

Study on the Effect of Preparation Methods on the Performance of Ag-Cu Bifunctional Catalysts for NH_3 -SCO

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Abstract

Ammonia selective catalytic oxidation ($\text{NH}_3\text{-SCO}$) can purify NH_3 waste gas, yet monometallic $\text{Ag}/\text{Al}_2\text{O}_3$ shows excellent low-temperature activity but poor N_2 selectivity with abundant N_2O byproducts. Herein, a series of 10 wt.% Ag-5 wt.% Cu bifunctional catalysts were prepared via different impregnation routes and metal loading sequences to balance catalytic performance. Performance tests reveal that co-impregnated $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-C}$ retains high low-temperature activity with limited selectivity improvement, while two-step Cu-first $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-T}$ slightly sacrifices conversion efficiency but achieves over 90% N_2 selectivity over the full temperature range. Multiple characterizations prove Cu occupies surface hydroxyl sites, reduces surface active oxygen and modulates Ag aggregation. In-situ DRIFTS indicates $\text{Ag}/\text{Al}_2\text{O}_3$ follows the low-selectivity imide pathway, whereas $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-T}$ shifts reactions toward the N_2^- route and partially reduces bidentate nitrates to restrain NO_2 formation. This work clarifies the structure-activity correlation and provides an optimized preparation strategy for high-efficiency $\text{NH}_3\text{-SCO}$ catalysts.

1 Introduction

- With the continuous advancement of fundamental science and applied technologies, environmental issues have attracted increasing attention from scholars. The World Health Organization and the United Nations Environment Programme have pointed out that airborne pollutants constitute a non-negligible threat to the lives of global urban residents and exert pervasive impacts on human beings^[1, 2]. Ammonia serves as an important product and raw material in the chemical industry^[3–6]. Owing to its high hydrogen density and carbon-free property, ammonia is also a promising clean energy carrier with safer transportation and storage performance compared with hydrogen^[7–11]. Nevertheless, ammonia is a toxic irritant gas hazardous to human health^[12]. Meanwhile, excessive ammonia emissions react in the atmosphere to form 2.5 μm particulate matter ($\text{PM}_{2.5}$), triggering adverse environmental outcomes including haze and soil acidification^[13, 14]. Statistics show that the total ammonia emission of the European Union reached approximately 3.419 million tons in 2020, while the figure of the United States was around 5.218 million tons^[15, 17]. Relevant reports and investigations estimated China's ammonia emission to be 9.60–9.724 million tons in the same year^[17]. At present, NH_3 is recognized as one of the primary nitrogen-containing pollutants contributing to haze formation, and ultra-low emission standards for ammonia have been enforced in China^[18–22].
- Conventional ammonia recovery technologies include physical condensation and water/acid scrubbing. Physical condensation separates ammonia based on boiling point differences. However, ammonia recovery from water inevitably generates massive ammonia-laden wastewater and causes severe secondary pollution. Inorganic acid solutions are highly corrosive and produce low-value salts, which limit their competitiveness in ammonia recycling^[23–29]. In recent years, mainstream ammonia abatement strategies have covered membrane separation, adsorption, biological

treatment, thermal combustion, selective catalytic oxidation and electrocatalytic oxidation^[22]. Among various NH_3 mitigation technologies, NH_3 selective catalytic oxidation (NH_3 -SCO) stands out as an extremely efficient route and has been widely adopted for industrial exhaust and diesel vehicle aftertreatment systems. The NH_3 -SCO reaction proceeds under mild conditions and completely eliminates NH_3 above a threshold temperature, producing only environmentally benign N_2 and H_2O , which renders it an ideal ammonia removal technology. To meet practical exhaust treatment demands, target catalysts are required to possess high low-temperature activity, low by-product yield, outstanding durability, strong water resistance and superior sulfur tolerance, which bring great challenges to catalyst development.

- NH_3 -SCO catalysts can be divided into three major categories: noble metal catalysts (Pt, Pd, Rh, Ir, Ru, Au, Ag)^[30–37], transition metal oxide catalysts (CuO , Fe_3O_4 , Co_3O_4 , NiO , V_2O_5)^[35–37], and bifunctional catalysts (Pt-Cu, Pt-Fe, Pt-V, Ag-Cu, Ag-Mn, Ag-Ce)^[38–43]. Noble metal catalysts deliver 100% NH_3 conversion below 200°C yet suffer N_2 selectivity lower than 70%. Transition metal oxides exhibit N_2 selectivity over 95% but barely show catalytic activity under 250°C . Bifunctional catalysts strike a balance between the two categories, generally achieving full NH_3 conversion near 200°C with N selectivity exceeding 80% across the whole temperature range. Among all noble metals, silver possesses unique merits. As the cheapest noble metal, Ag/ Al_2O_3 catalysts cost merely 1/30 of Pt/ Al_2O_3 counterparts with identical metal loading. Besides, Ag-based catalysts exhibit extraordinary low-temperature oxidation capacity and can fully decompose NH_3 at very low temperatures.
- Wang et al.^[44] demonstrated that Ag particle size and Ag valence states are decisive factors for NH_3 -SCO activity and N_2 selectivity. They found that enhanced activation of oxygen species on metallic Ag accelerates NH_3 over-oxidation and elevates N_2O generation. Experimental data also verified that H_2 pretreatment remarkably improves the NH_3 -SCO performance of Ag/ Al_2O_3 and reduces T_{50} . Metallic Ag facilitates O_2 activation, thereby boosting catalytic activity. Both pristine and H_2 -reduced Ag/ Al_2O_3 follow the i-SCR mechanism. When normalizing reaction rates by acid site quantity, Brønsted acid sites deliver higher turnover frequencies than Lewis acid sites, verifying their superior capability for low-temperature NH_3 oxidation. The enriched B acid sites on H_2 -treated Ag/ Al_2O_3 are a core contributor to improved catalytic activity.
- In the research of Xu et al.^[45], Ag/ Al_2O_3 exhibited favorable low-temperature NH_3 oxidation activity, producing N_2 and N_2O simultaneously. The formation rates of both products rise rapidly with temperature. In the high NH_3 conversion region, N_2 production grows steadily while N_2O yield declines, corresponding to a peak N_2 selectivity. At elevated temperatures, N_2 selectivity gradually drops accompanied by increased NO by-product formation.
- The NH_3 -SCO cycle initiates with NH_3 adsorption and subsequent activation by active oxygen species, followed by H abstraction to form amide intermediates. The generation of active oxygen via dissociative or non-dissociative adsorption on catalysts is the key step for NH_3 activation. Silver plays an irreplaceable role in O_2 activation, which is critical for dehydrogenation of adsorbed NH_3 . Four types of oxygen species are commonly detected on NH_3 -SCO catalysts: physically adsorbed

molecular oxygen, adsorbed atomic oxygen, surface lattice oxygen and reactive active oxygen. Experimental evidence suggests that re-oxidation of Ag nanoparticles is the rate-determining step within this reaction zone, and $\text{NH} = \text{NH}$ intermediates react with $[\text{O}]$ and $[\text{O}_2]$ to generate N_2 and N_2O .

