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# Catalytic activity and mechanism of selective catalytic oxidation of ammonia by Ag–CeO<sub>2</sub> under different preparation conditions

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Given the problem of the high-temperature window of CeO<sub>2</sub> catalyst activity, this study evaluated the catalytic properties of Ag/CeO<sub>2</sub> prepared by changing the preparation methods and loadings. Our experiments showed that Ag/CeO<sub>2</sub>-IM catalysts prepared by the equal volume impregnation method could have better activity at lower temperatures. The Ag/CeO<sub>2</sub>-IM catalyst achieves 90% NH<sub>3</sub> conversion at 200 °C, and the main reason is that the Ag/CeO<sub>2</sub>-IM catalyst has more vital redox properties, and the NH<sub>3</sub> catalytic oxidation temperature is lower. However, its high-temperature N<sub>2</sub> selectivity still needs to be improved and may be related to the less acidic sites on the catalyst surface. On both catalyst surfaces, the i-SCR mechanism governs the NH<sub>3</sub>-SCO reaction.

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## 1. Introduction

In recent years, ammonia has gradually been increasingly considered as a harmful gas. Excessive emission of ammonia will not only cause a series of impacts on the environment and the decline of biodiversity,<sup>1,2</sup> but also cause serious risks to human health. The lowest ammonia concentration that humans can perceive is 5.3 ppm,<sup>3</sup> and the increased ammonia emissions will greatly irritate the eyes, respiratory tract, *etc.*<sup>4</sup> Ammonia emissions in cities mainly come from diesel vehicle exhaust,<sup>5</sup> as an unexpected result of introducing technology to reduce NO<sub>x</sub> emissions.<sup>6</sup> However, after implementing China's National VI Standard, ammonia emissions have strict requirements, and the treatment of excess ammonia gas becomes necessary.

Technologies to reduce ammonia emissions include adsorption, absorption, biodegradation, catalytic oxidation, thermal decomposition, direct decomposition, and membrane separation.<sup>7–9</sup> Ammonia selective catalytic oxidation technique (NH<sub>3</sub>-SCO) is a highly effective and eco-friendly method of

treating waste gases that contain ammonia. NH<sub>3</sub>-SCO uses catalysts to oxidize NH<sub>3</sub> to N<sub>2</sub> and H<sub>2</sub>O under aerobic conditions selectively. Its mechanism has been extensively studied, mainly including three pathways, namely the imide mechanism (–NH mechanism), hydrazine mechanism (N<sub>2</sub>H<sub>4</sub> mechanism), and internal selective catalytic reduction mechanism (an i-SCR mechanism). In the imide mechanism, the adsorbed NH<sub>3(ad)</sub> is dehydrogenated twice to form –NH, and –NH reacts with O to form the characteristic intermediate –HNO, after which –HNO combines with –NH to produce N<sub>2</sub> and/or N<sub>2</sub>O;<sup>10–12</sup> in the hydrazine mechanism, NH<sub>3(ad)</sub> removes H to become –NH<sub>2</sub> and the two combine to form the characteristic intermediate hydrazine (NH<sub>2</sub>–NH<sub>2</sub>), and then NH<sub>2</sub>–NH<sub>2</sub> reacts with O to produce N<sub>2</sub> and H<sub>2</sub>O;<sup>10,13</sup> in the i-SCR mechanism, NH<sub>3(ad)</sub> first removes H to form –NH<sub>x</sub>, which reacts with O<sub>2</sub> to form NO<sub>x</sub>, and then is reduced to N<sub>2</sub> and H<sub>2</sub>O by –NH<sub>x</sub>.<sup>14–16</sup>

Research on NH<sub>3</sub>-SCO catalysts has focused on catalysts made of molecular sieves, noble metals, and transition metals. The surface of molecular sieve catalysts has acidic sites, and the active centers are equally distributed, but the hydrothermal stability is poor.<sup>17–19</sup> Noble metal catalysts are characterized by Ag, Pt, Au, Pd, and other precious elements as active components, and precious metals are usually loaded on different carriers. Generally, they have excellent low-temperature catalytic activity and can achieve a high NH<sub>3</sub> conversion at 300 °C. But its N<sub>2</sub> selectivity is poor, easy to sinter, and the cost is high.<sup>20–22</sup> Transition metal catalysts mainly refer to transition metals and their oxides, characterized by low price, abundant and easy availability, and have obtained extensive attention in catalytic oxidation. However, their low-temperature catalytic capacity needs to be improved.<sup>23,24</sup> Among them, CeO<sub>2</sub> has apparent advantages in catalytic oxidation due to its unique

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physicochemical properties, oxygen storage, and release capabilities.

In our previous NH<sub>3</sub>-SCO experiments, although the CeO<sub>2</sub> catalyst exhibits excellent redox performance, its activity at cold temperatures needs further improvement. Therefore, we use the combination of Ag and CeO<sub>2</sub> to prepare noble metal-supported catalysts to attain high NH<sub>3</sub> conversion at cold temperatures and evaluate the performance of Ag/CeO<sub>2</sub> catalysts with various preparation methods and loadings. To explore the differences in NH<sub>3</sub>-SCO properties of Ag/CeO<sub>2</sub> catalysts prepared in multiple ways, we adopted XRD, XPS, H<sub>2</sub>-TPR, and NH<sub>3</sub>-TPD characterization methods and *in situ* DRIFTS characterization was adopted to deduce the mechanism of the response.

## 2. Experimental

### 2.1 Catalyst synthesis

0.5 g of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Tianjin Comio Chemical Co., Ltd) and 0.2 g of PVP (Tianjin Hienceoptech Co., Ltd) were dissolved in 15 mL ethylene glycol, and then the above solution was slowly added to 15 mL deionized water. After continuous stirring for 30 min, the clarified liquor was transferred to a 50 mL PTFE-lined autoclave and kept at 160 °C for 8 h. After the autoclave was cooled at indoor temperature, the samples were gathered by centrifugal washing. Then, the samples were dried overnight at 110 °C in an oven. Finally, the specimens were heat treated at 500 °C for 3 h in a muffle furnace to obtain a CeO<sub>2</sub> carrier.

**2.1.1 Constant volume impregnation method.** 0.0786 g of silver nitrate (Beijing Inokai Technology Co., Ltd) was weighed using an electronic balance, dissolved in deionized water, and prepared into 1 mg mL<sup>-1</sup> of silver nitrate solution. After that, a certain amount of carrier CeO<sub>2</sub> was weighed into the beaker, and a particular volume of silver nitrate solution was added to CeO<sub>2</sub> drop by drop. The mixture was continuously stirred while dropping. After dropping, the mixture was mixed evenly for 30 min. Then, the specimens were kept in an air-blast drying oven and dried at 120 °C for 12 h. Eventually, the dried sample was burned in a muffle furnace at 500 °C for 3 h to obtain the catalyst, *x* Ag/CeO<sub>2</sub>-IM-*T*, where *x* represents the mass ratio of Ag to CeO<sub>2</sub>, and *T* stands for different calcination temperatures (°C).

**2.1.2 Deposition-precipitation method.** An appropriate amount of CeO<sub>2</sub> was weighed using an electronic balance and then dissolved in deionized water. After stirring for 15 min, ammonium carbonate solution was added for proper alkalization. A certain amount of silver nitrate was dropped into the CeO<sub>2</sub> solution and stirred continuously. After the dripping, the solution was allowed to stand for 30 min. The combination was aged indoors for 1 h and then washed by centrifugation with deionized water. Consequently, the material was dried at 120 °C for an entire night. Finally, the sample was placed in a quartz boat, burned in a hydrogen tube furnace, and reduced by passing a mixture of 200 mL min<sup>-1</sup> (90% N<sub>2</sub> and 10% H<sub>2</sub>) at 400 °C for 2 h to obtain *x* Ag/CeO<sub>2</sub>-DP catalyst, where *x* represents the mass ratio of Ag to CeO<sub>2</sub>.

### 2.2 Catalyst characterization

X-ray powder diffraction (XRD) characterization test was performed in a d8-Focus Type X-ray diffractometer produced by Germany Brock AXS Co., Ltd, using Cu target K $\alpha$  ray ( $\lambda$  = 0.1540598 nm), and Jade 6.5 was used for XRD data analysis.

X-ray photoelectron spectroscopy (XPS) uses ESCALAB 250Xi X-ray photoelectron spectroscopy (USA), with a limit energy resolution of 0.43 eV, a ray source of Al K $\alpha$  (1486.6 eV, power 150 W, 500  $\mu$ m beam spots), and the resulting XPS spectrogram uses C 1s (284.8 eV) for charge correction for standard peaks and peak fitting using XPS Peak software.

