Mechanism of selective catalytic oxidation of ammonia to nitrogen over Ag/Al$_2$O$_3$

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ABSTRACT

The mechanism of selective catalytic oxidation (SCO) of NH$_3$ over Ag/Al$_2$O$_3$ was studied by NH$_3$ temperature-programed oxidation, O$_2$-pulse adsorption, and in situ DRIFTS of NH$_3$ adsorption and oxidation. The essence which affects the low temperature activity of Ag/Al$_2$O$_3$ has been elucidated through the mechanism study. Different Ag species on Ag/Al$_2$O$_3$ significantly influence O$_2$ uptake by catalysts; while different oxygen species affect the activity of NH$_3$ oxidation at low temperature. The activated –NH could react with the atomic oxygen (O) at low temperatures (<140 °C); however, the –NH could also interact with the O$_2$ at temperatures above 140 °C. At low temperatures (<140 °C), NH$_3$ oxidation follows the –NH mechanism. However, at temperatures above 140 °C, NH$_3$ oxidation follows an in situ selective catalytic reduction (iSCR) mechanism (two-step formation of N$_2$ via the reduction of an in situ-produced NO$_x$ species by a NH$_x$ species).

1. Introduction

Selective catalytic oxidation (SCO) of ammonia (NH$_3$) with O$_2$ to nitrogen gas (N$_2$) and H$_2$O at low temperatures is an efficient method to abate NH$_3$ pollution. This SCO reaction has two important parameters: the selectivity and the application temperature. To rationally develop a process for NH$_3$ oxidation to N$_2$ over catalysts, the reaction mechanism must be clarified.

While several studies have examined the SCO process, the mechanism of NH$_3$ oxidation and N$_2$ formation is still uncertain. Three major reaction pathways have been proposed for the SCO of NH$_3$ to N$_2$ over different catalysts [1–13]. Zawadzki [1] proposed an imide (NH) mechanism in which the first step yields NH, and then the NH reacts with atomic oxygen (O) to form nitroxyl (HNO) and further conversion to N$_2$ or nitrous oxide (N$_2$O), or NH could even react with molecular O$_2$ to produce nitric oxide (NO). This mechanism was mainly supported by the results obtained on Pt or transition metal oxide catalysts [1–5]. Two other insights into the reaction mechanism of NH$_3$ oxidation have been proposed in recent years [6–13]. One is the SCO by a direct route involving a hydrazinium-type intermediate [7,8]. This mechanism has been reported mainly on the transition metal oxide catalysts such as CuO/Al$_2$O$_3$, Fe$_2$O$_3$/TiO$_2$, CrO$_x$/TiO$_2$, CoO$_x$/TiO$_2$, and CuO/TiO$_2$ [7,8]. The other is a two-step mechanism called in situ or "internal" selective catalytic reduction (iSCR), which involves the oxidation of a significant percentage of NH$_3$ into NO$_x$ species, and

the NO$_x$ species subsequently react with NH$_3$ to form N$_2$ [9–11]. Many noble metal catalysts, such as Ag (powder), Pt, Pt/Al$_2$O$_3$, Rh/Al$_2$O$_3$, Pd/Al$_2$O$_3$, Pt-ZSM-5, Pd-ZSM-5, and Rh-ZSM-5, have been suggested to follow this iSCR route [9–11].

Different reaction mechanisms of NH$_3$ oxidation are reportedly associated with different oxygen species [1,7,14–16]. Zawadzki [1] proposed that O was necessary for the very rapid formation of NH, as well as for the HNO intermediate and N$_2$O production. The hydrazinium-type intermediate mechanism had been suggested under conditions of little or limited O$_2$ availability; the only oxygen available was that associated with the metal oxide catalysts, and the catalyst testing was carried out in an essentially reducing environment. At higher O$_2$ concentrations, NH$_3$ mainly interacts with molecular O$_2$ and follows the iSCR mechanism [7,14].

Recently, Gang et al. [11,13] reported that alumina-supported Ag (Ag/Al$_2$O$_3$) catalysts were extremely active in NH$_3$ oxidation at low temperatures, and the performance of the Ag/Al$_2$O$_3$ catalyst was even superior to that of noble metal catalysts. We investigated the role of Ag species on Ag/Al$_2$O$_3$ in the activity and selectivity of NH$_3$ oxidation [17]. The state of the Ag species and Ag particle size was found to significantly influence the activity and selectivity of NH$_3$ oxidation over Ag/Al$_2$O$_3$. Ag^0 was proposed to be the main active species of NH$_3$ oxidation at low temperatures (<140 °C), whereas Ag$^+$ was also active at higher temperatures (>140 °C).

Gang et al. [11,13] revealed that the NH$_3$ oxidation over the Ag-based catalysts followed the iSCR mechanism. They reported that the NH$_3$ oxidation activity at low temperatures was related to the catalyst's ability to promote dissociative or non-dissociative adsorption of O$_2$ [11]. However, the roles of different oxygen

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species in the activity and the reaction mechanism over the Ag/Al_2O_3 have not been studied in detail. The role of different oxygen species in the activity and reaction mechanism of NH_3 oxidation over Ag/Al_2O_3 needs to be determined. Since the active species on Ag/Al_2O_3 for NH_3 oxidation are different in different temperature regions [17], investigating the role of different Ag species in the reaction process is important. Such information may be useful in the development of an improved process of NH_3 oxidation over Ag/Al_2O_3.

In this study, the role of different oxygen species in the activity and reaction mechanism of SCO of NH_3 over Ag/Al_2O_3 was studied in detail. O_2-pulse adsorption was used to measure the O_2 uptake on Ag/Al_2O_3. Temperature-programed oxidation (TPO) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were used to clarify the possible reaction mechanisms.

In this article, we have elucidated the essence which affects the low temperature activity of Ag/Al_2O_3 through the mechanism study. Different Ag species significantly influence O_2 uptake by catalysts, and different oxygen species affect low temperature activity and reaction routes. Adsorbed NH_3 mainly interacts with chemisorbed oxygen atom on Ag/Al_2O_3 at low temperatures (<140 °C). In contrast, at temperatures above 140 °C, adsorbed NH_3 can also react with gas phase O_2 to produce N_2. Accordingly, the reaction route of NH_3 oxidation over Ag/Al_2O_3 is different in different temperature regions. At low temperatures (<140 °C), NH_3 oxidation follows the –NH mechanism, while at temperatures above 140 °C, it follows the iSCR mechanism.

2. Materials and methods

2.1. Catalyst preparation

The catalyst used in this study was 10 wt.% Ag/Al_2O_3 prepared by an impregnation method using γ-Al_2O_3 powder (250 m^2 g^{-1}) and an appropriate amount of $AgNO_3$ (7.874 mg cm^{-3}) aqueous solution. After impregnation, the excess water was removed in a rotary evaporator at 80 °C. The sample was first dried at 120 °C overnight followed by calcination at 600 °C in air for 3 h. The weight ratio of Ag is measured with respect to the support γ-Al_2O_3.

