



Effect of the pressure on the catalytic oxidation of volatile organic compounds over Ag/Al₂O₃ catalyst

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ABSTRACT

The catalytic oxidation of volatile organic compounds (VOCs: ethanol, 1-propanol and 2-propanol) over Ag/Al₂O₃ catalyst under low and normal atmospheric pressure conditions has been studied with synchrotron vacuum ultraviolet (VUV) photoionization mass spectrometry (PIMS). The partial oxidation intermediates of the VOCs under different pressures were identified by PIMS and their photoionization efficiency (PIE) spectra. Alkene is preferentially formed under the low pressure conditions, while aldehyde and acid are favored under the normal atmospheric pressure conditions. In addition, the low pressure conditions are more suitable for observing the active intermediates, such as ethenol, ketene and propenal. The results indicate that the pressure has a significant effect on the oxidation pathway of VOCs over Ag/Al₂O₃ catalyst.

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1. Introduction

Increasing interest is being shown in catalytic combustion processes, which are convenient ways for the prevention of emission (including the control of nitrogen oxides (NO_x) and unburned hydrocarbons in heat and power generation plants) as well as clean-up processes (VOC removal and automobile exhaust converters) [1]. Compared with flame or thermal combustion, catalytic combustion exhibits advantages such as high efficiency, ultra low pollutant emissions, stable combustion, and so on. Fundamental knowledge of catalytic oxidation mechanisms is valuable for the development of effective methods for using catalysts to control air pollution.

The catalytic oxidation of VOCs over various catalysts, as a means to control air pollution, has been investigated [2]. Although silver is not the best oxidation catalyst, it is a well-known catalyst for the conversion of alcohols to aldehydes and ketones, and the only metal that selectively catalyzes ethylene epoxidation to ethylene oxide [3,4]. Some researchers have studied the catalytic oxidation of alcohols over silver based catalysts [5–11]. Yao [5] studied the catalytic oxidation of ethanol at low concentrations, and found that nearly 100% ethanol could be oxidized to acetaldehyde over Ag/Al₂O₃ catalyst, accompanied by a small amount of CO, C₂H₄ and CH₃COOH. Cordi and Falconer [6] studied

the oxidation of five VOCs including methanol, ethanol, acetaldehyde, formic acid and acetic acid over Ag/Al₂O₃ catalyst using temperature-programmed desorption (TPD) and oxidation (TPO). They reported that acetaldehyde and acetic acid were the partial oxidation products of ethanol, while formic acid was the partial oxidation product of methanol.

The selective catalytic reduction (SCR) of NO_x by hydrocarbons is a potential method for removing NO_x from oxygen rich exhausts of automobiles and stationary combustion facilities. Ag/Al₂O₃ is known to be one of the most effective catalysts for the SCR of NO_x by hydrocarbons. He et al. [9–12] found that an enolic surface species could be formed on Ag/Al₂O₃ during the partial oxidation of CH₃CHO, C₂H₅OH, C₃H₆, 1-propanol and 2-propanol over Ag/Al₂O₃ catalyst using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and found that this highly active species was the key intermediate in the process of NO_x reduction by hydrocarbons. Recently, Taatjes et al. [13] studied 24 different flames of 14 prototypical single fuels and low-pressure flames of commercial gasoline using synchrotron VUV photoionization mass spectrometry, and found that enols are common intermediates in hydrocarbon oxidation. It is well known that there is less collision between molecules under low pressure, so that one could expect to obtain rarer partial oxidation intermediates of VOC catalytic oxidation under such reaction conditions. More recently, enols with two to four carbon atoms have been found in propanols and butanols fueled low-pressure flames [14,15]. It is very interesting to note that enols can be formed from low-pressure plasma discharges of alcohols as well [16]. In addition, Ferguson et al. [17]

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reported that elevated pressure could accelerate the oxidation reactions showing that the effect of pressure was important for the investigation of the reaction products.

In this article, the reaction mechanism of catalytic partial oxidation of VOCs (such as ethanol, 1-propanol, and 2-propanol) over $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst was studied under low and normal atmospheric pressure conditions using tunable synchrotron VUV photoionization mass spectrometry (PIMS) combining with molecular-beam sampling technique. The intermediates of partial oxidation were identified by the measurements of PIMS and photoionization efficiency (PIE) spectra. The results could provide new insights into the mechanisms for the SCR of NO_x by alcohols and provide significant contributions to the practical use of $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of $\text{Ag}/\text{Al}_2\text{O}_3$ powders

The 4% $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts were prepared by an impregnation method using an aqueous solution of silver nitrate. After impregnation, the excess water was removed in a rotary evaporator at 333 K. The samples were first dried at 393 K for 12 h, followed by calcination at 873 K for 3 h.