NH<sub>3</sub>-temperature-programmed desorption (NH<sub>3</sub>-TPD) uses AutoChem II 2920 and Chembet TPDTPR-type chemisorbents. 100 mg of the sample was put in an N<sub>2</sub> atmosphere at a 10 °C min<sup>-1</sup> heating rate to 300 °C, thermostatic pretreatment was 1 h, and was cooled to 50 °C after completion. Then, 500 ppm NH<sub>3</sub> is passed for 1 h until adsorption saturation. After that, the flow of NH<sub>3</sub> is stopped and purged with N<sub>2</sub> for 30 min. After the signal is stabilized, it is heated from 50 °C to 900 °C at 10 °C min<sup>-1</sup> in an N<sub>2</sub> atmosphere while the NH<sub>3</sub> concentration is continuously recorded and output with a TCD signal.

H<sub>2</sub>-temperature-programmed reduction (H<sub>2</sub>-TPR) is performed on AutoChem II 2920 and Chemobelt TPDTPR-type chemisorption instruments. 100 mg of sample is placed in an N<sub>2</sub> atmosphere at a 10 °C min<sup>-1</sup> heating rate to 300 °C and pretreated at a constant temperature for 1 h. The samples were cooled to 50 °C after pretreatment. At the end of the cooling, a 10% H<sub>2</sub>/Ar gas mixture is introduced, and the temperature rises to 900 °C at a rate of 10 °C min<sup>-1</sup>. During this process, the H<sub>2</sub> consumption is recorded by the TCD detector.

*In situ* diffuse filter infrared spectroscopy (*in situ* DRIFTS) was performed using the German Bruker company Tensor II Fourier transform infrared spectrometer, supporting the MCT (Mercury Cadmium Telluride) detector, and the accessory is connected to the *in situ* diffuse reflection reaction cell. The adsorption, transient, and steady-state reaction experiments of the catalyst surface reaction species involved in this study were performed in this instrument, with a scanning range of 400–4000 cm<sup>-1</sup>, a diaphragm of 6 mm, a resolution of 4 cm<sup>-1</sup>, and several scans (64 times).

### 2.3 Activity testing

The NH<sub>3</sub>-SCO activity analyses in this study were operated in the laboratory-made fixed-bed quartz reaction device for all catalysts. The composition and concentration of the inlet reaction gas were as follows: [O<sub>2</sub>] = 10 vol, [NH<sub>3</sub>] = 500 ppm, N<sub>2</sub> was the equilibrium gas, and 300 mL min<sup>-1</sup> was the overall gas flow rate. The reaction temperature range of this study was 90–400 °C, and every temperature was constant for 30 min, controlled by a tubular reactor thermostat and a thermocouple. The exhaust gas detection system uses the German Bruker Tensor II infrared spectrometer to detect the concentration of NH<sub>3</sub>, N<sub>2</sub>O, NO<sub>2</sub>, and NO in import and export and uses computer supporting software for data analysis.



The evaluation indexes of NH<sub>3</sub>-SCO catalyst performance are NH<sub>3</sub> conversion and N<sub>2</sub> selectivity, which are determined by applying eqn (1) and (2), respectively:

$$\text{NH}_3 \text{ conversion (\%)} = \frac{\text{NH}_{3\text{in}} - \text{NH}_{3\text{out}}}{\text{NH}_{3\text{in}}} \times 100\% \quad (1)$$

$$\text{N}_2 \text{ selectivity (\%)} = \left( \frac{\text{NH}_{3\text{in}} - \text{NO}_{\text{out}} - \text{NO}_{2\text{out}} - 2\text{N}_2\text{O}_{\text{out}}}{\text{NH}_{3\text{in}}} \right) \times 100\% \quad (2)$$

### 3. Findings and analysis

#### 3.1 Catalytic effectiveness

Different preparation methods have a huge effect on NH<sub>3</sub>-SCO activity, so we adopted the constant volume impregnation method and deposition-precipitation method to prepare Ag-based catalysts, and the NH<sub>3</sub>-SCO activities for catalysts with different methods are shown in Fig. 1. Fig. 1a shows the NH<sub>3</sub> conversion results, and the T<sub>50</sub> of NH<sub>3</sub> conversion is 250 °C on the Ag/CeO<sub>2</sub>-DP catalyst, which is 50 °C lower than the CeO<sub>2</sub> support. Still, the T<sub>90</sub> of NH<sub>3</sub> conversion is above 400 °C on the Ag/CeO<sub>2</sub>-DP catalyst, higher than the CeO<sub>2</sub> support

(T<sub>90</sub> = 400 °C). The NH<sub>3</sub> conversion of Ag/CeO<sub>2</sub>-IM catalyst reaches 90% at 200 °C, and the T<sub>90</sub> is lower at 200 °C than the Ag/CeO<sub>2</sub>-DP catalyst and has a more excellent ammonia oxidation activity. The results of N<sub>2</sub> selectivity are shown in Fig. 1b. The N<sub>2</sub> selectivity of the Ag/CeO<sub>2</sub>-IM catalyst begins to decrease at 125 °C, and the N<sub>2</sub> selectivity is 70% at 200 °C, which then continues to decline with the increase in temperature. The Ag/CeO<sub>2</sub>-DP catalyst's N<sub>2</sub> selectivity is marginally higher than that of the Ag/CeO<sub>2</sub>-IM catalyst, and the N<sub>2</sub> selectivity starts to decrease at 150 °C, still higher than 90% at 200 °C, but the N<sub>2</sub> selectivity is less than 60% at 400 °C. The graphic shows that the CeO<sub>2</sub> has better N<sub>2</sub> selectivity than Ag/CeO<sub>2</sub>-DP catalyst and Ag/CeO<sub>2</sub>-IM catalyst from 100 °C to 300 °C, but the N<sub>2</sub> selectivity declined sharply from 300 °C to 30% at 400 °C. We have compared the catalytic performance of this work with other catalysts in recent years listed in Table 1, and it can be found that the Ag/CeO<sub>2</sub>-IM catalyst in this study exhibits a high rate of ammonia oxidation over a wide temperature window. While other catalysts with good low-temperature activity have a narrow temperature window and catalysts with good high-temperature ammonia oxidation performance are less active in the low-temperature region, the Ag/CeO<sub>2</sub>-IM catalyst maintains a more balanced ammonia oxidation performance with an ammonia conversion rate greater than 90% within a wider temperature window from low-temperature 200 °C to high-temperature 400 °C

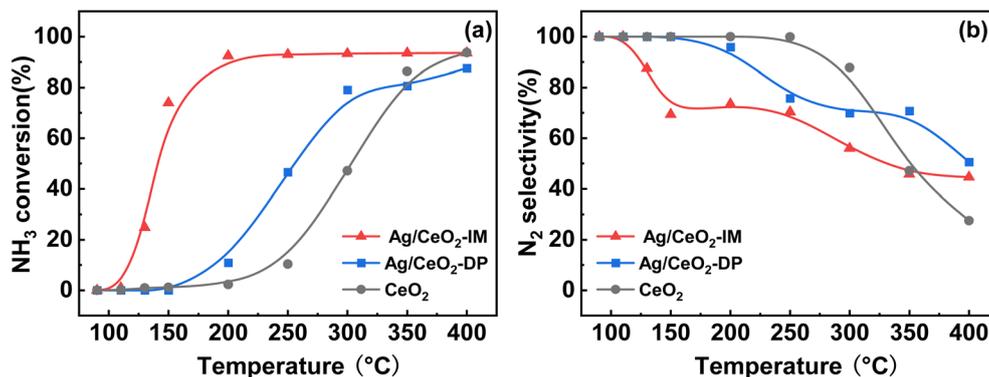


Fig. 1 (a) NH<sub>3</sub> conversion (b) N<sub>2</sub> selectivity of CeO<sub>2</sub>, Ag/CeO<sub>2</sub>-DP, and Ag/CeO<sub>2</sub>-IM catalysts (inlet reaction gas composition: [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 10 vol%, N<sub>2</sub> is equilibrium gas, GHSV = 60 000 h<sup>-1</sup>).