2.2. NH_3 temperature-programed oxidation (NH_3-TPO)

NH_3 temperature-programed oxidation (NH_3-TPO) experiments were carried out over fresh and H_2-pretreated Ag/Al_2O_3 catalysts using a fixed-bed continuous flow micro-reactor system equipped with a computer-interfaced quadruple mass spectrometer (Hiden WR13012 UK). Typically, 100 mg of sample was pretreated by heating in a flowing stream (40 cm^3 min^{-1}) of O_2/He (10 vol.%) from room temperature to 500 °C (25 °C min^{-1}). This was done to remove the water and desorb unwanted impurities. The temperature was held at 500 °C for 0.5 h and then cooled to room temperature under flowing gas (O_2/He). Prior to the NH_3 oxidation, the catalyst was reduced in situ by heating from room temperature to 400 °C (10 °C min^{-1}) in a H_2/Ar (5 vol.%) flow (40 cm^3 min^{-1}). Subsequently, the sample was kept at this temperature for 2 h; the temperature was then lowered to 50 °C, followed by a He flushing period for 1 h. At 50 °C, the He flow was switched to a flow of NH_3 500 ppm, O_2 10 vol.%, He as carrier for 2 h, and the total flow rate was 100 cm^3 min^{-1}. Then the sample temperature was increased from 50 °C to 500 °C at a rate of 10 °C min^{-1} and the TPO data were recorded with mass spectrometer. A similar experiment, without the H_2 pretreatment prior to the NH_3-TPO, was also performed over fresh Ag/Al_2O_3.

2.3. O_2-pulse adsorption

O_2 uptake was determined by O_2-pulse adsorption at various temperatures over the fresh and H_2-pretreated Ag/Al_2O_3 catalysts using a Quantasorb-18 automatic instrument (Quanta Chrome Instrument Co.). Prior to the O_2-pulse adsorption, 300 mg of sample was pretreated in situ with a flow of 5 vol.% H_2/Ar (40 cm^3 min^{-1}, 10 °C min^{-1}) at 400 °C for 2 h. Then, He gas (40 cm^3 min^{-1}) was passed over the sample for 1.5 h. After cooling to the desired temperature in He, O_2 pulses (4.46 μmol) were then injected in a He carrier over the sample, with a time interval between O_2 pulses of almost 100 s. The O_2 signal was analyzed online with an Autosorb-1-C TCD controller. A similar O_2-pulse adsorption experiment was performed over the fresh Ag/Al_2O_3, without the H_2 pretreatment prior to the O_2-pulse adsorption.

2.4. Fourier transform infrared (FTIR) spectroscopy studies

In situ DRIFTS spectra were recorded in a NEXUS 670-FTIR equipped with a smart collector and a liquid N_2-cooled MCT detector. The sample (about 30 mg) for study was finely ground and placed in a ceramic crucible. A feed gas mixture, controlled by mass flow meters, was supplied at a flow rate of 100 cm^3 min^{-1}. The wafers were first treated at 500 °C in a flow of high purity 10 vol.% O_2/N_2 for 0.5 h and then cooled to room temperature. At each temperature, the background spectrum was recorded in flowing N_2 and was subtracted from the sample spectrum obtained at the same temperature. All spectra were recorded at a resolution of 4 cm^{-1} with 100 accumulated scans.

The isotope experiment was performed in an IR cell, which was connected to a vacuum system, and it could be kept below 10^{-4} Torr by the pump. In this paper, the spectra are displayed in absorbance.

3. Results

3.1. NH_3-TPO

NH_3-TPO experiments were performed separately on the fresh and H_2-pretreated 10 wt.% Ag/Al_2O_3 catalysts to investigate the NH_3 oxidation activity over the two catalysts and the variety of products produced in different temperature regions (Fig. 1). NH_3
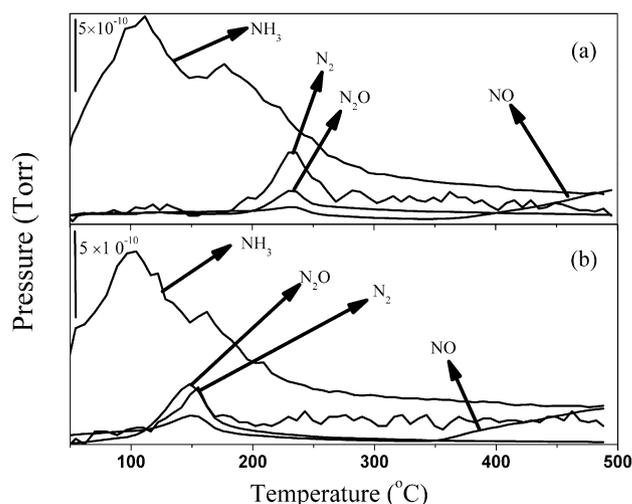

Fig. 1. NH_3 temperature-programed oxidation (NH_3-TPO) profiles over fresh (a) and H_2-pretreated (b) 10 wt.% Ag/Al_2O_3 catalysts. Reaction conditions: NH_3, 500 ppm; O_2, 10 vol.%; He as carrier; flow rate, 100 cm^3 min^{-1}; catalyst weight, 0.1 g (W/F = 0.06 g s cm^{-1}).

desorbed over the fresh Ag/Al_2O_3 (Fig. 1a) at temperatures from 50 °C to 300 °C. No product was formed below 140 °C. Upon heating, N_2 was formed/desorbed as the main product from 160 °C to 500 °C; N_2O was the second main product detected in the temperature range (160–350 °C), while at higher temperatures (>350 °C), significant amounts of NO were formed/desorbed. However, over the H_2-pretreated Ag/Al_2O_3 (Fig. 1b), NH_3 desorbed mainly at low temperatures (<160 °C). The selectivity of products of NH_3–TPO strongly depended on the reaction temperature. N_2O and N_2 were the main products detected in the low temperature range (80–160 °C); N_2 was found to be the main reaction product at temperatures above 160 °C, while at higher temperatures (>350 °C), significant amounts of NO were formed.

Compared to the fresh Ag/Al_2O_3, NH_3 could be oxidized at a lower temperature (<140 °C) over the H_2-pretreated Ag/Al_2O_3. Most products of NH_3 oxidation at low temperatures were N_2O and N_2. However, at higher temperatures, the main products of NH_3 oxidization over the fresh and H_2-pretreated Ag/Al_2O_3 catalysts were similar. This demonstrates that H_2 pretreatment enhances the low temperature activity of NH_3 oxidation over Ag/Al_2O_3 and that the low temperature (<140 °C) products are different from those produced at higher temperatures.

3.2. O_2-pulse adsorption

The effect of the O_2-pulse adsorption on the fresh and H_2-pretreated Ag/Al_2O_3 catalysts was investigated to elucidate the O_2 uptake of the catalysts at 100 °C and 160 °C. As seen in Fig. 2, molecular O_2 was readily chemisorbed on the H_2-pretreated Ag/Al_2O_3; in contrast, little molecular O_2 was adsorbed on the fresh Ag/Al_2O_3.