2.1.2. Preparation of washcoated honeycomb catalysts

Washcoated honeycomb catalysts were prepared using the 4% $\text{Ag}/\text{Al}_2\text{O}_3$ powder. Washcoat slurries were then prepared by mixing 250 g $\text{Ag}/\text{Al}_2\text{O}_3$ powder and 750 g water in a ball mill. Cordierite honeycombs with 400 cells per square inch (90 mm in diameter \times 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 and calcined at 873 K for 3 h. The washcoat loading was 110 g l^{-1} after calcination.

2.2. Experimental setup

The 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 and selective method for the analysis of individual intermediates and products of the reaction. Synchrotron radiation from a bend magnet of the 800 MeV electron storage ring was monochromized with a 1-m Seya-Namioka monochromator equipped with two gratings (2400 and 1200 grooves/mm), which provided single-photon ionization (SPI) and minimized fragmentation due to the near-threshold ionization. The wavelength of the monochromator was calibrated with the known ionization energies of the inert gases. The energy resolving power ($E/\Delta E$) was about 500–1000, depending on the slit widths. A LiF window with 1.0 mm thickness was used to eliminate higher order radiation of the dispersed light in the wavelength region longer than 105 nm.

With the tunability of the light source, a series of mass spectra from 8.63 to 11.15 eV were measured. 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 IE could be directly obtained from the PIE spectra. Considering the energy resolution of the monochromator and the cooling effect of molecular beam [18], the experimental error of the measured IEs was less than 0.05 eV. Thus, all components could be identified by their molecular weights from the photoionization mass spectrometry near threshold ionization and the ionization energies from photoionization efficiency spectra. The experimental IEs were compared with known literature values. According to our previous studies under the same conditions, the final products of VOCs oxidation over $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst are CO_2 and small amount of CO [10]. In this study, we focused on the intermediates of catalytic partial oxidation of VOCs, which are not in the same magnitude with the final products of CO_2 and CO, thereby we did not measure the photoionization efficiency (PIE) spectra of final products.

The details of MBMS have been described elsewhere [18]. It was originally designed for the study of combustion. Some modifications were made to detect products of the catalytic oxidation in this study. In brief, a schematic diagram of the experimental instrument is shown in Fig. 1. A syringe pump (ISCO Inc., USA) was used to control the flow rate of the VOC aqueous solution (ethanol, 1-propanol, and 2-propanol) at 0.500 ml/min. The aqueous

