

CeO₂添加对Ag/Al₂O₃催化剂低温氨氧化性能的影响

张 丽, 刘福东, 余运波, 刘永春, 张长斌, 贺 泓

摘要: 采用活性测试和氮气吸附、X射线衍射、X射线光电子能谱、紫外-可见漫反射吸收光谱、高倍透射电镜、原位漫反射傅里叶变换红外光谱和O₂脉冲吸附等研究了铈添加对Ag/Al₂O₃催化剂低温氨氧化性能的影响。结果表明, 适量铈的添加可以明显促进Ag/Al₂O₃催化剂的低温氨氧化活性, 且对催化剂的选择性影响不大。添加铈不仅可以促进Ag/Al₂O₃催化剂表面吸附和活化O₂的能力, 而且可促进催化剂表面吸附氨的解离吸附和活化。这是铈促进Ag/Al₂O₃催化剂低温氨氧化活性的主要原因。

关键词: 氨; 银; 铈; 氧化铝; 负载型催化剂; 氧气吸附; 高倍透射电镜; 原位漫反射傅里叶变换红外光谱

Abstract: The effects of adding CeO₂ to Ag/Al₂O₃ on the selective catalytic oxidation of ammonia to nitrogen were investigated by activity test and N₂ physisorption, X-ray diffraction, X-ray photoelectron spectroscopy, UV-Vis diffuse-reflectance spectroscopy, high resolution transmission electron microscopy, in situ diffuse reflectance infrared Fourier transform spectroscopy of NH₃ adsorption, and O₂-pulse adsorption. Adding a suitable amount of CeO₂ improved the catalytic activity of Ag/Al₂O₃ for NH₃ oxidation at temperatures below 160 °C, and slightly influenced N₂ selectivity by improving the catalyst’s ability to adsorb and activate O₂ and the adsorption and activation of NH₃.

Key words: ammonia; silver; cerium; alumina oxide; supported catalyst; oxygen uptake; high resolution transmission electron microscopy; in situ diffuse reflectance infrared Fourier transform spectroscopy

Effects of Adding CeO₂ to Ag/Al₂O₃ Catalyst for Ammonia Oxidation at Low Temperatures

ZHANG Li, LIU Fudong, YU Yunbo, LIU Yongchun, ZHANG Changbin, HE Hong

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Abstract: The effects of adding CeO₂ to Ag/Al₂O₃ on the selective catalytic oxidation of ammonia to nitrogen were investigated by activity test and N₂ physisorption, X-ray diffraction, X-ray photoelectron spectroscopy, UV-Vis diffuse-reflectance spectroscopy, high resolution transmission electron microscopy, in situ diffuse reflectance infrared Fourier transform spectroscopy of NH₃ adsorption, and O₂-pulse adsorption. Adding a suitable amount of CeO₂ improved the catalytic activity of Ag/Al₂O₃ for NH₃ oxidation at temperatures below 160 °C, and slightly influenced N₂ selectivity by improving the catalyst’s ability to adsorb and activate O₂ and the adsorption and activation of NH₃.

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The selective catalytic oxidation (SCO) of NH₃ to nitrogen (N₂) and water can reduce NH₃ emissions from chemical processes such as the selective catalytic reduction (SCR) of NOₓ by NH₃ and from soda production [1–5]. In particu-
lar, the low temperature oxidation of NH₃ to N₂ has important environmental applications. Noble metals such as Pt and Ir are the most active but least selective [5–7]. Gang et al. [6,8] reported that an alumina-supported Ag (10 wt% Ag/Al₂O₃) catalyst was extremely active for NH₃ oxidation at low temperatures, and was superior to the noble metals. Nonetheless, there is still a considerable need for better catalysts that are active at low temperatures. The addition of CeO₂ improves the NH₃ oxidation activities of Au-, Cu-, and Ag-based catalysts [2,3]. Lippits et al. [3] found that adding CeO₂ to Ag-based catalyst lowered the temperature for the onset of oxidation from 300 to 200 °C. However, the role of CeO₂ in the Ag-based catalyst has not been studied in detail. Recently, we investigated the SCO of NH₃ over a 10 wt% Ag/Al₂O₃ catalyst and discovered that the Ag valence state and particle size were significant for activity and N₂ selectivity at low temperatures [7]. To further improve the catalytic performance at low temperatures, we investigated the catalytic effects and the role of CeO₂ addition on Ag/Al₂O₃ for the oxidation of NH₃.

