Promotion Effect of H_2 on Ethanol Oxidation and NO_x Reduction with Ethanol over Ag/Al_2O_3 Catalyst

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S *Supporting Information*

ABSTRACT: The catalytic partial oxidation of ethanol and selective catalytic reduction of NO_x with ethanol (ethanol−SCR) over Ag/Al_2O_3 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 H_2 promotes the partial oxidation of ethanol to acetaldehyde over Ag/Al_2O_3, while the simultaneously occurring processes of dehydration and dehydrogenation were inhibited. H_2 addition favors the formation of ammonia during ethanol−SCR over Ag/Al_2O_3, the occurrence of which creates an effective pathway for NO_x reduction by direct reaction with NH_3. 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/Al_2O_3 by H_2. Using VUV−PIMS, the reactive vinyloxy radical was observed in the gas phase during the NO_x reduction by ethanol for the first time, particularly in the presence of H_2. Identification of such a reaction occurring in the gas phase may be crucial for understanding the reaction pathway of HC−SCR over Ag/Al_2O_3.
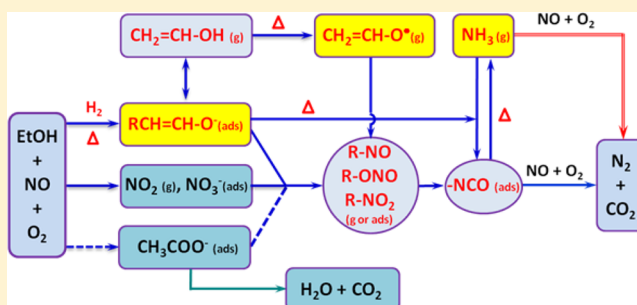
1. INTRODUCTION

The diesel engine, which is a typical lean-burn engine, has the advantage of lower consumption of fuel and lower emissions of CO_2, CO and HC than the stoichiometric gasoline engine. However, the control of NO_x emission from lean-burn engines remains one of the major challenges for environmental catalysis. Among the NO_x 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 NH_3/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/Al_2O_3) is known as one of the most effective catalysts.[1−6] When using oxygenated hydrocarbons as reductants, particularly ethanol, Ag/Al_2O_3 shows high activity even in the presence of SO_2 and H_2O.[7] More importantly, the low-temperature activity of Ag catalysts can be significantly boosted by H_2 addition, both under laboratory conditions and on a full-scale vehicle equipped with a Ag/Al_2O_3 converter.[8,9]

However, the origin of the promotion effect of H_2 on the HC−SCR over silver catalysts is still under debate, with possibilities including structural change of active sites and chemical effect on NO_x reduction.[10−12] Over Ag/Al_2O_3, Satsuma and co-workers proposed that hydrogen would be indispensable for the formation of oxidized silver clusters ($Ag_n^{\delta+}$), the presence of which is necessary for the promotion of C_3H_8 oxidation, and thus

