

Article

Phosphate Modification Promotes Low-Temperature NH_3 -SCO over Cu/CeO_2 Through Coupled Regulation of Surface Acidity and Oxygen Species

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Abstract

Selective catalytic oxidation of ammonia (NH_3 -SCO) is a promising technology for ammonia abatement. Cu/CeO_2 catalysts have attracted extensive attention because of their strong metal–support interaction and favorable redox properties. However, their practical application is still limited by insufficient low-temperature catalytic activity and unsatisfactory control of by-product formation. Herein, phosphate-functionalized Cu/CeO_2 catalysts were fabricated to regulate surface acidity and oxygen species behavior, thereby promoting low-temperature NH_3 -SCO activity. The optimal Acid- Cu/CeO_2 catalyst achieved 90% NH_3 conversion at 260 °C, corresponding to a 192 °C decrease in T_{90} compared with pristine Cu/CeO_2 (452 °C). Kinetic analysis showed that the apparent activation energy decreased from 125.78 to 84.70 kJ mol^{-1} after phosphoric acid modification. In addition, Acid- Cu/CeO_2 maintained relatively high N_2 selectivity and lower NO_x selectivity over the tested temperature range, indicating that phosphate modification suppresses the deep oxidation of NH_3 to NO_x by-products. Structural and surface characterization results demonstrated that Cu species remained highly dispersed on CeO_2 after modification, while surface phosphate species modified the local electronic environment and redistributed oxygen species. O 1s XPS and O_2 -TPD results revealed that phosphate modification decreased the static surface adsorbed/defect-related oxygen fraction but improved the accessibility and mobility of labile surface/subsurface or weakly bound lattice oxygen species. Py-IR and DRIFTS results further showed that phosphate modification increased Brønsted/Lewis acidity, enhanced NH_3 adsorption and N-H activation, and facilitated the formation and subsequent consumption of NH_x /-NHO-related intermediates under reaction conditions. This work provides insights into phosphate-mediated regulation of surface acidity and oxygen mobility and offers a strategy for designing efficient low-temperature Cu/CeO_2 -based NH_3 -SCO catalysts.

Keywords: Cu/CeO_2 catalyst; NH_3 -SCO; acid treatment; active oxygen species; surface acid sites

Academic Editor: Sónia Carabineiro

Received: 4 June 2026

Revised: 29 June 2026

Accepted: 1 July 2026

Published: 11 July 2026

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1. Introduction

Ammonia (NH_3) has been recognized as a critical atmospheric pollutant that contributes significantly to the formation of fine particulate matter ($\text{PM}_{2.5}$) and tropospheric

ozone, leading to severe air quality degradation and adverse impacts on human health and ecosystems [1]. With the widespread implementation of selective catalytic reduction (SCR) technology for NO_x abatement in industrial flue gas and diesel vehicles, ammonia slip has become an increasingly prominent environmental issue [2]. NH_3 -SCO, which selectively converts NH_3 into N_2 and H_2O , has emerged as a promising approach for ammonia emission control because of its high efficiency, relatively low operating cost, and potential to suppress secondary pollutants when high N_2 selectivity is achieved [3]. The core challenge in NH_3 -SCO technology lies in developing catalysts that can achieve complete ammonia conversion at low temperatures ($<300^\circ\text{C}$) while maintaining high N_2 selectivity and long-term stability under complex industrial conditions [4]. Extensive research has demonstrated that the catalytic performance of NH_3 -SCO catalysts is primarily governed by surface acidity and redox properties [4–7]. Surface acidic sites play a fundamental role in NH_3 adsorption and activation, which are the initial steps of the NH_3 -SCO reaction. In this context, the acid-site concentration affects the ability of the catalyst to adsorb NH_3 , whereas acid-site strength influences the stability and reactivity of adsorbed NH_3 species. Acid-site strength can be considered from two related aspects: the thermodynamic interaction strength between NH_3 and surface acid sites, and the thermal stability of adsorbed NH_3 species, which is commonly reflected by the NH_3 desorption temperature range in NH_3 -TPD or NH_3 -TPD-FTIR measurements. For low-temperature NH_3 -SCO, suitable acid strength is essential: weak acid sites may not retain NH_3 effectively under reaction conditions, whereas excessively strong acid sites may hinder NH_3 activation and subsequent conversion. Therefore, optimizing both the acid-site concentration and strength distribution of surface acid sites is important for improving low-temperature NH_3 -SCO performance. Jablonska et al. [4] systematically reviewed the role of surface acidity in transition metal oxide catalysts for NH_3 -SCO and concluded that both Brønsted (B) and Lewis (L) acid sites are essential for efficient ammonia activation. Specifically, Lewis acid sites are responsible for the adsorption of NH_3 to form coordinated NH_3 species, while Brønsted acid sites facilitate the formation of NH_4^+ intermediates [5,7]. Phosphorus-containing zeolitic catalysts also provide important guidance for understanding the role of phosphorus-related structures in NH_3 adsorption and activation. SAPO-34, a representative CHA-type silicoaluminophosphate molecular sieve, contains phosphorus as an intrinsic framework element and possesses abundant acid sites that are beneficial for NH_3 storage and low-temperature NH_3 -related reactions. Previous studies on Cu/SAPO-34 have shown that the acid content of SAPO-34 can significantly influence low-temperature NH_3 -SCR activity, while excessive acidity may also affect NH_3 oxidation behavior at higher temperatures [8]. Cu- and Fe-modified SAPO-34 catalysts have also been widely investigated for NH_3 -SCR, where isolated Cu^{2+} species, Fe-related species, and framework-derived acid sites jointly contribute to NH_3/NO_x adsorption, redox cycling, and broad-temperature catalytic activity [9,10]. In addition, Cu-containing silicoaluminophosphate CHA catalysts have been examined in both NH_3 -SCR and NH_3 -SCO reactions, further demonstrating that phosphorus-containing zeolitic frameworks can regulate Cu dispersion, surface acidity, NH_3 adsorption, and oxidation selectivity [11–14]. These studies indicate that phosphorus-containing structures are effective for constructing NH_3 -affinitive acidic environments and provide a useful conceptual basis for introducing phosphate species onto Cu/ CeO_2 to regulate surface acidity and NH_3 activation behavior [10].

Although these systems are mainly used in NH_3 -SCR rather than NH_3 -SCO, they demonstrate that phosphorus-containing structures can effectively regulate acid-site distribution and NH_3 activation behavior. Therefore, introducing phosphate species onto Cu/ CeO_2 is a rational strategy to tune surface acidity while simultaneously modifying the oxygen-related redox properties of CeO_2 . Sun et al. [15] reported that the construction of abundant surface acid sites on CuO/ CeO_2 catalysts significantly enhanced NH_3 adsorption