- Compared with other Ag-based catalysts, the 10 wt.% Ag/ Al_2O_3 sample in their work displayed low N_2 selectivity at low temperatures due to abundant N_2O generation. As temperature rises, surface reactions are accelerated, and the rate-determining step shifts from Ag nanoparticle re-oxidation to NH_3 adsorption and initial dehydrogenation. Gaseous O_2 undergoes rapid dissociation to produce active $[\text{O}]$ species, jointly suppressing N_2O formation at higher temperatures. Further temperature elevation triggers fast dehydrogenation of NH_3 to form atomic $[\text{N}]$, which readily reacts with excess $[\text{O}]$ to generate NO . The characterization results confirmed that nitrate species remain stable on the catalyst surface without participating in reactions, proving that detected NO does not originate from nitrate decomposition and clarifying the source of NO by-products.
- Li et al.^[46] aimed to fabricate low-cost high-efficiency Ag/ Al_2O_3 catalysts. They proposed that tuning H_2 reduction temperature to shrink Ag particle size enables high Ag dispersion under limited metal loading, an effect hardly achieved by traditional calcination. Catalytic activity follows the sequence: 600 Fresh > 700 Fresh > 800 Fresh > 900 Fresh > 500 Fresh > 400 Fresh (X Fresh represents catalysts reduced under X °C H_2 atmosphere). At 1 wt.% Ag loading, Ag particle size and dispersion dominate catalytic performance, and the 600 Fresh sample achieves optimal balance between the two parameters, delivering the best NH_3 -SCO activity. For catalysts reduced below 500°C, Ag can be transformed into metallic state, yet the tiny particle size restrains the O_2 activation efficiency of Ag^0 and lowers overall activity. Higher reduction temperatures enlarge Ag nanoparticles, and poor dispersion of active sites exerts negative impacts on catalytic reactions. Even with a tenfold reduction in Ag loading, H_2 -pretreated catalysts deliver comparable activity and N_2 selectivity to the 10 wt.% Ag/ Al_2O_3 reference, with N_2O as the primary by-product and NO/NO_2 selectivity far below 10%. However, the 600 Fresh sample nearly loses all activity under humid conditions, with only 6% NH_3 conversion at 300°C, revealing poor water tolerance of highly dispersed tiny Ag nanoparticles. In contrast, 800 Fresh retains partial activity and achieves complete NH_3 conversion at 275°C.
- Wet-dry cycling tests further evaluate catalyst water resistance. Both 600 Fresh and 800 Fresh maintain 100% NH_3 conversion without water vapor at 275°C. After introducing steam for 60 min, 600 Fresh rapidly deactivates within 4 min, while 800 Fresh sustains 80% conversion. Once water supply is cut off, the activity of 600 Fresh only recovers to 40% of its initial level and plateaus, whereas 800 Fresh regains full activity within 5 min. Silver atoms tend to aggregate under reductive atmospheres, while Ag nanoparticles can re-disperse during redox cycles. After one cycle, 600 Fresh suffers severe activity loss with merely 62% NH_3 conversion at 300°C. Two cycles cause slight activity decay for 800 Fresh, and 900 Fresh barely deactivates. It can be concluded that catalyst stability improves with rising reduction temperature and peaks at 900°C. Post-reaction re-dispersion of Ag^0 active sites is hindered by large Ag aggregates formed under low H_2 reduction temperatures, leading to activity decay. Higher reduction temperatures produce larger Ag nanoparticles and enhance hydrothermal durability.

- In practical NH_3 -SCO applications, steam is ubiquitous in exhaust streams. Catalysts are required to possess long service lives for industrial utilization. Therefore, water resistance and durability are vital evaluation indicators. Experiments reveal that catalyst activity and water/durability show opposite trends when the H_2 reduction temperature exceeds 600°C . Further research on water-resistant $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts is needed to develop low-cost, high-performance materials with prolonged service life.
- Wang et al.^[47] investigated the influence of calcination temperature and Ag loading on catalytic activity. NH_3 conversion gradually declines with elevated calcination temperature. $\text{Ag}/\text{Al}_2\text{O}_3$ -800 (calcined at 800°C) reaches full NH_3 conversion at approximately 170°C , 50°C higher than the counterpart calcined at 400°C . N_2O is the sole by-product over $\text{Ag}/\text{Al}_2\text{O}_3$ -X, and highly dispersed Ag species (AgHD) are detected on the catalysts. On one hand, NH_3 conversion rises with increased Ag loading and is greatly boosted after H_2 reduction. On the other hand, AgHD catalysts with low loading (5, 10, 20 wt.%) achieve over 95% N_2 selectivity at full NH_3 conversion. N_2O is more readily generated over Ag nanoparticle (AgNP) catalysts. AgHD catalysts exhibit superior N_2 selectivity and outstanding cycling stability, retaining $\sim 90\%$ NH_3 conversion and $\sim 97\%$ N_2 selectivity after ten cycles. Kinetic analysis indicates that the reaction orders of O_2 and NH_3 shift with calcination temperature: O_2 dominates the reaction rate at 400 – 600°C , while NH_3 becomes the rate-controlling factor at 700 and 800°C . The surface concentrations of adsorbed NO_3ads and NH_2ads intermediates on $\text{AgHD}/\text{Al}_2\text{O}_3$ far exceed those on $\text{AgNP}/\text{Al}_2\text{O}_3$, facilitating the formation and decomposition of $\text{N} = \text{N} - \text{M}$ intermediates to produce N_2 . Excess reactive $[\text{O}]$ is continuously consumed on AgNPs, accelerating the generation of $[\text{O}] - \text{N} = \text{N} - \text{O} - \text{M}$ intermediates that decompose into N_2O , which explains the inferior N_2 selectivity of AgNP catalysts with N_2O as the unique by-product.
- Zhang et al.^[43] studied Ag catalysts supported on CeSnO_x . Synergistic interaction between Ce and Sn enhances redox capacity and enriches acid sites favorable for NH_3 adsorption and activation^[48]. Ag loading significantly improves the redox performance of CeSnO_x . Ag deposition induces precipitation of partial Sn from the bulk to form surface SnO_2 particles and reduces the proportion of Ce^{3+} , lowering oxygen vacancy concentration^[49–51]. Sn doping modulates the electronic structure of AgO and accelerates electron transfer via the support. Electron density transfers from CeSnO_x (CSO) to AgO, enhancing AgO oxidation and CSO reduction performance, balancing NH_3 oxidation and NO_x reduction rates, boosting N_2 selectivity and facilitating NH_3 adsorption on CSO^[52]. On $1.75\text{Ag}/\text{CeSnO}_x$, Sn atoms disperse uniformly while partial SnO_2 aggregates. Higher Ag loading intensifies the low-temperature desorption peak of active oxygen and raises total oxygen content, contributing to its excellent low-temperature activity. On this catalyst, adsorbed NH_3 on Ag sites is first over-oxidized into NO_x . Below 200°C , partial NO_x reacts with NH_3 adsorbed on Ag nanoparticles to form N_2 , and residual NO_x diffuses onto CeSnO_x to form nitrates. Above 200°C , NO_x is reduced by $\text{NH}_3/\text{NH}_4^+$ adsorbed on the support to generate N_2 . Therefore, loading Ag on Ce-Sn binary oxides enables efficient conversion of NH_3 to N_2 over a wide temperature window via a dual-site tandem mechanism. Meanwhile, Ag deposition blocks partial micropores and reduces the BET specific surface area and pore volume of CeSnO_x . Mass transfer of NH_3 and NO_x is hindered by diffusion

resistance between dual components. Activity loss after water introduction is attributed to reversible competitive adsorption between H_2O and NH_3 ; active sites are re-exposed after water removal to recover catalytic performance^[53]. Hydrothermally aged catalysts maintain N_2 selectivity above 70% at high temperatures, demonstrating reliable stability. Severe hydrothermal treatment triggers partial aggregation of AgO nanoparticles, yet the binding energy of Ag remains unchanged, preserving favorable low-temperature activity. Hydrothermal aging increases oxygen vacancy density and surface adsorbed active oxygen, promoting further oxidation of adsorbed $-\text{NH}_2$ and reducing N_2 selectivity, which can be attributed to aggregated AgO nanoparticles and enriched active oxygen species after steam treatment.

