Promotion Effect of H₂ on Ethanol Oxidation and NOₓ Reduction with Ethanol over Ag/Al₂O₃ Catalyst

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ABSTRACT: The catalytic partial oxidation of ethanol and selective catalytic reduction of NOₓ with ethanol (ethanol–SCR) over Ag/Al₂O₃ were studied using synchrotron vacuum ultraviolet (VUV) photoionization mass spectrometry (PIMS). The intermediates were identified by PIMS and their photoionization efficiency (PIE) spectra. The results indicate that H₂ promotes the partial oxidation of ethanol to acetaldehyde over Ag/Al₂O₃, while the simultaneously occurring processes of dehydration and dehydrogenation were inhibited. H₂ addition favors the formation of ammonia during ethanol–SCR over Ag/Al₂O₃; the occurrence of which creates an effective pathway for NOₓ reduction by direct reaction with NH₃. Simultaneously, the enhancement of the formation of ammonia benefits its reaction with surface enolic species, resulting in producing NCO species again, leading to enhancement of ethanol–SCR over Ag/Al₂O₃ by H₂. Using VUV–PIMS, the reactive vinyloxy radical was observed in the gas phase during the NOₓ reduction by ethanol for the first time, particularly in the presence of H₂. Identification of such a reaction occurring in the gas phase may be crucial for understanding the reaction pathway of HC–SCR over Ag/Al₂O₃.

1. INTRODUCTION

The diesel engine, which is a typical lean-burn engine, has the advantage of lower consumption of fuel and lower emissions of CO₂, CO and HC than the stoichiometric gasoline engine. However, the control of NOₓ emission from lean-burn engines remains one of the major challenges for environmental catalysis. Among the NOₓ reduction technologies being developed for controlling diesel engine emissions, selective catalytic reduction by hydrocarbons (HC–SCR) has attracted much attention as a more environmentally friendly alternative to the commercially used NH₃/Urea–SCR.1−3 To date, numerous catalysts such as zeolitic oxide, base oxide/metal and noble metal catalysts have been found to be effective for HC–SCR, among which alumina supported silver (Ag/Al₂O₃) is known as one of the most effective catalysts.1−5 When using oxygenated hydrocarbons as reductants, particularly ethanol, Ag/Al₂O₃ shows high activity even in the presence of SO₂ and H₂O.5 More importantly, the low-temperature activity of Ag catalysts can be significantly boosted by H₂ addition, both under laboratory conditions and on a full-scale vehicle equipped with a Ag/Al₂O₃ converter.5,6

However, the origin of the promotion effect of H₂ on the HC–SCR over silver catalysts is still under debate, with possibilities including structural change of active sites and chemical effect on NOₓ reduction.10−12 Over Ag/Al₂O₃, Satsuma and co-workers proposed that hydrogen would be indispensable for the formation of oxidized silver clusters (Agₓ⁺), the presence of which is necessary for the promotion of C₃H₈ oxidation, and thus contributes to NOx reduction.3,12,13 Such transformation of Ag⁺ to Agₙ⁺ on Ag/Al₂O₃ was further observed by Kim et al.14 during NOₓ reduction by a mixture of ethanol and simulated diesel in the presence of H₂, accompanied by the creation of highly active oxygen species, enhancing the low-temperature activity of Ag/Al₂O₃ for NOₓ reduction. The formation of oxidized Ag clusters was also identified by Burch and co-workers11,15 during C₈H₁₈–SCR in the presence of H₂ and CO over Ag/Al₂O₃, respectively, however CO did not promote the HC–SCR activity. As a result, it was proposed that the promoting effect of H₂ on HC–SCR should not be attributed to structural changes of the active sites but rather to a chemical effect, which was also concluded by Szazma et al.16 and Korhonen et al.17