capacity and improved low-temperature catalytic activity. Similarly, Liu et al. [16] demonstrated that phosphorus modification of CuCeZr mixed metal catalysts increased both the number and strength of surface acid sites, leading to superior NH_3 -SCO performance. In addition, Sun et al. [17] demonstrated that the catalytic conversion of NH_3 to N_2 can be promoted by optimizing the balance between Brønsted and Lewis acid sites on Pt/SiO₂-Al₂O₃ catalysts. Specifically, Brønsted acid sites can stabilize NH_3 in the form of NH_4^+ species, whereas Lewis acid sites facilitate coordinated NH_3 adsorption and N-H bond activation to generate reactive NH_x intermediates. Therefore, an appropriate Brønsted/Lewis acid-site distribution is essential for coupling NH_3 adsorption-activation with subsequent nitrogen-forming reaction steps. The second key factor governing NH_3 -SCO performance is the presence and reactivity of surface active oxygen species, which are responsible for the oxidation of activated NH_3 intermediates. Surface active oxygen species, including superoxide (O_2^-), peroxide (O_2^{2-}), and lattice oxygen (O^{2-}), participate in the dehydrogenation of adsorbed NH_3 and the formation of key reaction intermediates such as nitrosyl (NO) and nitrate (NO_3^-) species. Guan et al. [18] designed reactive bridging O^{2-} species within atomic Cu-O-Fe sites, which enabled fast Cu redox for NH_3 conversion and direct NO adsorption to promote N-N coupling toward N_2 , achieving 99% N_2 selectivity at 100% conversion. Karatok et al. [19] demonstrated that surface atomic oxygen species on Ag (111) selectively catalyzed N-H bond cleavage, yielding mostly N_2 along with minor amounts of NO and N_2O . For Cu-based catalysts, Sun et al. [15] found that the concentration of $\text{Cu}^+/\text{O}_v/\text{Ce}^{3+}$ interfacial sites, which are rich in active lattice oxygen, was positively correlated with NH_3 oxidation activity. Similarly, Ran et al. [20] reported that support-dependent N_2 selectivity of CuO-based NH_3 -SCO catalysts was closely related to the mobility and reactivity of surface lattice oxygen species. Recent studies by Guan et al. [21] also revealed that the catalytic activity of NH_3 -SCO at low temperatures scaled proportionally with the concentration of Cu(II) superoxo species. Furthermore, Jablonska et al. [4] reported that surface-active oxygen species can react with adsorbed NH_3 to form nitrate/nitrite-related intermediates, which may further participate in nitrogen-forming reaction steps with adsorbed NH_3 or NH_x species. Cu/CeO₂ composites have attracted extensive research attention due to the fact that the high dispersion of active Cu species facilitated the formation of oxygen vacancies and enhanced the redox properties of the catalyst through the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox cycle [22]. Phosphate species can form P-O-Ce structures, regulate acid-site distribution, and modify redox/oxygen behavior of CeO₂-based catalysts. Surface phosphate species can interact with CeO₂ through P-O-Ce bonding and electron-withdrawing effects, thereby modifying the $\text{Ce}^{3+}/\text{Ce}^{4+}$ distribution, surface oxygen species behavior, and acid-site properties of ceria-based catalysts. In this context, phosphate modification provides a feasible strategy to regulate both acidity and redox-related oxygen behavior in Cu/CeO₂ catalysts for low-temperature NH_3 -SCO [23]. Although previous studies have shown that both sulfate and phosphate modification can improve the performance of CeO₂-based catalysts in NH_3 -SCR, the selection of phosphate modification in this work is based on the specific requirements of Cu/CeO₂-catalyzed low-temperature NH_3 -SCO. Phosphate species can form stable P-O-Ce surface structures on CeO₂, thereby modifying the surface electronic environment and oxygen species behavior. Meanwhile, phosphorus-containing surface species can regulate the distribution of acid sites, which is beneficial for NH_3 adsorption and activation. Compared with sulfate modification, phosphate modification avoids the pre-introduction of sulfur-containing species, which could interfere with the evaluation of SO₂ poisoning and sulfur resistance. In addition, compared with SiO₂ or H₃BO₃ modification, H₃PO₄ provides a more direct route to construct phosphate-related surface structures on Cu/CeO₂. Therefore, phosphoric acid was selected as the surface modifier in this work to regulate both surface acidity and oxygen species behavior of Cu/CeO₂ catalysts for low-temperature NH_3 -SCO. However, despite the prom-

ising NH_3 -SCO performance of Cu/CeO₂-based catalysts arising from the synergistic interaction between Cu species and CeO₂, their practical application still requires further improvement in low-temperature activity and durability under complex reaction atmospheres, particularly in the presence of SO₂ and H₂O [24,25]. Herein, phosphate-modified Cu/CeO₂ catalysts were prepared through a facile phosphoric acid treatment strategy for low-temperature NH_3 -SCO. The aim of this work is to investigate how surface phosphate modification regulates the physicochemical properties, surface acidity, oxygen species, and catalytic behavior of Cu/CeO₂ catalysts. The relationship between phosphate modification and NH_3 -SCO performance was systematically examined by catalytic activity tests, kinetic analysis, XRD, XPS, O₂-TPD, Py-IR, and operando DRIFTS measurements. This study is expected to provide useful insights into the role of phosphate modification in Cu/CeO₂-based NH_3 -SCO catalysts and provide a rational strategy for designing advanced low-temperature NH_3 -SCO catalysts.

2. Results and Discussion

2.1. Structural Characterization

To investigate the crystalline structure of the CeO₂ support and the dispersion state of Cu species, CeO₂, Cu/CeO₂, and Acid-Cu/CeO₂ were characterized by XRD, TEM, and HRTEM. As shown in Figure 1a, all samples exhibited a series of characteristic diffraction peaks at $2\theta = 28.5^\circ, 33.1^\circ, 47.4^\circ, 56.3^\circ, 59.1^\circ, 69.4^\circ, 76.7^\circ$, and 79.1° , which can be assigned to the (111), (200), (220), (311), (222), (400), (331), and (420) planes of cubic fluorite CeO₂, respectively [26,27]. No additional diffraction peaks corresponding to crystalline CuO, Cu₂O, or metallic Cu species were observed in Cu/CeO₂ or Acid-Cu/CeO₂, indicating that no large crystalline Cu-containing phase was formed after Cu introduction or phosphoric acid treatment.

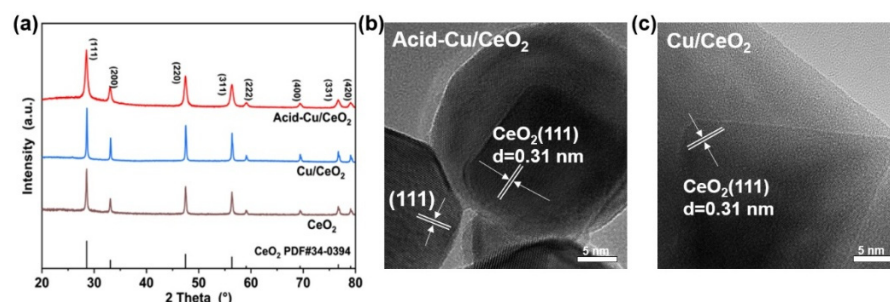


Figure 1. (a) XRD patterns of CeO₂, Cu/CeO₂, and Acid-Cu/CeO₂ catalysts; HRTEM images of (b) Acid-Cu/CeO₂ and (c) Cu/CeO₂ catalysts.

Compared with pristine CeO₂, Cu/CeO₂ showed slight changes in peak intensity and peak width, suggesting that the introduction of Cu species influenced the crystallization behavior and local structural environment of CeO₂ [28]. After phosphoric acid treatment, Acid-Cu/CeO₂ retained the main diffraction peaks of cubic fluorite CeO₂, indicating that the bulk CeO₂ crystalline framework was preserved.

Meanwhile, no phosphate-related crystalline phases were detected for Acid-Cu/CeO₂. This result suggests that the introduced phosphate species may be highly dispersed on the catalyst surface or present in an amorphous state below the XRD detection limit. Similar structural features have been reported for phosphate-modified ceria systems, where surface phosphate species were introduced while the fluorite CeO₂ framework was largely retained [29,30]. The slight variation in diffraction intensity after phosphoric acid treatment is mainly associated with surface etching and surface reconstruction rather than the formation of a new crystalline phase.

The TEM/HRTEM results further support this interpretation. Compared with Cu/CeO₂, Acid-Cu/CeO₂ exhibits a more irregular morphology with locally roughened and reconstructed edges, indicating that phosphoric acid treatment induces surface etching of CeO₂ (Figure 1b,c). Nevertheless, clear lattice fringes with an interplanar spacing of 0.31 nm are observed for both Cu/CeO₂ and Acid-Cu/CeO₂, corresponding to the CeO₂ (111) plane [31]. This confirms that the fluorite CeO₂ framework is retained after phosphoric acid treatment. In addition, no distinguishable Cu-containing nanoparticles or crystalline CuO_x domains are observed in the selected TEM/HRTEM regions. Corroborating the XRD results, these observations suggest that the Cu species are highly dispersed on the CeO₂ support without forming detectable crystalline Cu-containing phases [15,32,33]. The ICP-OES results further confirm the successful introduction of Cu species (Table S1). The Cu contents of Cu/CeO₂ and Acid-Cu/CeO₂ are 1.37 and 1.11 wt%, respectively, which are close to the nominal Cu loading of 1.5 wt%. The slight decrease in Cu content after phosphoric acid treatment may be related to the partial removal of weakly attached Cu species during acid etching and washing. Meanwhile, the Ce contents of Cu/CeO₂ and Acid-Cu/CeO₂ remain comparable, indicating that the bulk Ce-containing framework is largely retained after phosphoric acid treatment.