1 Experimental

1.1 Catalyst preparation and H₂-pretreatment

The Ag-Ce/Al₂O₃ catalysts used had different Ce loadings and were prepared by co-impregnating γ-Al₂O₃ powder (250 m²/g) with appropriate amounts of AgNO₃ and Ce(NO₃)₃·6H₂O in aqueous solution. After impregnation, excess water was removed in a rotary evaporator at 80 °C and the samples were dried overnight at 120 °C before calcination at 600 °C in air for 3 h. The mass ratio of Ag to γ-Al₂O₃ was maintained at 0.1 and the resulting Ag-Ce/Al₂O₃ samples were designated as AgₓCeᵧ/Al₂O₃, where γ was the Ce/Al₂O₃ mass ratio. The catalysts were sieved to a particle size of 20–40 mesh and pretreated in a H₂/N₂ flow (20 vol% H₂, 60 cm³/min) at 400 °C for 2 h before testing.

1.2 Activity test

1.2.1 Steady state activity for NH₃ oxidation

The SCO activity was measured in a fixed-bed quartz reactor using 0.2 g catalyst. The reactant gas was obtained from blends of different gas flows at a combined flow rate of 200 cm³/min (W/F = 0.06 (g·s)/cm³). A typical reactant gas composition was 0.05 vol% NH₃ and 10 vol% O₂, with N₂ providing the balance. The individual NH₃, O₂, and N₂ flow rates were controlled by mass flow controllers. Inlet and outlet gas compositions were analyzed using an online NEXUS 670-FTIR spectrometer fitted with a 200 cm³ gas cell. N₂ balance was calculated using M_NH₃ (inlet) = M_NH₃ (outlet) + 2M_N₂O + M_N₂O + 2M_N₂. These operating conditions were used as the standard.

1.2.2 Evolution of NH₃ oxidation with time at various temperatures

A H₂-pretreated Ag₀.₁Ce₀.₁/Al₂O₃ catalyst was fed with the reactant mixture and kept at temperatures of 100 and 160 °C, respectively, to evaluate the activity of the catalyst under these different conditions. The evolution of NH₃ oxidation versus time was recorded at both 100 and 160 °C.

1.3 Characterization of catalyst

N₂ adsorption-desorption isotherms were obtained by the adsorption of N₂ at –196 °C using a Quantasorb-18 automatic instrument (Autosorb-IC, Quanta Chrome Instrument, USA). Specific areas were computed from these isotherms by the Brunauer- Emmett-Teller (BET) method. The pore size distribution was calculated using the Barrett-Joinder-Halenda (BJH) method. Before measurement, samples were degassed at 300 °C for 4 h.

Powder X-ray diffraction (XRD) scans of the catalysts were conducted in the 2θ range of 20° to 70° at a scan speed of 6°/min using a Rigaku D/max-RB X-ray diffractometer (Japan) with Cu Kα radiation, operating at 40 kV and 40 mA.

The surface structure and concentration of the active species on the catalysts were characterized by X-ray photoelectron spectroscopy (XPS). Spectra were recorded using a PHI Quantera spectrometer (ULVAC-PHI, Inc. USA) with Al Kα radiation (hν = 1486.7 eV). The binding energies were calibrated against the C 1s peak of C present as a contaminant on the catalyst (284.8 eV).

UV-Vis diffuse-reflectance spectra (UV-Vis DRS) were recorded under ambient conditions using a U-3010 (Hitachi, Japan) spectrometer with a standard diffuse reflectance unit. The scan range was 190–850 nm and the scan rate was 300 nm/min. The measured spectra were treated by Kubelka-Munk functions and deconvoluted into Gaussian peaks that were used for the quantitative assignment of different Ag and Ce species [9–18].

High-resolution transmission electron microscopy (HR-TEM) images were recorded on an H-800 (Hitachi, Japan) instrument. The accelerating voltage for the microscope was 200 kV, the point resolution was 0.204 nm, and 200–300 particles were counted to evaluate the particle size (diameter) distribution.

In situ diffuse reflectance infrared Fourier transform spectra (in situ DRIFTS) were recorded using a Nexus 670 (Thermo Nicolet) FT-IR spectrometer equipped with an in
situ diffuse reflection chamber and a high sensitivity mercury-cadmium-telluride (MCT) detector. A sample of ca. 30 mg was ground finely and placed into a ceramic crucible. A feed gas mixture, controlled by mass flow meters, was supplied at a flow rate of 100 cm$^3$/min. The samples were first treated in a flow of high purity 10 vol% O$_2$/N$_2$ at 500 $^\circ$C for 0.5 h and then cooled to room temperature, followed by H$_2$-pretreatment in a flow of H$_2$/N$_2$ (20 vol% H$_2$) at 400 $^\circ$C for 1 h before being cooled to the desired temperature in a flow of high purity N$_2$. At each temperature, the background spectrum was recorded in flowing N$_2$, and it 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.