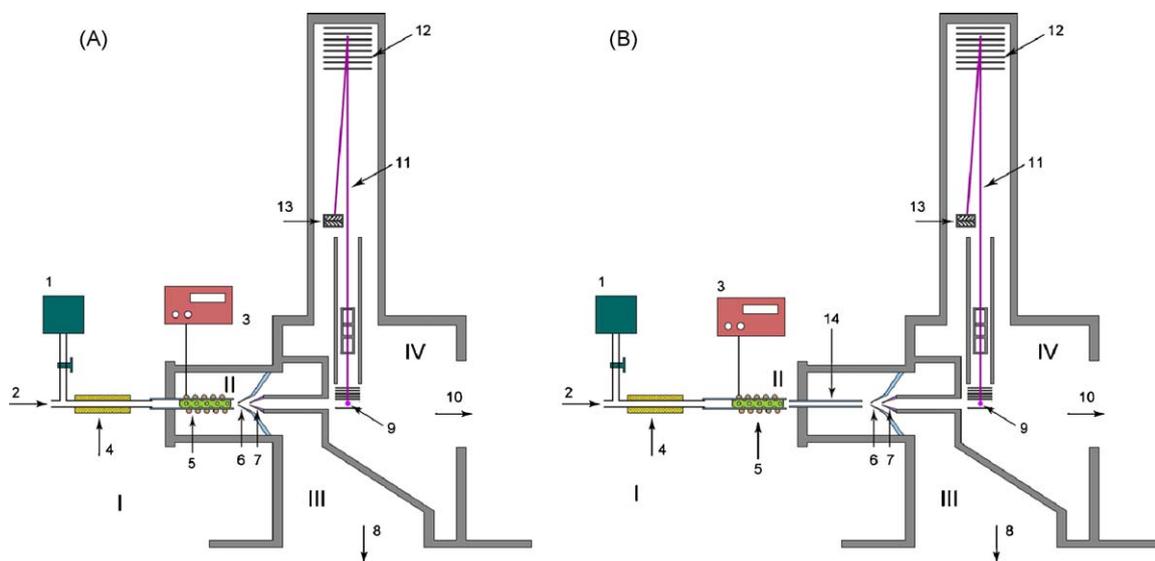


Fig. 1. Schematic diagram of the instrument under low pressure (A) and normal atmospheric pressure (B), including the sample inlet system (I), the catalyst bed (II), the differential pumped system (III), and the photoionization chamber with the reflectron TOF MS (IV). The other components include: (1) the syringe pump; (2) the carrier helium inlet; (3) the temperature controller; (4) the vaporizer; (5) the catalyst bed; (6) the quartz nozzle with an orifice of 500 μm at the tip; (7) the nickel skimmer; (8) to a turbo molecular pump with the pump speed of 3500 l/s; (9) the ionization region; (10) to a turbo molecular pump with the pump speed of 1600 l/s; (11) the ion trajectory; (12) the ion optics of the reflectron; (13) the MCP detector; (14) the quartz sampling tube.

solution of VOCs was vaporized with the carrier gas (Ar) and passed into the catalyst bed (II). The temperature of the vaporizer was maintained at 423 K to ensure that the aqueous solution was vaporized completely. As shown in Fig. 1A, 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 (Fig. 1B). The temperature of the catalyst bed was controlled by a temperature controller. The appropriate temperatures were adjusted to keep the conversion of VOCs at about 50%. The flow rates of Ar and O₂ were 1.500 and 0.500 standard liters per minute (SLM), respectively, controlled by a mass flow controller (MKS Instruments Inc.). For the low pressure experiments, the gas-phase mixture of unburned VOCs, partial oxidation products of VOCs and water from the catalyst bed outlet was sampled through a quartz cone-like nozzle with an orifice of ~ 500 μm in diameter. A nickel skimmer with a 2-mm diameter aperture was located at 18 mm downstream from the sampling nozzle. For the experiments under normal atmospheric pressure conditions, a quartz tube with 2.0 mm in diameter was used to sample the gases, as shown in Fig. 1B. The sample gases formed a molecular beam, which passed horizontally through the 10 mm gap between the repeller and extractor plates of the reflectron TOF MS [19]. The molecular beam intersected perpendicularly with the synchrotron VUV light beam. The ion signal was detected with the reflectron TOF MS, which was installed vertically in the photoionization chamber (see Fig. 1). A pulsed voltage of 200 V was used to propel ions into the flight tube, and finally to a microchannel plate (MCP) detector. Detailed information on the RTOF MS can be found in previous reports [18,19]. For the low pressure experiments, the pressures in the sample inlet chamber, the differentially pumped chamber and the ionization chamber were 800, 10^{-3} and 10^{-3} Pa, respectively. For the experiments under normal atmospheric pressure conditions, the pressures in the sample inlet chamber, the differentially pumped chamber and the ionization chamber were 800, 10^{-2} and 10^{-3} Pa, respectively.

3. Results and discussion

3.1. Catalytic partial oxidation of ethanol over Ag/Al₂O₃ catalyst under low and normal atmospheric pressure conditions

The partial catalytic oxidation of ethanol on the Ag/Al₂O₃ catalyst was conducted at 603 K under low pressure and at 563 K under normal atmospheric pressure.

Fig. 2 shows four VUV photoionization mass spectra of the partial oxidation of ethanol on Ag/Al₂O₃ catalyst under low pressure and at different photon energies. Several peaks in the mass range of 20–70 are observed at the photon energy of 10.78 eV, which correspond to hydrocarbons ranging from C₂ to C₄. However, some peaks do not originate from ethanol oxidation. The peaks with odd m/z are attributed to ¹³C isotope contribution. Furthermore, the peaks with odd m/z can also be produced from the fragmentation of large hydrocarbons, as the photon energy is high enough to produce fragmentation. In this study, the measurement of the PIE spectra of mass 45 is attributed to the fragmentation of ethanol.

Comparing the experimental IEs with the known values from the literature [20], several kinds of catalytic partial oxidation intermediates are identified. The measured ionization thresholds and ion intensity for all the observed peaks are listed in Table 1. Under low pressure conditions, ethylene, ketene, acetaldehyde, ethenol, propenal, acetone and 2-butenal can be identified; while under normal atmospheric pressure conditions, acetaldehyde, acetone, acetic acid, 2-butenal and ethyl ether are identified. Based on these results, it is obvious that the pressure has a significant effect on the partial catalytic oxidation pathway of ethanol over Ag/Al₂O₃ catalyst.