2.2. Surface Electronic Structure Analysis

To further analyze the effects of phosphate modification on the surface elemental composition, electronic structure and oxygen species distribution of the Cu/CeO₂ samples, XPS characterization was performed on both catalysts. The high-resolution Ce 3d XPS spectra of the Cu/CeO₂ and Acid-Cu/CeO₂ samples are presented in Figure 2a. Both samples exhibit typical Ce 3d spin-orbit splitting features, in which the Ce 3d_{5/2} and Ce 3d_{3/2} components are denoted as the v and u series, respectively. According to previous reports, the v' and u' peaks can be assigned to Ce³⁺ species, whereas the remaining peaks are mainly associated with Ce⁴⁺ species [34,35]. This indicates the coexistence of Ce³⁺ and Ce⁴⁺ on the surfaces of both Cu/CeO₂ and Acid-Cu/CeO₂, reflecting the non-stoichiometric nature of the CeO₂ surface. As summarized in Table S2, the relative Ce³⁺ content decreases from 20.52% for Cu/CeO₂ to 18.44% for Acid-Cu/CeO₂ after phosphoric acid treatment, accompanied by an increase in the Ce⁴⁺ proportion. This result indicates that phosphate modification does not promote Ce³⁺ formation. Instead, the electron-withdrawing phosphate species decrease the relative concentration of surface Ce³⁺ and shift the surface cerium species toward a higher oxidation state [15,29,30]. Therefore, phosphate modification mainly alters the surface electronic environment and Ce³⁺/Ce⁴⁺ distribution of Cu/CeO₂, rather than increasing the amount of Ce³⁺-related oxygen vacancies [29,36]. As shown in Figure 2b, analysis of the Cu 2p XPS spectra indicates that the copper species on the surfaces of both Cu/CeO₂ and Acid-Cu/CeO₂ catalysts exist in mixed valence states. Both samples exhibit characteristic spin-orbit splitting peaks corresponding to Cu 2p_{3/2} and Cu 2p_{1/2}, as well as characteristic satellite peaks of Cu²⁺ species in the range of 940.0–948.0 eV [37,38]. After deconvolution, the relative contents of Cu⁺ and Cu²⁺ were calculated and summarized in Table S3. For Cu/CeO₂, the surface Cu species are mainly composed of Cu²⁺, with Cu⁺ and Cu²⁺ contents of 33.73% and 66.27%, respectively. After phosphoric acid treatment, the Cu⁺ content increases to 49.82%, whereas the Cu²⁺ content decreases to 50.18% in Acid-Cu/CeO₂. This result indicates that phosphoric acid modification increases the relative proportion of reduced Cu⁺ species and promotes a more balanced Cu⁺/Cu²⁺ distribution on the catalyst surface [39]. The increased Cu⁺ fraction suggests that phosphate modification modifies the local electronic environment of Cu species and may facilitate the Cu⁺/Cu²⁺ redox cycle, which is beneficial for NH₃ activation and subsequent oxidation steps in NH₃-SCO [15,31,36].

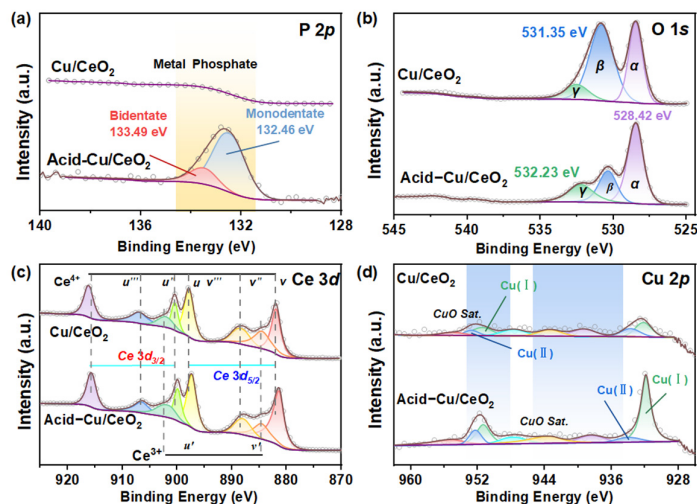


Figure 2. XPS spectra of Cu/CeO₂ and Acid-Cu/CeO₂: (a) Ce 3d; (b) Cu 2p; (c) O 1s; (d) P 2p.

Combined with the absence of copper-related crystalline diffraction peaks in the XRD patterns and the lack of observable CuO_x nanoparticles in TEM/HRTEM images, these XPS results are consistent with the highly dispersed state of Cu species on the CeO₂ support before and after phosphoric acid treatment. The O 1s spectra were further analyzed to clarify the evolution of surface oxygen species. As shown in Figure 2c, the O 1s spectra can be divided into three components, denoted as O_α, O_β, and O_γ [40]. Among them, O_α is mainly assigned to lattice oxygen species, O_β is generally associated with surface adsorbed oxygen or defect-related oxygen species, and O_γ is primarily related to surface hydroxyl groups, adsorbed water, or weakly adsorbed oxygen species [41].

As shown in Table S4, the O_β content of Cu/CeO₂ is 55.56%, and its O_{rela} ((O_β + O_γ)/(O_α + O_β + O_γ)) value reaches 66.11%, indicating a relatively high proportion of surface-related oxygen species. After phosphoric acid treatment, the O_α content of Acid-Cu/CeO₂ significantly increases from 33.89% to 55.25%, whereas the O_β content decreases from 55.56% to 24.86%, and the O_{rela} value also decreases to 44.75%. These results demonstrate that phosphoric acid modification markedly alters the distribution of surface oxygen species over Cu/CeO₂ and increases the relative proportion of lattice oxygen species [15,31,40].

Combined with the catalytic activity results, Acid-Cu/CeO₂ exhibits higher NH₃-SCO activity despite its lower proportion of O_β species. This indicates that the enhanced catalytic activity is not governed solely by the static surface adsorbed oxygen/defect-related oxygen fraction obtained from XPS. Instead, the availability and mobility of lattice or subsurface oxygen species may be more closely related to the superior NH₃-SCO performance of Acid-Cu/CeO₂, which is further supported by the O₂-TPD results discussed below. Therefore, compared with the total amount of surface adsorbed oxygen species, the lattice/subsurface oxygen behavior regulated by phosphate modification is more relevant to the improved catalytic performance [15,20,41]. Figure 2d presents the P 2p XPS spectra of Cu/CeO₂ and Acid-Cu/CeO₂. The untreated Cu/CeO₂ sample shows no discernible P 2p signal, whereas Acid-Cu/CeO₂ exhibits a clear P 2p signal in the 132–134 eV range, confirming that phosphorus species were successfully introduced onto the catalyst surface by phosphoric acid treatment [29,30,42]. In addition, the surface elemental composition was semi-quantitatively analyzed from the XPS survey spectrum (Table S5). For Acid-Cu/CeO₂, the surface P concentration is estimated to be 3.75 at. %, and the corresponding surface P: Cu atomic ratio is approximately 0.76. This result further supports the successful introduction of phosphorus-containing species on the catalyst surface [29,30,43]. The P 2p spectrum of Acid-Cu/CeO₂ can be deconvoluted into two components centered at 132.46 and

133.49 eV, which can be assigned to phosphate species with different coordination environments, generally associated with monodentate and bidentate phosphate species [43,44]. This interpretation is consistent with previous studies on phosphate-modified ceria and P/CeO₂ catalysts, where surface phosphate species were shown to interact with CeO₂ through phosphate–ceria interfacial structures and to modify the local electronic environment, acid-site distribution, and redox behavior of ceria [6,29].

Monodentate phosphate species containing terminal P-OH groups may contribute to the formation of Brønsted acid sites and surface electron-withdrawing effects, while bidentate phosphate species can interact with adjacent Ce sites through Ce-O-P linkages, thereby modifying the local coordination environment and oxygen species mobility [30,43,44]. Because phosphate species possess electron-withdrawing characteristics, their introduction can decrease the surface electron density around Ce species and modify the surface Ce³⁺/Ce⁴⁺ equilibrium [29,30,43]. This interpretation is consistent with the Ce 3d XPS results, where the relative Ce³⁺ content decreases and the Ce⁴⁺ proportion increases after phosphate modification. Therefore, the introduced phosphate species are considered an important factor responsible for the changes in surface acidity, surface electronic structure, and oxygen species distribution of Acid-Cu/CeO₂. However, the individual catalytic contributions of monodentate and bidentate phosphate species cannot be quantitatively separated based solely on P 2p XPS.