O$_2$ uptake was determined by O$_2$-pulse adsorption at various temperatures over H$_2$-pretreated Ag$_{0.1}$/Al$_2$O$_3$, Ce$_{0.1}$/Al$_2$O$_3$, and Ag$_{0.1}$Ce$_{0.1}$/Al$_2$O$_3$ catalysts using a Quantabors-18 automatic instrument (Quanta Chrome Instrument Co, USA). Prior to the O$_2$-pulse adsorption, 300 mg sample was reduced in situ with a flow of 5 vol% H$_2$/Ar (40 cm$^3$/min, 10 $^\circ$C/min) at 400 $^\circ$C for 2 h. Then He gas (40 cm$^3$/min) was passed over the sample for 1.5 h. After cooling to the desired temperature in He, O$_2$ pulses (4.46 µmol) were injected into a He carrier flowing over the sample. The time intervals between the O$_2$ pulses were about 100 s. The O$_2$ signal was analyzed online with an Autosorb-1-C TCD controller.

2 Results and discussion

2.1 NH$_3$ oxidation over different Ag$_{0.1}$Ce$_y$/Al$_2$O$_3$ catalysts

After similar pretreatment, the catalysts (200 mg) were tested under standard conditions for their activities. The activities of the Ag$_{0.1}$Ce$_y$/Al$_2$O$_3$ catalysts with different Ce/Al$_2$O$_3$ mass ratios are illustrated in Fig. 1. The NH$_3$ conversion over Ce-promoted Ag/Al$_2$O$_3$ catalysts at low temperature was increased comparing with unpromoted Ag$_{0.1}$/Al$_2$O$_3$. However, although increasing the mass ratio to 0.1 enhanced NH$_3$ oxidation to the highest conversion, further increase of this ratio gave lower NH$_3$ conversion. This indicated that adding CeO$_2$ to Ag/Al$_2$O$_3$ improved the catalytic activity of Ag/Al$_2$O$_3$ at temperatures below 160 $^\circ$C, and the best Ce/Al$_2$O$_3$ mass ratio was 0.1. The conversion of NH$_3$ using the Ag$_{0.1}$Ce$_{0.1}$/Al$_2$O$_3$ catalyst at 100 $^\circ$C was 73%, which was significantly higher than the 30% obtained with unpromoted Ag$_{0.1}$/Al$_2$O$_3$ catalyst under standard conditions.

The effects of H$_2$-pretreatment and the effects of CeO$_2$ on NH$_3$ oxidation at low temperatures over the Ag$_{0.1}$Ce$_{0.1}$/Al$_2$O$_3$ catalyst were also investigated (results not shown here) by comparing the activities of H$_2$-pretreated Ag$_{0.1}$Ce$_{0.1}$/Al$_2$O$_3$, and fresh Ag$_{0.1}$Ce$_{0.1}$/Al$_2$O$_3$ catalysts. Both the fresh Ag$_{0.1}$Ce$_{0.1}$/Al$_2$O$_3$ and H$_2$-pretreated Ce$_{0.1}$/Al$_2$O$_3$ catalysts showed little or no activity below 160 $^\circ$C, while high NH$_3$ conversion occurred with the H$_2$-pretreated Ag$_{0.1}$Ce$_{0.1}$/Al$_2$O$_3$ catalyst at temperatures below 160 $^\circ$C. Clearly, H$_2$-pretreatment enhanced significantly the low temperature activity of Ag$_{0.1}$Ce$_{0.1}$/Al$_2$O$_3$, although Ce$_{0.1}$/Al$_2$O$_3$ was inactive at low temperatures ($\leq$160 $^\circ$C). The stability of H$_2$-pretreated Ag$_{0.1}$Ce$_{0.1}$/Al$_2$O$_3$ for NH$_3$ oxidation was evaluated at 100 and 160 $^\circ$C. The results are shown in Fig. 2. NH$_3$ conversion at 100 $^\circ$C decreased gradually over 48 h from 73% to 37%, while the 100% NH$_3$ conversion at 160 $^\circ$C continued for more than 96 h.

![Fig. 1. Catalytic performance of the H$_2$-pretreated Ag$_{0.1}$Ce$_{0.1}$/Al$_2$O$_3$ catalysts with different Ce/Al$_2$O$_3$ mass ratios for NH$_3$ oxidation at different temperatures. Reaction conditions: NH$_3$ 0.05 vol%, O$_2$ 10 vol%, N$_2$ as balance, flow rate 200 cm$^3$/min, catalyst 0.2 g (W/F = 0.06 (g·s)/cm$^3$).](image)

![Fig. 2. Stability test of the H$_2$-pretreated Ag$_{0.1}$Ce$_{0.1}$/Al$_2$O$_3$ catalyst at various temperatures. Reaction conditions: NH$_3$ 0.05 vol%, O$_2$ 10 vol%, N$_2$ as balance, flow rate 200 cm$^3$/min, catalyst 0.2 g (W/F = 0.06 (g·s)/cm$^3$).](image)
was superior to that of the Ag/Al2O3 and other noble catalysts at low temperatures and its N2 selectivity (about 50% at temperatures below 160 °C) was similar to that of Ag/Al2O3. N2O was the main by-product over Ag0.1Ce0.1/Al2O3 at low temperatures. With further improvement, this catalyst would be promising as a suitable catalyst at low temperatures (≤ 160 °C).