Gang et al. [11,13] reported that adsorbed oxygen atom appeared on the reduced Ag catalysts, and the dissociation of O_2 was believed to be the rate-controlling step for NH_3 oxidation [13]. Lefferts et al. [18] also detected oxygen atom on a H_2-pretreated Ag surface, and the molecular O_2 was only present for a short time after removing air from the sample. Based on our O_2-pulse adsorption results, we conclude that molecular O_2 can be dissociatively chemisorbed on the surface of H_2-pretreated Ag/Al_2O_3
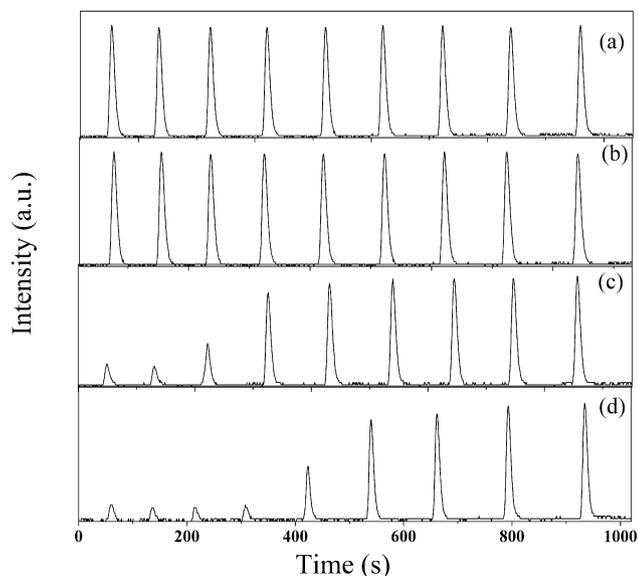

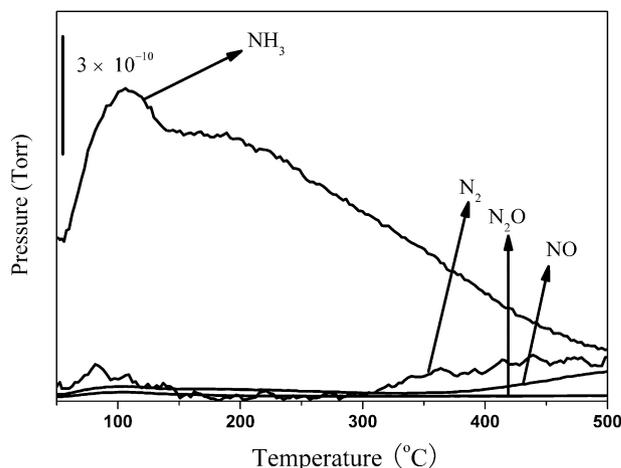**Fig. 3.** NH_3–TPO profiles over the fresh 10 wt.% Ag/Al_2O_3 catalyst, reaction conditions: NH_3, 500 ppm; He as carrier; flow rate, 100 cm³ min⁻¹; catalyst weight, 0.1 g (W/F = 0.06 g s cm⁻¹).

to form O species, while molecular O_2 cannot be adsorbed dissociatively on the surface of fresh Ag/Al_2O_3. In conjunction with our TPO results mentioned above (Fig. 1), we found that the NH_3 could be oxidized at a lower temperature (<140 °C) over the H_2-pretreated Ag/Al_2O_3 in the presence of the chemisorbed oxygen atom. However, over the fresh Ag/Al_2O_3, NH_3 could also be oxidized at higher temperatures in the absence of O. Because the molecular O_2 could not be adsorbed on the fresh catalyst, the adsorbed NH_3 mainly interacted with the gas phase O_2 or the lattice oxygen under these conditions. According to our other TPO experiment over fresh Ag/Al_2O_3 (Fig. 3) in the absence of gaseous O_2 (NH_3–He feed), we found that little product of NH_3 oxidation was formed below 300 °C. The adsorbed NH_3 mainly reacts with the gas phase O_2 over fresh Ag/Al_2O_3 in the presence of gaseous O_2. This demonstrates that the oxygen species have a significant influence on the low temperature (<140 °C) activity of NH_3 oxidation over Ag/Al_2O_3. This means that the dissociation of O_2 is the rate-controlling step for NH_3 oxidation.

Ag^0 is the main Ag species on H_2-pretreated Ag/Al_2O_3, while Ag^+ is the main Ag species on fresh Ag/Al_2O_3 [17]. The presence of different Ag species on the catalyst clearly affects the chemisorption of O_2. The presence of Ag^0 caused the adsorption of O species and must have been a reason for the enhanced low temperature activity of NH_3 oxidation over H_2-pretreated Ag/Al_2O_3.

O_2 uptake of H_2-pretreated Ag/Al_2O_3 at 160 °C (76.58 μmol g⁻¹) was higher than that at 100 °C (45.73 μmol g⁻¹). This demonstrates that the chemisorption of O_2 on Ag/Al_2O_3 is affected by temperature, in agreement with other reports [11,18,19].

3.3. FTIR study of NH_3 adsorption

FTIR spectra of the adsorbed species due to contact with the fresh and H_2-pretreated 10 wt.% Ag/Al_2O_3 catalysts at different temperatures with NH_3 are presented in Figs. 4 and 5. As shown in Fig. 4, after the sample was treated with NH_3 at room temperature, the bands were observed at 1695, 1614, 1483, 1389, and 1232 cm⁻¹. The bands at 1695 and 1483 cm⁻¹ were due to the asymmetric and symmetric deformation modes of NH_3 coordinated on Brønsted acid sites (NH_4^+) [6,20–23], respectively. The band at 1389 cm⁻¹ was observed under similar conditions on Ni/Al_2O_3 by Amblard et al. [6] and on $Au/MO_x/\gamma$-Al_2O_3 by Lin et al. [24]. According to the literature [6,24] and the peak behavior when the sample was heated, the band at 1389 cm⁻¹ could be assigned to NH_4^+ ad-species on the γ-Al_2O_3 support. The bands at 1614 and 1232 cm⁻¹ could be assigned to the asymmetric and symmetric