2.3. NH₃-SCO Catalytic Performance Evaluation

To evaluate the effect of phosphoric acid surface modification on the NH₃-SCO performance of Cu/CeO₂ catalysts, NH₃ conversion activity, stability, and kinetic tests were conducted over Cu/CeO₂ and Acid-Cu/CeO₂. Overall, Acid-Cu/CeO₂ exhibited markedly higher NH₃ conversion than pristine Cu/CeO₂ in the low- and medium-temperature range, together with improved reaction stability and a lower apparent activation energy, indicating that phosphoric acid surface modification effectively enhanced the NH₃-SCO performance of Cu/CeO₂ [15,16,24]. As shown in Figure 3a, the NH₃ conversion over both Cu/CeO₂ and Acid-Cu/CeO₂ gradually increased with increasing reaction temperature, but their temperature-dependent catalytic behaviors were markedly different. Below 200 °C, both catalysts exhibited very limited NH₃ conversion, indicating that NH₃ adsorption, activation, and oxidative conversion were insufficient in this temperature range [20,24]. When the temperature increased above 200 °C, the NH₃ conversion over Acid-Cu/CeO₂ increased sharply and reached approximately 90% at 260 °C. In contrast, Cu/CeO₂ showed a much slower increase in NH₃ conversion and required a significantly higher temperature to reach the same conversion level. The T₉₀ values of Acid-Cu/CeO₂ and Cu/CeO₂ were 260 °C and 452 °C, respectively, demonstrating that phosphoric acid modification substantially improved the low-temperature NH₃-SCO activity of Cu/CeO₂.

Figure 3b further compares the NH₃ conversion of the two catalysts at 240, 270, and 300 °C based on the same catalytic activity data shown in Figure 3a. Acid-Cu/CeO₂ showed much higher NH₃ conversion than Cu/CeO₂ at all three temperatures. Specifically, Acid-Cu/CeO₂ achieved approximately 84.4%, 92.7%, and 95.4% NH₃ conversion at 240, 270, and 300 °C, respectively, whereas Cu/CeO₂ showed only about 18.25%, 36.58%, and 57.9% conversion at the same temperatures. These results further confirm that phosphoric acid modification effectively enhances the low-temperature NH₃-SCO activity of Cu/CeO₂.

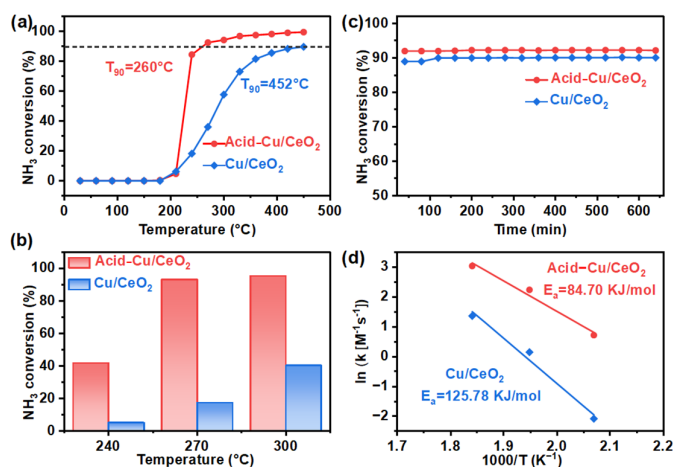


Figure 3. Catalytic NH₃ oxidation performance of Cu/CeO₂ and Acid-Cu/CeO₂: (a) NH₃ conversion as a function of reaction temperature; (b) NH₃ conversion at three selected temperatures (240, 270, and 300 °C). Reaction conditions: 500 ppm NH₃, 2 vol% O₂, total flow rate = 50 mL/min, and WHSV = 30,000 mL gcat⁻¹h⁻¹; (c) Long-term stability test for NH₃ conversion at T₉₀ over 600 min; (d) Arrhenius plots and apparent activation energies.

The catalytic stability results are shown in Figure 3c. Under T₉₀ conditions, the NH₃ conversion over Acid-Cu/CeO₂ remained above 90% during 600 min of continuous reaction, with no obvious deactivation observed, indicating its good reaction stability. By comparison, the NH₃ conversion over Cu/CeO₂ was generally lower than that over Acid-Cu/CeO₂. This result suggests that phosphoric acid surface modification not only improves the low- and medium-temperature activity of Cu/CeO₂ but also helps maintain a high NH₃ conversion level during long-term reaction. To further compare the kinetic behavior of the two catalysts, the apparent activation energies of Cu/CeO₂ and Acid-Cu/CeO₂ in the NH₃-SCO reaction were calculated based on the Arrhenius equation. As shown in Figure 3d, the E_a values of Cu/CeO₂ and Acid-Cu/CeO₂ were 125.78 kJ/mol and 84.70 kJ/mol, respectively. Compared with Cu/CeO₂, Acid-Cu/CeO₂ exhibited a lower apparent activation energy, indicating that phosphoric acid modification reduced the energy barrier of the NH₃-SCO reaction and enabled NH₃ adsorption, activation, and subsequent oxidative conversion to proceed more readily at lower temperatures [3,15,24]. This result is consistent with the lower T₉₀ value of Acid-Cu/CeO₂, further confirming the positive role of phosphoric acid surface modification in enhancing the low- and medium-temperature reaction activity of Cu/CeO₂.

In summary, phosphoric acid surface modification significantly improved the NH₃-SCO performance of Cu/CeO₂, resulting in higher NH₃ conversion in the low- and medium-temperature range, a lower T₉₀ value, good reaction stability, and a lower apparent activation energy. These results indicate that the introduction of surface phosphate species effectively optimizes the surface reaction environment of Cu/CeO₂ and promotes low-temperature NH₃ conversion, providing an experimental basis for further elucidating the performance enhancement mechanism from the perspectives of surface acidity, oxygen species distribution, and electronic structure [15,29,31].

The product selectivity was further analyzed to evaluate the N₂ formation ability and NO_x by-product formation over the two catalysts [24,27]. As shown in Figure 4a, Acid-Cu/CeO₂ maintains relatively high N₂ selectivity over the tested temperature range, with the N₂ selectivity remaining mostly above 70%. In contrast, the N₂ selectivity of Cu/CeO₂ gradually decreases as the reaction temperature increases, especially above 200 °C. This indicates that phosphoric acid modification is beneficial for maintaining N₂ selectivity

during $\text{NH}_3\text{-SCO}$. The NO_x selectivity results further support this conclusion. As shown in Figure 4b, the NO_x selectivity of Cu/CeO_2 increases continuously with increasing temperature, reaching a much higher value at elevated temperatures. This suggests that NH_3 is more readily over-oxidized to NO_x species on unmodified Cu/CeO_2 [21,24]. In comparison, Acid-Cu/CeO_2 shows lower and more stable NO_x selectivity over the same temperature range, indicating that phosphoric acid modification suppresses the deep oxidation of NH_3 to NO_x . Combined with the higher NH_3 conversion and improved N_2 selectivity, these results demonstrate that Acid-Cu/CeO_2 not only promotes NH_3 activation but also favors the selective conversion of NH_3 toward N_2 rather than NO_x by-products.

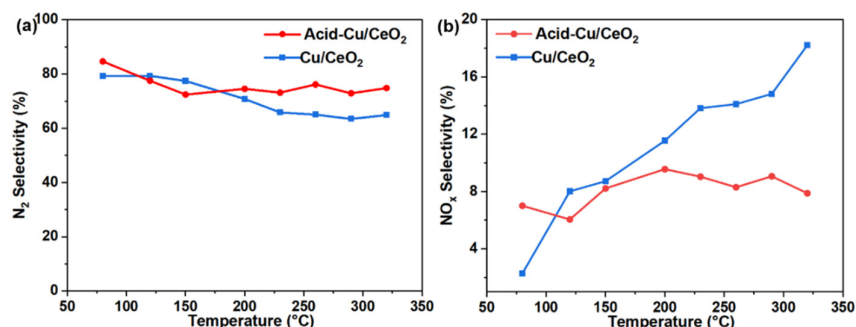


Figure 4. Temperature-dependent product selectivity over Acid-Cu/CeO_2 and Cu/CeO_2 catalysts during $\text{NH}_3\text{-SCO}$: (a) N_2 selectivity and (b) NO_x selectivity. Reaction conditions: 500 ppm NH_3 , 2 vol% O_2 , N_2 balance, total flow rate = 50 mL min^{-1} , catalyst mass = 0.10 g.