2.2 Characterization results

2.2.1 N2 physisorption

The effects of CeO2 addition on the textural characteristics of the co-impregnated Ag/Al2O3 samples were assessed by measuring N2 adsorption-desorption isotherms. The results are shown in Table 1. The BET surface area, pore size, and pore volume of the Ce-promoted Ag/Al2O3 catalysts decreased with increasing Ce/Al2O3 ratio. At lower Ce loadings, the decrease in pore size can be attributed to the blockage by Ce species formed from excess Ce. At higher Ce loadings, this could be due to the smaller pores of CeO2 deposited on the Al2O3 surface. The results showed that the activities of the Ag0.1Ce/Al2O3 catalysts at low temperatures (Fig. 1) were not related to their BET surface areas.

Table 1 BET surface area and pore size of Ag0.1Ce/Al2O3 catalysts with different Ce/Al2O3 mass ratios

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3</td>
<td>250</td>
<td>0.81</td>
<td>13.0</td>
</tr>
<tr>
<td>Ag0.1Ce0/Al2O3</td>
<td>249</td>
<td>0.80</td>
<td>12.9</td>
</tr>
<tr>
<td>Ag0.1Ce0.05/Al2O3</td>
<td>205</td>
<td>0.65</td>
<td>12.7</td>
</tr>
<tr>
<td>Ag0.1Ce0.1/Al2O3</td>
<td>206</td>
<td>0.63</td>
<td>12.2</td>
</tr>
<tr>
<td>Ag0.1Ce0.15/Al2O3</td>
<td>197</td>
<td>0.53</td>
<td>10.8</td>
</tr>
<tr>
<td>Ag0.1Ce0.2/Al2O3</td>
<td>173</td>
<td>0.52</td>
<td>12.0</td>
</tr>
<tr>
<td>Ag0.1Ce0.3/Al2O3</td>
<td>168</td>
<td>0.42</td>
<td>10.1</td>
</tr>
</tbody>
</table>

2.2.2 XRD

The XRD patterns of the Ag0.1Ce/Al2O3 catalysts are shown in Fig. 3. In the unpromoted Ag/Al2O3, γ-Al2O3 was the only phase. With the Ce-promoted samples, diffraction lines from CeO2 were present in addition to those of γ-Al2O3. The intensities of the CeO2 lines became stronger and sharper with increasing Ce loading, demonstrating that the size of the CeO2 particles on the γ-Al2O3 matrix increased with increasing Ce loading leading to a decrease in CeO2 dispersion. This coincided with the decrease in BET surface area (Table 1). As shown in Fig. 1, the activity of the Ag0.1Ce/Al2O3 catalyst at low temperatures first increased with increasing Ce loading (y ≤ 0.1), then decreased at higher loadings. This implied that a suitable Ce loading (y ≤ 0.1) gave the best dispersion of CeO2 in Ag0.1Ce/Al2O3, which gave the highest NH3 conversion at low temperatures. Conversely, the reduced dispersion of CeO2 at higher Ce loadings (y > 0.1) was one cause for the decrease in NH3 oxidation activity over the Ag0.1Ce/Al2O3 catalysts at temperatures below 160 °C.

2.2.3 XPS

XPS was used to determine the element compositions and their chemical valences on the surfaces of fresh, H2-pretreated Ag0.1Ce/Al2O3 catalysts and the samples after the stability test. The results for Ag are not shown here, but previous data [4] indicated that the binding energies of the 3d electrons in Ag0, Ag+, or Ag2+ were similar. Therefore, it was difficult to get the oxidation state of the Ag species from the XPS results. Instead, these were obtained from UV-Vis DRS results.

The experimental and fitted Ce 3d spectra of the catalysts are shown in Fig. 4. The broad line for the Ce 3d core level indicated that both Ce3+ and Ce4+ existed. The curves were fitted with eight peaks, which corresponded to the four pairs of spin-orbit doublets [19–21]. The letters V and U refer to the Ce 3d5/2 and Ce 3d3/2 spin-orbit components, respectively. The relative percentage of the two Ce species was obtained from the area ratio of the Ce4+ 3d5/2 (V, V'', V''') relative to Ce3+ 3d5/2 (V').