Fig. 2. O_2 uptakes on fresh 10 wt.% Ag/Al_2O_3 and on H_2-pretreated 10 wt.% Ag/Al_2O_3 at various temperatures. Fresh 10 wt.% Ag/Al_2O_3: 100 °C (a), 160 °C (b); H_2-pretreated 10 wt.% Ag/Al_2O_3: 100 °C (c); 160 °C (d). Reaction conditions: O_2, 4.46 μmol/pulse; He as carrier; flow rate, 40 cm³ min⁻¹; catalyst weight, 0.3 g.
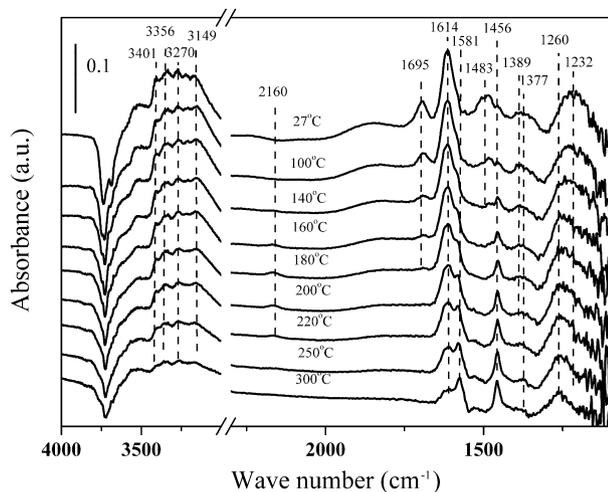
Fig. 4. FTIR spectra of the adsorbed species arising from contact of NH_3 (500 ppm) with the fresh 10 wt.% Ag/Al_2O_3 at room temperature and successive purging with N_2 at various temperatures.
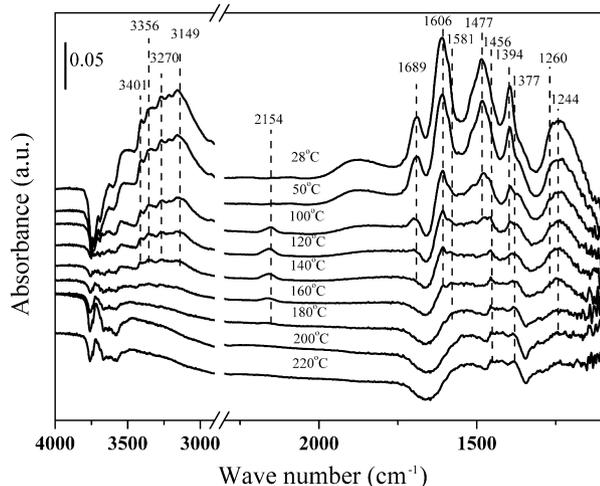

Fig. 5. FTIR spectra of the adsorbed species arising from contact of NH_3 (500 ppm) with the H_2-pretreated 10 wt.% Ag/Al_2O_3 at room temperature and successive purging with N_2 at various temperatures.

deformation modes of NH_3 coordinated on Lewis acid sites [6,20-23], respectively. Correspondingly, the bands in the NH stretching region were also observed at 3401, 3356, 3270, and 3149 cm^{-1} [8,14,25].

The intensities of these bands decreased gradually with the increase in the sample temperature (Fig. 4). Upon heating, first, the bands of NH_3 coordinated on Brønsted acid sites disappeared, followed by the bands ascribed to NH_3 coordinated on Lewis acid sites. This desorption sequence seemed to coincide with the expected adsorption strength of these ad-species. The NH_3 coordinated on Brønsted acid sites was weaker than that coordinated on Lewis acid sites. Desorption of the unreacted NH_3 and the activation of NH_3 were responsible for these decreases. A new weak band was visible at 2160 cm^{-1} from 160 °C to 220 °C, but vanished at temperatures above 220 °C. The assignment of this new peak will be discussed in the following section.

With increasing temperatures, intensities of three bands, 1581, 1456, and 1377 cm^{-1}, increased following the decrease of the bands assignable to NH_3. The bands at 1581 and 1377 cm^{-1} were assigned to amide (–NH_2) scissorings and (–NH_2) waggings,

respectively. The band at 1456 cm^{-1} was ascribed to –NH deformation modes [8,14,24,25]. These results indicate that upon heating, the adsorbed NH_3 can be activated to form –NH_2 and –NH intermediates through abstraction of hydrogen.

$$NH_3 \rightarrow NH_2 + H \tag{1}$$

$$NH_2 \rightarrow NH + H \tag{2}$$

The same experiment was performed on the H_2-pretreated Ag/Al_2O_3 catalyst. Similar bands at 1689, 1606, 1477, 1394, and 1244 cm^{-1} were observed after NH_3 adsorption (Fig. 5). Upon heating, the bands of NH_3 coordinated on Brønsted acid sites disappeared, followed by the bands ascribed to NH_3 coordinated on Lewis acid sites, and finally the band of –NH. A new weak band at 2154 cm^{-1} was observed from 100 °C to 160 °C, which disappeared at temperatures above 160 °C.

The bands at 2222 cm^{-1} are reportedly due to N–N stretching modes of gas phase N_2O over the reduced Ag catalyst [26]. A similar band at 2200 cm^{-1} upon NH_3 oxidation on ZnO has been assigned to adsorbed N_2O [27]. The appearance of more than one form of adsorbed N_2O is often explained by the simultaneous presence of N- and O-bonded molecules and/or by adsorption on different sites. However, the N–O modes of N_2O were not observable in many cases because of the strong bands associated with the substrate. When the N–O modes of adsorbed N_2O were detected, they were registered in the 1262–1220 cm^{-1} region [28]. As shown in Figs. 4 and 5, a band was observable at 1260 cm^{-1}, but it did not disappear synchronously with the band at 2160 cm^{-1}; hence these two bands should not be assigned to one ad-species. The band at 1260 cm^{-1} might be due to the shift in the band of NH_3 coordinated at Lewis acid sites (1244, 1232 cm^{-1}).

To assure the correct assignment of the band (2154, 2160 cm^{-1}), we investigated the interaction of N_2O and Ag/Al_2O_3 (the results are shown in Supplementary material). We found that the bands in the 2150–2300 cm^{-1} region were observable due to the asymmetric N–N–O stretching modes of gas phase N_2O, but they disappeared quickly after purging with N_2 for several minutes. Therefore, the band at 2154 (2160) cm^{-1} should not be assigned to the gas phase N_2O over the Ag/Al_2O_3. Our results suggest that this band (2154, 2160 cm^{-1}) should be assigned to adsorbed N_2O.

Compared to the results on the fresh Ag/Al_2O_3 (Fig. 4), the bands of NH_3 adsorbed on Brønsted and Lewis acid sites of the H_2-pretreated Ag/Al_2O_3 disappeared at lower temperatures. While the intensity of these bands decreased with a reduction in temperature, the bands of –NH_2 (1581, 1377 cm^{-1}) and –NH (1456 cm^{-1}) appeared, indicating that NH_3 adsorbed on H_2-pretreated Ag/Al_2O_3 can be activated to form –NH_2 and –NH intermediates at lower temperatures. Together with our O_2-pulse adsorption results (Fig. 2), this indicates that both adsorbed NH_3 and O_2 can be activated at lower temperatures (<140 °C) on H_2-pretreated Ag/Al_2O_3, which may explain the enhanced low temperature activity of NH_3 oxidation.