contributes to NOx reduction.[3,12,13] Such transformation of Ag^+ to $Ag_n^{\delta+}$ on Ag/Al_2O_3 was further observed by Kim et al.[14] during NO_x reduction by a mixture of ethanol and simulated diesel in the presence of H_2, accompanied by the creation of highly active oxygen species, enhancing the low-temperature activity of Ag/Al_2O_3 for NO_x reduction. The formation of oxidized Ag clusters was also identified by Burch and co-workers[11,15] during C_8H_{18}−SCR in the presence of H_2 and CO over Ag/Al_2O_3, respectively, however CO did not promote the HC−SCR activity. As a result, it was proposed that the promoting effect of H_2 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 Sazama 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 H_2 addition at low temperatures, thus enhancing NO_x reduction.[3,12,18] Based on in situ DRIFTS, it was proposed that the addition of H_2 results in remarkable promotion of partial oxidation of C_3H_8 over Ag/Al_2O_3, mainly to surface acetate.[12,18] During the partial oxidation of hydrocarbons containing two or three carbon atoms (such as C_2H_2, C_2H_4, C_3H_6, and C_3H_8) over Ag/Al_2O_3, however, He and co-workers proposed that H_2
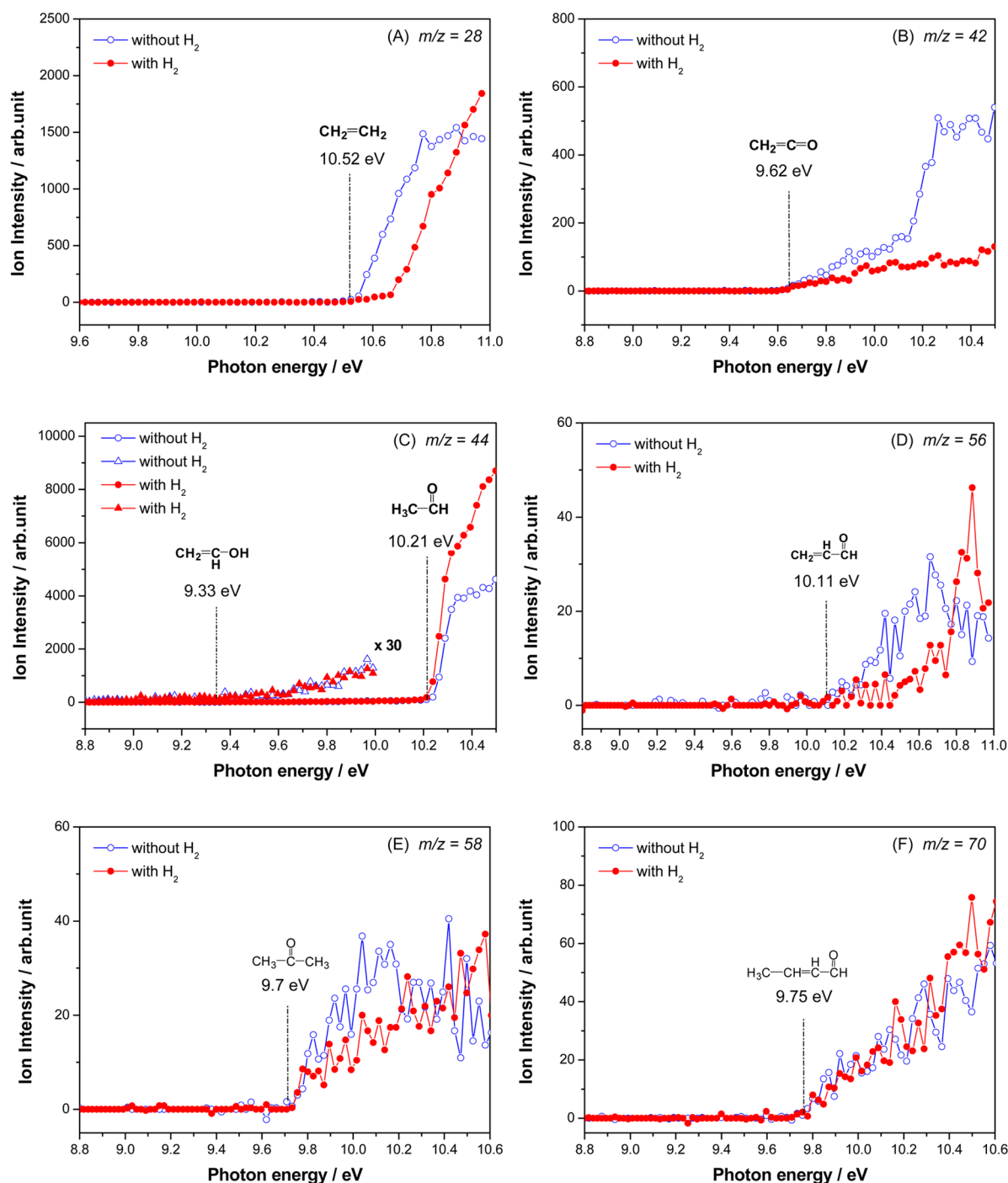
Figure 1. PIE spectra for m/z = 28 (A), 42 (B), 44 (C), 56 (D), 58 (E), and 70 (F) measured in the flow of ethanol + O_2 over Ag/Al$_2$O$_3$ under low pressure at 603 K in the absence or presence of H$_2$.