- Although Ag-based catalysts exhibit promising NH_3 -SCO performance, they suffer prominent drawbacks: toxic by-products form at different temperatures. Stricter emission regulations demand further optimization of Ag catalysts. Especially for Ag/ Al_2O_3 , massive N_2O generates below 250°C and abundant NO_x forms above 250°C . Constructing bifunctional catalysts effectively elevates N_2 selectivity.
- However, existing research on bifunctional catalysts mostly adopts fixed synthetic routes, and systematic investigations into how preparation methods and metal loading sequences regulate catalytic performance remain scarce. Comprehensive screening of bifunctional catalysts with identical metal contents but distinct fabrication procedures is required to identify optimal formulations. Despite the excellent low-temperature activity of Ag/ Al_2O_3 , doping foreign metals generally leads to severe activity decay. Given the low exhaust temperature of ammonia-fueled engines, NH_3 -SCO catalysts must retain high low-temperature activity. Systematic research on Ag-based bifunctional catalysts is therefore critical to enhance their low-temperature performance and improve competitiveness for ammonia engine aftertreatment systems.
- The optimal calcination temperature and atmosphere for monometallic catalysts have been thoroughly studied, whereas dual-component systems contain multiple active phases with disparate optimal thermal treatment conditions. The synergistic effect of different metal species determines overall catalytic performance, so it is necessary to explore how calcination conditions alter the state of each component and regulate catalytic properties.
- As environmentally hazardous gas, NH_3 emission standards are becoming increasingly stringent. Among all deamination technologies, NH_3 -SCO converts NH_3 into harmless N_2 and H_2O under mild conditions with prominent advantages in conversion efficiency and reaction conditions. Low-temperature activity and N_2 selectivity are the two most vital indicators for NH_3 -SCO catalysts; durability, water resistance, oxidation resistance and cost also cannot be ignored during material design. Noble metal catalysts represented by Ag/ Al_2O_3 deliver outstanding low-temperature activity yet low N_2 selectivity accompanied by abundant N_2O at low temperatures, along with insufficient hydrothermal stability. Existing studies reveal that doping transition metals into Pt-based catalysts greatly improves N_2 selectivity at the cost of partial activity loss, while relevant research on Ag-based systems is limited. Given the superior low-temperature activity of Ag/ Al_2O_3 , introducing

transition metals into this system is a promising strategy to develop catalysts with balanced activity and selectivity.

- To meet the working conditions of ammonia-fueled ships featuring low exhaust temperature and high NH_3 leakage, this work investigates the effects of fabrication routes and metal loading sequences on Ag-Cu/ Al_2O_3 catalysts. For dual-metal catalysts, the loading order of two active components needs to be rationally designed. Ag/ Al_2O_3 serves as an outstanding noble metal substrate for bifunctional catalyst construction. Cu is the most widely adopted transition metal for Pt-based bifunctional NH_3 -SCO catalysts. Although Cu doping sacrifices partial low-temperature activity, it significantly improves N_2 selectivity. In this paper, a series of Ag-Cu/ Al_2O_3 catalysts with fixed Ag and Cu loadings are fabricated via diverse preparation methods and metal loading orders. Their low-temperature activity and N_2 selectivity are compared with monometallic Ag/ Al_2O_3 . Multiple characterizations including BET, UV-vis, XRD, XPS, NH_3 -TPR, H_2 -TPD, ^1H MAS NMR and in-situ Raman are carried out to analyze catalyst texture, surface acidity and redox properties, revealing the dispersion state of Ag and Cu on $\gamma\text{-Al}_2\text{O}_3$ and their impacts on catalytic performance^[57]. In-situ DRIFTS is further adopted to clarify reaction pathways over Ag-Cu catalysts prepared by different routes and uncover how Cu introduction modifies NH_3 oxidation mechanisms.

2 Experimental

2.1 Catalyst Preparation

- In this study, three facile synthetic routes including solid impregnation, liquid impregnation and deposition-precipitation were adopted to load Ag and Cu onto $\gamma\text{-Al}_2\text{O}_3$ support, which can guarantee favorable metal dispersion after loading. A series of catalyst samples were prepared by adjusting metal loading sequences and combining different preparation processes, with fixed nominal Ag loading of 10 wt.% and Cu loading of 5 wt.%.
- First is the wet impregnation method. Taking the reference Ag/ Al_2O_3 sample as an example, 2.00 g $\gamma\text{-Al}_2\text{O}_3$ was accurately weighed and transferred into a beaker, followed by the addition of approximately 80 mL deionized water under continuous stirring. Meanwhile, 0.315 g silver nitrate solid was precisely weighed and dissolved in another beaker containing 20 mL deionized water with 15 min stirring. The silver nitrate solution was dropwise added into the $\gamma\text{-Al}_2\text{O}_3$ suspension and stirred continuously for another 2 h. After stirring, the mixed solution was transferred to a rotary evaporator for vacuum evaporation at a constant water bath temperature of 60°C until the liquid phase was completely removed. The solid residue was collected and dried in a constant-temperature oven at 80°C for no less than 12 h. After thorough drying, the powder was placed in a crucible and calcined under air atmosphere at 600°C for 3 h. Different post-processing operations were performed after calcination according to subsequent experimental requirements: if further metal loading steps were required, the solid was fully ground into fine powder; if the sample was the final catalyst, the cooled solid was tableted and sieved. Particles with 40–60 mesh were used for

catalytic performance tests, and finer powders were reserved for subsequent physicochemical characterizations.