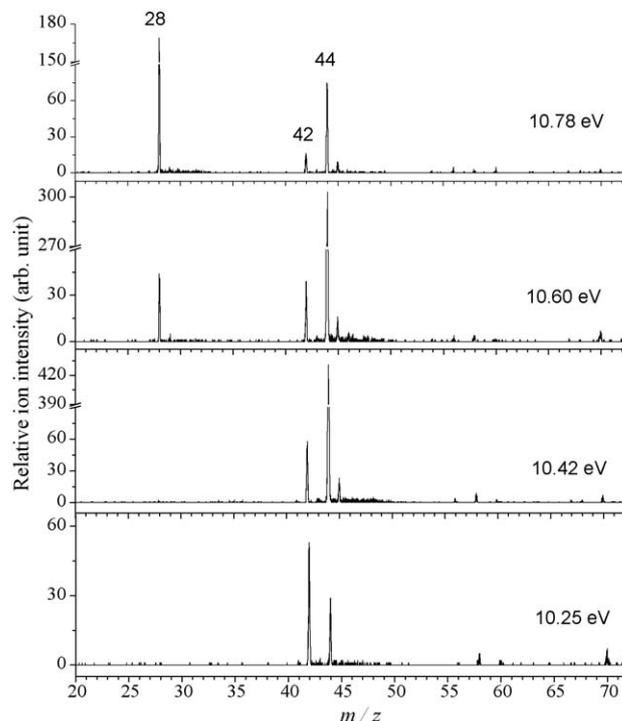


Fig. 2. VUV photoionization mass spectra of partial oxidation of ethanol over Ag/Al₂O₃ catalyst under low pressure at the photon energies of 10.78, 10.60, 10.42, and 10.25 eV, respectively.

As can be seen in Table 1, acetaldehyde, acetone, and 2-butenal are all present during the partial oxidation of C₂H₅OH over Ag/Al₂O₃ catalyst under both low and normal atmospheric pressure conditions, and acetaldehyde is the main product with the highest intensity among them. It is considered that acetaldehyde is produced from the dehydrogenation of ethanol over Ag/Al₂O₃ catalyst; acetone is formed by the oxidation of ethanol with molecular oxygen; and 2-butenal is formed from the self-condensation of acetaldehyde. Based on a previous study [6], acetaldehyde was the main partial oxidation product of ethanol during the TPO experiment and oxygen adsorbed on the silver site activates neighboring silver sites for dehydrogenation, forming acetaldehyde and H₂. Yao [5] found that Ag is a well-known catalyst for the conversion of alcohols to aldehydes and ketones, and nearly 100% ethanol was oxidized to acetaldehyde over Ag/Al₂O₃ catalysts under appropriate experimental conditions. They also found that acetone was formed by ethanol oxidation with molecular oxygen during the catalytic oxidation of ethanol over Pd/Al₂O₃ catalysts. Furthermore, the aldol condensation reaction is an important method for the synthesis of unsaturated carbonyl compounds in organic chemistry.

The ethylene, ketene, ethenol and propenal in Table 1 are only identified under low pressure conditions, whereas only acetic acid and ethyl ether are identified under normal atmospheric pressure conditions. Ethenol, as the isomer of acetaldehyde, has the same molecular weight as acetaldehyde and is only observed under low pressure conditions. Here the ethenol and acetaldehyde can be differentiated by comparing their different IEs from the PIE spectra with literature values. The PIE spectra of $m/z = 44$ (C₂H₄O) (Fig. 3) illustrate how to identify the isomers. Under low pressure, 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 [20]. Ethenol (CH₂=HC-OH), bearing OH groups adjacent to carbon-carbon double bonds, is thermodynamically unstable relative to acetaldehyde (CH₃-HC=O). Until now, only a few experimental data are available on neutral enol

Table 1

List of the partial oxidation species of ethanol identified by their IEs in the flow of ethanol over Ag/Al₂O₃ catalyst under low pressure at 603 K and normal atmospheric pressure at 563 K.

m/z	Formula	Low pressure		Normal atmospheric pressure		Species	Ref. [20]
		Measured (±0.05 eV)	Ion intensity (arb. unit)	Measured (±0.05 eV)	Ion intensity (arb. unit)		
28	C ₂ H ₄	10.52	22.46	–	–	Ethylene	10.50 ± 0.02
42	C ₂ H ₂ O	9.62	7.49	–	–	Ketene	9.614 ± 0.008
44	C ₂ H ₄ O	10.21	67.37	10.21	87.72	Acetaldehyde	10.21 ± 0.01
	C ₂ H ₄ O	9.33	0.90	–	–	Ethenol	9.33 ± 0.01
56	C ₃ H ₄ O	10.11	0.45	–	–	Propenal	10.10 ± 0.01
58	C ₃ H ₆ O	9.7	0.45	9.7	0.88	Acetone	9.71 ± 0.01
60	C ₂ H ₄ O ₂	–	–	10.65	6.58	Acetic acid	10.66 ± 0.05
70	C ₄ H ₆ O	9.74	0.90	9.74	2.19	2-Butenal	9.73 ± 0.01
74	C ₄ H ₁₀ O	–	–	9.53	2.63	Ethyl ether	9.53 ± 0.02