3.4. FTIR study of the interaction of NH_3 with O_2

The NH_3 oxidation mechanism was studied with respect to the behavior of adsorbed NH_3 species interacting with O_2 on the surfaces of fresh and H_2-pretreated 10 wt.% Ag/Al_2O_3 catalysts using in situ DRIFTS. Fig. 6 shows the in situ DRIFT spectra of the fresh Ag/Al_2O_3 in a flow of $NH_3 + O_2$ at various temperatures. The bands of NH_3 coordinated on Brønsted acid sites (1691, 1487, 1389 cm^{-1}) disappeared at temperatures above 140 °C. However, the bands coordinated on Lewis acid sites (1614, 1232 cm^{-1}) decreased gradually and vanished at higher temperatures (>220 °C). While these band intensities decreased, the band intensity of –NH (1456 cm^{-1}) increased from 100 °C. Three new bands appeared at
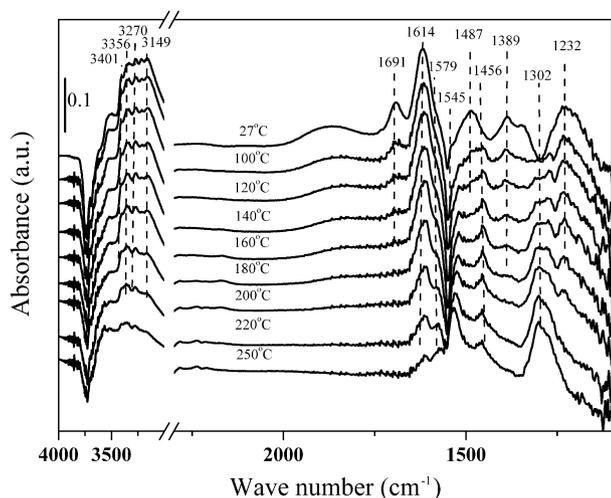
Fig. 6. FTIR spectra of the fresh 10 wt.% Ag/Al$_2$O$_3$ catalyst treated with a flow of 500 ppm NH$_3$ + 10 vol.% O$_2$/N$_2$ at various temperatures.
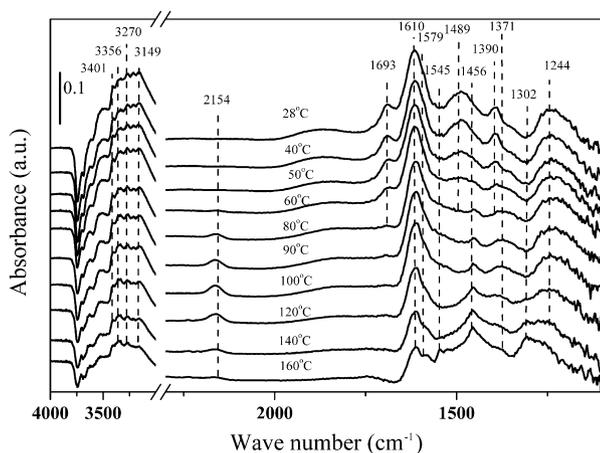

Fig. 7. FTIR spectra of the H$_2$-pretreated 10 wt.% Ag/Al$_2$O$_3$ catalyst treated with a flow of 500 ppm NH$_3$ + 10 vol.% O$_2$/N$_2$ at various temperatures.

1576, 1545, and 1302 cm^{-1} at temperatures above 140 °C and increased significantly with rising temperature. These bands could be assigned to nitrate ad-species [28,29], and the assignments of different nitrates are discussed in a more detailed manner in the following section.

Fig. 7 shows the results of the similar experiment performed on the H$_2$-pretreated Ag/Al$_2$O$_3$. The bands of NH$_3$ coordinated on Brønsted acid sites and Lewis acid sites decreased at a lower temperature in the presence of O$_2$ than without O$_2$ (Fig. 5). The –NH band (1456 cm^{-1}) appeared at 80 °C and increased significantly at temperatures above 140 °C. The band of adsorbed N$_2$O (2154 cm^{-1}) was visible from 80 °C to 140 °C. In addition, it could be noted that the band assigned to nitrate ad-species (1302, 1579 cm^{-1}) appeared at 140 °C. The bands at 1579, 1545,1456, and 1302 cm^{-1} increased significantly when the temperature rose to 160 °C, demonstrating that at higher temperatures (>140 °C) some nitrate ad-species are formed on the H$_2$-pretreated Ag/Al$_2$O$_3$, similar to the results found on the fresh Ag/Al$_2$O$_3$ (Fig. 6). However, on the fresh Ag/Al$_2$O$_3$ (Fig. 6), no N$_2$O (2154 cm^{-1}) ad-species appeared with the –NH band (1456 cm^{-1}) at low temperatures (<140 °C). Based on these findings, together with the TPO results (Fig. 1), we conclude that the adsorbed NH$_3$ could be activated to form –NH and further be converted to produce N$_2$

and N$_2$O on the H$_2$-pretreated Ag/Al$_2$O$_3$ at low temperatures (<140 °C; Fig. 7). In contrast, no adsorbed NH$_3$ was oxidized on the fresh Ag/Al$_2$O$_3$ under this condition, although it could have been activated to form some –NH intermediates (Fig. 6).

The presence of surface –NH indicates the dissociative adsorption of NH$_3$ and/or the presence of H-abstraction on the surface. Our DRIFT results (Fig. 7) showed that at lower temperatures, the bands of adsorbed NH$_3$ were smaller in the presence of O$_2$ than without O$_2$ (Fig. 5). Considering that gas phase O$_2$ can be chemisorbed as oxygen atom on the surface of H$_2$-pretreated Ag/Al$_2$O$_3$, this indicates that the adsorbed NH$_3$ is more readily activated to form –NH in the presence of oxygen atom, confirming the previous reports [1]. The first elementary process in NH$_3$ oxidation on H$_2$-pretreated Ag/Al$_2$O$_3$ is likely the reaction of NH$_3$ with O as follows:

$$NH_3 + O \rightarrow NH + H_2O \tag{3}$$

As shown in Fig. 7, –NH and the adsorbed N$_2$O bands were visible at low temperatures (<140 °C); some nitrate ad-species were observed at temperatures above 140 °C, as seen on the fresh Ag/Al$_2$O$_3$ (Fig. 6). This clearly shows that over the H$_2$-pretreated Ag/Al$_2$O$_3$, –NH is the key intermediate of NH$_3$ oxidation at low temperatures (<140 °C), and the SCO pathway at low temperatures is different from the reaction route at temperatures above 140 °C. In contrast, at temperatures above 140 °C, the SCO of NH$_3$ over fresh and H$_2$-pretreated Ag/Al$_2$O$_3$ catalysts both follow a similar reaction route.

A key role of –NH and –HNO species in NH$_3$ oxidation was proposed by Zawadzki [1] and supported by Germain and Perez [30]. Zawadzki [1] suggested that on Pt or metal oxide catalysts, the –NH could interact with oxygen atom to form –HNO species; then the –NH and –HNO could react with each other giving rise to N$_2$, while two –HNO species would be intermediates in N$_2$O formation. However, we found no band assignable to –HNO (Fig. 7), perhaps because the –HNO reacted quickly.

