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Promotional mechanism of enhanced denitration activity with Cu modification in a Ce/TiO₂–ZrO₂ catalyst for a low temperature NH₃-SCR system†

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This study aims to investigate the enhanced low temperature denitration activity and promotional mechanism of a cerium-based catalyst through copper modification. In this paper, copper and cerium oxides were supported on TiO₂–ZrO₂ by an impregnation method, their catalytic activity tests of selective catalytic reduction (SCR) of NO with NH₃ were carried out and their physicochemical properties were characterized. The CuCe/TiO₂–ZrO₂ catalyst shows obviously enhanced NH₃-SCR activity at low temperature (<300 °C), which is associated with the well dispersed active ingredients and the synergistic effect between copper and cerium species (Cu²⁺ + Ce³⁺ ↔ Cu⁺ + Ce⁴⁺), and the increased ratios of surface chemisorbed oxygen and Cu⁺/Cu²⁺ lead to the enhanced low-temperature SCR activity. The denitration reaction mechanism over the CuCe/TiO₂–ZrO₂ catalyst was investigated by *in situ* DRIFTS and DFT studies. Results illustrate that the NH₃ is inclined to adsorb on the Cu acidic sites (Lewis acid sites), and the NH₂ and NH₂NO species are the key intermediates in the low-temperature NH₃-SCR process, which can explain the promotional effect of Cu modification on denitration activity of Ce/TiO₂–ZrO₂ at the molecular level. Finally, we have reasonably concluded a NH₃-SCR catalytic cycle involving the Eley–Rideal mechanism and Langmuir–Hinshelwood mechanism, and the former mechanism dominates in the NH₃-SCR reaction.

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1. Introduction

Nitrogen oxides (NO_x) from automobile exhaust emissions and industrial processes can cause harmful effects on the ecological environment, such as photochemical smog, ozone depletion, acid rain, and the greenhouse effect.^{1,2} The selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is the most efficient and widely used technology for the control of NO_x emission.^{3,4} Traditional commercial vanadium–titanium catalysts have been used in various industrial fields due to their stability and high efficiency, but industrial application is still restrained by their inevitable drawbacks, including high operation temperature window, poisoning and deactivation of catalyst by deposited alkaline metal, and vanadium poisoning.^{5–7} Therefore, it is necessary to develop NH₃-SCR catalysts with excellent denitration activity in low temperature ranges.

Due to its preferable oxygen storage and redox properties, cerium-based catalyst has been extensively investigated to eliminate NO_x during the past several years.⁸ However, the NH₃-SCR activity of pure ceria is still very low, it is necessary to dope other transitional metals to improve the denitration performance of CeO₂. Copper containing materials have been commonly employed as catalysts due to the good low-temperature activity in NH₃-SCR process. Among them catalysts modified with copper, such as Cu-ZSM-5,⁹ Cu-MCM-41,¹⁰ Cu/SAPO-34,¹¹ and Cu/TiO₂ (ref. 12) have presented a high catalytic activity in the low temperature range. Moreover, it is reported that the synergistic interaction between Cu with Ce species can contribute to the enhancement of low temperature catalytic activity.¹³ Understanding the reaction mechanism over the catalyst is one of the core interests for the development of the NH₃-SCR catalyst with high catalytic activity. The generally accepted NH₃-SCR reaction mechanism includes two mechanisms in low temperature section, Eley–Rideal mechanism (adsorbed NH₃ reacts with gaseous NO and then decomposes to N₂ and H₂O) and Langmuir–Hinshelwood mechanism (adsorbed NO reacts with adsorbed NH₃ on the adjacent sites and then decomposes to N₂ and H₂O).^{14,15} Previously, it has been shown that a mixed Eley–Rideal mechanism and Langmuir–Hinshelwood mechanism for NH₃-SCR reaction over Cu/SSZ-39 catalyst

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at low temperature.¹⁶ Moreover, Lewis acid sites on the Cu–Ce–USY catalyst surface play a crucial role in its excellent low temperature SCR performance.¹⁷ Although there are many studies on reaction mechanism of copper and copper–cerium catalysts, details on reaction path and mechanism still need to be further investigated.

In addition to the experimental methods, the quantum chemical theoretical calculation methods of molecular simulation, especially the density functional theory (DFT), has been widely used to study the reaction mechanism in the field of catalyst denitration.¹⁸ On the one hand, the theoretical calculations can solve several problems difficultly dealt with the experimental study, such as active intermediates and molecular reaction details. On the other hand, the mutual verification with the experimental results improves the credibility of the experiment. As the first step and important part in the SCR reaction, the NH₃ and NO adsorption are related to the active acid sites and can lead to the generation of highly active intermediaries, which can be well discussed with DFT calculations.

In this paper, we explored the promotional mechanism of enhanced denitration activity on the cerium-based catalyst with copper modification for low temperature NH₃-SCR reaction. Textural, morphological and redox properties of the catalysts were researched with a few physicochemical characterized measurements, such as XRD, SEM, and XPS techniques. The active adsorbed species and intermediates were detected with *in situ* diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS), and the adsorptions of NH₃ and NO molecules were calculated with DFT method. The NH₃-SCR reaction mechanism over CuCe/TiO₂-ZrO₂ catalyst was systematically investigated by the *in situ* DRIFTS measurements combined with DFT calculations, and the catalytic cycle was deduced. Elucidating the NH₃-SCR reaction mechanism over CuCe/TiO₂-ZrO₂ catalyst in the molecular level could provide theoretical guidance for the design and development of modification on denitration catalysts.

2. Experimental and computational details

2.1 Catalyst preparation

The CuCe/TiO₂-ZrO₂ catalyst was prepared by impregnation method, and the amount of copper and cerium loading on the TiO₂-ZrO₂ support were 20 wt% and 10 wt%, respectively. The TiO₂-ZrO₂ (molar ratio of 1 : 1) support was synthesized by sol-gel method. Firstly, a certain quantity of Ti(OC₄H₉)₄ and ZrOCl₂·8H₂O (Guoyao Group Chemical Reagent Co., Ltd.) were dissolved in ethanol absolute, followed by dropwise addition of pre-prepared solution (the deionized water : acetic acid : ethanol absolute = 2 : 2 : 1 volume ratio). As addition of pre-prepared solution progressed to a certain extent, the precursor solution gradually became transparent and the pH of the solution increased to around 2. Afterwards, the mixed solution was stirred magnetically at room temperature until transparent sol was formed. Next, the mixture heated in a thermostatic water bath at 50 °C for 1 h and aged at room temperature for 12 h till

the hydrosol became transparent gel. Finally, the gel was incubated at 80 °C for 5 h and kept at 120 °C overnight in an oven. The obtained product was ground and calcined at 500 °C for 3 h in the muffle furnace. Certain amount of Ce(NO₃)₃·6H₂O (Tianjin Guangfu Fine Chemical Research Institute) and TiO₂-ZrO₂ were dissolved in deionized water, then the solution with magnetic stirring at 80 °C for 1 h. The obtained product was aged at room temperature for 12 h. Then, the mixture dried at 105 °C overnight in the oven and calcined at 450 °C for 4 h in a muffle furnace to obtain the Ce/TiO₂-ZrO₂ catalyst. The Cu/TiO₂-ZrO₂ catalyst was prepared with Cu(NO₃)₂·3H₂O (Tianjin Fuchen Chemical Reagents Company) and TiO₂-ZrO₂ as precursors followed the same method. The Ce/TiO₂-ZrO₂ sample and corresponding amount of Cu(NO₃)₂·3H₂O were dissolved in deionized water, then through magnetic stirring, evaporation, and calcination as with the above preparation method, and the catalyst prepared was denoted as CuCe/TiO₂-ZrO₂.