- Second is the solid impregnation method, which is mainly used for introducing the second metal component in stepwise impregnation. Taking the bifunctional catalyst prepared via liquid-solid two-step impregnation (Ag loaded first followed by Cu with nitrate precursors) mentioned in Chap. 3 as an example, sufficient Ag/Al₂O₃ powder was pre-synthesized by the above wet impregnation method, and 2.00 g of the powder was accurately weighed into an agate mortar. According to the target Cu loading of 5 wt.%, 0.295 g copper nitrate solid (or 0.251 g copper sulfate solid for sulfate precursor) was weighed and mixed with Ag/Al₂O₃ powder in the mortar. The mixture was fully ground until the color no longer changed. The mixed solid was transferred into an oven for 12 h drying, followed by calcination. The calcination parameters and post-treatment operations were consistent with those of the wet impregnation method.
- Third is the deposition-precipitation method, which is mainly applied for Ag loading on γ -Al₂O₃. 2.00 g γ -Al₂O₃ was accurately weighed into a beaker and mixed with about 80 mL deionized water under continuous stirring. Meanwhile, 0.315 g silver nitrate solid was dissolved in 20 mL deionized water with full stirring until complete dissolution. The silver nitrate solution was poured into the γ -Al₂O₃ suspension and stirred to achieve uniform mixing. A pH meter was immersed in the mixed solution, and ammonia water or ammonium carbonate was added dropwise under stirring with real-time pH monitoring. The addition of alkaline reagent was stopped when the pH value stabilized at 10.0^[54], and the mixture was stirred for another 10 min. After stirring, the suspension was transferred to a rotary evaporator placed in a fume hood for solvent evaporation. The evaporation temperature and all subsequent operations were identical to the wet impregnation process.
- For samples synthesized by co-impregnation, the preparation procedure was basically the same as wet impregnation, except that both silver nitrate and copper nitrate solids were dissolved together to prepare the impregnating solution, and all other steps remained unchanged. Catalysts prepared by multi-step routes were synthesized in accordance with the corresponding loading sequence and individual loading method of each metal.
- All catalysts were labeled based on metal composition, loading sequence and preparation method, namely Ag/Al₂O₃, Ag-Cu/Al₂O₃-C, Ag-Cu/Al₂O₃-T, Cu-Ag/Al₂O₃-T, Ag-Cu/Al₂O₃-S-N, Cu-Ag/Al₂O₃-S-N, Cu-Ag/Al₂O₃-DP and Cu-Ag/Al₂O₃-DP-S-S. The corresponding relationship between catalyst labels and their definitions is shown in Table 1, among which Ag/Al₂O₃ served as the reference sample for comparisons of catalytic performance and microstructure with Cu-doped bimetallic catalysts.

Table 1
Catalyst Name and Meaning Correspondence Table

Catalyst Label	Definition
Ag/Al ₂ O ₃	Reference catalyst prepared by wet impregnation
Ag-Cu/Al ₂ O ₃ -C	Ag-Cu bifunctional catalyst synthesized via co-impregnation
Cu-Ag/Al ₂ O ₃ -T	Ag-Cu bifunctional catalyst by two-step liquid impregnation (Ag loaded before Cu)
Ag-Cu/Al ₂ O ₃ -T	Ag-Cu bifunctional catalyst by two-step liquid impregnation (Cu loaded before Ag)
Cu-Ag/Al ₂ O ₃ -S-N	Bifunctional catalyst fabricated via liquid-solid two-step impregnation with nitrate precursors (Ag prior to Cu)
Ag-Cu/Al ₂ O ₃ -S-N	Bifunctional catalyst fabricated via liquid-solid two-step impregnation with nitrate precursors (Cu prior to Ag)
Cu-Ag/Al ₂ O ₃ -DP	Bifunctional catalyst combining deposition-precipitation and liquid impregnation
Cu-Ag/Al ₂ O ₃ -DP-S-S	Bifunctional catalyst combining deposition-precipitation and solid impregnation with sulfate precursors

2.2 Catalyst performance evaluation system and physicochemical characterization methods

The catalyst activity evaluation system consists of gas cylinders, pressure reducing valves, pipelines, mass flow controllers, digital display instruments, temperature-programmed tubular furnace, gas cell, vacuum pump, Fourier transform infrared (FTIR) spectrometer and computer. Quantifiable parameters were set for all components to guarantee identical testing conditions for all catalyst samples.

- First, the standard test conditions were defined. The total gas flow rate was fixed at 100 mL/min, and the feed gas consisted of 10 vol.% O₂, 500 ppm NH₃ with N₂ as the balance gas. The dosage of each catalyst sample was 0.1 g, corresponding to a weight hourly space velocity (WHSV) of 60000 mL/(g·h).
- Second, all mass flow meters were calibrated in the gas preparation stage. Multi-point sampling and linear fitting were adopted to establish the functional relationship between digital readings and actual gas flow rates with the coefficient of determination $R^2 > 0.99$. The fitted curves were verified by real-time flow measurement during formal tests, and the corresponding display parameters were recorded. In addition, 10 ammonia standard gas mixtures with different concentrations were prepared for FTIR calibration. The peak area of ammonia located at 910–982 cm⁻¹ was correlated with corresponding concentrations via cubic polynomial fitting. The same calibration method was applied to by-products N₂O, NO and NO₂.
- Third, a unified temperature program was set for the tubular furnace. Each catalyst sample was pretreated under N₂ atmosphere at 200°C for 2 h with a heating rate of 5°C/min, then cooled down

to 100°C to start formal activity testing. Each temperature point was held for 25 min: the first 20 min was reserved for reaction equilibrium, and FTIR spectra were collected three times and averaged in the last 5 min to reduce random errors. The heating ramp between adjacent temperature points was 5°C/min. Gas supply and heating were terminated once data at 300°C were collected to finish the experiment.

- Finally, the collected FTIR spectra were processed to quantify the outlet concentrations of NH_3 , N_2O , NO and NO_2 . The peak areas of each gas species were calculated and substituted into pre-calibrated formulas to obtain concentrations, based on which catalytic performance indexes were calculated. For samples with outstanding catalytic activity, comprehensive physicochemical characterizations were carried out to reveal the intrinsic structure-performance relationship, and all characterization techniques adopted in this work are illustrated as follows.
- A combination of multiple characterization techniques and DFT theoretical calculations was used to systematically investigate metal loading efficiency, pore structure, crystal phase, elemental valence, surface acid-base property, redox capacity, active oxygen species, surface hydroxyl groups and the evolution of reaction intermediates, so as to clarify the catalytic mechanism. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to measure the actual metal loadings. Qualitative and quantitative elemental analysis was realized via characteristic spectral lines excited by plasma, and the metal loading efficiency was calculated by comparing measured values with theoretical loadings. The specific surface area and pore parameters were measured by nitrogen adsorption-desorption (BET method). A total of 0.1000 g sample was pretreated at high temperature with vacuum-helium purging to eliminate impurity interference, followed by adsorption-desorption measurement at 88 K under liquid nitrogen environment. The specific surface area, pore volume and average pore size were derived from adsorption isotherms.
- X-ray diffraction (XRD) was employed to analyze crystal structures with a Cu ceramic X-ray tube. The scanning range of 2θ was 10–90 ° at a rate of 6 °/min. After spectrum normalization, standard PDF cards were matched to identify crystalline phases and semi-quantitatively evaluate the relative content of each component. X-ray photoelectron spectroscopy (XPS) was used to detect elemental composition, valence state and relative content, with a resolution of 0.48 eV for $\text{Ag } 3d_{5/2}$. C 1s spectrum was used for charge correction, and Avantage software was applied for peak deconvolution to distinguish elemental chemical states. UV-vis spectra were recorded within 200–800 nm at a spectral bandwidth of 1 nm, and standard spectra were referenced to identify the existing forms of Ag and dopant elements.
- NH_3 -TPD and H_2 -TPR tests were performed on a temperature-programmed tubular furnace equipped with a TCD detector to characterize surface acidity and redox property, respectively. For NH_3 -TPD measurements, samples were pretreated under inert gas at 300°C for over 30 min, cooled to room temperature for 1 h NH_3 adsorption, and purged to stabilize the baseline. Then the temperature was raised to 550°C at 5°C/min. Peakfit software was used for baseline subtraction and peak fitting. Desorption peaks were classified into α (< 150°C), β (150–250°C) and γ (> 250°C) sites, and the relative amount of each acid site was evaluated by peak area. The pretreatment procedure of H_2 -

TPR was consistent with NH_3 -TPD. After baseline stabilization under 5 vol.% H_2/N_2 mixed gas, the furnace was heated to 800°C at 5°C/min. Different surface active components were assigned according to the reduction temperature of deconvoluted peaks.