addition promoted the formation of surface enolic species (RCH=CH−O$^-$)−M, particularly in the low temperature range.[19,20] Compared with surface acetate, the surface enolic species exhibited higher activity toward NO + O$_2$ to produce the key intermediate of isocyanate (−NCO), and thus contributed to the promoting effect of H$_2$ on HC−SCR. As a common feature of H$_2$-assisted HC−SCR over Ag/Al$_2$O$_3$, an increased intensity of reactive enolic species triggered by H$_2$ addition was also observed during partial oxidation of ethanol and ethanol−SCR.[14,21] Using VUV−PIMS analysis, interestingly, Taatjes and co-workers identified that enols in the gas phase are common intermediates in hydrocarbon oxidation.[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.[23,24] With this powerful method, ethenol in the gas phase was unambiguously identified during the catalytic oxidation of C$_2$−C$_4$ alcohols over a Ag/Al$_2$O$_3$ catalyst.[25]

Table 1. Intermediates Produced during Partial Oxidation of Ethanol at 603 K over Ag/Al$_2$O$_3$ under Low Pressure

		without H$_2$		with H$_2$			
m/z	formula	measured (±0.05 eV)	ion intensity (arb.unit)	measured (±0.05 eV)	ion intensity (arb.unit)	species	ref 28
28	C$_2$H$_4$	10.52	22.46	10.52	15.32	ethylene	10.50 ± 0.02
42	C$_2$H$_2$O	9.62	7.49	9.62	3.33	ketene	9.614 ± 0.008
44	C$_2$H$_4$O	10.21	67.37	10.21	79.47	acetaldehyde	10.21 ± 0.01
	C$_2$H$_4$O	9.33	0.90	9.33	0.50	ethenol	9.33 ± 0.01
56	C$_3$H$_4$O	10.11	0.45	10.11	0.25	propenal	10.10 ± 0.01
58	C$_3$H$_6$O	9.7	0.45	9.7	0.29	acetone	9.71 ± 0.01
70	C$_4$H$_6$O	9.74	0.90	9.75	0.84	2-butenal	9.73 ± 0.01

Herein, the VUV−PIMS technique was employed to investigate the partial oxidation of ethanol and ethanol−SCR with or without H$_2$ over Ag/Al$_2$O$_3$. 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 H$_2$ on the mechanisms for ethanol oxidation and the SCR of NO$_x$ by alcohols over Ag/Al$_2$O$_3$ catalysts.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. *2.1.1. Preparation of Ag/Al$_2$O$_3$ Powders.* As described in our earlier papers,[2,26] a Ag/Al$_2$O$_3$ 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/Al$_2$O$_3$ powder prepared as mentioned above. Washcoat slurries were prepared by mixing 250 g Ag/Al$_2$O$_3$ powder and 750 g water in a ball mill.[25] 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.[23,25] 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,[23,25] 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 % C$_2$H$_5$OH, 25 vol % O$_2$, 10 vol % H$_2$O, 0.8 vol % NO (if used), 1 vol % H$_2$ (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/Al$_2$O$_3$ catalyst are N$_2$, CO$_2$, H$_2$O and CO.[26,27] 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 H$_2$ on the Ethanol Oxidation Over Ag/Al$_2$O$_3$ Catalyst. The effect of H$_2$ on the ethanol oxidation over Ag/Al$_2$O$_3$ catalyst under low pressure conditions was investigated at 603 K. Comparing the experimental IEs with the known values from the literature,[28] 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 (C$_2$H$_4$) with the ionization threshold of 10.52 eV (Figure 1A).

It is noteworthy that isomers can be determined by the PIE experiments. Ethenol (CH$_2$=HC−OH), as the isomer of acetaldehyde (CH$_3$−HC=O), has the same molecular weight as the latter. Here the ethenol and acetaldehyde can be distinguished by comparing their IEs from the PIE spectra with literature values. The PIE spectra for *m/z* = 44 (C$_2$H$_4$O) 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 ethenol and acetaldehyde according to the literature values of 9.33 ± 0.01, and 10.21 ± 0.01 eV.[28] Ethenol, 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