2.2 Catalyst activity test

The catalyst activity tests were carried out in a bench-scale experimental system at the temperature range of 150–400 °C. During each test, 0.2 g catalyst was put in the quartz tube of tubular furnace filled with the simulated flue gas. The reactant gas mixture contained 500 ppm NO, 500 ppm NH₃, 5% O₂ and N₂ balanced, and the total flow rate of the feeding gas was 500 mL min⁻¹, corresponding to a gas hourly space velocity (GHSV) of 60 000 h⁻¹. During each catalytic test, the temperature reached around the preset value, then reaction continued for 10 min until the readings of temperature and NO concentration were stable. Afterwards, the temperature and NO concentration were recorded every 30 s in 5 min, the average value was calculated and used to obtain the NO conversion. NO concentrations in the inlet and outlet gas were collected with a professional flue gas analyzer (Madur Photon & PGD-100, Austria). The denitration activity was determined by NO conversion, which was calculated by the following equation:

$$\text{NO conversion} = \frac{\text{NO}(\text{in}) - \text{NO}(\text{out})}{\text{NO}(\text{in})}$$

where NO (in) represented the NO concentration in the feed gas and NO (out) expressed the NO concentration in the effluent stream.

2.3 Catalyst characterization

The X-ray diffraction (XRD) patterns of the different catalysts were collected with a D8 Advanced diffractometer (Bruker, Germany) with Cu K α radiation in the 2 θ range from 10° to 80°. The working voltage was 40 kV, and the working current was 30 mA.

The Scanning electron microscopy (SEM) images of the samples were taken with a Quanta 250 FEG scanning electron microscope (FEI, USA) at an accelerating voltage of 30 kV.

The X-ray photoelectron spectroscopy (XPS) measurements were recorded on an Axis Ultra DLD spectrometer (Kratos, UK), Al K α radiation was used as the excitation source. The binding



energies were corrected by C1s peak at 284.6 eV to compensate the charging effect.

In situ DRIFTS experiments were performed on a Nicolet iS 50 FTIR spectrometer (Thermo Fisher, USA) equipped with an MCT/A detector. The catalyst was pretreated in the cell at 400 °C for 1 hour to remove adsorbed impurities, and then cooled down to 200 °C in N₂ gas flow. The background spectrum was recorded in a flow of pure N₂ atmosphere and subtracted automatically from the catalyst sample at 200 °C.

2.4 DFT calculations

The structural optimization, intermediates, transition states search, and calculated energy were analyzed in the DMol3 module in Materials Studio 2019. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was used to describe the electron exchange–correlation potential.¹⁹ The interaction between the valence and the core electrons was described by the projector augmented wave (PAW).²⁰ Brillouin zone was sampled by employing the 2 × 2 × 1 Monkhorst–Pack *k*-point grid and the plane wave cutoff energy was 400 eV. The maximum force of geometry optimization to 0.05 eV Å⁻¹. The convergence tolerance values of total energy, maximum atomic forces and maximum displacement were 1 × 10⁻⁵ Hartree, 4 × 10⁻³ Hartree Å⁻¹ and 5 × 10⁻³ Å, respectively.²¹

CeO₂ (1 1 1) has been previously reported to be the most stable among low index CeO₂ facets,^{22,23} which is also in harmony with the experimental result in this paper. Therefore, the low-doped copper–ceria surface model was obtained from a CeO₂ (1 1 1) slab, with a *p* (3 × 3) expansion of the surface unit cell, by substituting one surface Ce atom by one Cu atom. The optimized lattice parameters of the three-layer model were *a* = *b* = 11.64 Å, *c* = 26.71 Å, containing a vacuum layer of 20 Å set in the vertical direction to minimize the interaction between neighboring slab surfaces.

The adsorption energy was evaluated to characterize the adsorption properties of catalysts, which was defined by the following equation:

$$E_{\text{ads}} = E_{\text{slab,molecule}} - E_{\text{slab}} - E_{\text{molecule}}$$

where, E_{ads} meant the adsorption energy, $E_{\text{slab,molecule}}$ meant the energy of slab and molecule after adsorption, E_{slab} meant the energy of the catalyst slab before adsorption and E_{molecule} meant the energy of NH₃ and NO molecule in the gas phase before adsorption.^{24,25}

3. Results and discussion

3.1 NH₃-SCR activity of the catalysts

NO conversion over the different catalysts under the simulated flue gas conditions were performed to evaluate the denitration activity of the catalysts. As seen in Fig. 1, the NO conversion of TiO₂-ZrO₂ support was worst and below 50% during the whole reaction temperature range. The catalytic activity of Ce/TiO₂-ZrO₂ catalyst was obviously higher than TiO₂-ZrO₂ support at 300–400 °C, but still unsatisfactory at 150–250 °C. The Cu/TiO₂-

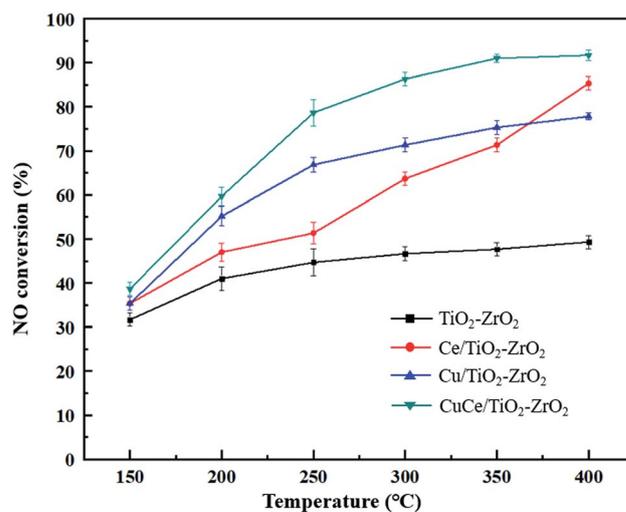


Fig. 1 NO conversion of TiO₂-ZrO₂, Ce/TiO₂-ZrO₂, Cu/TiO₂-ZrO₂ and CuCe/TiO₂-ZrO₂ catalysts.