Table 1 Literature review of catalytic performance results related to Ag or Ce based catalysts

| Catalysis   | Preparation method       | Reaction conditions   | Temperature window/°C | NH <sub>3</sub> conversion/% | Ref.      |
|---|--------------------------|---|-----------------------|------------------------------|-----------|
| Ag/CeO <sub>2</sub> -IM                           | Impregnation             | [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 10%, GHSV = 60 000 h <sup>-1</sup>  | 200–400               | >90                          | This work |
| Ag/CeO <sub>2</sub> -DP                           | Deposition-precipitation |   | 400                   | 87                           |           |
| 1.75Ag/CeSnO <sub>x</sub>                         | Impregnation             | [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 10%, GHSV = 100 000 h <sup>-1</sup> | 250–400               | 100                          | 14        |
| Ag/Al <sub>2</sub> O <sub>3</sub>                 | Rotary evaporator        | [NH <sub>3</sub> ] = 1000 ppm, [O <sub>2</sub> ] = 10%, GHSV = 35 000 h <sup>-1</sup> | 130–180               | 100                          | 25        |
| Ag/ZSM-5  |                          |   | 110–140               | 100                          |           |
| Ag/meso-TiO <sub>2</sub>                          | Wet impregnation         | [NH <sub>3</sub> ] = 5000 ppm, [O <sub>2</sub> ] = 2.5%                               | 350–400               | 100                          | 26        |
| Ag/Al <sub>2</sub> O <sub>3</sub> -H <sub>2</sub> | Impregnation             | [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 10%, GHSV = 28 000 h <sup>-1</sup>  | 120–180               | 100                          | 27        |
| Ag/nano-Al <sub>2</sub> O <sub>3</sub>            | Impregnation             | [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 10%, GHSV = 28 000 h <sup>-1</sup>  | 100–180               | 100                          | 28        |
| Ag/SiO <sub>2</sub> -TiO <sub>2</sub>             | Impregnation             | [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 10%, GHSV = 28 000 h <sup>-1</sup>  | 140–240               | 100                          | 29        |
| CuO/CeO <sub>2</sub> -NR                          | Wetness impregnation     | [NH <sub>3</sub> ] = 1000 ppm, [O <sub>2</sub> ] = 10%, GHSV = 40 000 h <sup>-1</sup> | 240–250               | 100                          | 30        |
| CeSnO <sub>x</sub>                                | Coprecipitation          | [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 10%, GHSV = 100 000 h <sup>-1</sup> | 300–400               | 90                           | 31        |



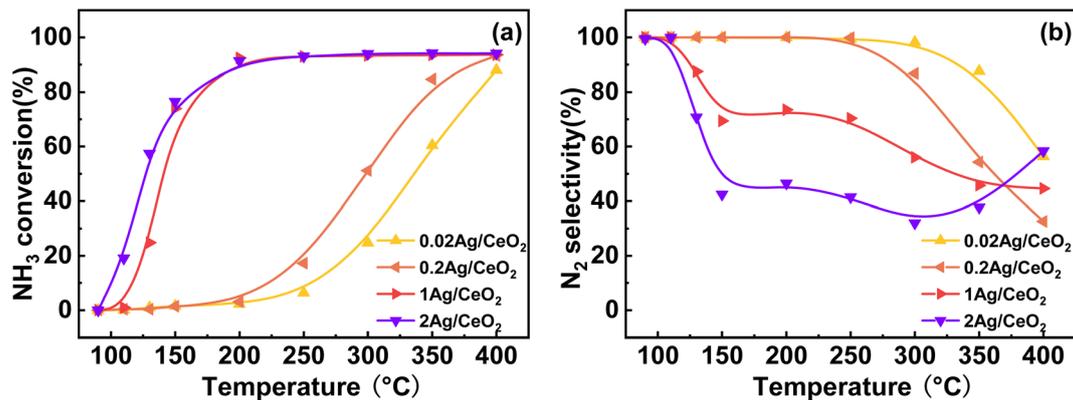


Fig. 2 (a) NH<sub>3</sub> conversion (b) N<sub>2</sub> selectivity of Ag/CeO<sub>2</sub>-IM catalyst with different Ag loading amounts (inlet reaction gas composition: [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 10 vol%, N<sub>2</sub> is equilibrium gas, GHSV = 60 000 h<sup>-1</sup>).

C. Overall, catalysts prepared by equal volume impregnation with better NH<sub>3</sub> conversion were preferred for further exploration.

Fig. 2 depicts the impact of various Ag loading amounts on the catalytic activity of Ag/CeO<sub>2</sub>-IM. As shown in Fig. 2a, with an increase in the amount of Ag loading from 0.2 wt% to 1 wt%,  $T_{90}$  of NH<sub>3</sub> conversion increased from 400 °C to 200 °C on the Ag/CeO<sub>2</sub>-IM catalysts. However, with the addition of Ag loading to 2 wt%, NH<sub>3</sub> conversion only increased a little at the low temperature. This is because the catalytic activity rises as the number of available surface-active sites increases.<sup>32</sup>{Azadi, 2012 #48} The increased Ag loading dispersed more Ag particles on the CeO<sub>2</sub> carrier. However, with an increase in the amount of Ag packing from 1 wt% to 2 wt%, the dispersion of Ag nanoparticles formed may not be further changed. Therefore, the number of exposed active sites no longer increases, so the NH<sub>3</sub> conversion has not increased much. Fig. 2b shows the influence of Ag loading on the N<sub>2</sub> selectivity of the catalyst. As Ag has a more vital oxidation capacity,<sup>33</sup> NH<sub>3</sub> is prone to excessive oxidation at high temperatures. Therefore, appropriate Ag loading can significantly improve NH<sub>3</sub> conversion and maintain good N<sub>2</sub> selectivity. When the loading reaches 1 wt%, the NH<sub>3</sub> conversion reaches 90% at 200 °C, and the N<sub>2</sub> selectivity of the catalyst remains above 50% at 125–400 °C, which is the optimum loading capacity for the Ag/CeO<sub>2</sub>-IM catalyst.

### 3.2 Catalyst phase analysis

The structure of the catalyst can be characterized by XRD. Fig. 3 displays the XRD results of Ag/CeO<sub>2</sub> catalysts formed by various preparation methods. It can be observed that the CeO<sub>2</sub> crystallinity increases after Ag loading, showing a typical CeO<sub>2</sub> cubic fluorite structure diffraction pattern. It also indicates that the Ag impregnation load will not significantly change the crystal structure of CeO<sub>2</sub> in the catalyst but also enhance the structural stability of CeO<sub>2</sub>. Notably, a slight shift in the diffraction angle towards the higher angle was observed, indicating that Ag<sup>+</sup> had merged into the CeO<sub>2</sub> lattice and changed the CeO<sub>2</sub> unit cell parameters.<sup>34</sup> In addition, the diffraction peak of Ag species was

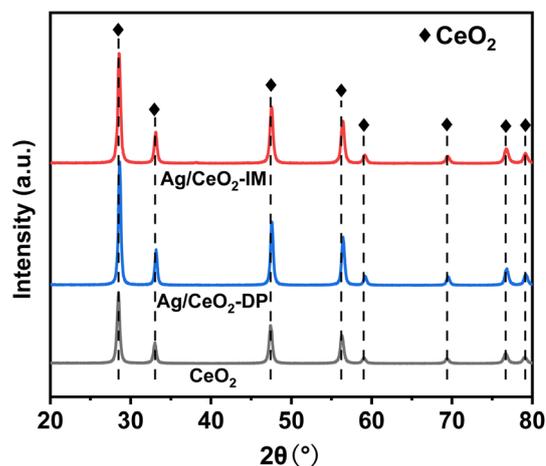


Fig. 3 Results of XRD tests on the catalysts CeO<sub>2</sub>, Ag/CeO<sub>2</sub>-DP, and Ag/CeO<sub>2</sub>-IM.

not observed, indicating that the Ag species were spread uniformly across the catalyst surface or did not reach the XRD detection limit.<sup>35</sup>

### 3.3 Surface element valence and oxygen content

The XPS results for determining the state of valence and oxygen concentration of the components on the catalyst's exterior are displayed in Fig. 4 and Table 2. Fig. 4a displays the XPS Ag 3d spectra of CeO<sub>2</sub>, Ag/CeO<sub>2</sub>-DP, and Ag/CeO<sub>2</sub>-IM, where the Ag 3d<sub>5/2</sub> core energy level binding energy appears at 367.9 and 368.4 eV. According to reports in the literature, 367.9 eV corresponds to Ag oxide,<sup>36</sup> and 368.4 eV correlates to the metal Ag.<sup>37</sup> The peak areas in the graph indicate that Ag/CeO<sub>2</sub>-IM catalysts have two types of Ag species on the surface: metallic Ag and Ag<sub>2</sub>O. From the deconvolution results of the peaks in Table 2, we can see that Ag/CeO<sub>2</sub>-IM has 56.02% of Ag<sup>0</sup>, which has more Ag<sup>0</sup> acting as the active site for ammonia oxidation than Ag/CeO<sub>2</sub>-DP, so Ag/CeO<sub>2</sub>-IM has superior low-temperature ammonia oxidation performance. Fig. 4b exhibits the XPS Ce 3d spectra of Ag/CeO<sub>2</sub>-DP, Ag/CeO<sub>2</sub>-IM, and CeO<sub>2</sub> catalysts. The