To discover the –HNO species, the concentration of NH$_3$ was reduced to lower the reaction rate. First, we evacuated the gaseous NH$_3$ after exposure of the H$_2$-pretreated Ag/Al$_2$O$_3$ to NH$_3$ for 1 h to leave the adsorbed NH$_3$ on the surface of the catalyst. A flow of O$_2$ was then supplied at various temperatures, and the subsequent spectra were collected (Fig. 8). Upon heating, –NH$_2$ (1371 cm^{-1}) and –NH (1456 cm^{-1}) appeared at temperatures above 70 °C; a new band was observed at 1529 cm^{-1} from 70 °C to 120 °C (Fig. 8). Similar behavior was observed for adsorbed
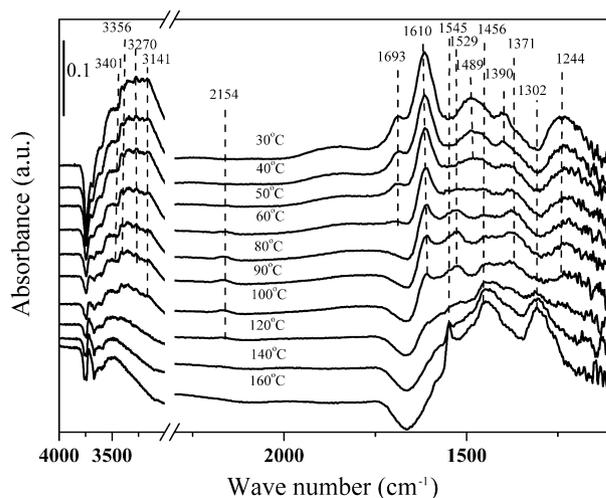

Fig. 8. FTIR spectra of the H$_2$-pretreated 10 wt.% Ag/Al$_2$O$_3$ taken after adsorption of NH$_3$ (500 ppm) at room temperature, followed by purging with N$_2$ for 30 min and successive heating in 10 vol.% O$_2$/N$_2$ at various temperatures.
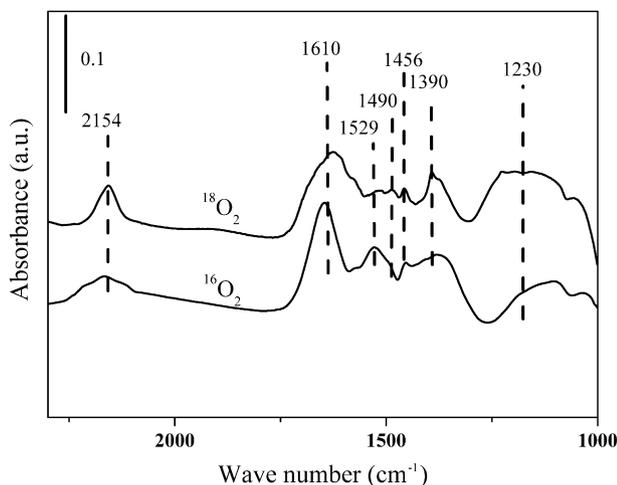
Fig. 9. FTIR spectra of the adsorbed NH_3 interacting with the $^{16}O_2$ and $^{18}O_2$ over H_2-pretreated 10 wt.% Ag/Al_2O_3 at 100 °C (The sample was exposed to 20 Torr NH_3 for 30 min firstly, and then it was out gassed and exposed to 30 Torr O_2).

Fig. 10. FTIR spectra of the adsorbed species arising from NO + O_2 (500 ppm NO, O_2 10 vol.%) adsorption over the H_2-pretreated 10 wt.% Ag/Al_2O_3 at 160 °C (a) and after successive purging with N_2 at 160 °C (b).

N_2O (2154 cm^{-1}) with a band at 1529 cm^{-1}; this band may have been an intermediate in the formation of N_2O, and the peak at around 1529 cm^{-1} was near the reported NO stretching band of –HNO species [7,8,24]. Alternatively, –HNO could be responsible for two bands. The adsorbed –HNO species have been proposed to be responsible for a N=O stretching band in the 1550–1400 cm^{-1} range, and for a –NH bending band in the 1450–1400 cm^{-1} region [7]. Since the two bands (1529, 1456 cm^{-1}) appear at the same time, this explanation is likely.

To help identify the –HNO species, the experiments were also conducted with $^{18}O_2$ and $^{16}O_2$ using FTIR. Fig. 9 illustrates the FTIR spectra obtained after either $^{18}O_2$ or $^{16}O_2$ interacting with the adsorbed NH_3 on the H_2-pretreated Ag/Al_2O_3 catalyst at 100 °C. The band near 1529 cm^{-1} after exposing to $^{16}O_2$ (Fig. 9) was red-shifted to around 1490 cm^{-1} after replacing with the $^{18}O_2$ (Fig. 9), which implies that this band is due to a species containing oxygen.

This implies that –NH may be converted to –HNO ad-species in the presence of O and that these ad-species must be the intermediates in the formation of N_2 and N_2O at low temperatures. At higher temperatures (>140 °C), the bands of –HNO (1529 cm^{-1}) and adsorbed N_2O (2154 cm^{-1}) vanished synchronously, while the bands of nitrates increased. This result indicates that the reaction route of NH_3 oxidation over Ag/Al_2O_3 is different in different temperature regions.

3.5. FTIR study of NO + O_2 adsorption

FTIR spectra of the adsorption of NO in the presence of O_2 on the H_2-pretreated 10 wt.% Ag/Al_2O_3 at 160 °C were observed to investigate the nitrate ad-species on the catalyst, and the results are shown in Fig. 10a. The bands at 1614, 1579, 1545, 1456, and 1302 cm^{-1} were detected. In addition, a weak band at 1750 cm^{-1} was also seen. Based on the previous studies of the NO + O_2 reaction on Al_2O_3 or Ag/Al_2O_3 catalysts, these peaks were tentatively assigned to adsorbed N_2O_4 (1750 cm^{-1}) and monodentate (1545 cm^{-1}), bidentate (1579 cm^{-1}), and bridging (1614 cm^{-1}) nitrates [26,28,31–34]. The bands at 1456 and 1302 cm^{-1} were close to the IR bands at 1411 and 1302 cm^{-1} for adsorbed water-solvated surface nitrates on Al_2O_3 [31]. Since the adsorbed water could be removed from the surface by purging with dry N_2 at 160 °C, band intensity of the water-solvated surface nitrates
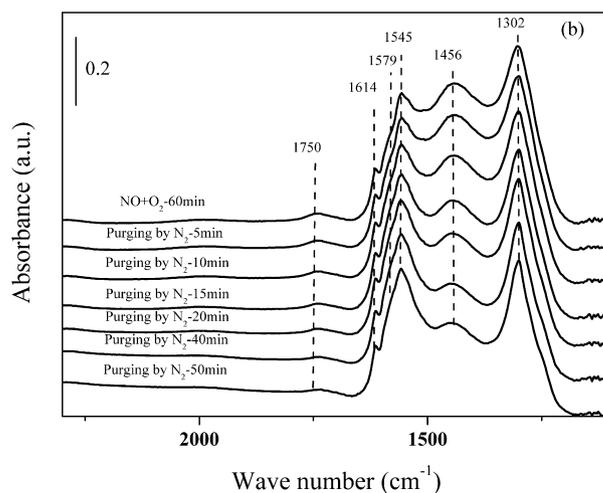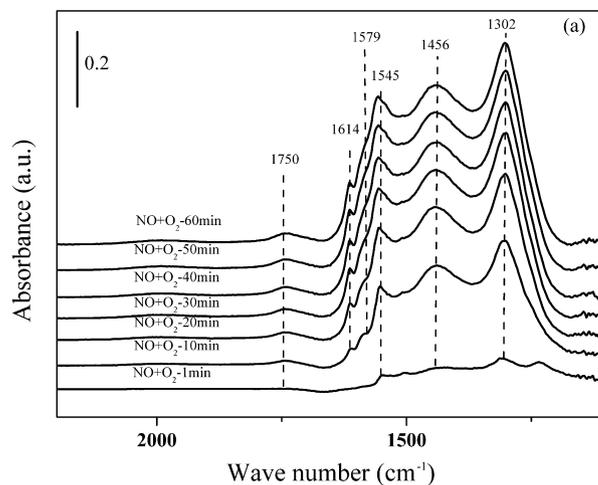
would decrease. According to our results (Fig. 10b), the band at 1456 cm^{-1} decreased significantly after purging with N_2, while the band at 1302 cm^{-1} did not vary in intensity. Therefore, the band at 1456 cm^{-1} should be assigned to adsorbed water-solvated surface nitrate ad-species on Ag/Al_2O_3. In addition, it could be noted that this band at 1456 cm^{-1} was in the same region as the –NH band. As shown in Fig. 7, –NH appeared at a lower temperature (80 °C) after NH_3 activation, while the water-solvated surface nitrate ad-species were visible at a higher temperature (160 °C) going with other nitrate ad-species; therefore, they should be assigned to different ad-species at different temperatures. The band at 1302 cm^{-1} was also close to that of bidentate nitrate on Ag/Al_2O_3 [32,33]; thus we are inclined to assign this band to bidentate nitrate.