ZrO₂ catalyst displayed a considerably enhanced activity at low temperature compared with TiO₂-ZrO₂ and Ce/TiO₂-ZrO₂ catalysts. NO conversion on CuCe/TiO₂-ZrO₂ catalyst exceeded 85% at the temperature above 300 °C. Moreover, the low-temperature NH₃-SCR activity of CuCe/TiO₂-ZrO₂ catalyst was markedly higher than other catalysts. It can be observed that copper modification is beneficial to strengthen the low-temperature denitration activity of the cerium-based catalyst. In order to explain the reasons of high NO conversion over CuCe/TiO₂-ZrO₂ catalyst at low temperature interval, XRD, SEM and XPS characterization tests were carried to study textural, morphological and redox properties of the catalysts, and the DRIFTS studies combined with DFT calculations were developed to further explore the adsorption and reaction mechanism of NH₃ and NO on CuCe/TiO₂-ZrO₂ catalyst.

3.2 Textural and morphological analysis

XRD measurement techniques were applied to determine the crystal structure of the catalysts and provide experimental foundation for the catalyst molecular model establishment in subsequent simulation calculation. As the results shown in Fig. 2, TiO₂-ZrO₂ support displays one characteristic peak at 2θ = 30.5°, the peak also shown in the XRD patterns of Ce/TiO₂-ZrO₂, Cu/TiO₂-ZrO₂ and CuCe/TiO₂-ZrO₂ catalysts, indicating the presence of ZrTiO₄ phase (PDF# 74-1504). The characteristic peaks of (111), (220), (311) crystal faces can be observed in Ce loaded catalysts (PDF# 34-0394), and these diffraction peaks are situated at 28.5°, 47.4° and 56.3°, respectively.²⁶ For Cu/TiO₂-ZrO₂ and CuCe/TiO₂-ZrO₂ catalysts, there are several diffraction peaks ascribed to CuO crystal structure locate at 32.5°, 35.6°, 38.7°, 48.8°, 53.4°, 58.2°, 61.6°, 66.3°, 68.0°, 72.3°, and 75.2° (PDF# 89-2529).²⁷ Furthermore, the peak intensity of CuCe/TiO₂-ZrO₂ is weaker than that of Ce/TiO₂-ZrO₂ and Cu/TiO₂-ZrO₂. Thus, it can be concluded that there is strong interaction between CeO₂ and CuO species, and the Cu and Ce active



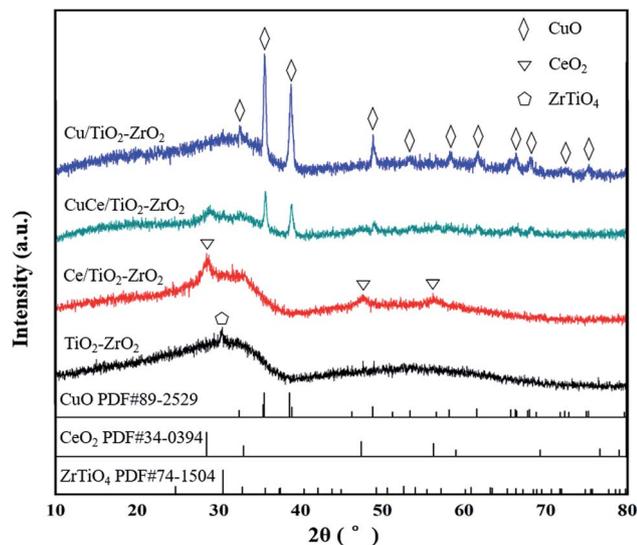


Fig. 2 XRD patterns of $\text{TiO}_2\text{-ZrO}_2$, $\text{Ce/TiO}_2\text{-ZrO}_2$, $\text{Cu/TiO}_2\text{-ZrO}_2$ and $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalysts.

components are dispersed well on the $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst surface.²⁸

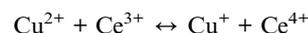
SEM experiments were conducted to investigate the morphology of the catalysts, and Fig. 3 displays SEM images of various catalysts. It suggests that $\text{TiO}_2\text{-ZrO}_2$ presents a block structure loaded with several dense particles. For $\text{Ce/TiO}_2\text{-ZrO}_2$ catalyst, CeO_2 particles agglomerate on the part region of the support. However, few particles deposit on the $\text{Cu/TiO}_2\text{-ZrO}_2$ catalyst surface. Both above cases will reduce the active surface area of the catalysts. Meanwhile, active components relative uniformly deposit on $\text{CuCe/TiO}_2\text{-ZrO}_2$, which is consistent with the XRD results. The high dispersibility is beneficial to increase the active surface area and low temperature denitration activity of the catalyst.

3.3 Redox properties analysis

XPS analysis were performed to investigate the chemical element states of copper and cerium as well as active oxygen species on the raw and modified catalyst surfaces. In the Fig. 4(a), the peaks detected at about 933.8 and 953.6 eV are assigned to $\text{Cu } 2p_{3/2}$ and $\text{Cu } 2p_{1/2}$, and some shake-up satellite peaks within 940–945 eV are relevant to Cu^{2+} and polycrystalline Cu_2O species.²⁹ By the peak deconvolution, the $\text{Cu } 2p_{3/2}$ splits into two peaks that are located at around 933.6 eV and 935.5 eV while the $\text{Cu } 2p_{1/2}$ splits into two peaks that are detected at around 953.5 eV and 955.4 eV. The peaks at 933.6 eV and 953.5 eV can be contributed to the Cu^+ species, while the peaks at 935.5 eV and 955.4 eV are corresponded to Cu^{2+} species. The result shows that both Cu^+ and Cu^{2+} coexist in the $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst, and Cu^+ species may be generated from strong interface between copper oxide with cerium oxide.³⁰ Fig. 4(b) shows the Ce 3d spectra for the catalysts, and the spectrum can be split into eight components. The peaks denoted as u' and v' are assigned to Ce^{3+} , while the peaks denoted as u, u'', u''', v, v'' and v''' are attributed to Ce^{4+} .^{31,32} The existence of $\text{Ce}^{4+}/\text{Ce}^{3+}$

redox couple contributes to the better $\text{NH}_3\text{-SCR}$ activity of the catalyst. Fig. 4(c) illustrates the O 1s spectra of different catalysts. The peak at low binding energy (529.8–530.1 eV) is assigned to the lattice oxygen (O_β), and the other peak at high binding energy (531.2–531.6 eV) is regarded as the surface chemisorbed oxygen (O_α). It should be mentioned that O_α has been reported to play an important role in low-temperature $\text{NH}_3\text{-SCR}$ reaction due to its strong mobility.³³

Table 1 shows the surface chemical composition of the catalysts obtained from XPS spectra. It can be seen that the $\text{CuCe/TiO}_2\text{-ZrO}_2$ represents the highest ratio of surface chemisorbed oxygen, which is helpful to improve the low-temperature activity. Besides, the decrease of copper oxidation state and increase of cerium oxidation state coexist on $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst compared to $\text{Ce/TiO}_2\text{-ZrO}_2$ and $\text{Cu/TiO}_2\text{-ZrO}_2$ catalysts. Therefore, the synergistic effect of copper and cerium occurs on catalyst surface, which is summarized as follows:



It has been mentioned earlier that surface chemisorbed oxygen contributes to enhance the low-temperature activity, which also accord with the results from Fig. 1 and Table 1. Besides, Ce^{3+} has been confirmed to favor the generation of oxygen vacancies, resulting in a higher proportion of surface chemisorbed oxygen.³⁴ However, $\text{Ce/TiO}_2\text{-ZrO}_2$ catalyst represents a higher ratio of Ce^{3+} and a lower ratio of O_α compared to $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst. This may be due to the presence of Cu–Ce interface, which promotes the formation of oxygen vacancies and mobility of oxygen species.³⁵ Therefore, the increased oxygen vacancies caused by the formation of Cu–Ce interface exceed the decreased oxygen vacancies resulted from the reduced Ce^{3+} concentration, causing more surface chemisorbed oxygen generated in $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst.