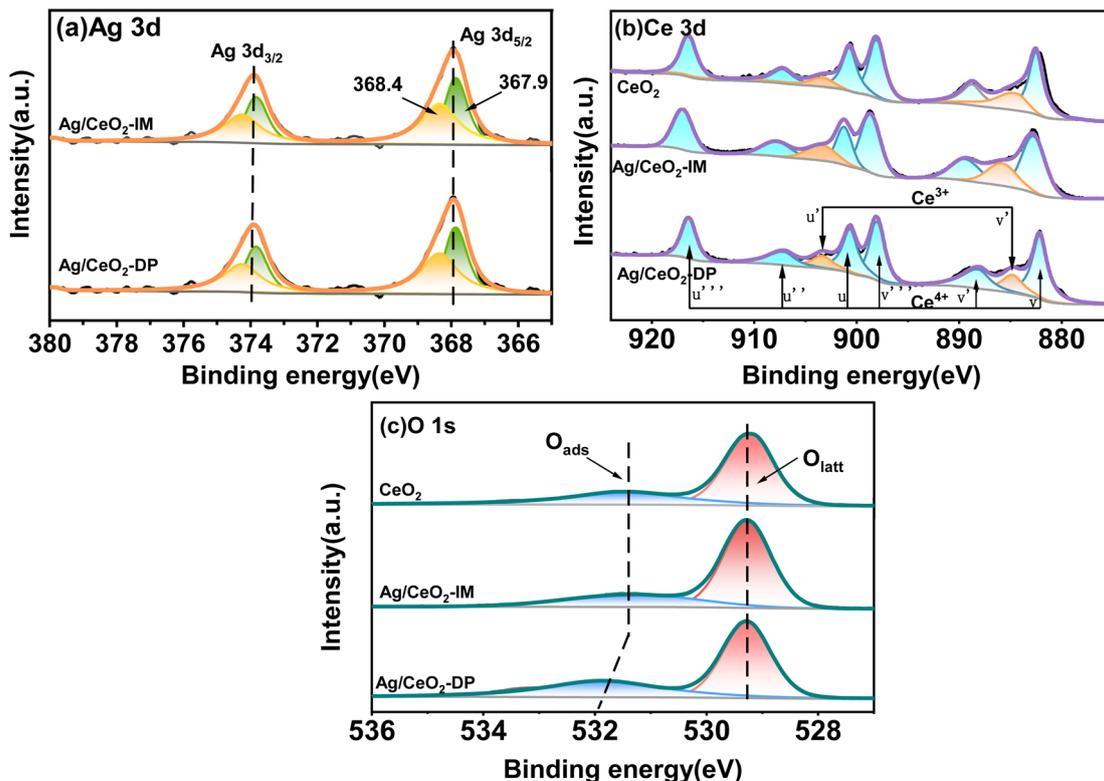


Fig. 4 Results of XPS tests on the catalysts  $\text{CeO}_2$ ,  $\text{Ag/CeO}_2\text{-DP}$ , and  $\text{Ag/CeO}_2\text{-IM}$ .

Table 2 XPS results

| Catalyst                    | Actual Ag content (wt%) | Atomic ratio (%)                          |  |  |
|-----------------------------|-------------------------|---|--|--|
|                             |                         | $\text{Ag}^0/(\text{Ag}^0 + \text{Ag}^+)$ | $\text{Ce}^{3+}/(\text{Ce}^{4+} + \text{Ce}^{3+})$ | $\text{O}_{\text{ads}}/(\text{O}_{\text{ads}} + \text{O}_{\text{latt}})$ |
| $\text{CeO}_2$              | —                       | —   | 18.30  | 26.64  |
| $\text{Ag/CeO}_2\text{-DP}$ | 1.19                    | 49.83                                     | 13.96  | 38.15  |
| $\text{Ag/CeO}_2\text{-IM}$ | 1.27                    | 56.02                                     | 10.80  | 33.95  |

markers  $u$ ,  $u''$ , and  $u'''$  correspond to  $\text{Ce}^{4+}$  of  $\text{Ce } 3d_{3/2}$ ,  $v$ ,  $v''$  and  $v'''$  correspond to  $\text{Ce}^{4+}$  of  $\text{Ce } 3d_{5/2}$ , while  $u'$  and  $v'$  correspond to  $\text{Ce}^{3+}$  of  $\text{Ce } 3d_{3/2}$  and  $\text{Ce } 3d_{5/2}$ , respectively.<sup>38,39</sup> The percentage  $\text{Ce}^{3+}$  content is shown in Table 2, with 18.30%  $\text{Ce}^{3+}$  on  $\text{CeO}_2$ , 13.96%  $\text{Ce}^{3+}$  in catalyst  $\text{Ag/CeO}_2\text{-DP}$ , and the least  $\text{Ce}^{3+}$  content of 10.8% in catalyst  $\text{Ag/CeO}_2\text{-IM}$ . This is due to the redox interaction between surface  $\text{Ce}^{3+}$  and  $\text{Ag}^+$ , which in turn produces the  $\text{Ag}^0\text{-CeO}_2$  interface.<sup>40</sup> The  $\text{Ce}^{3+}$  sites are involved in  $\text{Ag}^+$  reduction to form more  $\text{Ag}^0$ , which also corresponds to the metal Ag content outside the catalyst.

Fig. 4c exhibits the XPS O1s spectra of  $\text{CeO}_2$ ,  $\text{Ag/CeO}_2\text{-DP}$ , and  $\text{Ag/CeO}_2\text{-IM}$ . The O1s spectra may be fitted to two peaks. The binding energy is about 531 eV for surface adsorption oxygen  $\text{O}_{\text{ads}}$ , and the surface lattice oxygen  $\text{O}_{\text{latt}}$  is at about 530 eV.<sup>41–43</sup> As seen in Table 2, the catalysts obtained by both methods have higher surface adsorption of oxygen. This indicates that species of Ag present affect the ability to activate oxygen by interacting with Ce. Similar phenomena are also

found in the literature.<sup>44</sup> The  $\text{Ag/CeO}_2\text{-IM}$  catalyst's surface had somewhat less adsorption oxygen  $\text{O}_{\text{ads}}$  than the  $\text{Ag/CeO}_2\text{-DP}$  catalyst due to the formation of the  $\text{Ag}^0\text{-CeO}_2$  interface resulting in a slight increase in surface lattice oxygen.<sup>40</sup>

### 3.4 Surface acidity

Fig. 5 depicts the results characterizing the quantity and potency of acid sites across the catalyst's exterior using  $\text{NH}_3\text{-TPD}$ . On the surface of the trigger, three different types of desorption peaks can be found:  $\text{NH}_3$  physically adsorbed or  $\text{NH}_4^{+*}$  species adsorbed on weak B-acid site is in charge of the temperature below 150 °C,  $\text{NH}_4^{+*}$  species adsorbed on robust B-acid site is in charge of the peak between 150 °C and 250 °C, and  $\text{NH}_3^*$  species adsorbed on Lewis acid site is responsible for the peak beyond 250 °C.<sup>38,45</sup> Fig. 5 demonstrates that the total number of acid sites is  $\text{CeO}_2 > \text{Ag/CeO}_2\text{-DP} > \text{Ag/CeO}_2\text{-IM}$  in sequence. The  $\text{Ag/CeO}_2\text{-DP}$  catalyst retains a narrow peak below 150 °C, but the  $\text{Ag/CeO}_2\text{-IM}$  catalyst only has a weak peak



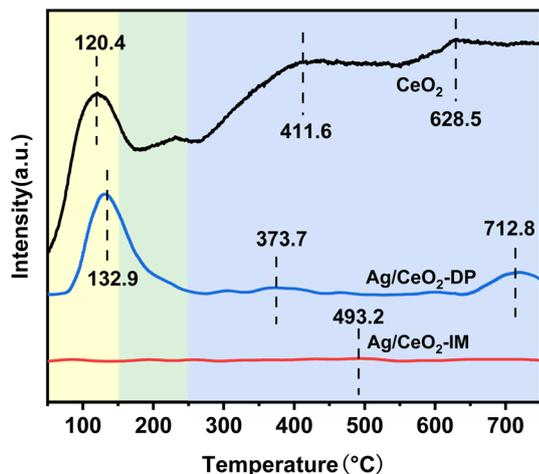


Fig. 5 Test results for the  $\text{NH}_3$ -TPD catalyst with  $\text{CeO}_2$ ,  $\text{Ag}/\text{CeO}_2$ -DP, and  $\text{Ag}/\text{CeO}_2$ -IM.

attributed to the L-acid site. The reduction of stimulus  $\text{NH}_3$  consumption after Ag support is mainly related to the drop in acid content brought on by the presence of surface silver species,<sup>26</sup> and  $\text{Ag}/\text{CeO}_2$ -IM has a very weak acidity due to the formation of the  $\text{Ag}^0$ - $\text{CeO}_2$  interface covering more acidic sites. In addition, it has been reported that the  $\text{N}_2$  selectivity of the ammonia oxidation catalyst will be impacted by its surface acidity,<sup>46,47</sup> which explains why the trigger with the lowest  $\text{N}_2$  selectivity is the  $\text{Ag}/\text{CeO}_2$ -IM.