chemistry. In the low-pressure flames of hydrocarbon oxidation, Taatjes et al. [13] found that enols are the common intermediates in hydrocarbon oxidation. Qi et al. [14,15] found that enols with two to four carbon atoms were in propanols and butanols fueled flames. Also, it is very interesting that enols can also be formed from plasma discharges of alcohols [16]. Under normal pressure, He et al. [9–12] observed the formation of the enolic species during the partial oxidation of alcohols on Ag/Al₂O₃ catalyst using in situ DRIFTS measurements, where the Ag/Al₂O₃ could provide a suitable surface to stabilize the ethenol. In the case of catalytic oxidation of ethanol over Ag/Al₂O₃, we deduce that C₂H₅OH is first adsorbed on the surface of Ag/Al₂O₃, an enolic anion (CH₂=CH–O)[–]M⁺ is then formed on the surface via the dehydrogenation of C₂H₅OH. A part of the enolic anion subsequently desorbs from the Ag/Al₂O₃ catalyst, becoming gaseous ethenol. Owing to its thermodynamic instability under normal pressure, ethenol subsequently transforms rapidly into acetaldehyde. Therefore, we consider that ethenol is the key intermediate during the catalytic partial oxidation of C₂H₅OH on the Ag/Al₂O₃ catalyst, and the formation of ethenol is significant for the SCR of NO_x by C₂H₅OH over the Ag/Al₂O₃ catalyst. In contrast, under normal atmospheric pressure conditions, ethenol cannot be observed in gas phase. However, in our previous study [9–12], we found that an enolic surface species was formed on Ag/Al₂O₃ under normal pressure during the partial oxidation of CH₃CHO, C₂H₅OH, C₃H₆, 1-propanol and 2-propanol over Ag/Al₂O₃ catalyst by in situ DRIFTS measurement. Therefore, we conclude that ethenol is formed on the surface of Ag/Al₂O₃ catalyst, but desorbed ethenol subsequently transforms rapidly into acetaldehyde in gas phase so that it cannot be detected even using

synchrotron VUV photoionization mass spectrometry under normal pressure conditions.

Besides ethenol, the ethylene, ketene and propenal can only be identified under low pressure conditions. It is deduced that ethylene is formed by the dehydration of ethanol over Ag/Al₂O₃ catalyst. Because of its high intensity, the formation of ethylene is another main reaction pathway for the partial oxidation of ethanol over Ag/Al₂O₃ catalyst under low pressure conditions. It is also supposed that ketene is formed by the further dehydrogenation of acetaldehyde and the formation of propenal is a result of the rearrangement and further dehydrogenation of acetone. According to the literature [6], ethylene may be formed by dehydration of ethanol on Al₂O₃.

On the other hand, acetic acid and ethoxy ethane are only observed under normal atmospheric pressure, as shown in Table 1. It is supposed that acetic acid is formed by the further oxidation of the generated acetaldehyde and ethyl ether is formed by the intermolecular dehydration of ethanol. In organic chemistry, the catalytic oxidation of aldehydes to the corresponding carboxylic acids is an important method for the preparation of acetic acid. Furthermore, in industrial applications, ethanol can be dehydrated to form ethyl ether on Al₂O₃ with more than 95% yield under suitable reaction conditions.

On the basis of the above results, we can conclude that pressure significantly affects the formation pathway of the partial oxidation intermediates on Ag/Al₂O₃ catalyst, as shown in Scheme 1. The low pressure conditions favor the dehydration and dehydrogenation of ethanol over the Ag/Al₂O₃ catalyst. However, normal atmospheric pressure conditions favor the partial catalytic oxidation of ethanol. In addition, low pressure conditions favor the observation of active intermediates, such as ethenol, ketene and propenal, and the