Generally, it has been accepted that, as an initial step of HC–SCR, the partial oxidation of hydrocarbons to active oxygenates is triggered by H₂ addition at low temperatures, thus enhancing NOₓ reduction.3,12,18 Based on in situ DRIFTS, it was proposed that the addition of H₂ results in remarkable promotion of partial oxidation of C₃H₈ over Ag/Al₂O₃, mainly to surface acetate.12,18 During the partial oxidation of hydrocarbons containing two or three carbon atoms (such as C₃H₆, C₃H₈, C₃H₁₀ and C₃H₁₂) over Ag/Al₂O₃, however, He and co-workers proposed that H₂
addition promoted the formation of surface enolic species \((\text{RCH} = \text{CH} - \text{O}^-) = \text{M}\), particularly in the low temperature range.\textsuperscript{19,20} Compared with surface acetate, the surface enolic species exhibited higher activity toward \(\text{NO} + \text{O}_2\) to produce the key intermediate of isocyanate \((-\text{NCO})\), and thus contributed to the promoting effect of \(\text{H}_2\) on \(\text{HC} - \text{SCR}\). As a common feature of \(\text{H}_2\)-assisted \(\text{HC} - \text{SCR}\) over \(\text{Ag/Al}_2\text{O}_3\), an increased intensity of reactive enolic species triggered by \(\text{H}_2\) addition was also observed during partial oxidation of ethanol and ethanol-\(\text{SCR}\).\textsuperscript{14,21} Using VUV−PIMS analysis, interestingly, Taatjes and co-workers identified that enols in the gas phase are common intermediates in hydrocarbon oxidation.\textsuperscript{22} The VUV−PIMS method provides an opportunity to identify the reactive gas phase intermediates during a chemical reaction, based on the following advantages: (1) molecular-beam sampling and high vacuum downstream can ensure free molecular flow of the sampled gas and reduce collision effects, making it possible to trap unstable intermediates; (2) the employed vacuum ultraviolet single-photon photoionization can minimize fragmentation of target molecules, thus the structural integrity of reactive intermediates would be preserved and detected.\textsuperscript{23,24} With this powerful method, ethenol in the gas phase was unambiguously identified during the catalytic oxidation of \(\text{C}_2 - \text{C}_4\) alcohols over a \(\text{Ag/Al}_2\text{O}_3\) catalyst.\textsuperscript{25}

Figure 1. PIE spectra for \(m/z = 28\) (A), \(42\) (B), \(44\) (C), \(56\) (D), \(58\) (E), and \(70\) (F) measured in the flow of ethanol + \(\text{O}_2\) over \(\text{Ag/Al}_2\text{O}_3\) under low pressure at 603 K in the absence or presence of \(\text{H}_2\).
Table 1. Intermediates Produced during Partial Oxidation of Ethanol at 603 K over Ag/Al2O3 under Low Pressure

<table>
<thead>
<tr>
<th>m/z</th>
<th>formula</th>
<th>without H2</th>
<th>with H2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>measured (±0.05 eV)</td>
<td>ion intensity (arb.unit)</td>
<td>measured (±0.05 eV)</td>
</tr>
<tr>
<td>28</td>
<td>C2H6</td>
<td>10.52</td>
<td>22.46</td>
</tr>
<tr>
<td>44</td>
<td>C2H3O</td>
<td>10.21</td>
<td>67.37</td>
</tr>
<tr>
<td></td>
<td>C2H4O</td>
<td>9.33</td>
<td>0.90</td>
</tr>
<tr>
<td>56</td>
<td>C2H4O</td>
<td>10.11</td>
<td>0.45</td>
</tr>
<tr>
<td>58</td>
<td>C2H4O</td>
<td>9.7</td>
<td>0.45</td>
</tr>
<tr>
<td>70</td>
<td>C2H6O</td>
<td>9.74</td>
<td>0.90</td>
</tr>
</tbody>
</table>

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Herein, the VUV–PIMS technique was employed to investigate the partial oxidation of ethanol and ethanol–SCR with or without H2 over Ag/Al2O3. Based on the intermediates identified by VUV–PIMS, the pathway of partial oxidation of ethanol was established. This result could provide new insights into the synergistic effect of H2 on the mechanisms for ethanol oxidation and the SCR of NOx by alcohols over Ag/Al2O3 catalysts.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. 2.1.1. Preparation of Ag/Al2O3 Powders. As described in our earlier papers, a Ag/Al2O3 catalyst with silver loading of 4 wt % was prepared by an impregnation method, immersing boehmite into an aqueous solution of silver nitrate. After impregnation, the excess water was removed in a rotary evaporator at 333 K, and then the sample was calcined in air at 873 K for 3 h.