Table 2 shows the results of the XPS quantitative analysis based on the atomic ratios obtained. The chemical valence of Ce on the surface of fresh Ag0.1Ce/Al2O3 was mainly Ce4+ with a small Ce3+ component. The surface ratio of Ce4+/Ce3+ on fresh Ag0.1Ce/Al2O3 decreased with H2-pretreatment, with some surface Ce4+ reduced to Ce3+. The surface ratio of Ce4+/Ce3+ increased during the stability test at 100 °C for 48 h (4.6), which indicated that some Ce3+...
was gradually oxidized at 100 °C over 48 h. In addition, the surface ratio of Ce\(^{4+}/\text{Ce}^{3+}\) increased further after testing at 160 °C for 96 h (5.2), which demonstrated that more Ce\(^{3+}\) was oxidized at the higher temperature with the longer period of time. Taking into account this and the activity test results shown in Fig. 2, it can be seen that while NH\(_3\) conversion at 100 °C decreased gradually together with the partial oxidation of Ce\(^{3+}\) in which Ce\(^{4+}/\text{Ce}^{3+}\) was increased to 4.6, the conversion did not decrease at the higher temperature of 160 °C despite more partial oxidation of Ce\(^{3+}\) in which Ce\(^{4+}/\text{Ce}^{3+}\) was increased to 5.2.

Table 2 XPS data (Ce\(^{4+}/\text{Ce}^{3+}\)) from the Ag\(_0.1\)Ce\(_0.1/\text{Al}_2\text{O}_3\) catalysts in Fig. 4

<table>
<thead>
<tr>
<th>Ag(_0.1)Ce(_0.1/\text{Al}_2\text{O}_3) catalyst</th>
<th>Ce(^{4+}/\text{Ce}^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)-pretreated</td>
<td>4.4</td>
</tr>
<tr>
<td>Retained at 100 °C for 48 h</td>
<td>4.6</td>
</tr>
<tr>
<td>Retained at 160 °C for 96 h</td>
<td>5.2</td>
</tr>
<tr>
<td>Fresh</td>
<td>6.3</td>
</tr>
</tbody>
</table>

2.2.4 UV-Vis DRS

The results of the UV-Vis DRS confirmed the details of the state of the supported Ag and Ce species. Fig. 5 shows the UV-Vis DRS of the fresh, H\(_2\)-pretreated Ag\(_0.1\)Ce\(_0.1/\text{Al}_2\text{O}_3\) catalyst and two samples after stability test as described above. The UV-Vis DRS analysis demonstrated the existence of different states of the Ag and Ce species, which can be seen after subtraction of the Al\(_2\text{O}_3\) spectrum. Fresh Ag\(_0.1\)Ce\(_0.1/\text{Al}_2\text{O}_3\) showed broad absorption bands at 206, 220, 260, and 305 nm, while the other three samples had an additional broad band at 450 nm (Fig. 5(a)). The bands at 206, 450, and 260 nm can be attributed to highly dispersed Ag\(^+\) ions, metallic silver (Ag\(^0\)) particles [9–15], and Ce\(^{3+}\) [17,18], respectively. The bands at 220 and 305 nm can be attributed to Ce\(^{4+}\) [16–18].

In Fig. 5(b), the measured spectra of the Ag\(_0.1\)Ce\(_0.1/\text{Al}_2\text{O}_3\) catalysts have been treated by Kubelka-Munk functions and deconvoluted into Gaussian peaks assigned to different Ag and Ce species [9–18]. Deconvolution was performed based on the above assignments. The relative intensities of these peaks are listed in Table 3, along with the quantification results for the different Ag and Ce species:

Table 3 Percentage of integrated area of the peaks derived from deconvolution of the UV-Vis DRS in Fig. 5

<table>
<thead>
<tr>
<th>Ag(_0.1)Ce(_0.1/\text{Al}_2\text{O}_3) catalyst</th>
<th>(I_1/%)</th>
<th>(I_2/%)</th>
<th>(I_3/%)</th>
<th>(I_4/%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>100</td>
<td>0</td>
<td>12.5</td>
<td>87.5</td>
</tr>
<tr>
<td>H(_2)-pretreated</td>
<td>1.8</td>
<td>98.2</td>
<td>27.6</td>
<td>72.4</td>
</tr>
<tr>
<td>Retained at 100 °C for 48 h</td>
<td>2.0</td>
<td>98.0</td>
<td>23.3</td>
<td>77.7</td>
</tr>
<tr>
<td>Retained at 160 °C for 96 h</td>
<td>7.3</td>
<td>92.7</td>
<td>21.5</td>
<td>78.5</td>
</tr>
</tbody>
</table>