The low-temperature activity is also related to the balanced populations of $\text{Cu}^+/\text{Cu}^{2+}$ sites and dominated by mobile NH_3 -solvated Cu species. In the low temperature range, Cu ions can form transient ion pairs and move through NH_3 solvation, thus leading to the better denitration activity. Moreover, the increased ratio of $\text{Cu}^+/\text{Cu}^{2+}$ leads to the enhanced low-temperature SCR activity.³⁶ The synergistic effect of copper and cerium also contributes to widen the operating temperature window for the SCR reaction below 300 °C,³⁰ which leads to the good low-temperature $\text{NH}_3\text{-SCR}$ activity of the catalyst.

According to the above physicochemical characterization, it is reasonable to conclude that the well dispersed active species and the synergistic effect between Cu and Ce species assist to the improvement in low temperature $\text{NH}_3\text{-SCR}$ activity of $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst.

3.4 In situ DRIFTS studies

The $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst with the best catalytic activity was selected for *in situ* DRIFTS characterization to identify the active sites, the adsorbed species and the intermediates on the catalyst surface, aiming at providing the experimental foundation for the adsorption of NH_3 and NO as well as reaction pathways of



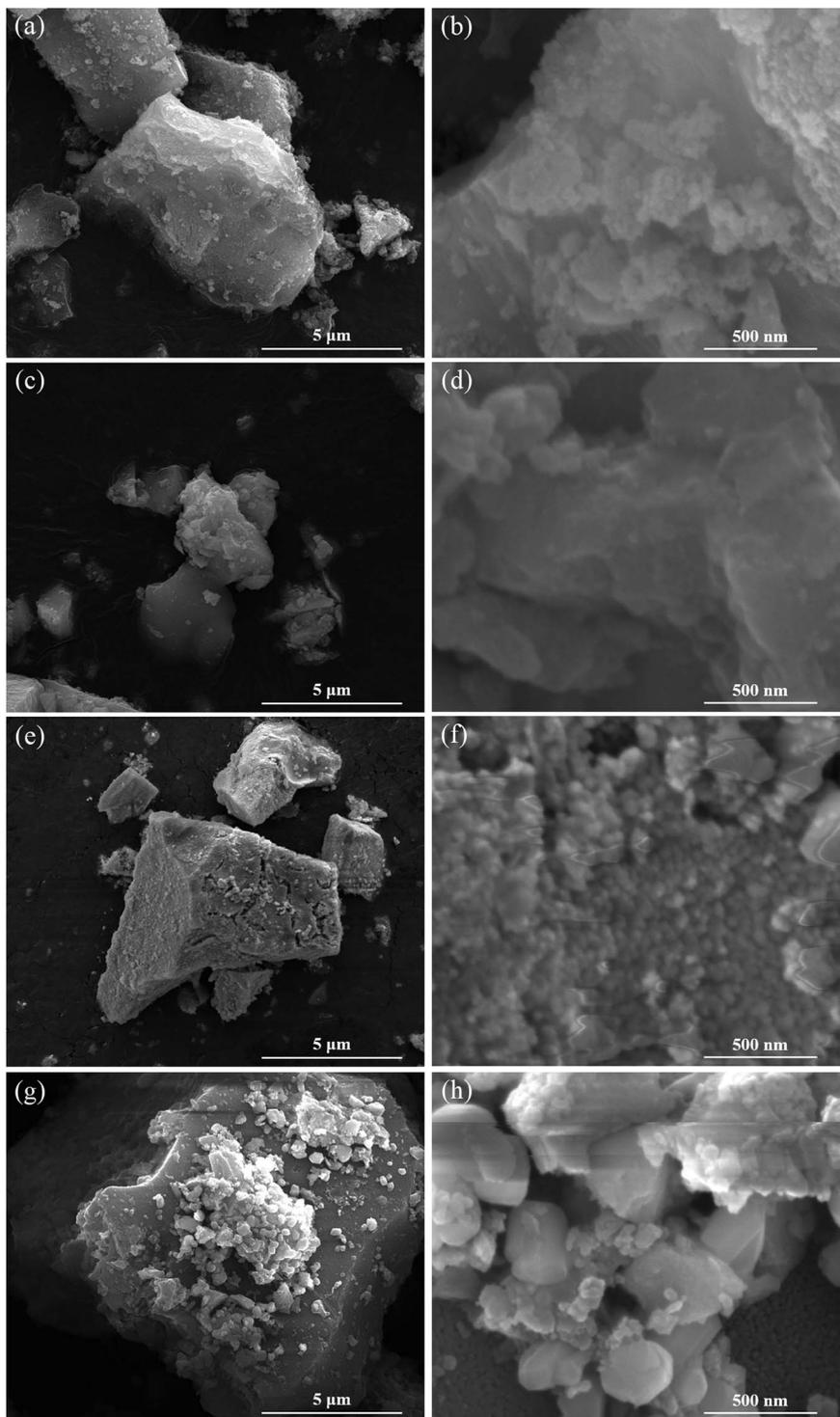


Fig. 3 SEM images of (a and b) $\text{TiO}_2\text{-ZrO}_2$, (c and d) $\text{Ce/TiO}_2\text{-ZrO}_2$, (e and f) $\text{Cu/TiO}_2\text{-ZrO}_2$, (g and h) $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst.

intermediates in DFT calculations, thus figuring out the reaction mechanism of Cu modification on $\text{Ce/TiO}_2\text{-ZrO}_2$ catalyst in low temperature $\text{NH}_3\text{-SCR}$ system.