- In-situ Raman spectroscopy with a 632 nm laser (resolution: 1 cm^{-1}) was used to evaluate O_2 activation capacity. The sample pretreatment procedure was identical to NH_3 -TPD. Background spectra were collected at 175°C, followed by continuous spectrum acquisition under 10 vol.% O_2/N_2 atmosphere after signal stabilization, and average values were taken to reduce experimental errors. The types and relative amounts of active oxygen species were identified from characteristic Raman shifts. ^1H MAS NMR was adopted to characterize surface hydroxyl groups. Samples were fully dried prior to testing to avoid paramagnetic impurities. The measurement was conducted under a magnetic field of 14.09 Tesla with a proton resonance frequency of 600 MHz. The obtained hydrogen spectra were normalized and symmetrized before Peakfit deconvolution, to quantitatively analyze two types of hydroxyl groups and clarify the occupation effect of metal dopants on surface hydroxyl sites.
- In-situ diffuse reflectance Fourier transform infrared spectroscopy (In situ DRIFTS) was applied to capture reaction intermediates and reveal NH_3 -SCO pathways. 0.1 g catalyst was pretreated under inert atmosphere at 500°C for 1 h and cooled to room temperature for testing. The feed gas was consistent with activity evaluation (10 vol.% O_2 , 500 ppm NH_3 , N_2 balance, total flow rate 100 mL/min). Spectra were collected three times and averaged after 10 min constant temperature at each gradient point. The dynamic variation of key intermediates at different temperatures was analyzed by comparing characteristic IR peaks to distinguish dominant reaction pathways.

3 Results and Discussion

3.1 Catalytic Performance Evaluation

- All prepared catalysts were subjected to activity tests, and the corresponding results are presented in Fig. 2. The reference $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst exhibited the optimal low-temperature activity, with NH_3 conversion exceeding 80% at 150°C and complete NH_3 elimination achieved at 175°C. The incorporation of Cu led to varying degrees of decline in low-temperature catalytic activity. Among all bimetallic samples, $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-C}$ synthesized via co-impregnation retained relatively superior low-temperature performance; it realized full NH_3 conversion at 175°C, while the conversion only reached 70% at 150°C. $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-S-N}$ displayed comparable low-temperature activity to $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-C}$. The $\text{Cu-Ag}/\text{Al}_2\text{O}_3\text{-DP}$ catalyst fabricated by the combination of deposition-precipitation and liquid impregnation also obtained 100% NH_3 conversion at 175°C, yet its conversion was merely approximately 50% at 150°C.
- The remaining catalysts failed to completely convert NH_3 at 175°C. For $\text{Cu-Ag}/\text{Al}_2\text{O}_3\text{-T}$ prepared by two-step liquid impregnation, the NH_3 conversion reached 90% at 175°C and full conversion was realized above 200°C. $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-T}$ delivered around 83% NH_3 conversion at 175°C and achieved total NH_3 removal at 200°C. Another liquid-solid two-step impregnated sample $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-S-N}$

showed much poorer low-temperature activity than Cu-Ag/Al₂O₃-S-N, only converting about 80% NH₃ at 175°C and reaching full conversion until 200°C. The Cu-Ag/Al₂O₃-DP-S-S catalyst prepared by deposition-precipitation coupled with solid impregnation using sulfate precursors barely possessed catalytic activity over the whole test temperature range. This phenomenon can be attributed to sulfur contamination introduced by sulfate precursors, which induces catalyst poisoning and deactivates the capability for NH₃ oxidation.

- In terms of N₂ selectivity, the monometallic Ag/Al₂O₃ reference catalyst delivered the lowest values across the entire test window. Its minimum N₂ selectivity was only around 60% during the rapid activity rising stage (150–175°C). N₂ selectivity rose slowly with increasing temperature and reached 75% at 300°C. Combined with the relationship between N₂O selectivity and temperature (Fig. 2C), N₂O served as the dominant by-product at low temperatures, while NO and NO₂ gradually became the main by-products as temperature increased. After Cu doping, all bimetallic catalysts exhibited improved N₂ selectivity to varying degrees. Most samples followed the trade-off rule for bifunctional NH₃-SCO catalysts: low-temperature activity and N₂ selectivity cannot be simultaneously maximized. High low-temperature activity is usually accompanied by poor N₂ selectivity, whereas strategies that greatly boost N₂ selectivity tend to sacrifice low catalytic activity.
- For co-impregnated Ag-Cu/Al₂O₃-C, N₂ selectivity only increased by approximately 3% relative to Ag/Al₂O₃ at 150°C where NH₃ conversion climbed rapidly. The promotion effect was strengthened with rising temperature, and N₂ selectivity exceeded 90% at 275°C. When the temperature further increased to 300°C, its N₂ selectivity slightly decreased. Although N₂O formation was further suppressed, massive NO₂ by-products were generated, jointly leading to the decline in overall N₂ selectivity.
- Ag-Cu/Al₂O₃-T exhibited the most prominent improvement in N₂ selectivity, maintaining values above 90% over the whole temperature range, with an enhancement of over 25% compared with Ag/Al₂O₃. Similar to Ag-Cu/Al₂O₃-C, abundant NO₂ formed above 275°C and slightly reduced N₂ selectivity. Cu-Ag/Al₂O₃-T (Ag loaded first via two-step impregnation) showed weaker selectivity improvement than Ag-Cu/Al₂O₃-T but outperformed other catalysts, with N₂ selectivity exceeding 85% at all tested temperatures. It achieved a better balance between activity and selectivity because it avoided severe loss of low-temperature activity observed on Ag-Cu/Al₂O₃-T.
- Cu-Ag/Al₂O₃-S-N (liquid-solid two-step) and Cu-Ag/Al₂O₃-DP (deposition-precipitation + liquid impregnation) displayed comparable N₂ selectivity improvement, both staying above 80°C throughout the experiment. Above 275°C, the generation of NO₂ and N₂O on these two samples was further inhibited, so their N₂ selectivity barely declined. When the metal loading sequence was reversed to prepare Ag-Cu/Al₂O₃-S-N (Cu first via liquid-solid impregnation), the promotion of N₂ selectivity was weakened. It only achieved 78% N₂ selectivity at 175°C; despite obvious improvement over Ag/Al₂O₃, its selectivity gain was inferior to other bimetallic catalysts, and its low-temperature activity was also unsatisfactory, resulting in the worst comprehensive performance among all samples.