Scheme 1. Possible Formation Pathways of Intermediates Produced during the Partial Oxidation of Ethanol Over Ag/Al$_2$O$_3$ under Low Pressure
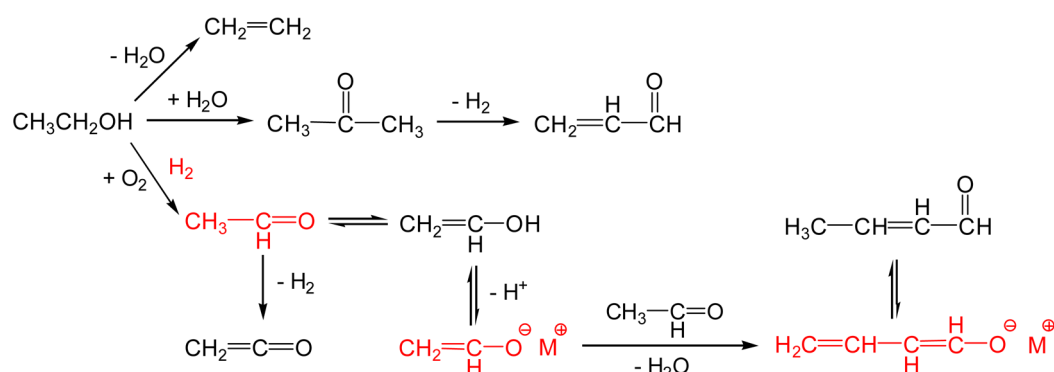
VUV−PIMS spectrometry, and found that enols are common intermediates in hydrocarbon oxidation.

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/Al$_2$O$_3$ was exposed to ethanol + O$_2$, while in the presence of H$_2$, 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 Al$_2$O$_3$ and TiO$_2$.[29,30] Over Ag/Al$_2$O$_3$, such condensation of acetaldehyde may also occur during the partial oxidation of ethanol, resulting in the formation of butenal (CH$_3$−CH=CH−CH=O, Figure 1F). As presented in Figure 1D−E and Table 1, trace amounts of propenal (CH$_2$=CH−CH=O) and acetone (CH$_3$−CO−CH$_3$) were also formed during the partial oxidation of ethanol over Ag/Al$_2$O$_3$, and lower relative concentrations were always observed when H$_2$ was introduced into the feed gas.

There are three pathways that could take place during the exposure of Ag/Al$_2$O$_3$ to ethanol + O$_2$ 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 + O$_2$ over Ag/Al$_2$O$_3$.[31,32] The presence of H$_2$ further promoted the formation of acetaldehyde, giving an ion intensity of 79.47%, which is 12.1% higher than that in the absence of H$_2$. Such enhancement of acetaldehyde formation by H$_2$ was also observed by Silva et al.[33] during ethanol−SCR over Ag/Al$_2$O$_3$. Combining these results with our previous in situ DRIFTS and TPD−MS measurements and DFT calculations, mainly pertaining to reaction on the surface of Ag/Al$_2$O$_3$,[26,27,34,35] 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 ethenol. Subsequently, a C$_2$ enolic anion (CH$_2$=CH−O$^-$)−M$^+$ is formed by hydrogen extraction when ethenol is adsorbed on the surface of Ag/Al$_2$O$_3$. Meanwhile, the occurrence of aldol condensation of acetaldehyde leads to the formation of C$_4$ enolic species (CH$_2$=CH−CH=CH−O$^-$)−M$^+$, the desorption of which results in the production of 2-butenal (CH$_3$−CH=CH−CHO). In addition, dehydrogenation of acetaldehyde possibly occurs to produce ketene (CH$_2$=C=O).

As shown in Table 1, the formation of acetaldehyde was clearly promoted by H$_2$ 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 H$_2$. On the surface of Ag/Al$_2$O$_3$, it should be noted that the adsorbed enolic species originating from hydrocarbon oxidation were significantly enhanced by H$_2$ addition, which has been identified by our previous DRIFTS studies,[19−21] and also by Kim et al.[14] Over silver catalysts, Shimizu et al.[12,13] proposed that the presence of H$_2$ promoted in situ generation of active oxygen species such as superoxide ions (O$_2^-$), and OOH species, the occurrence of which is crucial for the partial oxidation of C$_3$H$_8$. In our case, it is possible that the reactive oxygen species mentioned above would be produced in the presence of H$_2$, and then enhance the formation of enolic species during partial oxidation of ethanol over Ag/Al$_2$O$_3$.