3.4.1 Adsorption of NH_3 . *In situ* DRIFTS measurement of the $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst after being exposed to 500 ppm NH_3 for different time at 200 °C was recorded to distinguish the active sites for NH_3 adsorption. Fig. 5 shows the adsorbed NH_3 ,

species over $\text{CuCe/TiO}_2\text{-ZrO}_2$ surface. When the sample is adsorbed by NH_3 saturation, strong bands at 1606 cm^{-1} and 1207 cm^{-1} can be observed for all the situation, attributed to symmetric and asymmetric N-H bending vibrations of adsorbed NH_3 linked to Lewis acid sites.³⁷ Besides, the band at 1085 cm^{-1} also represents the symmetric N-H bending vibrations.³⁸ In the N-H region, several bands are observed at 3372,



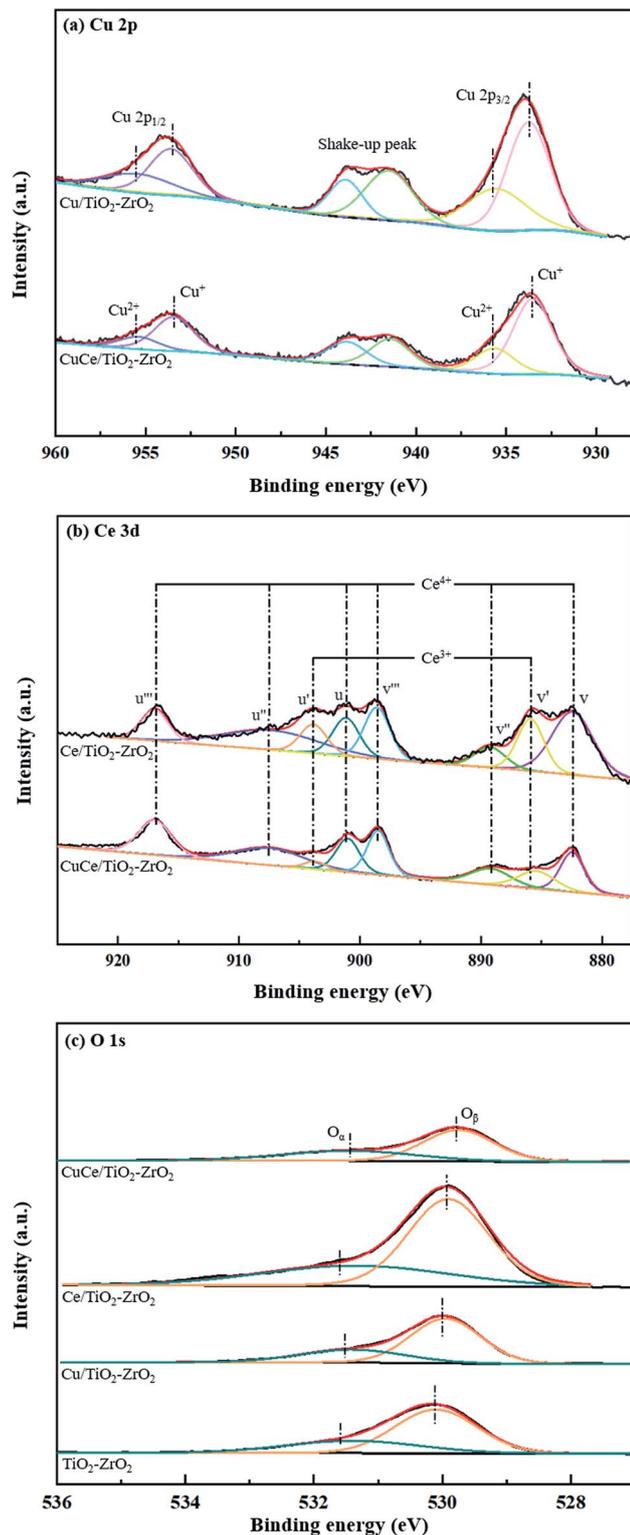


Fig. 4 XPS spectra of the raw and modified catalysts: (a) Cu 2p, (b) Ce 3d, (c) O 1s.

3247 and 3145 cm^{-1} , corresponding to the symmetric and asymmetric N–H stretching vibrations of the coordinated NH_3 on Lewis acid sites.³⁹ Accordingly, the band at 1521 cm^{-1} is assigned to the intermediate of amide species ($-\text{NH}_2$).⁴⁰ The

Table 1 Surface chemical composition of the catalysts obtained from XPS spectra

Catalysts	$\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$	$\text{Cu}^+ / (\text{Cu}^{2+} + \text{Cu}^+)$	$\text{Ce}^{3+} / (\text{Ce}^{3+} + \text{Ce}^{4+})$
$\text{TiO}_2\text{-ZrO}_2$	0.314	—	—
$\text{Ce/TiO}_2\text{-ZrO}_2$	0.339	—	0.208
$\text{Cu/TiO}_2\text{-ZrO}_2$	0.301	0.473	—
$\text{CuCe/TiO}_2\text{-ZrO}_2$	0.376	0.554	0.127

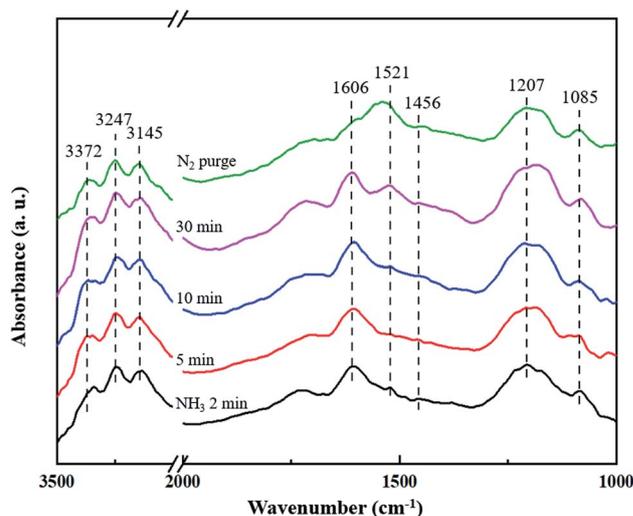


Fig. 5 *In situ* DRIFTS spectra of $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst treated in flow of 500 ppm NH_3 at 200 °C for different times.

band at 1456 cm^{-1} is attributed to the NH_4^+ species adsorbed on the Brønsted acid sites,⁴¹ which is much lower than other bands in intensities. All the changes on the states of NH_3 adsorption suggest that the quantity of coordinated NH_3 on the Lewis acid sites is much larger than that of the NH_4^+ ions on the Brønsted acid sites, indicating that NH_3 is inclined to adsorb on the Lewis acid sites and NH_3 adsorption on the Lewis acid sites is more stable at the reaction process.