3.2 Analysis of Redox Property and Surface Acidity

- Redox capability and surface acidity are critical to NH_3 -SCO performance and strongly correlate with low-temperature activity. Redox capacity refers to the adsorption and activation ability toward oxidants, namely O_2 activation in this reaction system. Surface acidity determines NH_3 adsorption capacity; stronger acidity facilitates NH_3 capture and increases collision probability between adsorbed NH_3 and active oxygen, thus accelerating catalytic oxidation.
- The redox characteristics of catalysts were analyzed from multiple perspectives including valence state and particle size of active metals, surface active oxygen content and O_2 activation capacity. XPS and H_2 -TPR were adopted to identify the chemical forms of surface metallic species. XPS quantification allowed calculation of the proportion of reactive oxygen relative to total surface oxygen (lattice oxygen + active oxygen). In-situ Raman spectroscopy was further utilized to characterize O_2 activation performance.
- NH_3 -TPD was applied to distinguish the type and quantify the amount of surface acid sites. The acquired desorption curves were deconvoluted, and the peak area reflected the relative content of different acid sites, while desorption temperature represented acid strength. Based on the above activity results, Ag-Cu/ Al_2O_3 -T showed the maximum enhancement of N_2 selectivity, while Ag-Cu/ Al_2O_3 -C retained the best low activity with limited selectivity improvement. Therefore, Ag/ Al_2O_3 , Ag-Cu/ Al_2O_3 -C and Ag-Cu/ Al_2O_3 -T were selected for comprehensive characterizations to obtain distinct comparative data and clarify the underlying structure-activity relationships.
- XPS spectra of the three catalysts are displayed in Figs. 3–5. The characteristic central positions of Ag $3d_{3/2}$ and Ag $3d_{5/2}$ are located at approximately 374.3 eV and 368.3 eV, respectively, which match the measured signals well, with minor binding energy shifts induced by different chemical microenvironments.
- Ag species supported on $\gamma\text{-Al}_2\text{O}_3$ exist as metallic Ag^0 aggregates and monovalent $\text{Ag}^+/\text{Ag}_2\text{O}$. For most metals, lower valence corresponds to lower binding energy, whereas Ag follows the opposite rule: Ag^+ possesses a lower binding energy than metallic Ag^0 ^[58, 59]. After peak fitting with Avantage software, the Ag^+ peak of Ag/ Al_2O_3 appeared at 368.1 eV and the Ag^0 peak at 368.8 eV. Although both peaks shifted slightly relative to the standard database, their energy interval remained unchanged, which was attributed to the altered chemical environment of Ag after loading on alumina.
- The Ag 3d spectra of the other two catalysts followed identical trends but differed in the relative proportion of Ag^0 . The $\text{Ag}^0/(\text{Ag}^0+\text{Ag}^+)$ ratio of Ag-Cu/ Al_2O_3 -C was slightly lower than that of Ag/ Al_2O_3 , while Ag-Cu/ Al_2O_3 -T contained the highest fraction of Ag^0 among the three samples. The content of Ag^0 positively correlated with catalytic low-temperature activity. Nevertheless, Ag-Cu/ Al_2O_3 -T with abundant Ag^0 still exhibited poor low activity. This can be explained by severe Ag^0 agglomeration, which generated large Ag nanoparticles or even micron-sized particles and impaired low-temperature oxidation performance.

- The deconvolution results of O 1s spectra for all catalysts are displayed in Figs. 3(B), 4(B) and 5(B). The overall O 1s peak centers at approximately 531.0 eV, which is close to the standard oxygen peak position of γ -Al₂O₃ (531.1 eV). The slight negative shift of binding energy originates from Ag and Cu oxides, whose oxygen signals appear at lower binding energies. Surface oxygen species on catalysts are divided into active oxygen and lattice oxygen. Active oxygen possesses higher binding energy and high reactivity for subsequent reactions, while lattice oxygen shows lower binding energy near the central position of O 1s peak and exhibits stable, inert properties.
- According to peak fitting results via Avantage software, Ag/Al₂O₃ has the highest proportion of active oxygen (O_a) with an area ratio of 0.34. After Cu introduction, the O_a ratios of Ag-Cu/Al₂O₃-C and Ag-Cu/Al₂O₃-T drop sharply to 0.13 and 0.14, respectively. The content of surface active oxygen is closely correlated with catalytic oxidation capacity; the remarkable decline of active oxygen upon Cu doping explains the weakened NH₃ oxidation activity. Nevertheless, Ag-Cu/Al₂O₃-C and Ag-Cu/Al₂O₃-T contain similar amounts of active oxygen but show distinct low-temperature activity, demonstrating that the quantity of active oxygen is not the sole decisive factor, and the intrinsic O₂ activation efficiency at given temperatures also plays a vital role.
- XPS Cu 2p spectra of Ag-Cu/Al₂O₃-C and Ag-Cu/Al₂O₃-T are presented in Figs. 3(C) and 4(C). As reported in standard XPS databases, Cu⁰, Cu⁺ and Cu²⁺ show Cu 2p_{3/2} signals at 932.6 eV, 932.7 eV and 933.1 eV, respectively^[60, 61]. Although their main peak positions are hard to distinguish directly, characteristic satellite peaks can be used to identify Cu valence states: metallic Cu only has Cu 2p_{1/2} and Cu 2p_{3/2} primary peaks without satellite peaks; Cu⁺ generates weak dual satellite peaks within 942–950 eV; Cu²⁺ produces dual satellite peaks at 938–945 eV and single satellite peaks at 958–965 eV.
- Peak deconvolution reveals that Cu on the two bimetallic catalysts mainly exists as metallic Cu⁰ and CuO (Cu²⁺), with negligible Cu⁺ species. The coexistence of multiple Cu valence states enables continuous redox cycling during catalytic reactions and accelerates each elementary step. The similar Cu valence distribution on Ag-Cu/Al₂O₃-C and Ag-Cu/Al₂O₃-T indicates that Cu chemical states are barely affected by metal loading sequences and preparation routes.
- H₂-TPR experiments were carried out to intuitively compare the redox capacity of the three catalysts, and the H₂ consumption profiles are illustrated in Fig. 6. A lower peak temperature corresponds to stronger redox ability of the related species, while a larger peak area represents a higher surface content of the corresponding component.
- Four H₂ consumption peaks are observed over Ag/Al₂O₃ at 130.8°C, 292.0°C, 399.2°C and 676.8°C, assigned to the reduction of surface active oxygen, large-sized Ag₂O, small-sized AgO and highly dispersed Ag⁺, respectively^[62–64]. Six reduction peaks emerge on Ag-Cu/Al₂O₃-C at 137.7°C, 155.0°C, 225.9°C, 249.6°C, 315.1°C and 681.5°C, corresponding to surface active oxygen, primary reduction of bulk CuO, co-reduction of small CuO and large Ag₂O, secondary reduction of CuO, reduction of fine Ag₂O and simultaneous reduction of highly dispersed Ag⁺ and Cu²⁺^[65]. Five reduction peaks appear for Ag-Cu/Al₂O₃-T at 122.2°C (T1), 153.7°C (T2), 201.5°C (T3), 229.5°C (T4) and 388.1°C (T5). T1 is attributed to surface active oxide reduction; T2 corresponds to one or

multiple reduction steps of CuO; T3 and T4 originate from secondary reduction of large Ag₂O and CuO; T5 is assigned to the reduction of small Ag₂O species.