2.1.2. Preparation of Washcoated Honeycomb Catalysts. Washcoated honeycomb catalysts were prepared using the 4 wt % Ag/Al2O3 powder prepared as mentioned above. Washcoat slurries were prepared by mixing 250 g Ag/Al2O3 powder and 750 g water in a ball mill. Cordierite honeycombs with 400 cells per square inch (90 mm in diameter ×110 mm in length) were dipped into the washcoat slips, and excess slurry was blown out with an air knife. The samples were then dried at 393 K for 12 h and calcined at 873 K for 3 h. The washcoat loading was 110 g·L−1 after calcination. Washcoated honeycomb catalyst with a volume of ca. 9 mL (15 mm in diameter ×51 mm in length) was used in VUV–PIMS experiments.

2.2. Experimental Setup for VUV–PIMS Measurement. The VUV–PIMS experiments were carried out at National Synchrotron Radiation Laboratory in Hefei, China. A molecular-beam mass spectrometer (MBMS) using synchrotron VUV light as the ionization source provided a novel method for the analysis of individual intermediates and products of the reaction. The details of the instrument have been reported elsewhere.

In brief, the apparatus consists of the sample inlet system, the catalyst bed, the differential pumped system, and the photo-ionization chamber with a reflectron TOF MS. The sampled gas forms a molecular beam, which is skimmed and passes into a differentially pumped ionization region where it is crossed by the tunable vacuum ultraviolet VUV light. By tuning the light source, a series of mass spectra from 8.5 to 11.7 eV were measured. In most cases, the measurement time for each mass spectrum was 120 s. The baseline was subtracted from the integrated ion intensity. Each mass peak was integrated to yield the PIE spectra, a plot of ion intensity vs photon energy. The value of ionization energies (IEs) could be directly obtained from the PIE spectra. Considering the energy resolution of the monochromator and the cooling effect of the molecular beam, the experimental error of the measured IEs was less than 0.05 eV. Thus, compared with known literature values, all components could be identified by their molecular weights from the PIMS and corresponding ionization thresholds obtained from PIE spectra.

A syringe pump (ISCO Inc.) was used to control the flow rate of aqueous ethanol solution, vaporized with the carrier gas (Ar) and passed into the catalyst bed. The temperature of the vaporizer was maintained at 423 K to ensure that the ethanol solution was vaporized completely. The catalyst bed was put in a low-pressure chamber (1.07 kPa) for the low pressure experiment and just outside the chamber for the experiment under normal atmospheric pressure conditions. The temperature of the catalyst bed was controlled by a temperature controller. A gaseous mixture of 1.92 vol % C2H5OH, 25 vol % O2, 10 vol % H2O, 0.8 vol % NO (if used), 1 vol % H2 (if used) in Ar balance was passed through the catalyst bed at a total flow rate of 2 000 mL min−1 (GHSV = 13 000 h−1).

According to our previous studies under the same conditions, the final products of ethanol oxidation and ethanol–SCR over Ag/Al2O3 catalyst are N2, CO2, H2O and CO. In this experiment, we focused on the intermediates produced in these two processes, the intensities of which are not of the same magnitude as the final products mentioned above; therefore, we did not measure the PIE spectra of final products.

3. RESULTS AND DISCUSSION

3.1. Promotion Effect of H2 on the Ethanol Oxidation Over Ag/Al2O3 Catalyst. The effect of H2 on the ethanol oxidation over Ag/Al2O3 catalyst under low pressure conditions was investigated at 603 K. Comparing the experimental IEs with the known values from the literature, intermediates originating from catalytic partial oxidation of ethanol were identified, with the PIE spectra shown in Figure 1. The measured ionization thresholds and ion intensity for all the observed peaks are listed in Table 1. The PIE spectra of m/z = 28 indicate the formation of ethylene (C2H4) with the ionization threshold of 10.52 eV (Figure 1A).

It is noteworthy that isomers can be determined by the PIE experiments. Ethanol (CH3OH), as the isomer of acetaldehyde (CH3CHO), has the same molecular weight as the latter. Here the ethanol and acetaldehyde can be distinguished by comparing their IEs from the PIE spectra with literature values. The PIE spectra for m/z = 44 (C2H4O) illustrate how to identify the isomers. As shown in Figure 1C, two onsets are clearly observed at 9.33 and 10.21 eV, which correspond to the IEs of ethanol and acetaldehyde according to the literature values of 9.33 ± 0.01 and 10.21 ± 0.01 eV. Ethanol, bearing OH groups adjacent to carbon–carbon double bonds, is thermodynamically unstable relative to acetaldehyde. Taatjes et al.22 studied 24 different flames of 14 prototypical single fuels and low-pressure flames of commercial gasoline using...
VUV-PIMS spectrometry, and found that enols are common intermediates in hydrocarbon oxidation.