\(^a\)For Ag\(^+\) (band at \(\lambda < 238\) nm).
\(^b\)For Ag\(^0\) (band at \(\lambda > 350\) nm).
\(^c\)For Ce\(^{3+}\) (band at 250 nm < \(\lambda < 300\) nm).
\(^d\)For Ce\(^{4+}\) (band at 210 < \(\lambda < 250\) nm and 260 < \(\lambda < 350\) nm).
The UV-Vis DRS results (Fig. 5) also confirmed that Ce³⁺ and Ce⁴⁺ coexisted on the alumina support. Furthermore, the relative amount of Ce⁴⁺ decreased following H₂-pretreatment but increased slightly following the stability test for 48 h at 100 °C and then increased more significantly after the stability test for 96 h at 160 °C. This was in agreement with the XPS results (Table 2). It can be concluded that some Ce³⁺ on the surface of the H₂-pretreated Ag₀.⁰₁Ce₀.⁰₁/Al₂O₃ catalyst was oxidized to Ce⁴⁺ at both 100 and 160 °C during the stability test, but the relative amounts of Ce⁴⁺ were lower than that in the fresh catalyst.

In fresh Ag₀.⁰₁Ce₀.⁰₁/Al₂O₃, Ag⁺ was the major Ag species present. On the H₂-pretreated catalyst, Ag₀ was the main Ag species present (Table 3), showing that most Ag₂O on the support was reduced to Ag₀ by the H₂-pretreatment. Taken together with the activity test results shown in Fig. 1, this showed that high NH₃ conversion was obtained over the H₂-pretreated Ag₀.⁰₁Ce₀.⁰₁/Al₂O₃ catalyst in the temperature range of 100–160 °C with the presence of Ag₀, while almost no NH₃ conversion was observed over the H₂-pretreated Ce₀.⁰₁/Al₂O₃ or fresh Ag₀.⁰₁Ce₀.⁰₁/Al₂O₃ due to the absence of Ag₀. That is, the presence of Ag₀ explains the enhanced low temperature activity of the H₂-pretreated Ag₀.⁰₁Ce₀.⁰₁/Al₂O₃ catalyst. It can therefore be concluded that Ag₀ is the main active species on this catalyst that is responsible for NH₃ oxidation at temperatures below 160 °C. However, a comparison with the H₂-pretreated Ag₀.⁰₁/Al₂O₃ catalyst showed that the H₂-pretreated Ag₀.⁰₁Ce₀.⁰₁/Al₂O₃ catalyst has a much higher NH₃ conversion in the presence of Ce. This showed that Ce has an important role in NH₃ oxidation at low temperature. This will be discussed in detail in the following section.

It was also found that Ag₀ was slightly oxidized after the stability test for more than 48 h at 100 °C while some Ce³⁺ on the surface of the catalyst was oxidized to Ce⁴⁺ under the same conditions. During this time, NH₃ conversion decreased gradually (Fig. 2). Consequently, Ce³⁺ oxidation can partly explain the decrease in catalytic activity at 100 °C with H₂-pretreated Ag₀.⁰₁Ce₀.⁰₁/Al₂O₃.

It is worth noting that both Ag₀ and Ce³⁺ were partly oxidized during the stability test at 160 °C for 96 h (Fig. 5), but that 100% NH₃ conversion was maintained throughout (Fig. 2).

2.2.5 HR-TEM

The HR-TEM images shown in Fig. 6 for the H₂-pretreated Ag₀.⁰₁/Al₂O₃ and Ag₀.⁰₁Ce₀.⁰₁/Al₂O₃ catalysts show the surface distribution of Ag particles. Statistical calculations of Ag particle size measured from these images provided the mean particle size (d) and degree of Ag dispersion (Table 4). The particles were assumed to be spherical.
These results indicated that Ag dispersion is not the primary contribution to the difference in activity observed between these two samples at low temperature. Indeed, the enhanced activity at low temperatures may be primarily linked to the role of the Ce species.

2.3 In situ DRIFTS study of NH₃ adsorption

In order to investigate the role of Ce and Ag for the adsorption of NH₃ on the catalysts, in situ DRIFTS spectra for the H₂-pretreated Ce₀.₁/Al₂O₃ and Ag₀.₁Ce₀.₁/Al₂O₃ catalysts exposed to NH₃ are shown in Fig. 7. In Fig. 7(a), the bands at 1695, 1481, and 1392 cm⁻¹ are from the deformation modes of NH₄⁺ formed by the interaction of NH₃ with Brønsted acid sites on γ-Al₂O₃ [2,23–27]. The bands at 1608 and 1240 cm⁻¹ can be attributed to the asymmetric and symmetric deformation modes, respectively, of NH₃ molecules coordinated on Lewis acid sites of the γ-Al₂O₃ [23–27]. The band at 1456 cm⁻¹ can be attributed to imide (–NH) deformation modes [2,28,29]. The two shoulders at 1580 and 1376 cm⁻¹ can be assigned to amide (–NH₂) scissoring and (–NH₂) wagging, respectively [2,28,29]. The bands in the N–H stretching region also occur at 3401, 3356, 3270, and 3149 cm⁻¹ [28,29].

