTS spectra of Ag/Al<sub>2</sub>O<sub>3</sub> in a steady state at 673 K in a flow of (a) C<sub>3</sub>H<sub>6</sub> (1714 ppm) + O<sub>2</sub> (10%), (b) CH<sub>3</sub>CHO (1636 ppm) + O<sub>2</sub> (10%), (c) C<sub>2</sub>H<sub>5</sub>OH (1565 ppm) + O<sub>2</sub> (10%), and (d) CO<sub>2</sub> (8%).

## Results and Discussion

Figure 1 shows the in situ DRIFT spectra of Ag/Al<sub>2</sub>O<sub>3</sub> in a flow of various gas mixtures at 673 K: (a) C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub>, (b) CH<sub>3</sub>CHO + O<sub>2</sub>, (c) C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub>, and (d) CO<sub>2</sub>. For C<sub>3</sub>H<sub>6</sub> oxidation (Figure 1a), two main bands observed at around 1579 and 1462 cm<sup>-1</sup> are assigned to  $\nu_{as}(\text{OCO})$  and  $\nu_s(\text{OCO})$  of acetate.<sup>6–9</sup> However, in the case of C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>CHO oxidation (Figure 1, spectra c and b), the peak at 1633 cm<sup>-1</sup> became predominant and peaks at 1416 and 1336 cm<sup>-1</sup> were also stronger than those in Figure 1a. Similar peaks at 1630, 1410, and 1300–1336 cm<sup>-1</sup> were observed on Ag/Al<sub>2</sub>O<sub>3</sub> in a flow of *n*-hexane + NO + O<sub>2</sub> and were assigned to carbonate species.<sup>6</sup> Turek et al.<sup>18</sup> reported that when CO<sub>2</sub> chemisorbed on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the main adsorbed species were carbonates such as bicarbonates and free carbonates. We also studied the adsorption of CO<sub>2</sub> on Ag/Al<sub>2</sub>O<sub>3</sub> at 673 K in this experiment (Figure 1d), but no peaks at 1633,

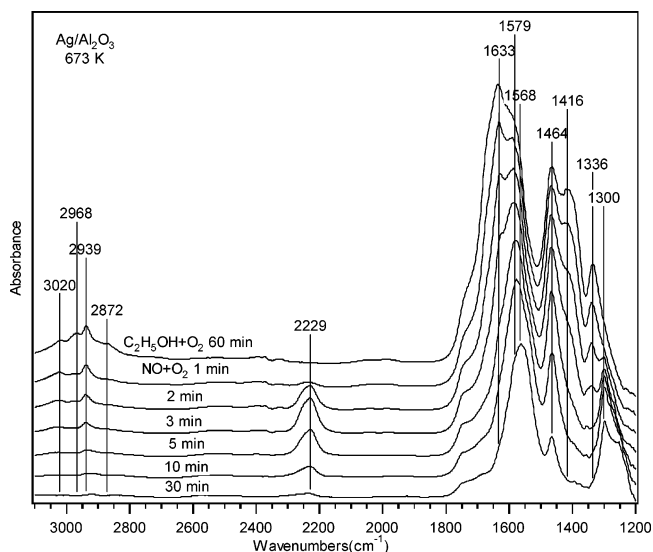
**SCHEME 1. Formation of an Enolic Species on Ag/Al<sub>2</sub>O<sub>3</sub> from CH<sub>3</sub>CHO and C<sub>2</sub>H<sub>5</sub>OH**

**SCHEME 2. Formation of an Enolic Species on Ag/Al<sub>2</sub>O<sub>3</sub> from C<sub>3</sub>H<sub>6</sub>**


1416, or 1336 cm<sup>-1</sup> were observed even when the concentration of CO<sub>2</sub> in the fed gas was as high as 8%.