According to our FTIR spectra results on NH_3 oxidation (Figs. 6 and 7), the bands assignable to nitrate ad-species (1614, 1579, 1545, 1456, and 1302 cm^{-1}) appeared in the same regions as NO + O_2 ad-species. This result indicates that adsorbed NH_3 could be oxidized to form NO and adsorbed as nitrate ad-species on the catalysts in the presence of O_2.

It could be noted that a band (1614 cm^{-1}) of bridging nitrates was located at the same position as the asymmetric deformation modes of NH_3 coordinated on the Lewis acid sites, which may explain the appearance of this peak at higher temperatures while the
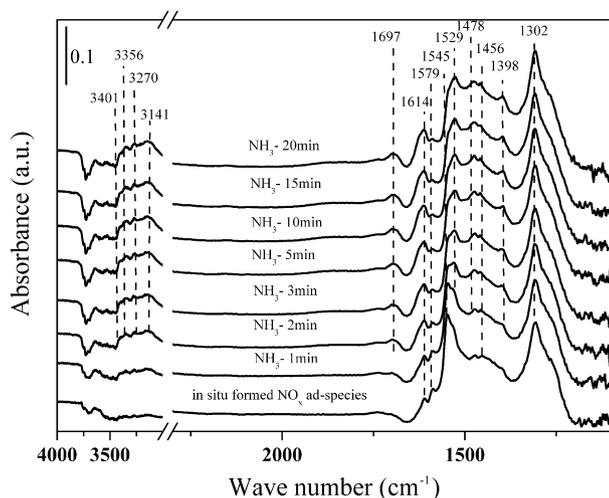
Fig. 11. FTIR spectra of the surface species arising from the interaction of NH$_3$ (500 ppm) with the in situ-formed NO$_x$ on the H$_2$-pretreated 10 wt.% Ag/Al$_2$O$_3$ at 160 °C.

other bands (1232, 1244 cm^{-1}) of NH$_3$ coordinated on the Lewis acid site disappeared (Figs. 6 and 7).

3.6. Interaction of NH$_3$ with the in situ-formed NO$_x$

To elucidate the reaction pathway, the interaction of NH$_3$ with the in situ-formed NO$_x$ species was investigated as follows: first, NO$_x$ ad-species were formed in situ on the H$_2$-pretreated Ag/ Al$_2$O$_3$ by exposing the catalyst to NH$_3$ and O$_2$ at 160 °C for 1 h. Then the sample was purged with N$_2$ at this temperature for 0.5 h. Finally, 500 ppm of NH$_3$ was introduced when the in situ DRIFTS spectra were recorded. As shown in Fig. 11, the bands attributable to nitrate ad-species (1614, 1579, 1545, 1456, 1302 cm^{-1}) were observed after exposing the Ag/Al$_2$O$_3$ to NH$_3$ and O$_2$ at 160 °C for a brief period. Following NH$_3$ inflow for 1 min, the monodentate nitrate band (1545 cm^{-1}) vanished, indicating that NH$_3$ reacted with the NO$_x$ ad-species quickly. However, the intensity of the bands (1579, 1302 cm^{-1}) attributable to bidentate nitrates only decreased slightly during this period. Therefore, we conclude that NO$_x$ adsorbed as monodentate nitrate reacted more favorably with NH$_x$ compared to the other nitrate ad-species. This result clearly indicates that the SCO of NH$_3$ on the H$_2$-pretreated Ag/Al$_2$O$_3$ at this temperature follows an iSCR mechanism, which involves the oxidation of a significant percentage of NH$_3$ into NO$_x$ species, along with adsorbed NO$_x$ species interacting with NH$_x$ and being reduced to N$_2$ with N$_2$O as a by-product. The in situ-formed NO is the intermediate of this iSCR mechanism.

The bands assignable to NH$_3$ ad-species (1697, 1614, 1478, and 1398 cm^{-1}) appeared on Ag/Al$_2$O$_3$ following NH$_3$ inflow, as shown in Fig. 11. Their intensity increased with the exposure time. However, the bands at 1529 and 1456 cm^{-1} assignable to –HNO species increased at the same time. Together with our results mentioned above, this indicates that the adsorbed –NH might have interacted with the previously adsorbed surface O to form –HNO species under this condition.

4. Discussion

4.1. NH$_3$ adsorption

As shown in Figs. 4 and 5, with the adsorption of NH$_3$ and an increase in temperature, –NH$_2$ and –NH intermediates appeared and

the bands assignable to adsorbed N$_2$O (2160, 2154 cm^{-1}) were observed in the absence of O$_2$. Other studies have found that in the absence of O$_2$, activated –NH could also interact with lattice oxygen (O^{2-}) to produce a small quantity of N$_2$O [7,8,14]. Our results (Figs. 4 and 5) demonstrate that in the absence of O$_2$, NH$_3$ can dehydrogenate to form –NH$_2$ and –NH intermediates and produce some products; however, this kind of reaction would not be sustainable under O$_2$-free conditions and will not be discussed here in detail.