### 3.5 Redox performance

Fig. 6 displays the data of the  $\text{H}_2$ -TPR analysis of the catalyst's redox capability. There are three reduction crests in the  $\text{H}_2$ -TPR spectra of  $\text{Ag}/\text{CeO}_2$ -IM,  $\text{Ag}/\text{CeO}_2$ -DP, and  $\text{CeO}_2$  catalysts. The reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  in bulk phase  $\text{CeO}_2$  causes the peak above 750 °C. In contrast, the removal of  $\text{CeO}_2$  on the exterior causes the peak between 350 and 650 °C,<sup>48–50</sup> and the graph shows that the catalyst's reducing peak at temperatures over

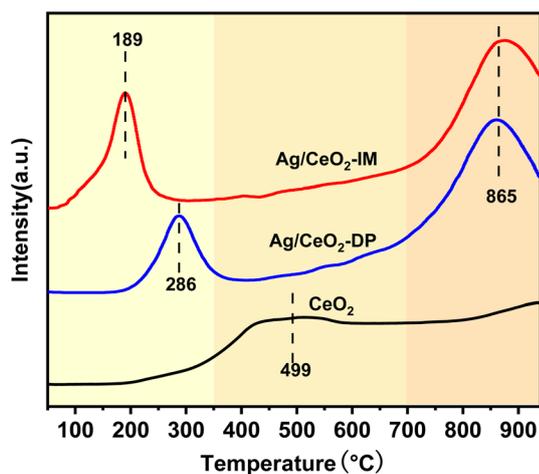


Fig. 6 Test results for the  $\text{H}_2$ -TPR catalyst with  $\text{CeO}_2$ ,  $\text{Ag}/\text{CeO}_2$ -DP, and  $\text{Ag}/\text{CeO}_2$ -IM.

750 °C after supporting Ag is more prominent than  $\text{CeO}_2$ 's, and the peak between 350–650 °C disappears. The reduction of silver oxide species or the removal of oxygen on the surface of the  $\text{Ag}^0$ - $\text{CeO}_2$  interface is responsible for the appearance of new prominent peaks at temperatures below 300 °C.<sup>51,52</sup> Moreover,  $\text{Ag}/\text{CeO}_2$ -IM catalyst has a lower reduction peak temperature, which is in line with the findings of the activity test and shows  $\text{Ag}/\text{CeO}_2$ -IM catalyst has a more extraordinary redox ability.

### 3.6 Surface reaction mechanism exploration

The DRIFTS findings of  $\text{NH}_3 + \text{O}_2$  co-adsorption at various temperatures were recorded to understand the surface response of  $\text{NH}_3$ -SCO on multiple catalysts, as shown in Fig. 7. The infrared spectra of  $\text{NH}_3$ -SCO reactions on the  $\text{Ag}/\text{CeO}_2$ -IM catalyst are shown in Fig. 7a, where  $965 \text{ cm}^{-1}$  correspond to physically adsorbed  $\text{NH}_3$ ,<sup>53</sup>  $1430 \text{ cm}^{-1}$  can be attributed to the  $\text{NH}_4^{+*}$  species adsorbed at the Brønsted acid site,<sup>47</sup> 1320, 1591, and  $1293 \text{ cm}^{-1}$  infrared peaks can be credited with  $\text{NH}_2$  (ref. 47 and 54) and  $\text{NH}$  species,<sup>46</sup>  $1030 \text{ cm}^{-1}$  corresponds to bidentate nitrate,<sup>55</sup> and 1222 and  $1246 \text{ cm}^{-1}$  correspond to bridge nitrate species.<sup>45</sup>  $\text{N}_2\text{O}_2^{2-}$  species, the intermediate that gives rise to  $\text{N}_2\text{O}$ , is responsible for the peak at  $1010 \text{ cm}^{-1}$ .<sup>56,57</sup> It can be seen from the figure that  $\text{NH}_2$  and  $\text{NH}$  species exist at 90 °C, and their peak strength is reduced to 150 °C and disappears, which indicates that some  $\text{NH}_3$  species adsorbed at low temperatures can be dehydrogenated on the surface.  $\text{NH}_4^{+*}$  species ( $1430 \text{ cm}^{-1}$ ) and  $\text{NH}_2$  species ( $1591$  and  $1320 \text{ cm}^{-1}$ ) adsorbed at the Brønsted acid site appeared at 110 °C, and their peak strength first increased and disappeared after 200 °C, indicating that the Brønsted acid site was involved in the ammonia oxidation reaction. After 200 °C, bidentate nitrate ( $1030 \text{ cm}^{-1}$ ), bridge nitrate ( $1222$  and  $1246 \text{ cm}^{-1}$ ), and intermediates of  $\text{N}_2\text{O}$  ( $1010 \text{ cm}^{-1}$ ) appeared, and with rising temperature, their peak strength increased. The above detection results show that during the ammonia oxidation reaction of the  $\text{Ag}/\text{CeO}_2$ -IM catalyst, the catalyst surface-adsorbed  $\text{NH}_3$  species underwent an ammonia oxidation process that was dehydrogenated to produce  $\text{NH}_2$  and  $\text{NH}$ . Some  $\text{NH}_x$  species were over-oxidized to form  $\text{NO}_x$ . Subsequently, nitrate adsorbed on the catalyst's exterior reacts with the  $\text{NH}_x$  species to produce  $\text{N}_2$  and a byproduct called  $\text{N}_2\text{O}$ ; that is, the ammonia oxidation reaction of the  $\text{Ag}/\text{CeO}_2$ -IM catalyst followed the i-SCR mechanism.

The infrared spectra of the  $\text{NH}_3$ -SCO reaction on the  $\text{Ag}/\text{CeO}_2$ -DP catalyst are shown in Fig. 7b. Brønsted acid sites' adsorbed  $\text{NH}_4^{+*}$  species are responsible for the peaks at 1398 and  $1467 \text{ cm}^{-1}$ ,<sup>47</sup>  $\text{NH}_3^*$  species adsorbed at Lewis acid sites are accountable for the peaks at 1145 and  $1052 \text{ cm}^{-1}$ ,<sup>45</sup>  $\text{NH}_2$  and  $\text{NH}$  species are responsible for the peaks at 1355 and  $1292 \text{ cm}^{-1}$ ,<sup>47</sup> and 1030, 1523, and  $1554 \text{ cm}^{-1}$  correspond to bidentate nitrates,<sup>55,58,59</sup> and  $1218 \text{ cm}^{-1}$  is classified as bridge nitrate.<sup>45</sup> The  $\text{Ag}/\text{CeO}_2$ -DP catalyst also follows the i-SCR reaction pathway, as shown in Fig. 7b. The double-toothed nitrate and bridge nitrate species were seen outside the  $\text{Ag}/\text{CeO}_2$ -DP catalyst at 300 °C. In contrast, these nitrate species were seen on the exterior of the  $\text{Ag}/\text{CeO}_2$ -IM catalyst at 200 °C, indicating that



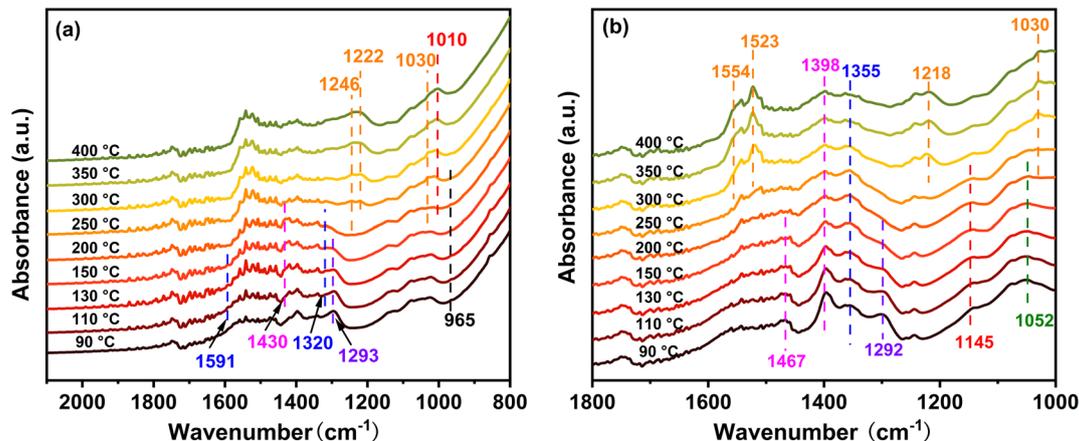


Fig. 7 Ag/CeO<sub>2</sub>-IM (a) and Ag/CeO<sub>2</sub>-DP (b) catalysts acting as NH<sub>3</sub>-SCO catalysts *in situ* DRIFTS reactions at various temperatures.