The PIE spectra of \( m/z = 42 \) with a feature threshold at 9.62 eV belong to ketene (Figure 1B), which possibly originates from the dehydrogenation of acetaldehyde. As shown in Table 1, the ketene gave the third strongest intensity (7.49%) among the measured intermediates when Ag/Al2O3 was exposed to ethanol + O2, while in the presence of H2, its intensity dropped to a much lower level of 3.33%. It is well-known that aldol condensation reactions of aldehydes are commonly catalyzed by metal oxides such as Al2O3 and TiO2. Over Ag/Al2O3, such condensation of acetaldehyde may also occur during the partial oxidation of ethanol, resulting in the formation of butenal (CH3−CH==CH−CH==O, Figure 1F). As presented in Figure 1D−E and Table 1, trace amounts of propenal (CH2−CHO) were also formed during the partial oxidation of ethanol over Ag/Al2O3, and lower relative concentrations were always observed when H2 was introduced into the feed gas.

There are three pathways that could take place during the exposure of Ag/Al2O3 to ethanol + O2 in the presence of water vapor: dehydration, dehydrogenation (by reaction with water), and partial oxidation of ethanol (Scheme 1). Comparing the ion intensities of intermediates listed in Table 1, it is clear that the partial oxidation of ethanol to acetaldehyde is the major pathway during the reaction of ethanol + O2 over Ag/Al2O3. The presence of H2 further promoted the formation of acetaldehyde, giving an ion intensity of 79.47%, which is 12.1% higher than that in the absence of H2. Such enhancement of acetaldehyde formation by H2 was also observed by Silva et al. during ethanol−SCR over Ag/Al2O3. Combining these results with our previous DRIFTS and TPD−MS measurements and DFT calculations, mainly pertaining to reaction on the surface of Ag/Al2O3, the whole pathway involving partial oxidation of ethanol was proposed as shown in Scheme 1. Ethanol principally reacts with oxygen to form acetaldehyde, which is followed by isomerization to ethanol. Subsequently, a C2 enolic anion (CH2==CH−O−)−M+ is formed by hydrogen extraction when ethanol is adsorbed on the surface of Ag/Al2O3. Meanwhile, the occurrence of aldol condensation of acetaldehyde leads to the formation of C2 enolic species (CH3==CH−CH==CH−O−)−M+, the desorption of which results in the production of 2-butenal (CH3−CH==CH−CHO). In addition, dehydrogenation of acetaldehyde possibly occurs to produce ketene (CH2==C==O).

As shown in Table 1, the formation of acetaldehyde was clearly promoted by H2 introduction; meanwhile, other products in the gas phase related to partial oxidation, such as ketene, ethenol, and 2-butenal, had lower concentrations compared with those obtained in the absence of H2. On the surface of Ag/Al2O3, it should be noted that the adsorbed enolic species originating from hydrocarbon oxidation were significantly enhanced by H2 addition, which has been identified by our previous DRIFTS studies and also by Kim et al. Over silver catalysts, Shimizu et al. proposed that the presence of H2 promoted in situ generation of active oxygen species such as superoxide ions (O2−), and OOH species, the occurrence of which is crucial for the partial oxidation of C2H4. In our case, it is possible that the reactive oxygen species mentioned above would be produced in the presence of H2, and then enhance the formation of enolic species during partial oxidation of ethanol over Ag/Al2O3.

It is well-known that the dehydration of alcohols is catalyzed by various solid acid catalysts. The production of C2H4 during exposure of Ag/Al2O3 to ethanol + O2 was also related to the acid sites (such as surface OH groups) on the surface of the silver catalyst. The introduction of H2 creates more reactive oxygen species over Ag/Al2O3, enhancing the partial oxidation of ethanol. As a result, ethanol available for dehydration to produce C2H4 decreased in the presence of H2. The reaction between ethanol and water relating to acetone production has been considered as a dehydrogenation process, the occurrence of which was catalyzed by metal oxides (2EtOH + H2O → Me2CO + CO2 + 4H2). The addition of H2 is therefore beneficial for the reverse reaction, decreasing the yield of acetone, and also its further dehydrogenation to CH2==CH−CHO, as shown in Table 1 and Scheme 1.