- Compared with Ag/Al₂O₃, both Cu-doped Ag-Cu/Al₂O₃-C and Ag-Cu/Al₂O₃-T display lower area ratios of the T₁ peak, which corresponds to less H₂ consumption and further verifies that Cu incorporation reduces the quantity of surface active oxygen species. Moreover, the high-temperature reduction peak T₄ in Fig. 6(A) completely disappears for step-impregnated samples, while only an extremely weak signal remains for the co-impregnated catalyst. This indicates that highly dispersed Ag⁺ almost vanishes after Cu doping. A plausible explanation is that Cu competes for anchoring sites on the support, driving the aggregation of silver oxides and increasing their particle size.
- Compared with Ag-Cu/Al₂O₃-C, Ag-Cu/Al₂O₃-T exhibits a narrower, smaller fifth H₂ consumption peak, which represents a lower content of small-sized Ag₂O. It can be inferred that silver oxides are more severely agglomerated on Ag-Cu/Al₂O₃-T with larger Ag₂ particles. The particle size sequence of Ag species derived from H₂-TPR is inversely consistent with the order of low-temperature activity, confirming that severe Ag aggregation deteriorates catalytic performance at low temperatures. Nevertheless, Ag particle size cannot fully determine N₂ selectivity, which implies that Cu plays a dominant role in improving N₂ selectivity for bifunctional catalysts.
- Catalytic oxidation performance relies not only on the total amount of surface active oxygen but also on the intrinsic O₂ activation capacity of the catalyst. In the NH₃-SCO cycle, gaseous O₂ must be adsorbed and activated before it can abstract hydrogen from NH₃ stepwise and realize ammonia oxidation. In-situ Raman measurements at 175°C (a temperature where all three catalysts show measurable activity) were carried out to compare their O₂ activation efficiency. The feed gas was consistent with formal reaction gas except for the absence of NH₃, and spectra were collected after signal stabilization, as presented in Fig. 7(A).
- Different oxygen species show characteristic Raman shifts: adsorbed molecular O₂ at 679 cm⁻¹, activated atomic O* at 245 cm⁻¹, superoxide O₂⁻ at 1057 cm⁻¹ and peroxide O₂²⁻ at 531 cm⁻¹[66, 67]. Physically adsorbed O₂ is inert and cannot participate in redox reactions directly. Among all activated oxygen species, atomic O* and superoxide O₂⁻ possess the strongest oxidation ability, whereas peroxide O₂²⁻ exhibits moderate reactivity.
- Abundant signals of adsorbed O₂, O* and O₂⁻ together with minor peroxide peaks are detected over Ag/Al₂O₃, demonstrating multiple O₂ activation pathways and efficient oxygen conversion at 175°C. For Ag-Cu/Al₂O₃-C, the characteristic peak of molecular O₂ and the strong O₂⁻ signal are barely observable, yet O* and O₂²⁻ can still be identified. Its O₂ adsorption and activation capacity are weakened relative to Ag/Al₂O₃ but remain acceptable. In contrast, Ag-Cu/Al₂O₃-T adsorbs massive molecular O₂, while the characteristic peaks of activated O*, O₂²⁻ and O₂⁻ are all very weak. This reveals that the catalyst can capture plenty of O₂ at 175°C but suffers poor activation efficiency, resulting in inferior low-temperature activity. The O₂ activation capability of the three catalysts matches their low-temperature activity ranking perfectly, proving that O₂ activation efficiency is a core factor governing low-temperature NH₃ conversion performance.

- Acidity determines the NH_3 adsorption capacity of catalysts, so it is another critical factor governing catalytic performance apart from redox capacity. NH_3 -TPD is the standard characterization technique to evaluate surface acidity for NH_3 -SCO catalysts, as ammonia acts as a typical alkaline probe molecule that can directly reflect the adsorption-desorption behavior of NH_3 . The NH_3 -TPD profiles of $\text{Ag}/\text{Al}_2\text{O}_3$, $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-C}$ and $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-T}$ were processed via peak deconvolution, and the results are displayed in Fig. 7(B).
- Combined with previous research, the desorption peaks were classified into three categories according to temperature ranges: low-temperature α peaks corresponding to NH_3 desorbed from weak Lewis acid sites, medium-temperature β peaks assigned to strong Lewis acid sites, and high-temperature γ peaks originating from Brønsted acid sites^[68, 69]. The $\text{Ag}/\text{Al}_2\text{O}_3$ sample exhibited prominent low-temperature desorption signals, indicating abundant weak Lewis acid sites. Below 175°C , NH_3 oxidation mainly proceeds over Lewis acid sites; when the temperature exceeds 175°C , adsorbed NH_3 gradually migrates to Brønsted acid sites, accompanied by improved N_2 selectivity. This phenomenon demonstrates that the reaction pathway on Brønsted acid sites favors the generation of N_2 rather than by-products.
- Distinct acid site distributions were observed on $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-C}$ after Cu doping. The quantity of weak Lewis acid sites decreased, while the amounts of strong Lewis and Brønsted acid sites increased simultaneously. Besides, the strength of weak Lewis acid sites on $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-C}$ was higher than that of $\text{Ag}/\text{Al}_2\text{O}_3$, the strength of strong Lewis acid sites remained comparable, and its Brønsted acid sites possessed the weakest acidity among the three catalysts. For $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-T}$, the number of weak Lewis acid sites further declined; the quantity of strong Lewis acid sites was similar to $\text{Ag}/\text{Al}_2\text{O}_3$ but with enhanced strength, and both the content and strength of Brønsted acid sites reached the maximum value. The strength of Lewis acid sites showed an inverse correlation with low-temperature activity, which implies that Brønsted acid sites serve as the major active sites for low-temperature NH_3 oxidation. On $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-T}$, NH_3 tends to be stably trapped on Lewis acid sites at low temperatures and fails to transfer to Brønsted sites efficiently, thus leading to inferior catalytic activity.

3.3 Characterizations of Catalyst Microstructure and Reaction Mechanism

- Apart from redox property and surface acidity, a series of characterizations were performed to analyze specific surface area, pore structure, crystal phase, metal dispersion, anchoring sites and reaction pathways. These characterizations further clarify the loading state of Ag and Cu on $\gamma\text{-Al}_2\text{O}_3$ as well as the influence of metal doping on support pore properties, and establish the correlation between preparation-induced variations in Ag particle size/crystallinity and the resulting low-temperature activity & N_2 selectivity.
- The BET adsorption-desorption isotherms and pore parameters of $\text{Ag}/\text{Al}_2\text{O}_3$, $\text{Ag-Cu}/\text{Al}_2\text{O}_3\text{-C}$ and $\text{Ag-Cu}/\text{Al}_2\text{O}_3$ are presented in Fig. 8(A) and Table 2. Pore structure parameters were calculated from gas

adsorption volumes at different relative pressures. All samples displayed type III isotherms with H3 hysteresis loops, consistent with the characteristic curve of nano γ - Al_2O_3 , which consists of loosely stacked particles with abundant interparticle mesopores. This indicates that Ag and Cu modification does not alter the intrinsic mesoporous structure of the support.

- Ag/ Al_2O_3 possessed the largest specific surface area due to its lower total metal loading. After Cu introduction, both Ag-Cu/ Al_2O_3 -C and Ag-Cu/ Al_2O_3 -T showed reduced specific surface area and remarkably enlarged average pore size. The pore volume of Ag-Cu/ Al_2O_3 -C was nearly identical to Ag/ Al_2O_3 , while Ag-Cu/ Al_2O_3 -T exhibited a slight increase in pore volume. It can be inferred that partial micropores are blocked after metal loading, reducing the number of effective adsorption sites for NH_3 and raising average pore diameter. For step-impregnated catalysts, partial exposure of metal species slightly elevates pore volume and surface area, yet severe micropore blockage hinders NH_3 adsorption and consequently suppresses low-temperature catalytic activity.