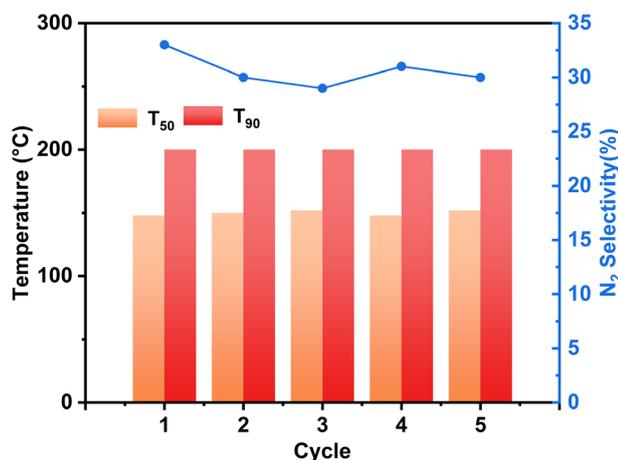


Fig. 8 Comparison of  $T_{50}$ ,  $T_{90}$ , and  $N_2$  selectivity at 400 °C for 5 cycles of stability testing of Ag/CeO<sub>2</sub>-IM catalysts (inlet reaction gas composition: [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 10 vol%, N<sub>2</sub> is equilibrium gas, GHSV = 100 000 h<sup>-1</sup>).

the Ag/CeO<sub>2</sub>-IM catalyst had a lower NH<sub>3</sub> ignition temperature and better NH<sub>3</sub> oxidation capacity, which agreed with the outcomes of the two catalytic activity tests as well.

### 3.7 Hydrothermal stability

In practical applications, the diesel engine will undergo a stop-cooling-restart process, which will impact the catalyst's action, so we conducted a cyclic stability test on the motivation and simulated the actual situation to investigate the tolerance of the stimulus. Fig. 8 displays the Ag/CeO<sub>2</sub>-IM catalyst's stability test results over numerous cycles. During the 5 processes of the cycling test, the NH<sub>3</sub> conversion results of the Ag/CeO<sub>2</sub>-IM catalyst remained constant,  $T_{90}$  was kept at 200 °C, and the N<sub>2</sub> selectivity at 400 °C remained relatively stable at about 30%, which indicates that the Ag/CeO<sub>2</sub>-IM catalyst has good cycling stability and no major changes in the active sites during the cycling process.

In addition, diesel engines in practical applications usually have exhaust temperatures higher than 600 °C due to the regeneration of diesel particulate filters and contain about 10% H<sub>2</sub>O.<sup>60,61</sup> Therefore, catalysts for diesel vehicles require high hydrothermal durability. Fig. 9 displays the Ag/CeO<sub>2</sub>-IM catalyst's activity test results before and after hydrothermal ageing at 700 °C for 12 h. Ag/CeO<sub>2</sub>-IM catalyst's hydrothermal ageing reduces NH<sub>3</sub> conversion at low temperatures, an increase of  $T_{90}$  by 50 °C, and a decrease in N<sub>2</sub> selectivity to about 50% at 200 °C,

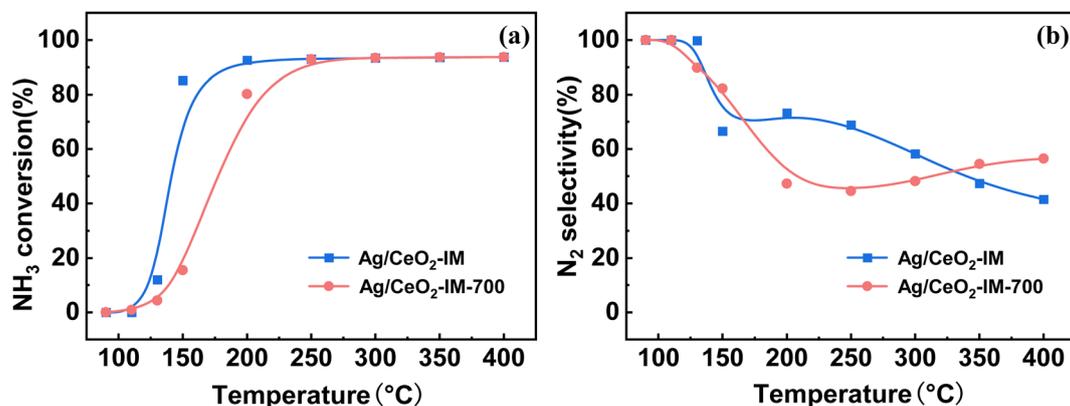


Fig. 9 (a) NH<sub>3</sub> conversion (b) N<sub>2</sub> selectivity of Ag/CeO<sub>2</sub>-IM catalyst and Ag/CeO<sub>2</sub>-IM-700 catalyst after hydrothermal testing.



which may be due to agglutination and sintering of Ag species at 700 °C. The hydrothermal stability of the Ag/CeO<sub>2</sub>-IM catalyst needs to be improved.

## 4. Conclusions

In this study, the deposition precipitation approach and equal volume impregnation method were used to create the Ag/CeO<sub>2</sub> catalyst, the impact of the preparation technique and load amount on ammonia oxidation performance was discussed, and the following conclusions were drawn:

(1) The Ag/CeO<sub>2</sub>-IM catalyst prepared by the equal volume impregnation method has a better NH<sub>3</sub> oxidation capacity than the Ag/CeO<sub>2</sub>-DP catalyst prepared by the deposition precipitation method. NH<sub>3</sub> conversion can reach 90% at 200 °C, and T<sub>50</sub> is below 150 °C. The Ag/CeO<sub>2</sub>-IM catalyst has good cycle stability, but its hydrothermal stability at 700 °C still needs to be improved.

(2) The Ag/CeO<sub>2</sub>-IM catalyst has a higher content of Ag<sup>0</sup> and stronger redox, which achieves low temperature and high NH<sub>3</sub> conversion, but its surface acidity is less than that of Ag/CeO<sub>2</sub>-DP, which results in N<sub>2</sub> selectivity decreasing slowly at 150–400 °C. According to the results of *in situ* DRIFTS, the Ag/CeO<sub>2</sub>-IM catalyst had a lower NH<sub>3</sub> ignition temperature and better NH<sub>3</sub> oxidation capacity, which was the main reason for the higher activities of the Ag/CeO<sub>2</sub>-IM catalyst.

(3) The mechanism of NH<sub>3</sub>-SCO on the Ag/CeO<sub>2</sub>-IM and Ag/CeO<sub>2</sub>-DP catalysts both followed the i-SCR mechanism.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## References