3.2. Promotion Effect of H2 on Ethanol−SCR Over Ag/Al2O3 Catalyst. To further investigate the synergistic effect of H2, we also studied the SCR of NOx by ethanol over the Ag/Al2O3 catalyst at 570 K under normal atmospheric pressure. Figure 2 shows VUV–PIMS spectra of the ethanol−SCR over Ag/Al2O3 at the photon energy of 11.7 eV. In this case, species with molecular weight of 28, 44, 56, 58, and 70 were observed, all of which were also detected during the partial oxidation of ethanol over Ag/Al2O3 under low pressure. These results clearly indicate that similar reaction pathways relating to ethanol oxidation occurred during exposure of Ag/Al2O3 to ethanol + O2 and to NO + ethanol + O2. The m/z value of 60 due to acetic acid (CH3COOH) was detected with low intensity, which originated from partial oxidation. The peak at m/z = 30 was due to NO.

To identify the origin of the species observed in VUV–PIMS experiment, we also measured the corresponding PIE spectra (Figure 3). The peaks at 31 and 45 exhibited appearance energies at 11.22 and 10.73 eV, respectively. These results indicate that the fragment ions of [CH3O]+ and [C2H5O]+ were formed when...
ethanol was ionized. As shown in Figure 3C, the formation of acetaldehyde was clearly identified, while ethenol was hardly observed. Interestingly, the PIE spectra of \( m/z = 43 \) exhibited an onset of 10.88 eV. According to the literature value of 10.85 eV,\(^{28} \) this indicates that vinyloxy radical (\( \text{CH}_2\equiv\text{CH}−\text{O} \)) was produced.

We also integrated the areas of PIMS peaks (Figure 3), with the result shown in SI Table S1. It is clear that introduction of H\(_2\) significantly decreased the concentration of NO, 33.4% lower than that in the absence of H\(_2\). In the presence of H\(_2\), meanwhile, the intensities of peaks assignable to ethanol (\( m/z = 31, 45, \) and 46) were also much lower than those in the absence of H\(_2\), dropping 77.1−81.9%. This result suggests that H\(_2\) promotes reactions among NO, ethanol, and O\(_2\). Meanwhile, increased intensities of acetaldehyde and vinyloxy radical were clearly observed in the presence of H\(_2\), rising 41.1% and 35.3%, respectively.

The vinyloxy radical is an important intermediate in a few chemical reactions involving atmospheric and combustion chemistry. It is a main product in the reaction of O(\(^{\text{3P}}\)) atoms with a few alkenes such as ethene and propene.\(^{40} \) Here, we found that the vinyloxy radical was also produced during ethanol−SCR over Ag/Al\(_2\)O\(_3\) at normal atmospheric pressure. As proposed by Bouchoux et al.,\(^{41} \) the vinyloxy radical could be formed by deprotonation from the hydroxyl group of the ionized ethenol, as presented in eq 1. With this in mind, it is reasonable that ethenol was hardly observed during the NO\(_x\) reduction by ethanol at normal atmospheric pressure (Figure 3C). During the partial oxidation of ethanol over Ag/Al\(_2\)O\(_3\) under low pressure, however, the vinyloxy radical was hardly observed. This possibly means that a higher pressure is beneficial for the deprotonation of ethenol to produce vinyloxy, by giving an opportunity for collision between ethenol and other species to facilitate hydrogen extraction. Previous studies also confirmed that even at room

![Figure 2. VUV photoionization mass spectra of ethanol−SCR at 570 K over Ag/Al\(_2\)O\(_3\) (A) without H\(_2\) and (B) with H\(_2\) under normal atmospheric pressure at the photon energy of 11.7 eV.](image1)

![Figure 3. PIE spectra for \( m/z = 31 \) (A), 43 (B), 44 (C), and 45 (D) measured in the flow of ethanol + O\(_2\) + NO + H\(_2\) over Ag/Al\(_2\)O\(_3\) under normal atmospheric pressure at 570 K.](image2)
temperature, the vinyloxy radical in the gas phase can react with NO and NO₂, particularly in the presence of O₂, all of which are present in the ethanol–SCR system.