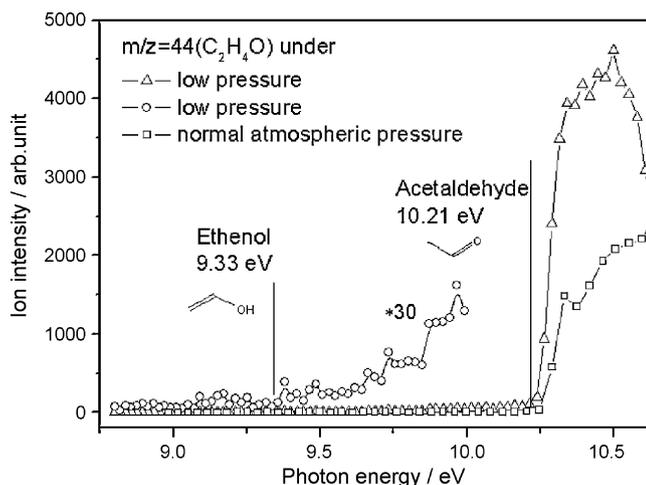
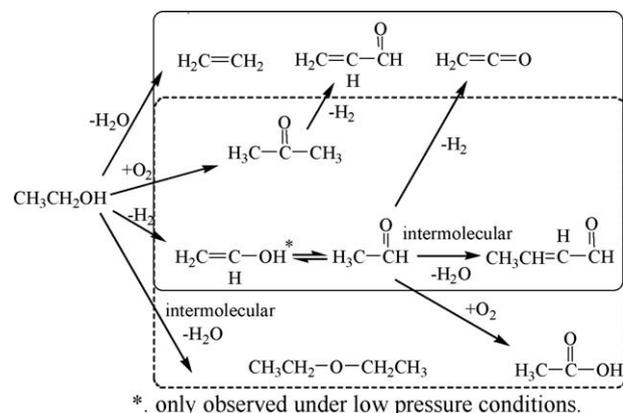


Fig. 3. The PIE spectra of $m/z = 44$ (C₂H₄O) measured in the flow of ethanol over Ag/Al₂O₃ catalyst under low pressure at 603 K and normal atmospheric pressure at 563 K.



Scheme 1. Possible formation pathways of ethanol partial oxidation intermediates over Ag/Al₂O₃ catalyst under low pressure at 603 K (solid frame) and normal atmospheric pressure at 563 K (dotted frame).

Table 2

List of the partial oxidation species of 1-propanol identified by their IEs in the flow of 1-propanol over Ag/Al₂O₃ catalyst under low pressure at 603 K and normal atmospheric pressure at 523 K.

m/z	Formula	Low pressure		Normal atmospheric pressure		Species	Ref. [20]
		Measured (±0.05 eV)	Ion intensity (arb. unit)	Measured (±0.05 eV)	Ion intensity (arb. unit)		
28	C ₂ H ₄	10.5	5.85	–	–	Ethylene	10.50 ± 0.02
42	C ₃ H ₆	9.73	70.26	–	–	Propene	9.73 ± 0.01
44	C ₂ H ₄ O	–	–	10.2	4.62	Acetaldehyde	10.21 ± 0.01
56	C ₃ H ₄ O	8.95	3.75	–	–	Propenal	8.95
58	C ₃ H ₆ O	9.96	16.39	9.96	86.71	Propanal	9.96
74	C ₃ H ₆ O ₂	–	–	10.21	8.67	Propanoic acid	10.24 ± 0.03
78	C ₆ H ₆	9.21	3.75	–	–	Benzene	9.2 ± 0.1

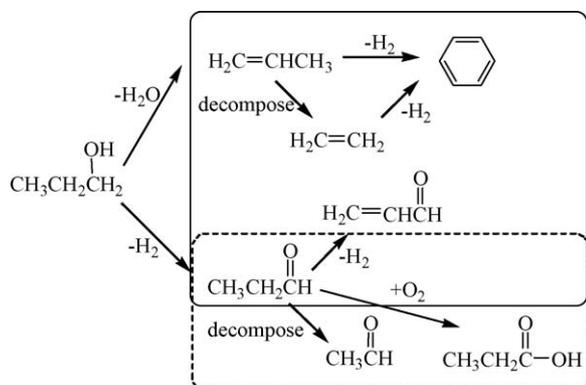
formation of ethenol is a key step during the catalytic oxidation of C₂H₅OH over the Ag/Al₂O₃ catalyst.

3.2. Catalytic partial oxidation of 1-propanol and 2-propanol over Ag/Al₂O₃ catalyst under low and normal atmospheric pressure conditions

To further investigate the effect of the pressure on the formation pathway of the partial oxidation products on Ag/Al₂O₃ catalyst, we also studied the catalytic partial oxidation of 1-propanol and 2-propanol over the catalyst. The catalytic partial oxidation of 1-propanol was carried out at 603 K under low pressure and 523 K under normal atmospheric pressure. The measured ionization thresholds and ion intensities for all observed peaks are listed in Table 2, along with the IEs from the literature [20].