It is well-known that the dehydration of alcohols is catalyzed by various solid acid catalysts.[36,37] The production of C$_2$H$_4$ during exposure of Ag/Al$_2$O$_3$ to ethanol + O$_2$ was also related to the acid sites (such as surface OH groups) on the surface of the silver catalyst.[38] The introduction of H$_2$ creates more reactive oxygen species over Ag/Al$_2$O$_3$, enhancing the partial oxidation of ethanol. As a result, ethanol available for dehydration to produce C$_2$H$_4$ decreased in the presence of H$_2$. 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 + H$_2$O → Me$_2$CO + CO$_2$ + 4H$_2$).[39] The addition of H$_2$ is therefore beneficial for the reverse reaction, decreasing the yield of acetone, and also its further dehydrogenation to CH$_2$=CH−CHO, as shown in Table 1 and Scheme 1.

3.2. Promotion Effect of H$_2$ on Ethanol−SCR Over Ag/Al$_2$O$_3$ Catalyst. To further investigate the synergistic effect of H$_2$, we also studied the SCR of NO$_x$ by ethanol over the Ag/Al$_2$O$_3$ catalyst at 570 K under normal atmospheric pressure. Figure 2 shows VUV−PIMS spectra of the ethanol−SCR over Ag/Al$_2$O$_3$ 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/Al$_2$O$_3$ under low pressure. These results clearly indicate that similar reaction pathways relating to ethanol oxidation occurred during exposure of Ag/Al$_2$O$_3$ to ethanol + O$_2$ and to NO + ethanol + O$_2$. The m/z value of 60 due to acetic acid (CH$_3$COOH) was detected with low intensity, which originated from partial oxidation.[1,2,4] 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 [CH$_3$O]$^+$ and [C$_2$H$_5$O]$^+$ were formed when
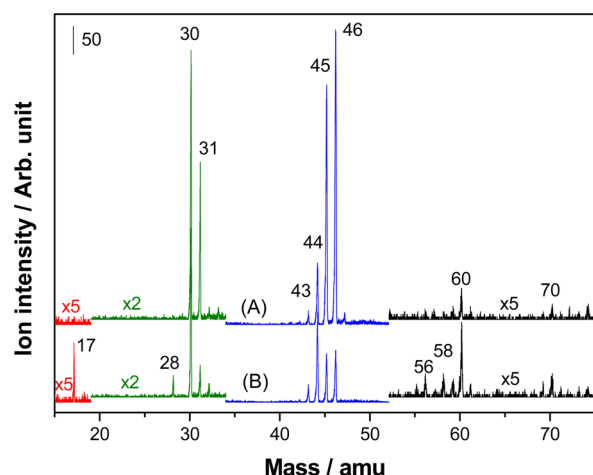
Figure 2. VUV photoionization mass spectra of ethanol−SCR at 570 K over Ag/Al$_2$O$_3$ (A) without H$_2$ and (B) with H$_2$ under normal atmospheric pressure at the photon energy of 11.7 eV.