\[
\text{CH}_2=\text{CH} \rightarrow \text{OH} \xrightarrow{\text{-H}^+} \text{[CH}_2=\text{CH} \rightarrow \text{O} \leftarrow \text{CH}_2=\text{CH} \rightarrow \text{O}]
\]

\[\text{CH}_2=\text{CH} \rightarrow \text{O} + \text{NO} \rightarrow \text{O} = \text{CH} \rightarrow \text{CH}_2 \rightarrow \text{NO} \]

\[\text{CH}_2=\text{CH} \rightarrow \text{O} + \text{NO} \rightarrow \text{CH}_2=\text{CH} \rightarrow \text{O} \rightarrow \text{O} = \text{CH} \rightarrow \text{CH}_2 \rightarrow \text{NO} \]

\[\text{O} = \text{CH} \rightarrow \text{CH}_2 \rightarrow \text{NO} \xrightarrow{\text{-OH}} \rightarrow \text{-N} + \text{H}_2 \text{O} + \text{CO} \]

\[= \text{N} = \text{C} = \text{O} \]

\[\text{CH}_2=\text{CH} \rightarrow \text{O} + \text{NO} \rightarrow \text{O} = \text{CH} \rightarrow \text{CH}_2 \rightarrow \text{NO} \]

\[\text{CH}_2=\text{CH} \rightarrow \text{O} + \text{NO} \rightarrow \text{CH}_2 \rightarrow \text{C} = \text{O} \rightarrow \text{HONO} \]

\[\text{O} = \text{CH} \rightarrow \text{CH}_2 \rightarrow \text{NO} \rightarrow \text{OH} \xrightarrow{\text{-OH}} \rightarrow \text{-C} = \text{N} \rightarrow \text{-N} = \text{C} \rightarrow \text{O} \]

As for HC–SCR of NO, most of the studies dealing with the reaction mechanism have been restricted to surface phenomena. However, Eränen and co-workers proposed that octane–SCR over Ag/Al₂O₃ not only occurs on the surface of the catalyst but also continues in the gas phase, leading to the final products of N₂, H₂O, and CO₂. The occurrence of such a gas-phase reaction was proved by placing a commercial Pt-supported oxidation catalyst after the Ag/Al₂O₃ catalyst. When the oxidation catalyst was placed immediately behind the Ag/Al₂O₃, NO conversion to N₂ was decreased dramatically. A similar gas-phase reaction was also observed during NO₂ reduction by ethanol over Ag/Al₂O₃. The above results strongly suggest that very active intermediates were present in the gas phase during HC–SCR over Ag/Al₂O₃. Here, we found that the reactive vinyloxy radical was produced during ethanol–SCR, the appearance of which may induce a sequence of reactions, beginning with interaction with NO in the gas phase.

The kinetics of the reaction of vinyloxy radical with NO was investigated by Delbos et al. over wide ranges of pressure (3.9–90.2 kPa) and temperature (295–413 K). In this process, an ab initio calculation further predicted that ON−CH₂CHO and CH₃=CHONO are the major products. 2-Nirososetanal, ON−CH₂CHO, can formally be considered as the addition product of NO to the carbon of the vinyloxy radical, CH₂=CHO (eq 2), whereas ethene nitrite (CH₂=CHONO) would be formed by addition of NO at the terminal oxygen of CH₂=CHO (eq 3). Considering that ON−CH₂CHO is the most stable product during the reaction of CH₂=CHONO with NO, the isomerization of CH₂=CHONO to ON−CH₂CHO may take place (eq 4).

\[\text{Transformation of ON−CH₂CHO to its enol tautomer, } \text{−CH} \equiv \text{N(OH)}, \text{with subsequent dehydration to } \text{−CN} \text{ and transformation to } \text{−NCO} \text{ (eq 5), has been proposed as a possible route for } \text{−NCO} \text{ formation.}^{1,2,46}\]

The gas-phase kinetics of the CH₂=CHO + NO reaction was measured by Barnhard et al., during which two reaction pathways would take place with no appreciable reaction barrier, as described in eqs 6 and 7. The produced organo-nitro compound of CHO−CH₂=NO₂ was also able to produce −NCO via enol and −CNO formation, as shown in eq 8.1,2,46