To further contextualize the catalytic performance of Acid-Cu/CeO_2 , representative $\text{NH}_3\text{-SCO}$ catalysts reported in the literature were compared [24,27]. As summarized in Table S6, CuO/TiO_2 catalysts with gradient oxidative dual sites achieved a T_{90} of approximately 270 °C under 500 ppm NH_3 and 5 vol% O_2 , while Cu-attapulgite catalysts generally required around 300 °C to reach 90% NH_3 conversion under similar NH_3/O_2 feeds [3,45,46]. CuO/CeO_2 nanorod catalysts also showed excellent $\text{NH}_3\text{-SCO}$ activity, with a T_{90} value of approximately 250 °C under the reported reaction conditions [15]. Cu-Ce-Zr mixed oxides exhibited a comparable T_{90} value of around 260 °C, where coordinated Cu species and reactive oxygen species were identified as key factors governing NH_3 activation and N_2 selectivity [40]. In addition, phosphate-containing hydroxyapatite-supported Cu catalysts required a higher temperature of approximately 350 °C to reach 90% NH_3 conversion, with an N_2 selectivity of about 84% [47]. In comparison, Acid-Cu/CeO_2 reaches a T_{90} of 260 °C under 500 ppm NH_3 , 2 vol% O_2 , and a WHSV of 30,000 mL $\text{gcat}^{-1} \text{h}^{-1}$, while maintaining relatively high N_2 selectivity and lower NO_x selectivity. These comparisons indicate that phosphate modification enables Cu/CeO_2 to achieve competitive low-temperature $\text{NH}_3\text{-SCO}$ performance under relatively mild oxygen concentration [15,24,27,40].

As a typical poison for $\text{NH}_3\text{-SCO}$, SO_2 causes catalyst deactivation via competing for active sites and forming inert sulfate species; thus, sulfur resistance is an important evaluation criterion for their practical application [6,24,26,48]. To evaluate the effect of phosphoric acid modification on sulfur resistance, 10 ppm SO_2 was introduced into the reaction atmosphere, and the SO_2 resistance of Cu/CeO_2 and Acid-Cu/CeO_2 was investigated, as shown in Figure 5a. Under SO_2 -free conditions, Acid-Cu/CeO_2 showed higher NH_3 conversion than Cu/CeO_2 , confirming its superior low- and medium-temperature activity. After SO_2 introduction, both catalysts were affected, and Acid-Cu/CeO_2 did not exhibit a clear sulfur-resistance advantage.

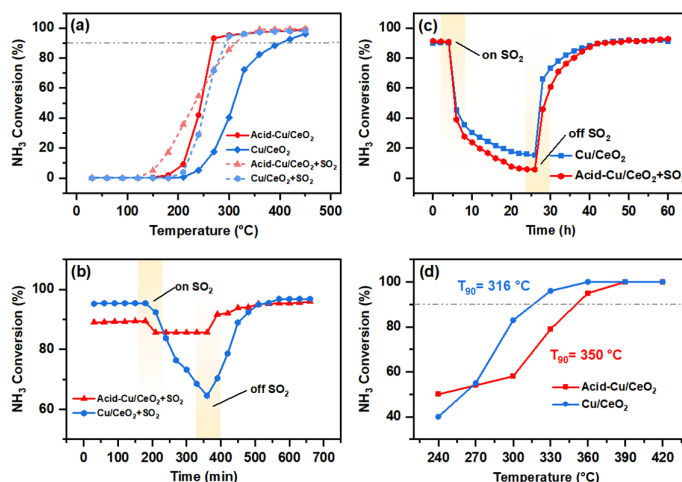


Figure 5. Sulfur resistance performance of Cu/CeO₂ and Acid-Cu/CeO₂: (a) Temperature-programmed NH₃ conversion curves of the samples in the presence and absence of SO₂; (b) 12 h long-term stability curves of the catalysts at T₉₀; (c) 48 h long-term stability curves of the catalysts at T₉₀; (d) Catalytic activity test of the catalysts after SO₂ poisoning test.

The 12 h SO₂-resistance tests were conducted at the corresponding T₉₀ temperatures determined under SO₂-free conditions, namely 452 °C for Cu/CeO₂ and 260 °C for Acid-Cu/CeO₂ (Figure 5b). After SO₂ introduction, the NH₃ conversion over both catalysts decreased to different extents, indicating the inhibitory effect of SO₂ on NH₃-SCO. After SO₂ removal, the NH₃ conversion recovered rapidly. For Cu/CeO₂, the conversion even became slightly higher than its initial SO₂-free level, which is regarded as a transient overshoot during the SO₂ on-off process rather than a stable promotional effect of SO₂ [49,50]. Therefore, this result mainly indicates that the SO₂-induced inhibition is reversible under the present test conditions.

When the SO₂ exposure time was extended to 48 h, the NH₃ conversion of both catalysts continuously decreased to below 20%, demonstrating severe deactivation under prolonged SO₂ treatment (Figure 5c). After SO₂ was removed from the feed gas, the NH₃ conversion over both catalysts recovered rapidly, indicating that the SO₂-induced inhibition was largely reversible under the present reaction conditions. This recovery behavior suggests that the deactivation during short-term SO₂ exposure was mainly associated with reversible adsorption or labile sulfur-containing surface species, rather than irreversible destruction of the active sites [51,52]. However, prolonged SO₂ exposure still caused a significant decrease in NH₃ conversion, demonstrating that SO₂ remains a critical poisoning component for both catalysts. After SO₂ removal, the activity partially recovered for both catalysts, but the post-treatment light-off behavior differed significantly between the two samples [49,52]. The T₉₀ of Cu/CeO₂ decreased by 102 °C, whereas that of Acid-Cu/CeO₂ increased by 56 °C, indicating different surface evolution behaviors during SO₂ treatment. Overall, SO₂ significantly inhibited the NH₃-SCO activity of both catalysts, especially under long-term exposure. Nevertheless, their rapid recovery after SO₂ removal suggests that the poisoning process was mainly reversible. Although phosphoric acid modification improved the intrinsic NH₃-SCO activity of Cu/CeO₂, it did not provide a consistently positive effect on SO₂ resistance [53].

2.4. Analysis of Surface Oxygen Species and Acidic Sites

As shown in Figure 6, the O₂-TPD profile of unmodified Cu/CeO₂ exhibits three main desorption features. The weak low-temperature peak at 175 °C can be assigned to weakly chemisorbed oxygen species [40,54,55]. The desorption peak centered at 397 °C is related to surface/subsurface labile oxygen species, while the high-temperature peak at 726 °C is generally associated with bulk lattice oxygen [56]. The relatively weak low-temperature desorption signal suggests that unmodified Cu/CeO₂ contains a limited amount of readily desorbed surface oxygen species. After phosphoric acid modification, the O₂ desorption behavior of Acid-Cu/CeO₂ changes markedly. Several desorption peaks appear at 289, 388, 490, 559, 666, and 784 °C, indicating a more complex distribution of oxygen species. The peak at 289 °C can be attributed to chemisorbed oxygen species with relatively weak binding [14,57]. More importantly, the medium-temperature desorption peaks at 388, 490, and 559 °C are more reasonably assigned to surface/subsurface labile oxygen species and weakly bound lattice oxygen species, rather than being solely attributed to surface adsorbed oxygen. These oxygen species can participate in the oxidative dehydrogenation of adsorbed NH₃ species and reaction intermediates during the NH₃-SCO reaction [15,24,40]. The high-temperature peaks at 666 and 784 °C are attributed to lattice oxygen species with stronger binding [56,58]. It should be noted that the enhanced medium-temperature O₂ desorption behavior of Acid-Cu/CeO₂ does not directly contradict the decreased O_β fraction observed in the O 1s XPS results. XPS reflects the quasi-static surface oxygen composition, whereas O₂-TPD reflects the temperature-dependent release and mobility of oxygen species during heating. Therefore, the decreased O_β fraction in XPS indicates a lower relative amount of static surface adsorbed/defect-related oxygen species, while the enhanced medium-temperature O₂ desorption peaks indicate improved accessibility and mobility of labile surface/subsurface or weakly bound lattice oxygen species [15,40]. This suggests that phosphoric acid modification redistributes oxygen species and improves the mobility of oxygen species involved in NH₃-SCO [29,30]. This interpretation is consistent with previous studies on Cu–Ce-based NH₃-SCO catalysts, in which the mobility and reactivity of surface/subsurface oxygen species, rather than only the static amount of adsorbed oxygen detected by XPS, were considered crucial for NH₃ activation and selective oxidation [15,28,40].