The band intensities from NH₃ coordinated on Brønsted (1695, 1481, and 1392 cm⁻¹) and Lewis acid sites (1608 and 1240 cm⁻¹) decreased gradually with increasing temperature. Those related to –NH₂ and –NH (1580, 1456, and 1376 cm⁻¹) appeared at room temperature together with those of NH₃, but disappeared at higher temperatures (Fig. 7(a)). These results showed that NH₃ adsorbed on H₂-pretreated Ce₀.₁/Al₂O₃ was adsorbed dissociatively to form –NH₂ and –NH intermediates and followed reactions (1) and (2) with the abstraction of hydrogen. Furthermore, these –NH₂ and –NH are stable on H₂-pretreated Ce₀.₁/Al₂O₃ and do not disappear until a temperature of 400 °C.

\[
\begin{align*}
\text{NH}_3 & \rightarrow \text{NH}_2 + \text{H} & (1) \\
\text{NH}_2 & \rightarrow \text{NH} + \text{H} & (2)
\end{align*}
\]

In the case of the H₂-pretreated Ag₀.₁Ce₀.₁/Al₂O₃ catalyst, similar bands occurred at 1695, 1608, 1481, 1456, 1392, 1365, and 1240 cm⁻¹ following NH₃ adsorption (Fig. 7(b)). The bands of NH₃ adsorbed on the Brønsted and Lewis acid sites of Ag₀.₁Ce₀.₁/Al₂O₃ disappeared at 160 °C. While the intensity of these bands decreased with increasing temperature, the bands corresponding to –NH₂ (1365 cm⁻¹) and –NH (1456 cm⁻¹) increased and then disappeared at temperatures below 160 °C, indicating that NH₃ adsorbed on H₂-pretreated Ag₀.₁Ce₀.₁/Al₂O₃ was activated to form –NH₂ and –NH intermediates first and then desorbed from the surface of the catalyst. Comparing with the in situ DRIFTS results in Fig. 7(a), it is seen that the adsorbed NH₃ on both H₂-pretreated Ag₀.₁Ce₀.₁/Al₂O₃ and Ce₀.₁/Al₂O₃ can be activated to form –NH₂ and –NH intermediates, but the –NH₂ and –NH formed can be activated and desorbed from the surface of H₂-pretreated Ag₀.₁Ce₀.₁/Al₂O₃ much faster in the presence of Ag. In addition, according to our previous in situ DRIFTS results of NH₃ adsorption on H₂-pretreated Ag₀.₁/Al₂O₃ [30], bands corresponding to –NH₂ and –NH did not appear at room temperature, which is different from that with H₂-pretreated Ce₀.₁/Al₂O₃. Hence, we conclude that CeO₂ addition promoted the dissociative adsorption of NH₃ to form –NH₂ and –NH intermediates.

![Fig. 7](image-url)
2.4 \textit{O}_2\text{-pulse adsorption}

The \textit{O}_2 uptakes of the catalysts were determined by measuring \textit{O}_2\text{-pulse adsorption at 100 °C. As shown in Fig. 8, \textit{O}_2 was chemisorbed on the three catalysts. As expected, the amount of \textit{O}_2 uptake on \textit{Ag}_0.1\text{Ce}_0.1/\text{Al}_2\text{O}_3 (69.71 \mu\text{mol/g}) was much higher than that on either \textit{Ag}_0.1/\text{Al}_2\text{O}_3 (45.73 \mu\text{mol/g}) or \textit{Ce}_0.1/\text{Al}_2\text{O}_3 (36.47 \mu\text{mol/g}).

Gang et al. [6,8] reported on adsorbed atomic oxygen (O) on reduced Ag catalysts, and considered the dissociation of \textit{O}_2 to be the rate controlling step in \textit{NH}_3 oxidation [8]. Leferts et al. [31] also detected O on a H\textsubscript{2}-pretreated Ag surface. From the present \textit{O}_2\text{-pulse adsorption results, it is likely that some molecular \textit{O}_2 was chemisorbed dissociatively on the surface of H\textsubscript{2}-pretreated \textit{Ag}_0.1/\text{Al}_2\text{O}_3 as O species.