As described above, the reaction involving vinyloxy radical occurring in the gas phase may contribute to NO₃ reduction, particularly in the presence of H₂, the identification of which may be crucial for understanding the mechanism of HC–SCR over Ag/Al₂O₃. Considering that both the gas-phase reaction of vinyloxy radical + NO and the surface reaction of enolic species + NO₂ may result in the formation of organo-nitrite and -nitro species, the presence of these organo-nitrogen compounds during ethanol–SCR over Ag/Al₂O₃ was further investigated by TPD–MS (Figure S1, see also Supporting Information (SI)). Comparing with the TPD spectra of Ag/Al₂O₃ exposed to NO + O₂ (SI Figure S1B), a new peak assignable to NO desorption was clearly observed at 703 K after exposure of the catalyst to a flow of NO + C₂H₅OH + O₂ (SI Figure S1C), which was accompanied by the appearance of CO₂ and CO (or N₂). At this temperature, however, the desorption of CO₂ and CO did not occur after exposing the Ag/Al₂O₃ to ethanol + O₂ (SI Figure S1A). Consequently, we think that these peaks of NO, CO₂, CO (or N₂) appearing at 703 K in SI Figure S1C were derived from the decomposition of nitrogen- and oxygen-containing compounds. During ethanol–SCR over Ag/Al₂O₃, the potential intermediates containing nitrogen and oxygen are organo-nitrogen species (R−NO, R−NO₂, and R−ONO₂), −NCO, and −CN, the latter two of which possess the molecular C/N ratio of 1:2. To further identify which species contributed to the desorption of NO, CO₂, CO (or N₂), the TPD spectra presented in SI Figure S1C were fitted on the basis of deconvoluted curves (SI Figure S2), and then peak areas were integrated. Based on this, the molecular ratio of C/N related to the desorption of NO, CO₂, and CO (or N₂) at 703 K was calculated, with an average value of 2.2. Such a C/N ratio is very close to that in the organo-nitrogen compounds ON−CH₂CHO, CHO−CH₂=NO₂, and CH₂=CHONO, which in turn confirms our speculation involving the formation of these intermediates during ethanol–SCR over Ag/Al₂O₃.

In the presence of H₂, it should be noted that a new peak at m/z = 17 was observed (Figure 2). Comparing the molecular weight from the PIMS, NH₃ can be identified. Back in 1973, Unland found that −NCO species adsorbed on the Pt/Al₂O₃ surface reacted with H₂O to yield NH₃ and CO₂. The hydrolysis of −NCO on Ag/Al₂O₃ catalysts was further demonstrated by DRIFTS and MS measurements during HC–SCR. In the presence of H₂, Richter et al. found that NH₃ exhibited high activity toward NO₂ reduction over Ag/Al₂O₃ over a wide temperature range of 473–823 K. Our results presented in SI Figure S3 also confirmed that H₂ significantly promoted NH₃−SCR over Ag/Al₂O₃, giving 100% NO conversion to N₂ at 480 K; while in the absence of H₂, the NO₂ conversion was below 20% over the whole temperature range during NO₂ reduction by NH₃.

More recently, using transient activity testing and in situ DRIFTS analysis of ethanol−SCR over Ag/Al₂O₃, we found that NH₃ originating from the hydrolysis of −NCO species can in turn react with enolic species, to produce −NCO. The reaction between ammonia and enolic species thus creates a cyclic pathway for NO₂ reduction by ethanol, which may guarantee the high efficiency of the ethanol−SCR system. With this in mind, it is possible that the cyclic pathway between enolic species and ammonia was also enhanced by H₂ addition during ethanol−SCR over Ag/Al₂O₃. As shown in Figure 2, the signal of NH₃ was much lower than that of NO and ethanol even in the presence of H₂. Yet, it is not necessarily true that only a trace amount of ammonia was produced during ethanol−SCR, because it is possible that large amount of the produced NH₃ was consumed by reaction with enolic species and/or with NO + H₂. As a result,
it is difficult to accurately measure the contribution of NH$_3$ in NO$_x$ reduction by ethanol.