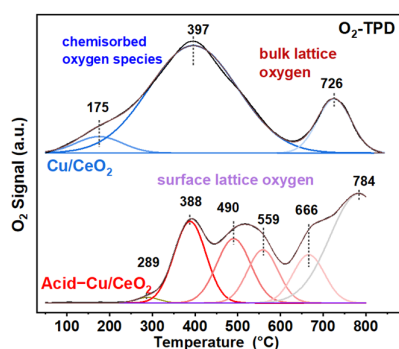


Figure 6. O₂-TPD profiles of Cu/CeO₂ and Acid-Cu/CeO₂ catalysts.

To further distinguish the surface acid properties associated with NH₃ adsorption and activation, Py-IR was performed over CeO₂, Cu/CeO₂, and Acid-Cu/CeO₂ [48,59,60]. As shown in Figure 7, the bands around 1540 cm^{−1} are assigned to pyridine adsorbed on Brønsted acid sites, while the bands around 1440 and 1600 cm^{−1} are attributed to pyridine coordinated to Lewis acid sites [61,62]. The band near 1490 cm^{−1} is generally associated with pyridine adsorbed on both Brønsted and Lewis acid sites [48,59]. In NH₃-SCO, Brønsted acid sites can stabilize NH₃ in the form of NH₄⁺ species, whereas Lewis acid sites

can adsorb NH_3 as coordinated NH_3 species and participate in N-H bond activation [60]. It should be noted that, for Cu/CeO₂-based redox catalysts, Lewis acid sites detected by Py-IR mainly correspond to pyridine-coordinated surface cationic sites, including Cu and Ce species. These sites may also participate in redox-related reaction steps. Therefore, the Py-IR results are mainly used here to compare the relative Brønsted/Lewis acid-site distribution among different samples under identical conditions, rather than to completely separate acidity from redox properties [61,62].

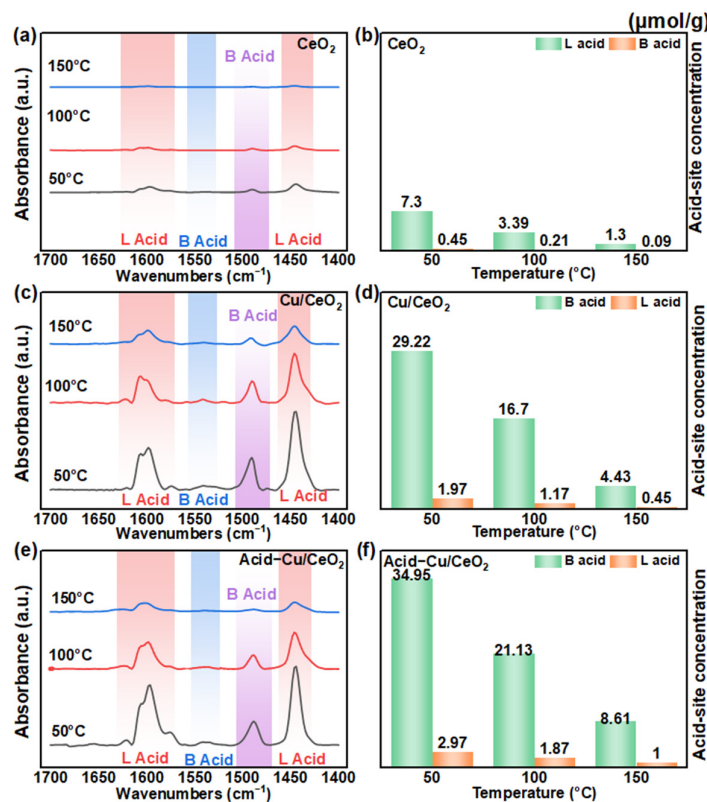


Figure 7. Py-IR spectra of (a) CeO₂, (b) Cu/CeO₂ and (c) Acid-Cu/CeO₂; (d–f) corresponding concentration of Brønsted acid sites and Lewis acid sites calculated from the above spectra.

For CeO₂, the intensities of both Brønsted and Lewis acid bands gradually decrease as the desorption temperature increases from 50 to 150 °C, indicating the progressive desorption of weakly adsorbed pyridine species (Figure 7a). As summarized in Table S7, the Brønsted acid-site concentrations of CeO₂ are 0.45, 0.21, and 0.09 μmol g^{−1} at 50, 100, and 150 °C, respectively, while the Lewis acid-site concentrations are 7.30, 3.39, and 1.30 μmol g^{−1}. The total acid-site concentration decreases from 7.75 to 1.39 μmol g^{−1} as the desorption temperature increases, indicating that most acid sites on CeO₂ are weak or medium-strength acid sites. After Cu introduction, Cu/CeO₂ exhibits a much higher acid-site concentration than CeO₂, especially in the Lewis acid region (Figure 7c,d). The total acid-site concentrations of Cu/CeO₂ are 31.19, 17.87, and 4.88 μmol g^{−1} at 50, 100, and 150 °C, respectively. Specifically, the Lewis acid-site concentrations increase to 29.22, 16.70, and 4.43 μmol g^{−1}, while the Brønsted acid-site concentrations increase to 1.97, 1.17, and 0.45 μmol g^{−1}. These results indicate that Cu introduction significantly increases the number of pyridine-accessible acid sites, with Lewis acid sites remaining the dominant acid species. The enhanced Lewis acidity is closely related to the formation of surface Cu species and Ce-related cationic sites, which can provide more coordination sites for NH_3 adsorption and activation [31,36,42]. After phosphoric acid treatment, Acid-Cu/CeO₂ shows further in-

creased acid-site concentration compared with Cu/CeO₂ (Figure 7e,f). The total acid-site concentrations of Acid-Cu/CeO₂ reach 37.92, 22.99, and 9.61 $\mu\text{mol g}^{-1}$ at 50, 100, and 150 °C, respectively, which are higher than those of Cu/CeO₂ at all corresponding desorption temperatures. Both Brønsted and Lewis acid sites are enhanced after phosphoric acid treatment. The Brønsted acid-site concentrations increase to 2.97, 1.87, and 1.00 $\mu\text{mol g}^{-1}$, while the Lewis acid-site concentrations increase to 34.95, 21.13, and 8.61 $\mu\text{mol g}^{-1}$ at 50, 100, and 150 °C, respectively. Moreover, Acid-Cu/CeO₂ retains higher total acid-site concentrations at 150 °C than Cu/CeO₂, suggesting that phosphoric acid modification not only increases the acid-site concentration but also improves the retention of medium-strength acid sites [6,29,63]. The acidity-regulation effect is also consistent with previous reports on H₃PO₄-modified CeO₂ and phosphate-functionalized ceria, where phosphate species were demonstrated to introduce or strengthen acid sites and simultaneously modify the redox behavior of ceria [6,29,48,63].

These Py-IR results demonstrate that phosphoric acid modification effectively regulates and strengthens the surface acidity of Cu/CeO₂. The increased Brønsted acid sites can promote NH₃ adsorption and stabilization as NH₄⁺ species, while the abundant Lewis acid sites can provide coordination sites for NH₃ activation [48]. Therefore, the superior NH₃-SCO performance of Acid-Cu/CeO₂ is closely related to the enhanced and redistributed Brønsted/Lewis acid sites, together with the modified Cu⁺/Cu²⁺ redox state and improved oxygen species mobility discussed above [15,24,63].