3.4.2 Co-adsorption of NO and O_2 . The co-adsorption of NO and O_2 over $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst is also investigated by the *in situ* DRIFTS characterization, Fig. 6 displays the spectra obtained with 500 ppm NO + 5% O_2 at 200 °C in different time intervals. The bands located at 1170 cm^{-1} and 1029 cm^{-1} are ascribed to the NO^- species and the *cis*- $\text{N}_2\text{O}_2^{2-}$ species, respectively.^{42,43} It can be observed that the bands at 1913 cm^{-1} and 1851 cm^{-1} can be detected when catalyst exposed to the NO + O_2 atmosphere, and decrease quickly upon the treatment with N_2 purge. These bands can be viewed as the gaseous or weakly adsorbed NO linked to the copper sites.^{38,44} The bands at 1430 cm^{-1} and 1361 cm^{-1} are both assigned to monodentate nitrate,^{42,45} whereas the band at 1567 cm^{-1} is attributed to bidentate nitrate.⁴⁶ Moreover, the latter adsorption band is much more intense than the former band, suggesting that the amount of bidentate nitrate is much larger than that of monodentate nitrate. The results show that the bidentate nitrate and



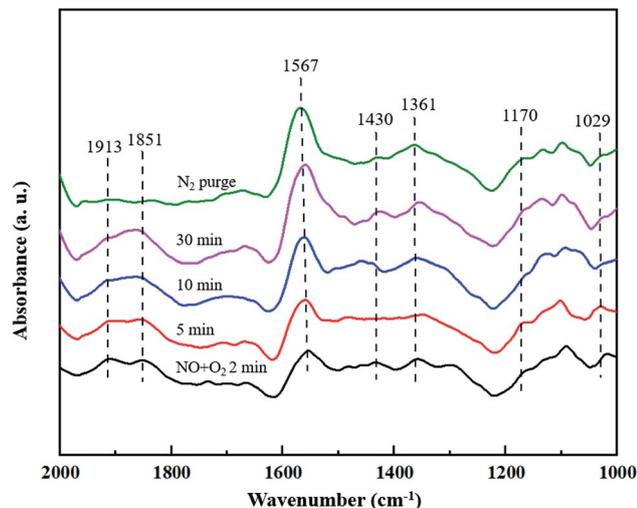


Fig. 6 *In situ* DRIFTS spectra of CuCe/TiO₂-ZrO₂ catalyst treated in flow of 500 ppm NO + 5% O₂ at 200 °C for different times.

monodentate nitrate both are the active intermediates on the catalyst surface during NH₃-SCR process.

3.5 DFT study

3.5.1 NH₃ adsorption on Cu-CeO₂ (1 1 1). It has been proved that the NH₃ adsorption is the primary factor in the NH₃-SCR reaction.⁴⁷ NH₃ molecules are placed near the Lewis acid sites (Cu-O, Ce1-O, Ce2-O) and Brønsted acid site (Cu-OH) of the catalyst surface to simulate the adsorption process. Surface cerium atoms Ce1 and Ce2 represent Ce-sites of different atomic environment, the former is the Ce atom adjacent to Cu atom and the latter is the Ce atom farther from Cu atom. The optimized geometric structures and energies of NH₃ adsorb on the Lewis and Brønsted acid sites are presented in Fig. 7. It can be concluded that the NH₃ molecule is more easily combined with the Cu acidic sites (Lewis acid sites). Because the distance between N atom and Cu atom is the shortest (1.922 Å), and the adsorption energy of NH₃ adsorbs on the top sites of Cu atom in

the way of the N-down orientation is the lowest (-188.69 kJ mol⁻¹). Compared with Cu sites serve as the Lewis acid sites, NH₃ molecule adsorbs on the Brønsted acid site connected with Cu atom has a weaker adsorption capacity, the length of N-H band and O-H band are 2.019 Å and 0.974 Å, and the adsorption energy is -130.70 kJ mol⁻¹. Besides, the bond length of NH₃ molecules on the two Ce atoms are 2.693 Å and 2.691 Å, and the adsorption energies of NH₃ molecules on the two Ce atoms are -78.56 kJ mol⁻¹ and -85.01 kJ mol⁻¹, indicating that the atomic environment has hardly influence on the NH₃ adsorption state on the acidic sites. In conclusion, NH₃ tends to connect with Lewis acid sites of CuCe/TiO₂-ZrO₂ catalyst during the reaction process, which is consistent with the *in situ* DRIFTS results. Although the Brønsted acid site linked to the Cu atom has higher adsorption energy than that of the Lewis acid site, the adsorption energy is still lower than the adsorption energy of Ce atoms, and the characteristic peak of the NH₄⁺ ions on the Brønsted acid sites can be detected in NH₃ adsorption in *in situ* DRIFTS tests. Therefore, we can speculate that some gaseous ammonia still adsorbs on the Brønsted acid sites.

Taking the above analysis results of NH₃ adsorption into consideration, we focus our attention on NH₃ dehydrogenation on the Cu atoms in this paper, the potential energy diagram and optimized structures of NH₃ dehydrogenation reaction over catalysts are present in Fig. 8, S1,[†] and Table 2 presents the energy changes of each step involved in the dehydrogenation reaction. On the process, NH₃ molecule firstly adsorbs on the top site of Cu atom with its nitrogen end (IM1). H-migration happens after the NH₃ adsorption on the catalyst surface, one H atom (H1) of the intermediate Cu-NH₃ migrates to the adjacent O atom to form a new Brønsted acid site, the reaction heat is 19.56 kJ mol⁻¹ while the activation energy barrier is 49.05 kJ mol⁻¹. Then the NH₂ fragment (IM2) continues to lose H atom (H2) to generate NH, the reaction heat is 20.08 kJ mol⁻¹ while the activation energy barrier can reach 39.38 kJ mol⁻¹. Finally, NH (IM3) can also be continuously dehydrogenated, one H atom (H3) is transferred to bond with the O atom and only one N atom left on the copper atom (IM4), and the reaction

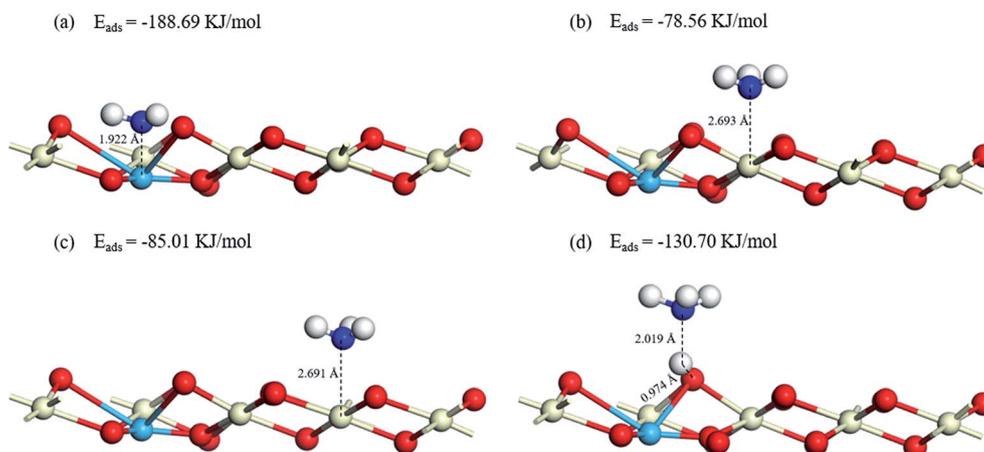


Fig. 7 Optimized structures and energies of NH₃ adsorptions on (a) Cu-O, (b) Ce1-O, (c) Ce2-O, (d) Cu-OH.