Based on the above information, we can conclude that the promotion effect of H$_2$ on the NO$_x$ reduction by ethanol over Ag/Al$_2$O$_3$ can be proposed as shown in Scheme 2. Addition of H$_2$ improves the formation of the surface enolic species during partial oxidation of ethanol over Ag/Al$_2$O$_3$ together with the formation of surface acetate. Compared with acetate, the surface enolic species show higher activity toward NO + O$_2$ to produce NCO via the formation of organic nitrogen species (R−N=O, R−NO, and R−NO$_2$), the occurrence of which is also promoted by H$_2$ introduction.\(^1,2\) The −NCO species, as a key intermediate in HC−SCR, further reacts with NO + O$_2$ to produce N$_2$.\(^1,2\) During this process, meanwhile, the hydrolysis of −NCO to NH$_3$ also occurred, which was enhanced by the presence of H$_2$. The formation of NH$_3$ therefore accelerated its reaction with enolic species to produce −NCO species again, benefiting ethanol−SCR over Ag/Al$_2$O$_3$. In the presence of H$_2$, meanwhile, the produced NH$_3$ is reactive toward NO + O$_2$ to form N$_2$, creating an effective NH$_3$−SCR pathway for NO$_x$ reduction. The presence of H$_2$ enhanced the formation of reactive vinyloxy radical, the appearance of which may create a gas-phase pathway contribution to the formation of organic nitrogen species in the gas phase. Identification of such a reaction occurring in the gas phase may be crucial for understanding the mechanism of HC−SCR over Ag/Al$_2$O$_3$.

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**REFERENCES**

2. He, H.; Yu, Y. B. Selective catalytic reduction of NOx over Ag/Al$_2$O$_3$ catalyst: From reaction mechanism to diesel engine test. Catal. Today 2005, 100, 37−47.
8. Satokawa, S. Enhancing the NO/C/H$_2$/O$_2$ reaction by using H$_2$ over Ag/Al$_2$O$_3$ catalysts under lean-exhaust conditions. Chem. Lett. 2000, 294−295.

**ASSOCIATED CONTENT**

Supporting Information

TPD−MS spectra, deconvolution results of TPD−MS, relevant discussion of TPD−MS, activity of Ag/Al$_2$O$_3$ for NH$_3$−SCR, and integrated areas of species (or their fragment ions) measured in ethanol−SCR under normal atmospheric pressure at 570 K are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.
(13) Shimizu, K.; Tsuzuki, M.; Kato, K.; Yokata, S.; Okumura, K.; Satsuma, A. Reductive activation of O\textsubscript{2} with H\textsubscript{2}-reduced silver clusters as a key step in the H\textsubscript{2}-promoted selective catalytic reduction of NO with C\textsubscript{2}H\textsubscript{4} over Ag/Al\textsubscript{2}O\textsubscript{3}. J. Phys. Chem. C 2007, 111, 950–959.

(14) Kim, P. S.; Kim, M. K.; Cho, B. K.; Nam, I. S.; Oh, S. H. Effect of H\textsubscript{2} on deNO\textsubscript{x} performance of HC–SCR over Ag/Al\textsubscript{2}O\textsubscript{3}: Morphological, chemical, and kinetic changes. J. Catal. 2013, 301, 65–76.

(15) Breen, J. F.; Burch, R.; Hardacre, C.; Hill, C. J. Structural investigation of the promotional effect of hydrogen during the selective catalytic reduction of NO\textsubscript{x} with hydrocarbons over Ag/Al\textsubscript{2}O\textsubscript{3} catalysts. J. Phys. Chem. B 2005, 109, 4805–4807.


(18) Bentrup, U.; Richter, M.; Fricke, R. Effect of H\textsubscript{2} admixture on the adsorption of NO, NO\textsubscript{x}, and propane at Ag/Al\textsubscript{2}O\textsubscript{3} catalyst as examined by in situ FTIR. Appl. Catal., B 2005, 55, 213–220.


(21) Zhang, X. L.; He, H.; Ma, Z. C. Hydrogen promotes the selective catalytic reduction of NO\textsubscript{x} by ethanol over Ag/Al\textsubscript{2}O\textsubscript{3}. Catal. Commun. 2007, 8, 187–192.


(26) Yu, Y. B.; Gao, H. W.; He, H. FTIR, TPD and DFT studies of intermediates on Ag/Al\textsubscript{2}O\textsubscript{3} during the catalytic reduction of NO\textsubscript{x} by C\textsubscript{2}H\textsubscript{4}OH. Catal. Today 2004, 93–95, 805–809.

(27) Yan, Y.; Yu, Y. B.; He, H.; Zhao, J. J. Intimate contact of enolic species with silver sites benefits the SCR of NO\textsubscript{x} by ethanol over Ag/Al\textsubscript{2}O\textsubscript{3}. J. Catal. 2012, 293, 13–26.


(31) Lee, J. H.; Schmiegel, S. J.; Oh, S. H. Improved NO\textsubscript{x} reduction over the staged Ag/Al\textsubscript{2}O\textsubscript{3} catalyst system. Appl. Catal., A 2008, 342, 78–86.