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 (CH$_2$=CH−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(^{3}P) 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
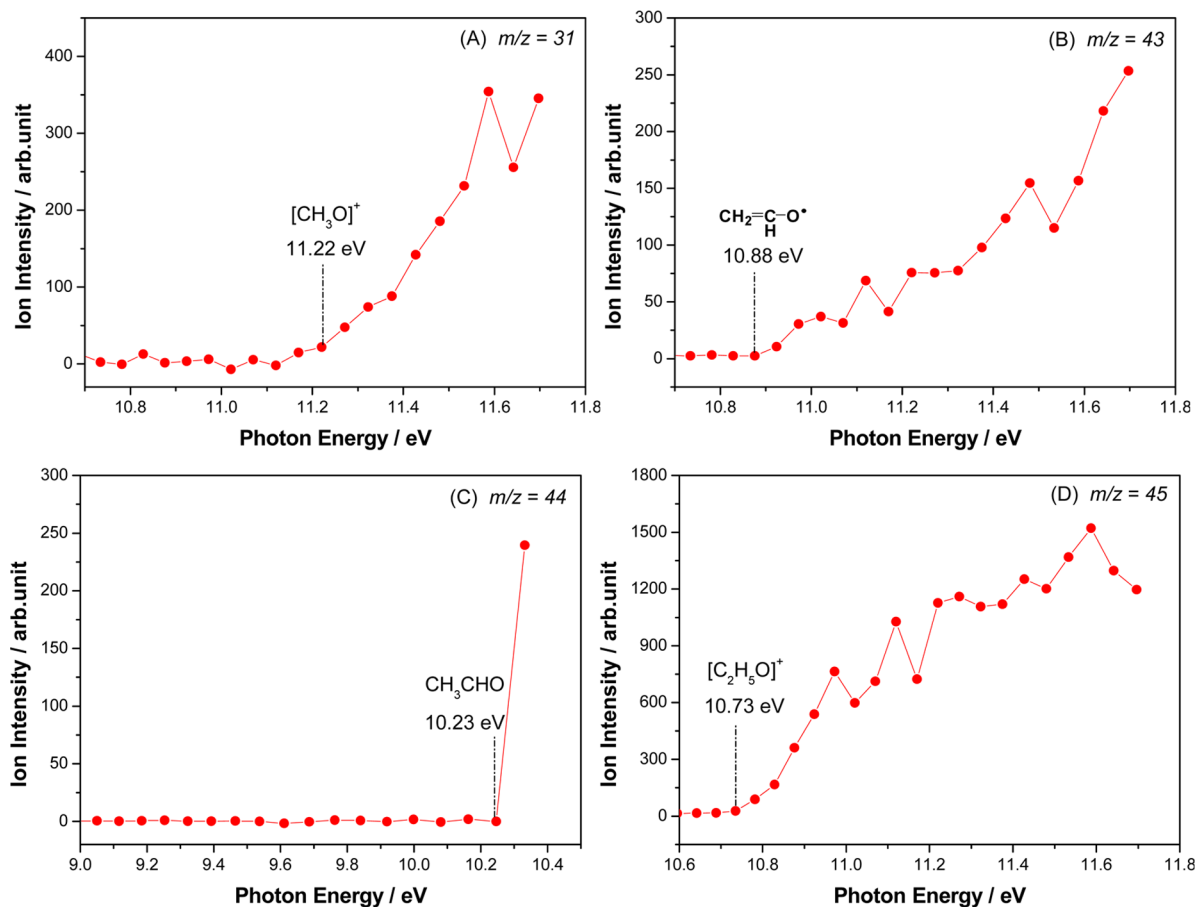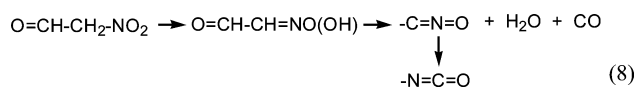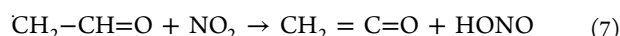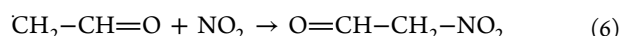

Figure 3. PIE spectra for m/z = 31 (A), 43 (B), 44 (C), and 45 (D) measured in the flow of ethanol + O$_2$ + NO + H$_2$ over Ag/Al$_2$O$_3$ under normal atmospheric pressure at 570 K.

temperature, the vinyloxy radical in the gas phase can react with NO and NO_2, particularly in the presence of O_2,[41,42] all of which are present in the ethanol−SCR system.
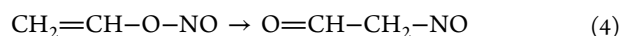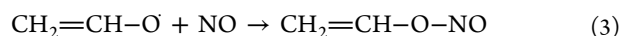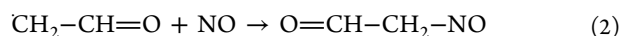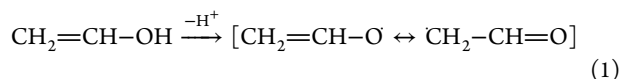
$$CH_2{=}CH{-}OH \xrightarrow{-H^+} [CH_2{=}CH{-}\overset{\cdot}{O} \leftrightarrow \overset{\cdot}{C}H_2{-}CH{=}O] \tag{1}$$

$$\overset{\cdot}{C}H_2{-}CH{=}O + NO \rightarrow O{=}CH{-}CH_2{-}NO \tag{2}$$

$$CH_2{=}CH{-}\overset{\cdot}{O} + NO \rightarrow CH_2{=}CH{-}O{-}NO \tag{3}$$

$$CH_2{=}CH{-}O{-}NO \rightarrow O{=}CH{-}CH_2{-}NO \tag{4}$$

$$O{=}CH{-}CH_2{-}NO \rightarrow O{=}CH{-}CH{=}N(OH) \rightarrow {-}C{\equiv}N + H_2O + CO$$
$$\downarrow$$
$$\qquad\qquad\qquad {-}C{=}N{=}O \rightarrow {-}N{=}C{=}O \tag{5}$$