Under low pressure conditions, ethylene, propene, propenal, propanal and benzene are identified, whereas acetaldehyde, propanal, and propanoic acid are identified under normal atmospheric pressure conditions. The formation pathways of the 1-propanol partial oxidation intermediates over Ag/Al₂O₃ catalyst are shown in Scheme 2.

Comparing the results under low pressure with those under normal atmospheric pressure in Table 2, only propanal is the common partial oxidation intermediate formed by the dehydrogenation of 1-propanol. The PIE spectra for propanal under both low and normal atmospheric pressure conditions are shown in Fig. 4. Under normal atmospheric pressure, propanal shows the highest signal intensity, indicating that it is the main intermediate of the partial oxidation of 1-propanol over Ag/Al₂O₃ catalyst. As shown in Table 2, ethylene, propene, propenal and benzene are only observed under low pressure. It is deduced that propenal is formed by the further dehydrogenation of propanal. Propene is formed by the dehydration of 1-propanol and shows the highest intensity, indicating that propene is the



Scheme 2. Possible formation pathways of 1-propanol partial oxidation intermediates over Ag/Al₂O₃ catalyst under low pressure at 603 K (solid frame) and normal atmospheric pressure at 523 K (dotted frame).

main intermediate of 1-propanol partial oxidation over Ag/Al₂O₃ catalyst. Subsequently, a part of propene decomposes to ethylene. Trace amounts of benzene are formed by further dehydrogenation and condensation of ethylene or propene or both. Under normal atmospheric pressure, only acetaldehyde and propanoic acid are observed. The formation of acetaldehyde can be explained by the decomposition of propanal over Ag/Al₂O₃ catalyst, and propanoic acid is formed by the further oxidation of propanal.

A similar experiment was performed for the catalytic partial oxidation of 2-propanol over Ag/Al₂O₃ catalyst at 603 K under low pressure and at 473 K under normal atmospheric pressure. The measured ionization thresholds and ion intensities for all observed peaks are listed in Table 3, along with the IEs from the literature [20].

Under low pressure conditions, propene, acetaldehyde, acetone, methylethyl ether and benzene are identified, whereas only acetone appears under normal atmospheric pressure conditions. The formation pathways of the partial oxidation intermediates of 2-propanol over Ag/Al₂O₃ catalyst are shown in Scheme 3.

The results in Table 3 show that acetone is the common partial oxidation intermediate, formed by the dehydrogenation of 2-propanol. The PIE spectra for acetone are shown in Fig. 5, its high intensity indicating that the formation of acetone is the main reaction pathway in the partial oxidation of 2-propanol over Ag/Al₂O₃ catalyst under low and normal atmospheric pressure conditions.

Under low pressure conditions, the other four products are observed, that is, propene, acetaldehyde, methylethyl ether and benzene. The formation of propene with high intensity can be

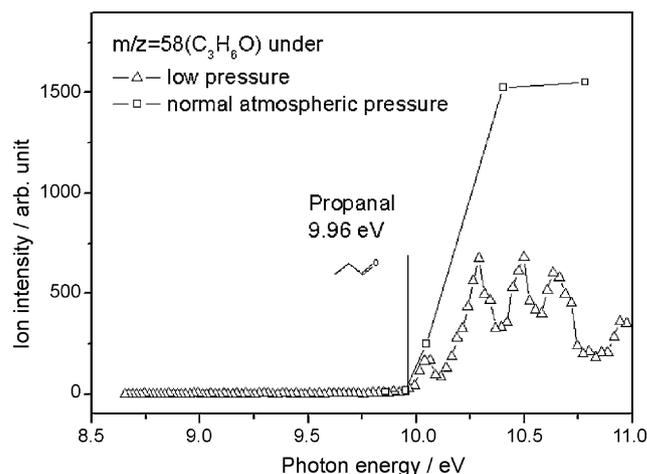
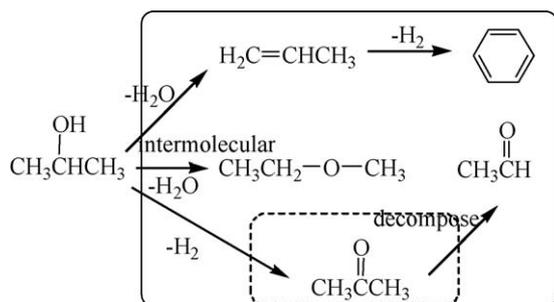


Fig. 4. The PIE spectra for $m/z = 58$ (C₃H₆O) measured in the flow of 1-propanol over Ag/Al₂O₃ catalyst under low pressure at 603 K and normal atmospheric pressure at 523 K.