2.5. Mechanistic Insights into NH₃-SCO

To clarify the NH₃ adsorption behavior and surface intermediate evolution over the two catalysts, DRIFTS experiments were first performed under NH₃ adsorption conditions, followed by operando DRIFTS measurements under NH₃ + O₂ reaction conditions. As shown in Figure 8a, Acid-Cu/CeO₂ exhibits several distinct bands at 3641, 3400, 1682, 1625, 1502, 1457, and 1268 cm⁻¹ under the NH₃ atmosphere. The negative band at 3641 cm⁻¹ is assigned to the consumption or perturbation of surface -OH groups, indicating that surface hydroxyl species participate in NH₃ adsorption and activation [64,65]. The band at 3400 cm⁻¹ corresponds to the N-H stretching vibration [66,67]. The band at 1682 cm⁻¹ is attributed to NH₃ adsorbed on Brønsted acid sites, while the band at 1268 cm⁻¹ is assigned to NH₃ coordinated on Lewis acid sites [68,69]. The band at 1502 cm⁻¹ can be assigned to -NH₂ species generated by the initial dehydrogenation of adsorbed NH₃, whereas the band at 1457 cm⁻¹ is associated with -NH species [70,71]. In addition, the band at 1625 cm⁻¹ can be attributed to -NHO-related intermediates [72,73]. With increasing temperature, the Lewis-acid-related NH₃ adsorption band gradually weakens, while the -NH₂, -NH, and -NHO-related bands first become evident and then decrease at higher temperatures. This evolution indicates that NH₃ adsorbed on Acid-Cu/CeO₂ is progressively activated through N-H bond cleavage. Specifically, Lewis-bound NH₃ is first dehydrogenated to form -NH₂ species, which are further converted into -NH species and subsequently into -NHO-related intermediates. At elevated temperatures, these reactive intermediates are further transformed or consumed during the NH₃-SCO reaction. In contrast, as shown in Figure 8b, Cu/CeO₂ shows much weaker NH₃ adsorption features, with bands observed at 3647, 1583, 1414, and 1159 cm⁻¹. The band at 3647 cm⁻¹ corresponds to the N-H stretching vibration. The bands at 1583 and 1159 cm⁻¹ are assigned to NH₃ coordinated on Lewis acid sites, while the band at 1414 cm⁻¹ is attributed to NH₃ adsorbed on Brønsted acid sites [74,75]. Compared with Acid-Cu/CeO₂, the weaker band intensities over Cu/CeO₂ indicate its limited NH₃ adsorption capacity. In addition, no obvious -NH₂, -NH, or -NHO-related bands are observed over Cu/CeO₂ under the NH₃ atmosphere, suggesting that the activation and stepwise dehydrogenation of adsorbed NH₃ are much less efficient on the unmodified catalyst. After introducing O₂, operando DRIFTS measurements were further

performed to investigate the oxidative transformation of NH_3 -derived intermediates during NH_3 -SCO. As shown in Figure 8c, Acid-Cu/CeO₂ exhibits characteristic bands at 3644, 3401, 1679, 1628, 1501, 1457, and 1270 cm^{-1} under the $\text{NH}_3 + \text{O}_2$ atmosphere. The negative band at 3644 cm^{-1} is assigned to the consumption or perturbation of surface -OH groups, indicating that surface hydroxyl species are involved in the NH_3 -SCO reaction. The band at 3401 cm^{-1} corresponds to the N-H stretching vibration [76–78]. The band at 1679 cm^{-1} is attributed to NH_3 adsorbed on Brønsted acid sites, while the band at 1270 cm^{-1} is assigned to NH_3 coordinated on Lewis acid sites. The band at 1501 cm^{-1} is assigned to $-\text{NH}_2$ species, and the band at 1457 cm^{-1} is associated with $-\text{NH}$ species [64,79]. The band at 1628 cm^{-1} is attributed to $-\text{NHO}$ -related intermediates formed through the interaction between dehydrogenated NH_x species and surface hydroxyl or oxygen species [80,81]. Compared with the NH_3 -only atmosphere, the presence of O_2 promotes the oxidative transformation of adsorbed NH_3 species. With increasing temperature, the bands associated with $-\text{NH}_2$, $-\text{NH}$, and $-\text{NHO}$ -related intermediates gradually decrease after their formation, indicating that these intermediates are continuously consumed through further oxidation or coupling reactions. As shown in Figure 8d, Cu/CeO₂ exhibits bands at 3612, 1576, 1524, 1414, 1308, 1256, 1156, and 1020 cm^{-1} under $\text{NH}_3 + \text{O}_2$ reaction conditions. The band at 3612 cm^{-1} corresponds to the N-H stretching vibration [82,83]. The bands at 1576 and 1156 cm^{-1} are assigned to NH_3 coordinated on Lewis acid sites, while the band at 1414 cm^{-1} is attributed to NH_3 adsorbed on Brønsted acid sites [3,84]. The band at 1524 cm^{-1} can be assigned to $-\text{NH}_2$ species, indicating that part of the adsorbed NH_3 can undergo initial dehydrogenation on Cu/CeO₂ [85–87]. The bands at 1308, 1256, and 1020 cm^{-1} are mainly assigned to nitrate/nitrite-related species generated from the oxidation of adsorbed NH_3 [15,68,75,88]. With increasing temperature, these NO_x -related bands become more pronounced, indicating that NH_3 -derived intermediates are readily oxidized to nitrate/nitrite species and tend to accumulate on the Cu/CeO₂ surface. These DRIFTS observations are consistent with previous NH_3 -SCO mechanistic studies, in which adsorbed NH_3 , NH_x intermediates, and nitrate/nitrite-related species were identified as key surface species during NH_3 activation and oxidative transformation [24,81,89,90].

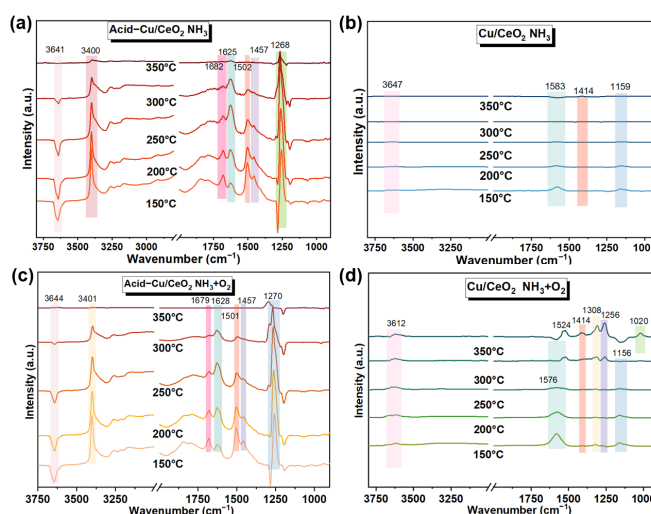


Figure 8. DRIFTS spectra of (a) Acid-Cu/CeO₂ and (b) Cu/CeO₂ under NH_3 adsorption conditions, and operando DRIFTS spectra of (c) Acid-Cu/CeO₂ and (d) Cu/CeO₂ under $\text{NH}_3 + \text{O}_2$ reaction conditions at different temperatures.

Overall, the DRIFTS results reveal distinct NH_3 activation and intermediate transformation behaviors over the two catalysts. Acid-Cu/CeO₂ shows stronger NH_3 adsorption

on Brønsted and Lewis acid sites, more evident formation of -NH_2 , -NH , and -NHO- related intermediates, and continuous consumption of these intermediates at elevated temperatures [42,48,63]. This indicates that phosphoric acid modification promotes NH_3 adsorption, N-H bond activation, and subsequent transformation of NH_x -derived species [68,71,72]. In contrast, Cu/CeO_2 exhibits weaker NH_3 adsorption and less efficient NH_x intermediate formation, while nitrate/nitrite-related species accumulate more obviously under $\text{NH}_3 + \text{O}_2$ conditions (Figure 9) [24,27,68].

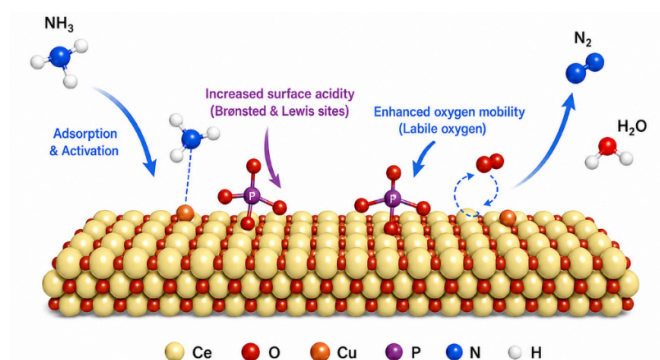


Figure 9. Schematic illustration of phosphate-modified Cu/CeO_2 for low-temperature NH_3 -SCO.

3. Experimental Section

3.1. Preparation of Catalysts

Cu/CeO_2 : 1.96 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (>99.5%, Shanghai Aladdin Co., Ltd., China) and 16.88 g NaOH (95%, Shanghai E & Chemical Technology Co., Ltd., China) were dissolved in 10 mL and 30 mL of deionized water, respectively. After mixing and stirring for 30 min, a calculated amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99%, Shanghai Aladdin Co., Ltd., China) corresponding to a nominal Cu loading of 1.5 wt% was added dropwise and stirred for another 30 min. Hydrothermal treatment was carried out at 180 °C for 24 h, followed by centrifugation, washing, and calcination at 500 °C for 4 h with a heating rate of 10 °C min^{-1} from room temperature.