$$\overset{\cdot}{C}H_2{-}CH{=}O + NO_2 \rightarrow O{=}CH{-}CH_2{-}NO_2 \tag{6}$$

$$\overset{\cdot}{C}H_2{-}CH{=}O + NO_2 \rightarrow CH_2{=}C{=}O + HONO \tag{7}$$

$$O{=}CH{-}CH_2{-}NO_2 \rightarrow O{=}CH{-}CH{=}NO(OH) \rightarrow {-}C{=}N{=}O + H_2O + CO$$
$$\downarrow$$
$$\qquad\qquad\qquad\qquad {-}N{=}C{=}O \tag{8}$$
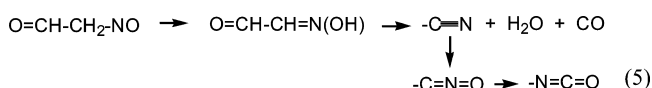
As for HC−SCR of NO_x, most of the studies dealing with the reaction mechanism have been restricted to surface phenomena. However, Eränen and co-workers[43] proposed that octane−SCR over Ag/Al_2O_3 not only occurs on the surface of the catalyst but also continues in the gas phase, leading to the final products of N_2, H_2O, and CO_2. The occurrence of such a gas-phase reaction was proved by placing a commercial Pt-supported oxidation catalyst after the Ag/Al_2O_3 catalyst. When the oxidation catalyst was placed immediately behind the Ag/Al_2O_3, NO_x conversion to N_2 was decreased dramatically. A similar gas-phase reaction was also observed during NO_x reduction by ethanol over Ag/Al_2O_3.[31,44] The above results strongly suggest that very active intermediates were present in the gas phase during HC−SCR over Ag/Al_2O_3. 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_x in the gas phase.

The kinetics of the reaction of vinyloxy radical with NO was investigated by Delbos et al.[45] 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 $ON{-}CH_2CHO$ and $CH_2{=}CHONO$ are the major products. 2-Nirosoethanal, $ON{-}CH_2CHO$, can formally be considered as the addition product of NO to the carbon of the vinyloxy radical, $\overset{\cdot}{C}H_2{-}CHO$ (eq 2), whereas ethene nitrite ($CH_2{=}CHONO$) would be formed by addition of NO at the terminal oxygen of $CH_2{=}CHO^{\cdot}$ (eq 3). Considering that $ON{-}CH_2CHO$ is the most stable product during the reaction of $CH_2{=}CHO$ with NO, the isomerization of $CH_2{=}CHONO$ to $ON{-}CH_2CHO$ may take place (eq 4).[45] Transformation of $ON{-}CH_2CHO$ to its enol tautomer, $-CH{=}N(OH)$, with subsequent dehydration to $-CN$ and transformation to $-NCO$ (eq 5), has been proposed as a possible route for $-NCO$ formation.[1,27,46] The gas-phase kinetics of the $CH_2{=}CHO + NO_2$ reaction was measured by Barnhard et al.,[47] 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 $CHO{-}CH_2{-}NO_2$ was also able to produce $-NCO$ via enol and $-CNO$ formation, as shown in eq 8.[1,27,46]

As described above, the reaction involving vinyloxy radical occurring in the gas phase may contribute to NO_x reduction,

particularly in the presence of H_2, the identification of which may be crucial for understanding the mechanism of HC−SCR over Ag/Al_2O_3. Considering that both the gas-phase reaction of vinyloxy radical + NO_x and the surface reaction of enolic species + NO_x may result in the formation of organo-nitrite and -nitro species, the presence of these organo-nitrogen compounds during ethanol−SCR over Ag/Al_2O_3 was further investigated by TPD−MS (Figure S1, see also Supporting Information (SI)). Compared with the TPD spectra of Ag/Al_2O_3 exposed to NO + O_2 (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 + C_2H_5OH + O_2 (SI Figure S1C), which was accompanied by the appearance of CO_2 and CO (or N_2). At this temperature, however, the desorption of CO_2 and CO did not occur after exposing the Ag/Al_2O_3 to ethanol + O_2 (SI Figure S1A). Consequently, we think that these peaks of NO, CO_2, CO (or N_2) appearing at 703 K in SI Figure S1C were derived from the decomposition of nitrogen- and oxygen-containing compounds. During ethanol−SCR over Ag/Al_2O_3, the potential intermediates containing nitrogen and oxygen are organo-nitrogen species (R−NO, R−NO_2, and R−ONO), −NCO, and −CN, the latter two of which possess the molecular C/N ratio of 1.[1,2] To further identify which species contributed to the desorption of NO, CO_2, CO (or N_2), 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, CO_2, and CO (or N_2) 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 $ON{-}CH_2CHO$, $CHO{-}CH_2{-}NO_2$, and $CH_2{=}CHONO$, which in turn confirms our speculation involving the formation of these intermediates during ethanol−SCR over Ag/Al_2O_3.