The peak at 1633 cm<sup>-1</sup> can be associated with the frequency of the double bond stretching vibration, such as  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{O})$ . However, stretching vibration frequencies of isolated C=C and C=O should be higher than 1633 cm<sup>-1</sup> in general. It should be noted that the IR spectra of gas-phase phenol and methoxy ethene give peaks between 1600 and 1650 cm<sup>-1</sup>,<sup>19</sup> as do the IR spectra of adsorbed catechol on a TiO<sub>2</sub> colloid and chemisorbed acetone–oxygen mixtures on nickel oxide.<sup>20,21</sup> Their common characteristic is an enolic structure. We conjecture that in this study, an enolic anion  $(\text{CH}_2-\text{CH}-\text{O})^-\text{M}^+$  was formed when CH<sub>3</sub>CHO adsorbed on the Ag/Al<sub>2</sub>O<sub>3</sub> surface. The conjugation of the  $(\text{CH}_2-\text{CH}-\text{O})^-$  group may induce the vibrational mode of C–C–O to shift to a frequency lower than  $\nu(\text{C}=\text{C})$  and higher than  $\nu(\text{C}=\text{O})$ .<sup>19–21</sup> The peaks between 2872 and 3020 cm<sup>-1</sup> in Figure 1 also accord with the distribution of  $\nu(\text{C}-\text{H})$  for a H<sub>2</sub>C=CH– group.<sup>19–21</sup> As a consequence, the peak at 1633 cm<sup>-1</sup> in Figure 1 could be tentatively assigned to an asymmetric stretching vibration mode of  $(\text{CH}_2-\text{CH}-\text{O})^-$ , and peaks at 1416 and 1336 cm<sup>-1</sup> could be tentatively attributed to a symmetric stretching vibration mode of  $(\text{CH}_2-\text{CH}-\text{O})^-$  and for a C–H deformation mode, respectively. However, these peaks are barely perceptible on Ag/Al<sub>2</sub>O<sub>3</sub> in the flow of C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> as shown in Figure 1a, indicating a low surface concentration of  $(\text{CH}_2-\text{CH}-\text{O})^-$ . As shown in Figure 1b,c, when Ag/Al<sub>2</sub>O<sub>3</sub> is exposed to CH<sub>3</sub>CHO + O<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub>, very strong peaks at 1633, 1416, and 1336 cm<sup>-1</sup> are observed, indicating that an enolic species is the main surface species.

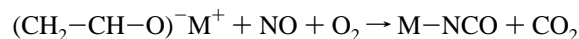
Summarizing this discussion, the formation of an enolic species on Ag/Al<sub>2</sub>O<sub>3</sub> can be proposed as shown in Schemes 1 and 2.

To exclude the possibility of attributing the three peaks previously mentioned to carbonates species, we introduce NO + O<sub>2</sub> to react with the surface species that is attributed to an enolic species. Figure 2 shows the dynamic changes of in situ DRIFTS spectra of Ag/Al<sub>2</sub>O<sub>3</sub> as a function of time in the flow of NO + O<sub>2</sub> at 673 K after exposure to a flow of C<sub>2</sub>H<sub>5</sub>OH + O<sub>2</sub> for 60 min at the same temperature. Enolic species peaks at 1633, 1416, and 1336 cm<sup>-1</sup> and its  $\nu(\text{C}-\text{H})$  peaks between 2872 and 3020 cm<sup>-1</sup> decreased sharply and disappeared completely after 10 min, indicating that the enolic species is quite reactive toward NO + O<sub>2</sub>. Meanwhile, the acetate peak at 1464 cm<sup>-1</sup> was still very strong. The peak at 2229 cm<sup>-1</sup> due to NCO<sup>3–9,11,15</sup> sharply increased initially, and reached a maximum after 3 min, then decreased gradually. Simultaneously, peaks at 1568 and 1300 cm<sup>-1</sup> were also observed and assigned to  $\nu(\text{N}=\text{O})$  and  $\nu_{\text{as}}(\text{ONO})$  of adsorbed NO<sub>3</sub><sup>-</sup>, respectively.<sup>3,5–9,11,15</sup> As a result,



**Figure 2.** Dynamic changes of in situ DRIFTS spectra of Ag/Al<sub>2</sub>O<sub>3</sub> as a function of time in a flow of NO (800 ppm) + O<sub>2</sub> (10%) at 673 K. Before the measurement, the catalyst was preexposed to a flow of C<sub>2</sub>H<sub>5</sub>OH (1565 ppm) + O<sub>2</sub> (10%) for 60 min at 673 K.

the reaction between enolic species with NO + O<sub>2</sub> is proposed as:



This result supports our assignment of an enolic species and suggests a novel reaction mechanism for the SCR of NO by C<sub>2</sub>H<sub>5</sub>OH. It has been suggested that the mechanism of NO reduction by ethanol was similar to that of the SCR of NO by C<sub>3</sub>H<sub>6</sub>, that is, NO<sub>x</sub> + C<sub>3</sub>H<sub>6</sub> or C<sub>2</sub>H<sub>5</sub>OH → R-NO<sub>2</sub> + R-ONO → NCO + NO + O<sub>2</sub> → N<sub>2</sub>.<sup>16,17</sup> However, using C<sub>2</sub>H<sub>5</sub>OH as a reductant results in significantly higher NO<sub>x</sub> conversion than using C<sub>3</sub>H<sub>6</sub>, especially in a low-temperature zone.<sup>1,4,15</sup> As shown in Figure 1, there are only two kinds of surface species on Ag/Al<sub>2</sub>O<sub>3</sub> during partial oxidation of ethanol: acetate and an enolic species. Figure 2 shows that a strong NCO peak is formed during the first 10 min of exposure to NO + O<sub>2</sub>. During the formation of the NCO peak, the peaks of the enolic species disappeared completely; however, the acetate hardly changed. These phenomena support our hypothesis that the enolic species plays a crucial role in the formation of NCO during reduction of NO by C<sub>2</sub>H<sub>5</sub>OH on Ag/Al<sub>2</sub>O<sub>3</sub>. Thus, the reaction mechanism for the SCR of NO by C<sub>2</sub>H<sub>5</sub>OH can be suggested as:

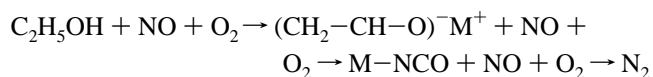
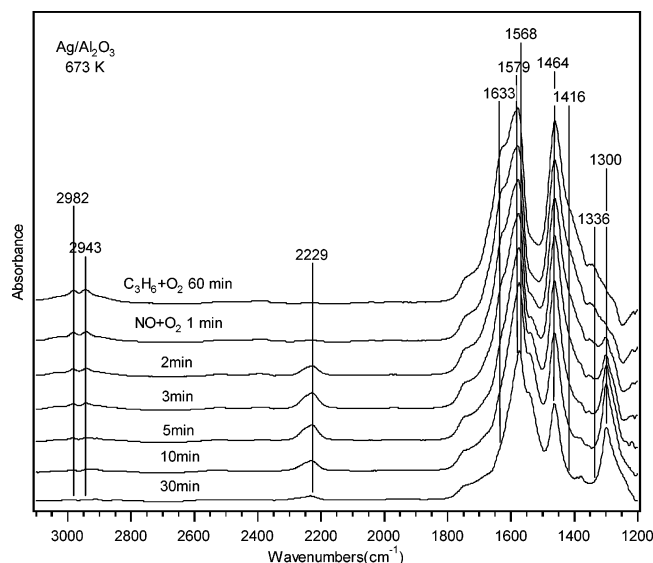


Figure 3 shows the dynamic changes of in situ DRIFTS spectra of Ag/Al<sub>2</sub>O<sub>3</sub> as a function of time in a flow of NO + O<sub>2</sub> at 673 K after exposure to the flow of C<sub>3</sub>H<sub>6</sub> + O<sub>2</sub> for 60 min at the same temperature. Similarly, enolic species peaks decreased promptly and disappeared in the first 10 min. In contrast, acetate peaks remained. It was the low surface concentration of the enolic species that led to a low surface concentration of NCO species.

**Conclusions**

In conclusion, a novel surface species, an enolic species, has been found on Ag/Al<sub>2</sub>O<sub>3</sub> surface by the assignments of peaks at 1633, 1416, and 1336 cm<sup>-1</sup> and a related C–H stretching mode. Two kinds of main surface species on Ag/Al<sub>2</sub>O<sub>3</sub>, enolic



**Figure 3.** Dynamic changes of in situ DRIFTS spectra of Ag/Al<sub>2</sub>O<sub>3</sub> as a function of time in a flow of NO (800 ppm) + O<sub>2</sub> at 673 K. Before the measurement, the catalyst was preexposed to a flow of C<sub>3</sub>H<sub>6</sub> (1714 ppm) + O<sub>2</sub> (10%) for 60 min at 673 K.

species and acetate are formed during the partial oxidation 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>. The enolic species has a higher reactivity with NO + O<sub>2</sub> than acetate. Therefore, the reaction between the enolic species and NO + O<sub>2</sub> is a main pathway for the formation of NCO. When using C<sub>3</sub>H<sub>6</sub> as a reductant in the SCR of NO over Ag/Al<sub>2</sub>O<sub>3</sub>, acetate is the dominant surface species, and its relatively low reactivity with NO + O<sub>2</sub> leads to a low surface concentration of NCO, and subsequently to a low NO conversion. In contrast, using C<sub>2</sub>H<sub>5</sub>OH as a reductant results in a higher surface concentration of enolic species and subsequent NCO species, and finally to the enhancement of NO conversion.

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