Based on the in situ DRIFTS results of NH$_3$ oxidation (Fig. 6) on the surface of fresh Ag/Al$_2$O$_3$, the bands of NH$_3$ coordinated on Brønsted acid sites disappeared at 140 °C, while the bands coordinated on Lewis acid sites decreased gradually at higher temperatures. However, our NH$_3$-TPO (Fig. 1) and in situ DRIFTS (Fig. 6) results showed that over the fresh catalyst, the adsorbed NH$_3$ could hardly be oxidized at low temperatures (<140 °C). Therefore, the NH$_3$ coordinated on Brønsted acid sites had no influence on the activity; only the NH$_3$ coordinated on Lewis acid sites contributed to this reaction activity. A similar result was found on the H$_2$-pretreated Ag/Al$_2$O$_3$ (Fig. 7). These results indicate that Brønsted acid sites are not necessary for NH$_3$ oxidation, in agreement with the previous findings in the literature [7,8,14].

4.2. Interaction of NH$_3$ with O$_2$
4.2.1. Interaction of NH$_3$ with O$_2$ at low temperatures (<140 °C)

It has been (Figs. 7 and 8) demonstrated that the reaction pathway at low temperatures (<140 °C) over H$_2$-pretreated Ag/Al$_2$O$_3$ is totally different from the route at temperatures above 140 °C. Oxygen atom has been found to be chemisorbed on the surface of H$_2$-pretreated Ag/Al$_2$O$_3$, and it is more active than the gaseous O$_2$ or lattice oxygen (O^{2-}). At low temperatures (<140 °C), O reacts more favorably with –NH to form –HNO intermediates (Fig. 8). The –NH and –HNO are the key intermediates of the –NH mechanism. Zawadzki [1] previously proposed the –NH mechanism, but provided no evidence of the –NH and –HNO intermediates or O$_2$ chemisorption. Since both the O$_2$ chemisorption and the intermediates of – NH and –HNO were detected in our experiments, we are inclined to attribute the low temperature reaction pathway of NH$_3$ oxidation over Ag/Al$_2$O$_3$ to the –NH mechanism. The main reaction routes at low temperatures (<140 °C) are as follows:

$$O_2 \rightarrow 2O \tag{4}$$
$$NH + O \rightarrow HNO \tag{5}$$
$$NH + HNO \rightarrow N_2 + H_2O \tag{6}$$
$$HNO + HNO \rightarrow N_2O + H_2O \tag{7}$$

4.2.2. Interaction of NH$_3$ with O$_2$ at high temperatures (>140 °C)

At higher temperatures (>140 °C), NH$_3$ oxidation over H$_2$-pretreated Ag/Al$_2$O$_3$ does not follow the –NH mechanism (Figs. 7 and 8) mentioned above. Under this condition (>140 °C), the interaction of NH$_3$ with O$_2$ caused the formation of NO$_x$ ad-species on the Ag/Al$_2$O$_3$, and the in situ-formed NO$_x$ species could react quickly with NH$_3$ following NH$_3$ inflow (Fig. 11). Ramis et al. [14] proposed an SCR route; i.e., in the presence of NO, the –NH$_2$ would react with NO to produce N$_2$, and –NH would react with NO to produce N$_2$O as a by-product. Zawadzki [1] also suggested that –NH would react with molecular O$_2$ to produce NO at higher temperatures, but the author did not propose the in situ reaction between the NO and –NH$_x$. Since the key intermediate (NO$_x$) of the SCR routes proposed by Ramis et al. [8,14,35–38] was detected in our experiment (Figs. 6 and 7), and the NH$_3$ could rapidly react with the in situ-formed NO$_x$ ad-species (Fig. 11), we are inclined to accept that the NH$_3$ oxidation over Ag/Al$_2$O$_3$ at higher temperatures (>140 °C) follows the iSCR mechanism. The reaction pathways are as follows:

$$NH + O_2 \rightarrow NO + OH \tag{8}$$

$$NH_2 + NO \rightarrow N_2 + H_2O \tag{9}$$

$$NH + NO \rightarrow N_2O + H \tag{10}$$

$$H + OH \rightarrow H_2O \tag{11}$$

A possible role of molecular O_2 in NH_3 oxidation to produce NO_x has also been proposed in the literature [1,8] but may require higher temperatures compared to the interaction of NH_3 with oxygen atom, which is in agreement with our above-mentioned results.

We found that O_2 could also be adsorbed dissociatively to form surface oxygen atom on H_2-pretreated Ag/Al_2O_3 at higher temperatures (160 °C; Fig. 2), and the coverage of active oxygen species increases with an increase of temperature up to160 °C. Fig. 8 shows that the adsorbed NH_3 could be quickly activated to form –NH intermediates via reaction (3) in the presence of oxygen atom. However, at higher temperatures (>140 °C), the –NH mainly interacted with the oxygen species to form NO intermediates (Fig. 8). This demonstrates that the increase of the ratio (O/NH) favors the formation of NO at higher temperatures. We could infer that the adsorbed NH_3 interacted with oxygen atom and gaseous O_2 at the same time over H_2-pretreated Ag/Al_2O_3 at higher temperatures (>140 °C). Firstly, the oxygen atom activated the adsorbed NH_3 to form –NH intermediates, and then the formed –NH interacted with the oxygen atom or gaseous O_2 to produce NO_x ad-species under this condition. However, at low temperatures (<140 °C), the adsorbed NH_3 mainly interacts with oxygen atom. This may explain the different reaction mechanisms of NH_3 oxidation over H_2-pretreated Ag/Al_2O_3 at low temperatures (<140 °C) and at temperatures above 140 °C.

It could be noted that at temperatures above 350 °C (Fig. 1) a significant amount of NO desorbed/formed over the Ag/Al_2O_3, primarily because at higher temperatures (>350 °C), the in situ-formed NO_x could directly desorb as one of the products.

Ag^0 has been proposed as the main active species on the Ag/Al_2O_3 in the oxidation of NH_3 at low temperatures (<140 °C), while Ag^+ could also be the active species at temperatures above 140 °C [17]. In this study, we found that both adsorbed NH_3 and O_2 could be activated by Ag^0, which explains the enhanced low temperature activity. However, the role of Ag^+ on the Ag/Al_2O_3 in NH_3 oxidation is only to activate the adsorbed NH_3.

5. Conclusions

Chemisorbed oxygen atom enhances the low temperature (<140 °C) activity of NH_3 oxidation over Ag/Al_2O_3; in contrast, gas phase O_2 mainly interacts with adsorbed NH_3 at temperatures above 140 °C. The pathway of NH_3 oxidation over Ag/Al_2O_3 at low temperatures (<140 °C) differs from that at temperatures above 140 °C. At low temperatures (<140 °C), NH_3 oxidation follows the –NH mechanism. That is, the adsorbed NH_3 first reacts with oxygen atom to form a –NH intermediate. Then the –NH interacts with the chemisorbed oxygen atom to form a –HNO intermediate. The interaction of –NH and –HNO would produce N_2 and H_2O directly, while two –HNO would interact to form a N_2O by-product. At temperatures above 140 °C, the SCO of NH_3 follows an iSCR mechanism. That is, the –NH mainly reacts with molecular O_2 to form NO. Then, the in situ-formed NO interacts with the NH_x and is reduced to N_2, with N_2O as a by-product.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2009.08.011.

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