In the presence of H_2, it should be noted that a new peak at $m/z = 17$ was observed (Figure 2). Comparing the molecular weight from the PIMS,[28] NH_3 can be identified. Back in 1973, Unland[48] found that −NCO species adsorbed on the Pt/Al_2O_3 surface reacted with H_2O to yield NH_3 and CO_2. The hydrolysis of −NCO on Ag/Al_2O_3 catalysts was further demonstrated by DRIFTS and MS measurements during HC−SCR.[49] In the presence of H_2, Richter et al. found that NH_3 exhibited high activity toward NO_x reduction over Ag/Al_2O_3 over a wide temperature range of 473−823 K.[50] Our results presented in SI Figure S3 also confirmed that H_2 significantly promoted NH_3−SCR over Ag/Al_2O_3, giving 100% NO_x conversion to N_2 at 480 K; while in the absence of H_2, the NO_x conversion was below 20% over the whole temperature range during NO_x reduction by NH_3.

More recently, using transient activity testing and in situ DRIFTS analysis of ethanol−SCR over Ag/Al_2O_3, we found that NH_3 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 NO_x reduction by ethanol, which may guarantee the high efficiency of the ethanol−SCR system.[51] With this in mind, it is possible that the cyclic pathway between enolic species and ammonia was also enhanced by H_2 addition during ethanol−SCR over Ag/Al_2O_3. As shown in Figure 2, the signal of NH_3 was much lower than that of NO and ethanol even in the presence of H_2. 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 NH_3 was consumed by reaction with enolic species and/or with NO + H_2. As a result,

Scheme 2. Possible Effect of H$_2$ on the SCR of NO$_x$ by Ethanol Over Ag/Al$_2$O$_3$
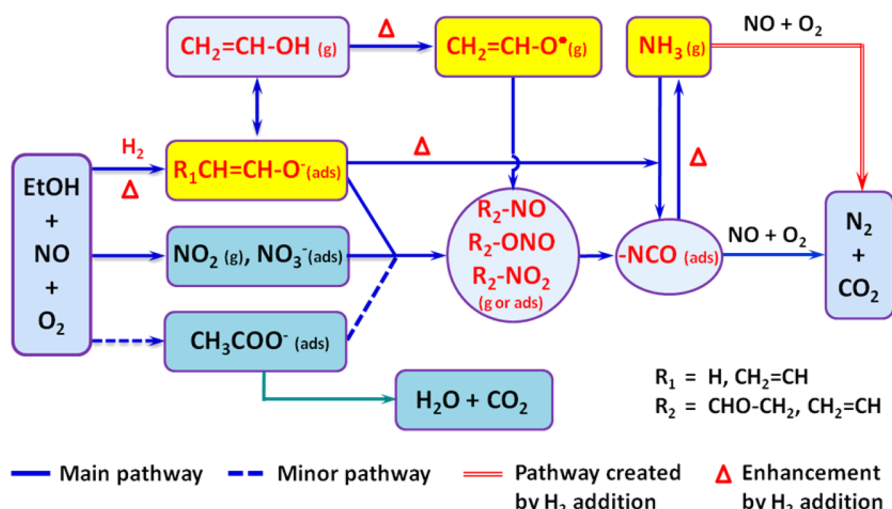
it is difficult to accurately measure the contribution of NH$_3$ in NO$_x$ reduction by ethanol.

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−NO, R−ONO, and R−NO$_2$), the occurrence of which is also promoted by H$_2$ introduction.[21] 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$_3$.

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.

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