- 1 Y. Zeng, S. Tian and Y. Pan, Revealing the Sources of Atmospheric Ammonia: a Review, *Curr. Pollut. Rep.*, 2018, **4**(3), 189–197.
- 2 C. M. Clark and D. Tilman, Loss of plant species after chronic low-level nitrogen deposition to prairie grasslands, *Nature*, 2008, **451**(7179), 712–715.
- 3 X. Qiang, M. Hu, B. Zhao, Y. Qin, T. Zhang, L. Zhou and J. Liang, Preparation of porous silicon/Pd-loaded WO<sub>3</sub> nanowires for enhancement of ammonia sensing properties at room temperature, *Mater. Sci. Semicond. Process.*, 2018, **79**, 113–118.
- 4 S. Gerrity, E. Clifford, C. Kennelly and G. Collins, Ammonia oxidizing bacteria and archaea in horizontal flow biofilm reactors treating ammonia-contaminated air at 10 degrees C, *J. Ind. Microbiol. Biotechnol.*, 2016, **43**(5), 651–661.
- 5 M. Gu, Y. Pan, W. W. Walters, Q. Sun, L. Song, Y. Wang, Y. Xue and Y. Fang, Vehicular Emissions Enhanced Ammonia Concentrations in Winter Mornings: Insights from Diurnal Nitrogen Isotopic Signatures, *Environ. Sci. Technol.*, 2022, **56**(3), 1578–1585.
- 6 N. J. Farren, J. Davison, R. A. Rose, R. L. Wagner and D. C. Carslaw, Underestimated Ammonia Emissions from Road Vehicles, *Environ. Sci. Technol.*, 2020, **54**(24), 15689–15697.
- 7 E. Liu, B. Sarkar, L. Wang and R. Naidu, Copper-complexed clay/poly-acrylic acid composites: Extremely efficient adsorbents of ammonia gas, *Appl. Clay Sci.*, 2016, **121–122**, 154–161.
- 8 E. Morral, D. Gabriel, A. D. Dorado and X. Gamisans, A review of biotechnologies for the abatement of ammonia emissions, *Chemosphere*, 2021, **273**, 128606.
- 9 M. Saeed, M. A. Arain, M. Naveed, M. Alagawany, M. E. Abd El-Hack, Z. A. Bhutto, M. Bednarczyk, M. U. Kakar, M. Abdel-Latif and S. Chao, *Yucca schidigera* can mitigate ammonia emissions from manure and promote poultry health and production, *Environ. Sci. Pollut. Res. Int.*, 2018, **25**(35), 35027–35033.
- 10 T. Lan, Y. Zhao, J. Deng, J. Zhang, L. Shi and D. Zhang, Selective catalytic oxidation of NH<sub>3</sub> over noble metal-based catalysts: state of the art and future prospects, *Catal. Sci. Technol.*, 2020, **10**(17), 5792–5810.
- 11 L. Zhang and H. He, Mechanism of selective catalytic oxidation of ammonia to nitrogen over Ag/Al<sub>2</sub>O<sub>3</sub>, *J. Catal.*, 2009, **268**(1), 18–25.
- 12 S. Ge, X. Liu, J. Liu, H. Liu, H. Liu, X. Chen, G. Wang, J. Chen, G. Zhang, Y. Zhang and J. Li, Synthesis of TixSn1-xO<sub>2</sub> mixed metal oxide for copper catalysts as high-efficiency NH<sub>3</sub> selective catalytic oxidation, *Fuel*, 2022, **314**, 123061.
- 13 M. Sun, J. Liu, C. Song, Y. Ogata, H. Rao, X. Zhao, H. Xu and Y. Chen, Different Reaction Mechanisms of Ammonia Oxidation Reaction on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeZrO<sub>2</sub> with Various Pt States, *ACS Appl. Mater. Interfaces*, 2019, **11**(26), 23102–23111.
- 14 Y. Zhang, M. Zhang, Y. Zang, H. Wang, C. Liu, L. Wei, Y. Wang, L. He, W. Wang, Z. Zhang, R. Han, N. Ji, C. Song, X. Lu, D. Ma, Y. Sun and Q. Liu, Elimination of NH<sub>3</sub> by Interfacial Charge Transfer over the Ag/CeSnO<sub>x</sub> Tandem Catalyst, *ACS Catal.*, 2023, 1449–1461.
- 15 H. Wang, T. Murayama, M. Lin, N. Sakaguchi, M. Haruta, H. Miura and T. Shishido, Understanding the Distinct Effects of Ag Nanoparticles and Highly Dispersed Ag Species on N<sub>2</sub> Selectivity in NH<sub>3</sub>-SCO Reaction, *ACS Catal.*, 2022, **12**(10), 6108–6118.
- 16 L. Peng, A. Guo, D. Chen, P. Liu, B. Peng, M. Fu, D. Ye and P. Chen, Ammonia Abatement via Selective Oxidation over Electron-Deficient Copper Catalysts, *Environ. Sci. Technol.*, 2022, **56**(19), 14008–14018.
- 17 L. Chmielarz and M. Jablonska, Advances in selective catalytic oxidation of ammonia to dinitrogen: a review, *RSC Adv.*, 2015, **5**(54), 43408–43431.



- 18 J. Guo, Y. Peng, Y. Zhang, W. Yang, L. Gan, K. Li, J. Chen and J. Li, Comparison of NH<sub>3</sub>-SCO performance over CuOx/H-SSZ-13 and CuOx/H-SAPO-34 catalysts, *Appl. Catal., A*, 2019, **585**, 117119.
- 19 F. Wang, Y. Zhu, Z. Li, Y. Shan, W. Shan, X. Shi, Y. Yu, C. Zhang, K. Li, P. Ning, Y. Zhang and H. He, Promoting effect of acid sites on NH<sub>3</sub>-SCO activity with water vapor participation for Pt-Fe/ZSM-5 catalyst, *Catal. Today*, 2021, **376**, 311–317.
- 20 T. Lan, Y. Zhao, J. Deng, J. Zhang, L. Shi and D. Zhang, Selective catalytic oxidation of NH<sub>3</sub> over noble metal-based catalysts: state of the art and future prospects, *Catal. Sci. Technol.*, 2020, **10**(17), 5792–5810.
- 21 H. Wang, T. Murayama, M. Lin, N. Sakaguchi, M. Haruta, H. Miura and T. Shishido, Understanding the Distinct Effects of Ag Nanoparticles and Highly Dispersed Ag Species on N<sub>2</sub> Selectivity in NH<sub>3</sub>-SCO Reaction, *ACS Catal.*, 2022, 6108–6118.
- 22 H. Wang, M. Lin, T. Murayama, S. Feng, M. Haruta, H. Miura and T. Shishido, Selective catalytic oxidation of ammonia to nitrogen over zeolite-supported Pt-Au catalysts: Effects of alloy formation and acid sites, *J. Catal.*, 2021, **402**, 101–113.
- 23 H. Zhao, Z. Qu and H. Sun, Rational design of spinel CoMn<sub>2</sub>O<sub>4</sub> with Co-enriched surface as high-activity catalysts for NH<sub>3</sub>-SCO reaction, *Appl. Surf. Sci.*, 2020, **529**, 147044.
- 24 W. Liu, Y. Long, X. Tong, Y. Yin, X. Li and J. Hu, Transition metals modified commercial SCR catalysts as efficient catalysts in NH<sub>3</sub>-SCO and NH<sub>3</sub>-SCR reactions, *Mol. Catal.*, 2021, **515**, 111888.
- 25 Z. Wang, Q. Sun, D. Wang, Z. Hong, Z. Qu and X. Li, Hollow ZSM-5 zeolite encapsulated Ag nanoparticles for SO<sub>2</sub>-resistant selective catalytic oxidation of ammonia to nitrogen, *Sep. Purif. Technol.*, 2019, **209**, 1016–1026.
- 26 M. Jablonska, W. Ciptonugroho, K. Gora-Marek, M. G. Al-Shaal and R. Palkovits, Preparation, characterization and catalytic performance of Ag-modified mesoporous TiO<sub>2</sub> in low-temperature selective ammonia oxidation into nitrogen and water vapour, *Microporous Mesoporous Mater.*, 2017, **245**, 31–44.
- 27 F. Wang, G. He, B. Zhang, M. Chen, X. Chen, C. Zhang and H. He, Insights into the Activation Effect of H<sub>2</sub> Pretreatment on Ag/Al<sub>2</sub>O<sub>3</sub> Catalyst for the Selective Oxidation of Ammonia, *ACS Catal.*, 2019, **9**(2), 1437–1445.
- 28 F. Wang, J. Ma, G. He, M. Chen, C. Zhang and H. He, Nanosize Effect of Al<sub>2</sub>O<sub>3</sub> in Ag/Al<sub>2</sub>O<sub>3</sub> Catalyst for the Selective Catalytic Oxidation of Ammonia, *ACS Catal.*, 2018, **8**(4), 2670–2682.
- 29 F. Wang, J. Ma, G. He, M. Chen, S. Wang, C. Zhang and H. He, Synergistic Effect of TiO<sub>2</sub>-SiO<sub>2</sub> in Ag/Si-Ti Catalyst for the Selective Catalytic Oxidation of Ammonia, *Ind. Eng. Chem. Res.*, 2018, **57**(35), 11903–11910.
- 30 H. Sun, H. Wang and Z. Qu, Construction of CuO/CeO<sub>2</sub> Catalysts via the Ceria Shape Effect for Selective Catalytic Oxidation of Ammonia, *ACS Catal.*, 2023, 1077–1088.
- 31 L. Zhou, M. Zhang, C. Liu, H. Wang, Y. Zhang, Y. Zang, Z. Zhang, R. Han, N. Ji, C. Song, X. Lu, W. Wang and Q. Liu, Synergistic Effect over CeSnO<sub>x</sub> Catalyst for the Selective Catalytic Oxidation of NH<sub>3</sub>, *ACS Appl. Energy Mater.*, 2022, **5**(11), 14211–14221.
- 32 P. Azadi, E. Afif, F. Azadi and R. Farnood, Screening of nickel catalysts for selective hydrogen production using supercritical water gasification of glucose, *Green Chem.*, 2012, **14**(6), 1766–1777.
- 33 W. J. Liu, Y. F. Long, S. N. Liu, Y. Y. Zhou, X. Tong, Y. J. Yin, X. Y. Li, K. Hu and J. J. Hu, Promotional effect of Ce in NH<sub>3</sub>-SCO and NH<sub>3</sub>-SCR reactions over Cu-Ce/SCR catalysts, *J. Ind. Eng. Chem.*, 2022, **107**, 197–206.
- 34 T. Montini, M. Melchionna, M. Monai and P. Fornasiero, Fundamentals and Catalytic Applications of CeO<sub>2</sub>-Based Materials, *Chem. Rev.*, 2016, **116**(10), 5987–6041.
- 35 Y. Su, K. Fu, Y. Zheng, N. Ji, C. Song, D. Ma, X. Lu, R. Han and Q. Liu, Catalytic oxidation of dichloromethane over Pt-Co/HZSM-5 catalyst: Synergistic effect of single-atom Pt, Co<sub>3</sub>O<sub>4</sub>, and HZSM-5, *Appl. Catal., B*, 2021, **288**, 119980.
- 36 S. Zhao, Z. Li, Z. Qu, N. Yan, W. Huang, W. Chen and H. Xu, Co-benefit of Ag and Mo for the catalytic oxidation of elemental mercury, *Fuel*, 2015, **158**, 891–897.
- 37 E. Sumesh, M. S. Bootharaju and A. T. Pradeep, A practical silver nanoparticle-based adsorbent for the removal of Hg<sup>2+</sup> from water, *J. Hazard. Mater.*, 2011, **189**(1–2), 450–457.
- 38 S. M. Lee, H. H. Lee and S. C. Hong, Influence of calcination temperature on Ce/TiO<sub>2</sub> catalysis of selective catalytic oxidation of NH<sub>3</sub> to N<sub>2</sub>, *Appl. Catal., A*, 2014, **470**, 189–198.
- 39 Z. Wang, Z. Qu, X. Quan, Z. Li, H. Wang and R. Fan, Selective catalytic oxidation of ammonia to nitrogen over CuO-CeO<sub>2</sub> mixed oxides prepared by surfactant-templated method, *Appl. Catal., B*, 2013, **134–135**, 153–166.
- 40 M. V. Grabchenko, G. V. Mamontov, V. I. Zaikovskii, V. La Parola, L. F. Liotta and O. V. Vodyankina, The role of metal-support interaction in Ag/CeO<sub>2</sub> catalysts for CO and soot oxidation, *Appl. Catal., B*, 2020, **260**, 118148.
- 41 M. Sun, S. Wang, Y. Li, H. Xu and Y. Chen, Promotion of catalytic performance by adding W into Pt/ZrO<sub>2</sub> catalyst for selective catalytic oxidation of ammonia, *Appl. Surf. Sci.*, 2017, **402**, 323–329.
- 42 J. H. Shin, G. J. Kim and S. C. Hong, Reaction properties of ruthenium over Ru/TiO<sub>2</sub> for selective catalytic oxidation of ammonia to nitrogen, *Appl. Surf. Sci.*, 2020, **506**, 144906.
- 43 Y. Wang, H. Chang, C. Shi, L. Duan, J. Li, G. Zhang, L. Guo and Y. You, Novel Fe-Ce-O mixed metal oxides catalyst prepared by hydrothermal method for Hg<sup>0</sup> oxidation in the presence of NH<sub>3</sub>, *Catal. Commun.*, 2017, **100**, 210–213.
- 44 X. L. Tang, Y. Y. Zhang, Y. R. Lei, Y. Y. Liu, H. H. Yi and F. Y. Gao, Promotional catalytic activity and reaction mechanism of Ag-modified Ce<sub>0.6</sub>Zr<sub>0.4</sub>O<sub>2</sub> catalyst for catalytic oxidation of ammonia, *J. Environ. Sci.*, 2023, **124**, 491–504.
- 45 H. Wang, Q. Zhang, T. Zhang, J. Wang, G. Wei, M. Liu and P. Ning, Structural tuning and NH<sub>3</sub>-SCO performance optimization of CuO-Fe<sub>2</sub>O<sub>3</sub> catalysts by impact of thermal treatment, *Appl. Surf. Sci.*, 2019, **485**, 81–91.
- 46 M. Lin, B. An, N. Niimi, Y. Jikihara, T. Nakayama, T. Honma, T. Takei, T. Shishido, T. Ishida, M. Haruta and T. Murayama,