Table 3

List of the partial oxidation species of 2-propanol identified by their IEs in the flow of 2-propanol over Ag/Al₂O₃ catalyst under low pressure at 603 K and normal atmospheric pressure at 473 K.

m/z	Formula	Low pressure		Normal atmospheric pressure		Species	Ref. [20]
		Measured (± 0.05 eV)	Ion intensity (arb. unit)	Measured (± 0.05 eV)	Ion intensity (arb. unit)		
42	C ₃ H ₆	9.73	21.34	–	–	Propene	9.73 \pm 0.01
44	C ₂ H ₄ O	10.21	2.78	–	–	Acetaldehyde	10.21 \pm 0.01
58	C ₃ H ₆ O	9.69	74.21	9.70	100.00	Acetone	9.69 \pm 0.01
60	C ₃ H ₈ O	9.7	0.93	–	–	Methylethyl ether	9.6 \pm 0.1
78	C ₆ H ₆	9.21	0.74	–	–	Benzene	9.2 \pm 0.1



Scheme 3. Possible formation pathways of the 2-propanol partial oxidation intermediates over Ag/Al₂O₃ catalyst under low pressure at 603 K (solid frame) and normal atmospheric pressure at 473 K (dotted frame).

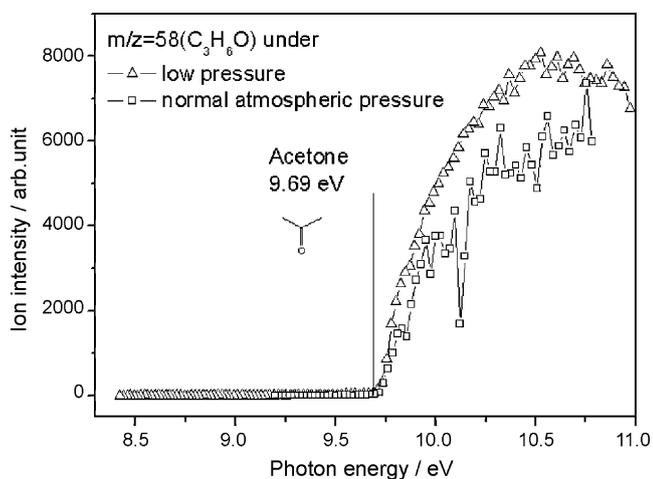


Fig. 5. The PIE spectra for $m/z = 58$ (C₃H₆O) measured in the flow of 2-propanol over Ag/Al₂O₃ catalyst under low pressure at 603 K and normal atmospheric pressure at 473 K.

explained by the dehydration of the adsorbed 2-propanol over Ag/Al₂O₃ catalyst, which is another main reaction pathway of the partial oxidation of 2-propanol on Ag/Al₂O₃ catalyst under low pressure. Subsequently, trace amounts of benzene are formed by further dehydrogenation and condensation of propene. It is also supposed that methylethyl ether is formed by the intermolecular dehydration and decomposition of 2-propanol. Further decomposition may produce acetaldehyde.

Based on these results, it is noteworthy that the pressure has a significant effect on the formation pathway of the partial oxidation products of 1-propanol and 2-propanol over Ag/Al₂O₃ catalyst. Low pressure conditions favor the dehydration and dehydrogenation of 1-propanol and 2-propanol over the Ag/Al₂O₃ catalyst. In contrast, normal atmospheric pressure conditions favor the partial oxidation of 1-propanol and 2-propanol. In addition, low pressure conditions favor observation of active intermediates such as propenal.

4. Conclusions

Synchrotron VUV photoionization mass spectrometry combined with a molecular-beam sampling technique has been used to study the partial catalytic oxidation of volatile organic compounds (ethanol, 1-propanol and 2-propanol) over Ag/Al₂O₃ catalyst under low pressure and normal atmospheric pressure conditions. It was found that the pressure has a significant effect on the reaction pathways for the partial oxidation of the VOCs. Low pressure conditions favor the dehydration and dehydrogenation of VOCs over the Ag/Al₂O₃ catalyst, and normal atmospheric pressure conditions favor the further partial oxidation of the VOCs. In addition, ethenol, ketene and propenal can be unambiguously identified as active reaction intermediates under low pressure conditions. For the oxidation of ethanol, the formation of ethenol is a key step during the catalytic oxidation of C₂H₅OH on the Ag/Al₂O₃ catalyst under both low pressure and normal atmospheric pressure conditions.

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