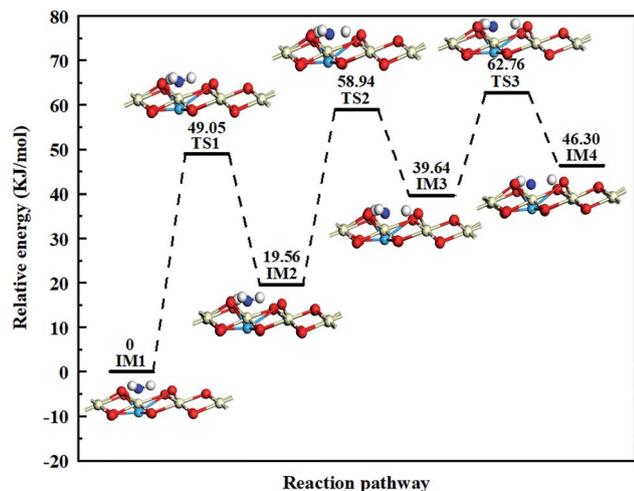


Fig. 8 Potential energy diagram and optimized structures of NH_3 dehydrogenation reaction on the Cu atoms. The energy of the reactant is taken as zero.

Table 2 The reaction energies and activation energy barriers of each step involved in the NH_3 dehydrogenation reaction on the Cu atoms

	Reaction energy (kJ mol^{-1})	Energy barrier (kJ mol^{-1})
$\text{IM1} \rightarrow \text{TS1} \rightarrow \text{IM2}$	19.56	49.05
$\text{IM2} \rightarrow \text{TS2} \rightarrow \text{IM3}$	20.08	39.38
$\text{IM3} \rightarrow \text{TS3} \rightarrow \text{IM4}$	6.66	23.12

heat is 6.66 kJ mol^{-1} while the activation energy barrier is $23.12 \text{ kJ mol}^{-1}$. The result shows that the activation energy barrier gradually decreases in the NH_3 dehydrogenation process, indicating the NH_3 dissociation reaction is getting easier. According to the optimized structures of the intermediates and the transition states shown in Fig. S1,[†] there are symmetric and asymmetric N–H stretching vibrations of the coordinated NH_3 on Lewis acid sites during the NH_3 dehydrogenation reaction process, which can be verified by the NH_3 adsorption results in *in situ* DRIFTS studies. Moreover, the reaction path shows that the NH_2 fragment has the lowest energy in the dehydrogenation products, showing it can steadily adsorb on the catalyst surface, which also in harmony with the experimental results.

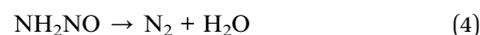
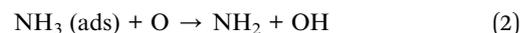
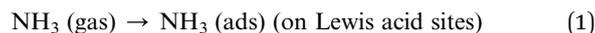
3.5.2 NO adsorption on Cu–CeO₂ (1 1 1). Firstly, the adsorption sites of the NO molecule are discussed. Based on the results of NH_3 adsorption and dehydrogenation on the catalyst surface, the NH_2 , NH , N , O1 and O2 active sites are consisted in the adsorption sites (O1 and O2 represent different oxygen active sites at NH_2 fragment environment, the former is the O atom in the hydroxyl group and the latter is the O atom adjacent to the Cu atom). The adsorption of the NO molecule is through N-down on, and the optimized adsorption structures and energies of NO molecules adsorb on the catalysts are present in Fig. 9 and S2.[†] It can be seen that the energies of NO adsorb on NH_2 , NH , and N are $-596.85 \text{ kJ mol}^{-1}$, $-609.12 \text{ kJ mol}^{-1}$, and

$-610.23 \text{ kJ mol}^{-1}$, respectively. The distances between N atom of NO and Cu atom are 4.145 \AA , 2.666 \AA , and 3.888 \AA for Cu– NH_2 , Cu– NH , and Cu– N sites. Compared to the NO adsorptions on the N atoms, the NO molecules adsorb on the O atoms have a worse adsorption capacity. The adsorption energies of NO adsorb on O1 and O2 atom are $-192.87 \text{ kJ mol}^{-1}$ and $-333.44 \text{ kJ mol}^{-1}$, but the adsorbed NO molecules have little effect on the adsorbed NH_3 molecules on the Lewis acid sites. It suggests that NO molecule is inclined to adsorb on the top sites of N atoms of the dehydrogenation products, and the NH_2 and NH_2NO intermediates are the important components in the NH_3 -SCR process.

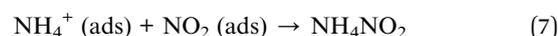
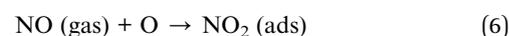
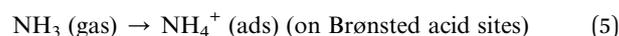
3.6 Proposed reaction mechanism

Combining the experimental and DFT results obtained in this paper and the results of previous studies,^{48–53} the NH_3 -SCR reaction mechanism on $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst at low temperature is exhibited and the explanation follows.

The foundational reaction involves the participation of NH_3 and NO to generate N_2 and H_2O , the H atom remained will be connected with the O atom adjacent to Cu atom to form new Brønsted acid site. In detail, the adsorbed NH_3 linked to the Lewis acid sites can be activated to form the amino group ($-\text{NH}_2$). Then it will further react with gaseous NO to form NH_2NO , which is the key intermediate product in the reaction process, and finally decomposes into gas phase N_2 and H_2O due to instability. The reaction follows Eley–Rideal reaction mechanism and the reaction steps are shown as reaction (1)–(4).



The regenerative reaction occurs on the Brønsted acid site formed from the foundational reaction, NH_3 and NO participate in the reaction to produce N_2 and H_2O , and the remaining H atom is removed and the Lewis acid site is restored. In this process, gaseous NH_3 adsorbs on the Brønsted acid site linked to the Cu atom to form NH_4^+ species. At the same time, gaseous NO bonds to the lattice oxygen atom to form monodentate nitrite ($-\text{NO}_2$), creating an oxygen vacancy on the catalyst surface, which can be replenished by the active oxygen. Then NH_4^+ species migrates to the NO_2 to form NH_4NO_2 intermediate product, and finally decomposes into gaseous N_2 and H_2O . The reaction follows Langmuir–Hinshelwood reaction mechanism and the reaction steps follow as reaction (5)–(8).