- Role of the Acid Site for Selective Catalytic Oxidation of NH<sub>3</sub> over Au/Nb<sub>2</sub>O<sub>5</sub>, *ACS Catal.*, 2019, **9**(3), 1753–1756.
- 47 Q. Zhang, T. Zhang, F. Xia, Y. Zhang, H. Wang and P. Ning, Promoting effects of acid enhancing on N<sub>2</sub> selectivity for selectivity catalytic oxidation of NH<sub>3</sub> over RuO<sub>x</sub>/TiO<sub>2</sub>: The mechanism study, *Appl. Surf. Sci.*, 2020, **500**, 144044.
- 48 A. Trovarelli, Catalytic properties of ceria and CeO<sub>2</sub>-containing materials, *Catal. Rev.*, 1996, **38**(4), 439–520.
- 49 E. Aneggi, D. Wiaterski, C. de Leitenburg, J. Llorca and A. Trovarelli, Shape-Dependent Activity of Ceria in Soot Combustion, *ACS Catal.*, 2013, **4**(1), 172–181.
- 50 K. Krishna, A. Bueno-López, M. Makkee and J. A. Moulijn, Potential rare-earth modified CeO<sub>2</sub> catalysts for soot oxidation part II: Characterisation and catalytic activity with NO+O<sub>2</sub>, *Appl. Catal., B*, 2007, **75**(3–4), 201–209.
- 51 L. Yu, R. Peng, L. Chen, M. Fu, J. Wu and D. Ye, Ag supported on CeO<sub>2</sub> with different morphologies for the catalytic oxidation of HCHO, *Chem. Eng. J.*, 2018, **334**, 2480–2487.
- 52 G. V. Mamontov, M. V. Grabchenko, V. I. Sobolev, V. I. Zaikovskii and O. V. Vodyankina, Ethanol dehydrogenation over Ag-CeO<sub>2</sub>/SiO<sub>2</sub> catalyst: Role of Ag-CeO<sub>2</sub> interface, *Appl. Catal., A*, 2016, **528**, 161–167.
- 53 D. M. Meng, W. C. Zhan, Y. Guo, Y. L. Guo, L. Wang and G. Z. Lu, A Highly Effective Catalyst of Sm-MnO<sub>x</sub> for the NH<sub>3</sub>-SCR of NO<sub>x</sub> at Low Temperature: Promotional Role of Sm and Its Catalytic Performance, *ACS Catal.*, 2015, **5**(10), 5973–5983.
- 54 Q. L. Zhang, H. M. Wang, P. Ning, Z. X. Song, X. Liu and Y. K. Duan, In situ DRIFTS studies on CuO-Fe<sub>2</sub>O<sub>3</sub> catalysts for low temperature selective catalytic oxidation of ammonia to nitrogen, *Appl. Surf. Sci.*, 2017, **419**, 733–743.
- 55 S. H. Zhan, H. Zhang, Y. Zhang, Q. Shi, Y. Li and X. J. Li, Efficient NH<sub>3</sub>-SCR removal of NO<sub>x</sub> with highly ordered mesoporous WO<sub>3</sub>(chi)-CeO<sub>2</sub> at low temperatures, *Appl. Catal., B*, 2017, **203**, 199–209.
- 56 M. Q. Shen, L. L. Xu, J. Q. Wang, C. X. Li, W. L. Wang, J. Wang and Y. P. Zhai, Effect of synthesis methods on activity of V<sub>2</sub>O<sub>5</sub>/CeO<sub>2</sub>/WO<sub>3</sub>-TiO<sub>2</sub> catalyst for selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>, *J. Rare Earths*, 2016, **34**(3), 259–267.
- 57 Y. Liu, T. T. Gu, X. L. Weng, Y. Wang, Z. B. Wu and H. Q. Wang, DRIFT Studies on the Selectivity Promotion Mechanism of Ca-Modified Ce-Mn/TiO<sub>2</sub> Catalysts for Low-Temperature NO Reduction with NH<sub>3</sub>, *J. Phys. Chem. C*, 2012, **116**(31), 16582–16592.
- 58 M. Jablonska, A. M. Beale, M. Nocun and R. Palkovits, Ag-Cu based catalysts for the selective ammonia oxidation into nitrogen and water vapour, *Appl. Catal., B*, 2018, **232**, 275–287.
- 59 L. Uran, J. Gallego, W. Ruiz, E. Bailon-Garcia, A. Bueno-Lopez and A. Santamaria, Monitoring intermediate species formation by DRIFT during the simultaneous removal of soot and NO<sub>x</sub> over LaAgMnO<sub>3</sub> catalyst, *Appl. Catal., A*, 2019, **588**, 117280.
- 60 B. Guan, R. Zhan, H. Lin and Z. Huang, Review of state of the art technologies of selective catalytic reduction of NO<sub>x</sub> from diesel engine exhaust, *Appl. Therm. Eng.*, 2014, **66**(1–2), 395–414.
- 61 A. Marberger, M. Elsener, R. J. G. Nuguid, D. Ferri and O. Kröcher, Thermal activation and aging of a V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub> catalyst for the selective catalytic reduction of NO with NH<sub>3</sub>, *Appl. Catal., A*, 2019, **573**, 64–72.