Acid- Cu/CeO_2 : 600 mg of Cu/CeO_2 was dispersed in 20 mL of anhydrous ethanol (analytical grade, Shanghai Sinopharm Chemical Reagent Co., Ltd., China) and ultrasonicated for 15 min. 18 mL of 0.1 mol/L H_3PO_4 (analytical reagent, Shanghai Sinopharm Chemical Reagent Co., Ltd., China) was added, corresponding to a nominal P amount of 1.80 mmol and a nominal P:Cu atomic ratio of 12.7:1 based on the 1.5 wt% Cu loading. The volume was adjusted to 20 mL with ethanol. Ultrasonic etching was performed for 20 min using a commercial ultrasonic cleaner (KT-5200DT, Nanjing Kulike Technology Co., Ltd., China) at a fixed power of 250 W and a frequency of 40 kHz under continuous-wave mode at room temperature. The product was centrifuged at 5000 rpm for 5 min, washed three times with deionized water, and dried at 80 °C in an oven overnight.

3.2. Catalytic Activity Evaluation

The NH_3 -SCO performance of all catalysts was evaluated in a fixed-bed quartz reactor. Typically, 0.10 g of catalyst powder with a particle size of 60–80 mesh was loaded into the reactor and fixed between two layers of quartz wool. The total gas flow rate was 50 mL min^{-1} , and the feed gas consisted of 500 ppm NH_3 (NH_3 purity $\geq 99.999\%$), 2 vol% O_2 (O_2 purity $\geq 99.999\%$), and N_2 as the balance gas. All gases used in the catalytic activity and SO_2 -resistance tests were supplied by Nanjing Special Gas Co., Ltd., China. The weight hourly space velocity (WHSV) was 30,000 $\text{mL gcat}^{-1} \text{h}^{-1}$. The temperature was increased from room temperature to 500 °C at a ramp rate of 6 °C min^{-1} . At each target

temperature, the catalyst was held for 25 min to reach steady state before the outlet gas was analyzed. The outlet NH_3 concentration was quantitatively measured using an ammonia gas analyzer (Thermo Scientific Model 17i, USA). NH_3 conversion was calculated according to the following equation:

$$X_{\text{NH}_3} = \frac{[\text{NH}_{3\text{inlet}}] - [\text{NH}_{3\text{outlet}}]}{[\text{NH}_{3\text{inlet}}]} \times 100\%$$

$$S_{\text{N}_2} = \frac{\{[\text{NH}_{3\text{inlet}}] - [\text{NH}_{3\text{outlet}}] - [\text{NO}_{\text{outlet}}] - [\text{NO}_{2\text{outlet}}] - 2 \times [\text{N}_2\text{O}_{\text{outlet}}]\}}{[\text{NH}_{3\text{inlet}}] - [\text{NH}_{3\text{outlet}}]} \times 100\%$$

For the kinetic analysis, the apparent reaction rates were calculated from the steady-state NH_3 conversion data obtained in the low-conversion region during the catalytic activity tests. The NH_3 conversion values used for the Arrhenius plots were selected from the light-off measurements under identical reaction conditions, rather than from the selected-temperature bar chart or the long-term stability tests. The apparent NH_3 conversion rate was calculated according to the inlet NH_3 molar flow rate, NH_3 conversion, and catalyst mass. The apparent activation energy was then obtained from the slope of the linear relationship between $\ln r$ and $1/T$ based on the Arrhenius equation.

To evaluate SO_2 resistance, 10 ppm SO_2 (99.99%) was introduced into the reaction atmosphere while maintaining the same NH_3 , O_2 , and N_2 balance gas composition, catalyst mass, and total flow rate. For the SO_2 -containing activity tests, the catalytic performance was measured under the same temperature-programmed protocol in the presence of 10 ppm SO_2 . For the SO_2 on-off stability tests, the catalysts were first stabilized under SO_2 -free reaction conditions at their corresponding T_{90} temperatures, followed by the introduction of 10 ppm SO_2 into the feed gas. After SO_2 exposure, SO_2 was removed from the gas stream, and the recovery behavior of NH_3 conversion was continuously monitored under the original SO_2 -free reaction atmosphere. In addition, post- SO_2 activity tests were conducted after the SO_2 -resistance experiments to evaluate the changes in catalytic light-off behavior.

3.3. Characterization of Catalysts

Comprehensive physicochemical characterization was conducted to establish the relationship between the structural properties, surface acidity, oxygen species characteristics, and NH_3 -SCO catalytic performance of the catalysts. X-ray diffraction (XRD) was employed to characterize the crystal structure and phase composition of the samples. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface elemental composition, chemical states, and electronic structure of the catalysts. Oxygen temperature-programmed desorption (O_2 -TPD) was performed to investigate the distribution, activity, and mobility of surface oxygen species. Pyridine adsorption infrared spectroscopy (Py-IR) was used to distinguish and quantify Brønsted and Lewis acid sites. Furthermore, operando diffuse reflectance infrared Fourier transform spectroscopy (operando DRIFTS) was applied to monitor the dynamic evolution of surface adsorbed species and key intermediates during the NH_3 -SCO reaction, thereby elucidating the reaction pathway and structure–activity relationship of the catalysts. The instrument models and detailed testing parameters are provided in the Supporting Information.

4. Conclusions

In this work, phosphate-modified Cu/CeO₂ catalysts were prepared by a facile phosphoric acid surface treatment and applied to low-temperature NH_3 -SCO. Acid-Cu/CeO₂ retained the cubic fluorite structure of CeO₂, while Cu species remained highly dispersed after modification. Compared with pristine Cu/CeO₂, Acid-Cu/CeO₂ showed markedly

enhanced NH_3 -SCO activity, with the T_{90} decreasing from 452 to 260 °C and the apparent activation energy decreasing from 125.78 to 84.70 kJ mol⁻¹. In addition, Acid-Cu/CeO₂ exhibited relatively higher N₂ selectivity and lower NO_x selectivity, indicating that phosphate modification promotes selective NH_3 conversion toward N₂ while suppressing excessive NO_x formation. Characterization results revealed that surface phosphate species regulate the surface electronic structure and reaction environment of Cu/CeO₂. XPS results showed that phosphate modification decreased the relative Ce³⁺ concentration, increased the Ce⁴⁺ proportion, and regulated the Cu⁺/Cu²⁺ distribution on the catalyst surface. Meanwhile, O 1s XPS and O₂-TPD results indicated that the improved activity is more closely related to oxygen species redistribution and mobility rather than simply to the amount of static surface adsorbed/defect-related oxygen species. Py-IR and DRIFTS results further confirmed that phosphate modification increased Brønsted/Lewis acidity, enhanced NH_3 adsorption and N-H activation, and promoted the formation and consumption of NH_3 -NHO-related intermediates. Overall, phosphate surface modification improves the low-temperature NH_3 -SCO performance of Cu/CeO₂ by jointly regulating surface acidity, Cu/Ce electronic states, and oxygen species mobility.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16070628/s1>, Figure S1: NH_3 conversion over CeO₂ catalyst as a function of temperature; Table S1: ICP-OES elemental analysis results of Cu/CeO₂ and Acid-Cu/CeO₂ catalysts; Table S2: Relative Ce³⁺ and Ce⁴⁺ contents calculated from the Ce 3d XPS spectra of Cu/CeO₂ and Acid-Cu/CeO₂ catalysts; Table S3: Relative Cu¹⁺ and Cu²⁺ contents calculated from the Cu 2p XPS spectra of Cu/CeO₂ and Acid-Cu/CeO₂ catalysts; Table S4: Relative contents of O α , O β , O γ and Orela obtained from the O 1s XPS fitting results of Cu/CeO₂ and Acid-Cu/CeO₂ catalysts; Table S5: Surface elemental composition of Acid-Cu/CeO₂ estimated from XPS survey spectra; Table S6: Comparison of Ammonia Selective Catalytic Oxidation Performance of Different Catalysts; Table S7: Quantitative acid site results of CeO₂, Cu/CeO₂ and Acid-Cu/CeO₂ catalysts measured by Py-IR at different desorption temperatures.

Author Contributions: Writing—original draft, Data curation, S.M.; Writing—review and editing, Formal analysis, H.L.; Data curation, Formal analysis, Y.H. (Yuchen Huang); Conceptualization, Data curation, K.S.; Conceptualization, Data curation, Y.H. (Yuejia Huang); Supervision, Funding acquisition, Project administration, Y.F.; Validation, Methodology, Y.D. All authors have read and agreed to the published version of the manuscript.

Funding: We acknowledge the National Natural Science Foundation of China (No. 22306094) for the financial support and Jiangsu Future Membrane Technology Innovation Center (No. BM2021804).

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Conflicts of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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