Li et al. [32] reported that molecular \textit{O}_2 was adsorbed on the surface of partially reduced cerium oxide to form a superoxide species (O\textsuperscript{2+}), which can be further chemisorbed dissociatively to O on the surface of H\textsubscript{2}-reduced cerium oxide. In the present study, some surface Ce\textsuperscript{3+} of the H\textsubscript{2}-pretreated \textit{Ag}_0.1\text{Ce}_0.1/\text{Al}_2\text{O}_3 was reduced to \textit{Ce}^{3+} by H\textsubscript{2} reduction (Tables 2 and 3). This can lead to the formation of surface oxygen nests together with bulk oxygen vacancies, to result in the dissociative adsorption of \textit{O}_2 on reduced cerium oxide. Taken together with the \textit{O}_2 pulse-adsorption results (Fig. 8), it can be concluded that some molecular \textit{O}_2 is chemisorbed dissociatively to form O on the surface of H\textsubscript{2}-pretreated \textit{Ce}_0.1/\text{Al}_2\text{O}_3, which would explain the enhanced \textit{O}_2 uptake on the H\textsubscript{2}-pretreated \textit{Ag}_0.1\text{Ce}_0.1/\text{Al}_2\text{O}_3 catalyst.

From these results, it can be concluded that adding \textit{CeO}_2 enhanced the \textit{O}_2 uptake of \textit{Ag/Al}_2\text{O}_3 by promoting the catalytic ability of \textit{Ag/Al}_2\text{O}_3 for dissociative or non-dissociative adsorption of \textit{O}_2 at low temperatures (100 °C). The \textit{NH}_3 oxidation activity of \textit{Ag/Al}_2\text{O}_3 at low temperatures is determined by its catalytic ability for both dissociative and non-dissociative adsorption of \textit{O}_2 [6]. Chemisorbed O enhanced \textit{NH}_3 oxidation below 140 °C on \textit{Ag/Al}_2\text{O}_3, while gas phase molecular \textit{O}_2 mainly interacted with adsorbed \textit{NH}_3 at temperatures above 140 °C [30]. From Fig. 1 it can be seen that higher \textit{NH}_3 conversion occurred on H\textsubscript{2}-pretreated \textit{Ag}_0.1\text{Ce}_0.1/\text{Al}_2\text{O}_3, with a higher \textit{O}_2 uptake at 100 °C. This confirmed that \textit{O}_2 uptake was the main factor causing the enhanced low temperature activity of the catalyst, since the addition of \textit{CeO}_2 improved the activation of \textit{NH}_3 to form –NH and –HNO intermediates (reactions (3)–(5)), which are the key intermediates for \textit{NH}_3 oxidation (route (6) and (7)) at low temperatures (< 140 °C).

The 100 °C/48 h stability test results (Fig. 2) showed that the high degree of \textit{NH}_3 conversion decreased gradually with the oxidation of some \textit{Ce}^{3+} (Tables 2 and 3), although \textit{Ag}^{0} showed little oxidation under these conditions. This presumably reflected a decrease in the ability of the catalyst to participate in the dissociative adsorption of \textit{O}_2 as a result of the oxidation of \textit{Ce}^{3+}, thus contributing to a decrease in \textit{NH}_3 oxidation activity at 100 °C.

The 160 °C/96 h stability test results, however, showed that 100% \textit{NH}_3 conversion was maintained throughout (Fig. 2), although both \textit{Ag}^{0} and \textit{Ce}^{2+} were partly oxidized during the test (Fig. 5). Gas phase molecular \textit{O}_2 mainly interacted with adsorbed \textit{NH}_3 at temperatures above 140 °C on \textit{Ag/Al}_2\text{O}_3 [30]. Hence, it can be inferred that at the higher temperature of 160 °C, adsorbed \textit{NH}_3 mainly interacted with \textit{O}_2 on \textit{Ag}_0.1\text{Ce}_0.1/\text{Al}_2\text{O}_3 and any partial oxidation of \textit{Ce}^{3+} did not affect the activity under these conditions. Furthermore,
Ag$^+$ is the active species on Ag/Al$_2$O$_3$ at temperatures above 140 °C [7], and thus Ag$^+$ on Ag$_{0.1}$Ce$_{0.1}$/Al$_2$O$_3$ is likely also the active species involved in NH$_3$ oxidation at 160 °C. Hence, high NH$_3$ conversion will persist in spite of the oxidation of some Ag$^0$ species.

3 Conclusions

The addition of an appropriate amount of CeO$_2$ to Ag/Al$_2$O$_3$ improved the catalytic oxidation of NH$_3$ at temperatures below 160 °C. Ag$^+$ on Ag$_{0.1}$Ce$_{0.1}$/Al$_2$O$_3$ is likely also the active species involved in NH$_3$ oxidation at 160 °C. Hence, high NH$_3$ conversion will persist in spite of the oxidation of some Ag$^0$ species.

References