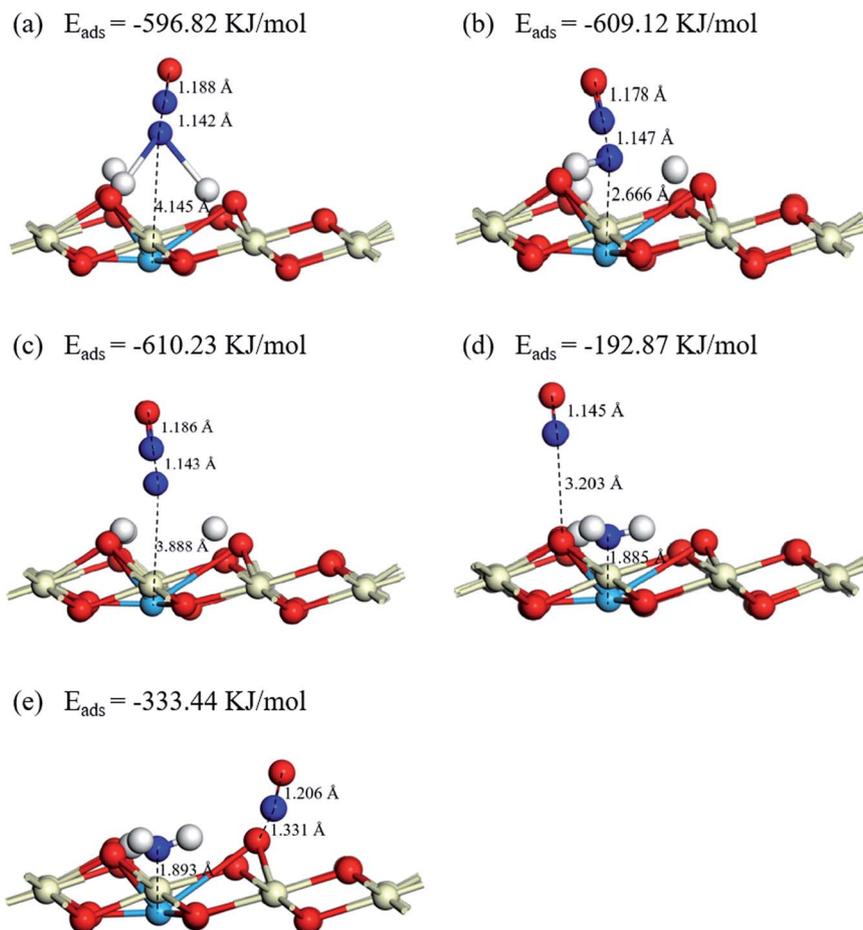


Fig. 9 Optimized structures and energies of NO adsorptions on (a) Cu-NH₂, (b) Cu-NH, (c) Cu-N, (d) NH₂-Cu-OH, (e) NH₂-Cu-O.

According to the *in situ* DRIFTS and DFT results obtained above, the NH₃ adsorption on the Lewis acid sites should be far greater than that on the Brønsted acid sites, suggesting that the Eley-Rideal reaction mechanism dominates in the NH₃-SCR reaction process.

As the final summarize comment, the multiple reaction mechanism herein proposed. It is developed from traditional lab-scale experiments and emerging quantum chemical simulations, involving *in situ* DRIFTS of NH₃ adsorption and co-adsorption of NO and O₂ as well as DFT calculations of NH₃ adsorption, NH₃ dehydrogenation and NO adsorption on the catalyst surface. The results can be reasonably extended to realistic operating conditions and provide support for the method of experiment combined with simulation in the NH₃-SCR mechanism studies. The multiple reaction mechanism (shown in Fig. 10) includes Eley-Rideal reaction mechanism and Langmuir-Hinshelwood reaction mechanism. At low temperatures, the presence of gaseous NH₃ ensures the continuous supply to the NH₃ adsorption on the catalyst surface. Besides, the NH₃ supplement can be divided into two parts to participate in the foundational reaction and regenerative reaction in the NH₃-SCR catalytic cycle, and the amount of ammonia involved in the foundational reaction is much higher than that in the regenerative reaction. The NH₃ feed will firstly

result in the consumption of the Lewis acid sites, and then, to the activation of the newly generated Brønsted acid sites. Moreover, the Eley-Rideal reaction mechanism dominates in the denitration reaction and the oxidation of NO assists to close the catalytic cycle.

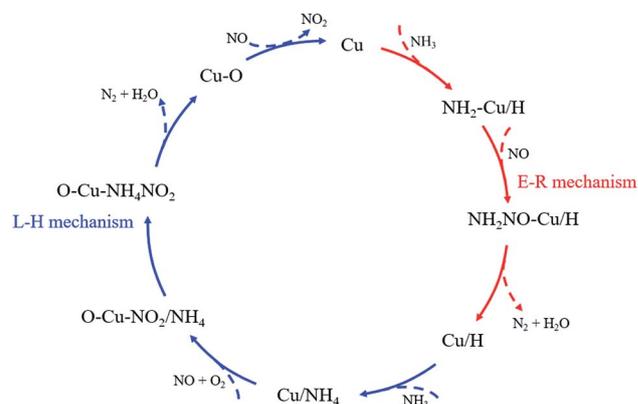


Fig. 10 NH₃-SCR catalytic cycle on the CuCe/TiO₂-ZrO₂ catalyst.



4. Conclusions

In this study, we investigated the improved denitration activity and promotional mechanism of cerium-based catalyst with copper modification in low temperature NH_3 -SCR denitration process. $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst has enhanced catalytic activity in the low temperature range comparing to $\text{TiO}_2\text{-ZrO}_2$, $\text{Ce/TiO}_2\text{-ZrO}_2$ and $\text{Cu/TiO}_2\text{-ZrO}_2$ catalysts, which is mainly attributable to the well distributed particulates and synergistic effect of copper and cerium on catalyst surface. The high dispersion degree is helpful to increase the active surface area, and the synergistic effect between copper and cerium ($\text{Cu}^{2+} + \text{Ce}^{3+} \leftrightarrow \text{Cu}^+ + \text{Ce}^{4+}$) contributes to increase the ratios of surface chemisorbed oxygen and $\text{Cu}^+/\text{Cu}^{2+}$, thus leading to the better low-temperature SCR activity. *In situ* DRIFTS results and DFT calculations were used to study the adsorption and reaction mechanism of NH_3 and NO on the $\text{CuCe/TiO}_2\text{-ZrO}_2$ catalyst for low-temperature NH_3 -SCR reaction. Results show that NH_3 is inclined to adsorb on the Cu acidic sites and the NH_2 and NH_2NO species are the key intermediates in the denitration reaction process. Therefore, copper modification will markedly improve the low temperature denitration activity of cerium-based catalyst. We also reasonably conclude a NH_3 -SCR catalytic cycle involving the foundational reaction and regenerative reaction. The Eley-Rideal mechanism and Langmuir-Hinshelwood mechanism both occur in the cycle, and the former mechanism dominates in the denitration reaction.

Author contributions

Wei Zhang: conceptualization, methodology, software, resources, data curation, supervision, project administration, funding acquisition. Yunhao Tang: formal analysis, writing-original draft, writing-review & editing, funding acquisition. Wei Xiao: investigation, visualization, validation. Min Ruan: writing-review & editing, funding acquisition. Yanshan Yin: writing-review & editing, funding acquisition. Quanbin Song: writing-review & editing, funding acquisition. Kang Xie: investigation, visualization. Chuan Qin: investigation, visualization. Mengyao Dong: investigation, validation. Yunhe Zhou: investigation, validation. Jie Li: investigation, validation.

Conflicts of interest

There are no conflicts of interest to declare.

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