Table 2

The specific surface area, pore volume, and average pore size of the Ag/ Al_2O_3 , Ag-Cu/ Al_2O_3 -C, and Ag-Cu/ Al_2O_3 -T samples calculated by the BJH method

Samples	Surface area (m^2/g)	Pore volume (cc/g)	Average pore size (nm)
Ag/ Al_2O_3	174.7	0.51	7.64
Ag-Cu/ Al_2O_3 -C	150.1	0.51	9.21
Ag-Cu/ Al_2O_3 -T	156.1	0.53	9.49

- To further identify the crystalline forms of supported metallic species, XRD measurements were carried out for Ag/ Al_2O_3 , Ag-Cu/ Al_2O_3 -C and Ag-Cu/ Al_2O_3 -T, and high-precision denoised patterns are shown in Fig. 8(B). Distinct diffraction peaks of γ - Al_2O_3 matching JCPDS#35-0121 were detected for all samples, verifying that the bulk support framework remains intact. For Ag species, reference cards (Ag: JCPDS#04-0783; Ag_2O : JCPDS#41-1104; Ag_3O_4 : JCPDS#30-1054) were applied for phase identification. Clear metallic Ag signals were observed on Ag/ Al_2O_3 , while no obvious Ag_2O diffraction peaks appeared. Combined with XPS data, Ag_2 is inferred to exist in amorphous or highly dispersed states on the support, and weak Ag_3O_4 peaks originate from partial aggregation of silver oxides.
- Compared with monometallic Ag/ Al_2O_3 , Ag-Cu/ Al_2O_3 -C and Ag-Cu/ Al_2O_3 -T exhibited intensified Ag diffraction peaks, demonstrating enhanced crystallinity of Ag species after Cu doping. Characteristic Ag_2O signals also emerged on both bimetallic catalysts, which can be attributed to altered dispersion and ordered stacking of Ag_2O induced by Cu introduction. Notably, the Ag_3O_4 peak intensity of Ag-Cu/ Al_2O_3 -T decreased drastically relative to Ag-Cu/ Al_2O_3 -C, revealing that sequential Cu loading is more effective in modulating the dispersion of silver oxides.
- Weak CuO diffraction peaks (JCPDS#48-1548) were detected on both bimetallic samples. The faint signals stem from the low nominal Cu loading (5 wt.%) and the much weaker intrinsic diffraction

intensity of CuO relative to Ag and $\gamma\text{-Al}_2\text{O}_3$. Moreover, Ag-Cu/ Al_2O_3 -C showed slightly stronger CuO peaks than Ag-Cu/ Al_2O_3 -T, indicating that the co-impregnation method better retains the crystallinity of copper oxides.

- XRD can only identify crystalline phases; highly dispersed or amorphous metal oxides fail to produce distinguishable diffraction signals. Therefore, UV-vis diffuse reflectance spectroscopy was adopted to supplement characterization, with spectra displayed in Fig. 9(A). Four characteristic absorption bands for Ag species were assigned as follows: 235 nm (Ag^+), 280 nm (Ag^{nan}), 338 nm (large aggregated Ag^0), 430 nm (Ag nanoparticles)^[66, 70]. Four characteristic bands of Cu species are located at 245 nm (Cu^{2+}), 299 nm (Cu^+), 352 nm (Cu^+), 624 nm (bulk CuO)^[68, 71].
- Multiple Ag species coexist on Ag/ Al_2O_3 , with cationic Ag species dominating; among zero-valent Ag, aggregated Ag^0 accounts for the majority while the Ag nanoparticle peak is negligible. After Cu doping, the Ag nanoparticle signal nearly disappears, the Ag^0 band weakens, and the peak intensity of Ag^+ rises sharply, which is consistent with XPS results. XPS confirms the absence of Cu^+ , so the spectral variations of Ag^{nan} are not interfered by cuprous species. The increased relative content of Ag^{nan} after Cu doping proves the formation of large cationic silver aggregates, which matches the H_2 -TPR conclusions.
- Differences in Cu speciation also exist between the two bimetallic catalysts. Both contain dispersed Cu^{2+} and aggregated CuO, yet Ag-Cu/ Al_2O_3 -C has a higher proportion of isolated Cu^{2+} , while Ag-Cu/ Al_2O_3 -T possesses more bulk CuO aggregates. Since low-temperature activity is primarily governed by Ag species, the distinct Cu states are presumed to be the key factor accounting for divergent N_2 selectivity. Aggregated CuO species serve as the key factor for improved N_2 selectivity, as they facilitate the reduction of over-oxidized NO^{int} intermediates.
- The dispersion of Ag and Cu species over the support exerts significant influences on both low-temperature activity and N_2 selectivity. Investigating the occupation of anchoring sites by Ag and Cu can further reveal how Cu introduced via different preparation methods affects metal dispersion, especially for Ag. Previous studies have demonstrated that metallic species are anchored mainly at two types of surface hydroxyl sites on $\gamma\text{-Al}_2\text{O}_3$: terminal hydroxyl groups and bridging hydroxyl groups. After anchoring, metal atoms form direct bonds with surface oxygen. Therefore, ^1H MAS NMR can be employed to quantify residual surface hydroxyl groups by detecting hydrogen signals, so as to evaluate the occupation of anchoring sites over different catalysts^[72, 73].
- In this work, ^1H MAS NMR measurements were performed on Ag/ Al_2O_3 , Ag-Cu/ Al_2O_3 -C and Ag-Cu/ Al_2O_3 -T. The acquired spectra were calibrated and processed to obtain symmetric ^1H signals. Peak deconvolution was conducted, and the resulting fitted spectra are presented in Fig. 9(B). The statistical peak-area results are summarized in Fig. 9(C), where the relative hydrogen content of all samples is normalized by setting the bridging-hydroxyl hydrogen content of Ag/ Al_2O_3 as 100%.
- ^1H MAS NMR results show that Ag/ Al_2O_3 possesses the highest amount of surface hydroxyl groups owing to its lower total metal loading. Upon Cu incorporation, the hydroxyl content decreases markedly, yet the reduction extents differ between terminal and bridging hydroxyls, which is related

to both site preference of Cu and the metal-introduction strategy. In general, Cu species anchor at both types of hydroxyl sites with slightly higher preference for terminal hydroxyls. Among the bimetallic samples, Ag-Cu/Al₂O₃-C consumes the largest fraction of hydroxyl sites, exhibiting the lowest content for both terminal and bridging hydroxyl groups. This indicates less severe metal aggregation on Ag-Cu/Al₂O₃-C. By contrast, severe metal aggregation occurs on Ag-Cu/Al₂O₃-T, which is predominantly attributed to substantial agglomeration of Ag and the formation of larger silver-oxide particles. Consequently, the number of available reactive sites declines and intrinsic reactivity deteriorates, leading to suppressed low-temperature catalytic activity.

- N₂ selectivity is another vital performance metric, and improving this property constitutes one major motivation for constructing bimetallic bifunctional catalysts. The catalytic pathway largely determines N₂-selectivity behavior. It is widely accepted that bifunctional NH₃-SCO catalysts mainly follow the i-SCR mechanism: noble-metal sites partially oxidize NH₃ into NO_x intermediates, and then transition-metal sites reduce these NO_x into N₂ with the assistance of unreacted NH₃.
- In-situ DRIFTS experiments were carried out on Ag/Al₂O₃, Ag-Cu/Al₂O₃-C and Ag-Cu/Al₂O₃-T to verify the above hypothesis. Temperature-dependent signals of key intermediates were monitored to identify dominant reaction pathways at different temperatures, as shown in Fig. 10. Characteristic bands are assigned as follows in ascending wavenumber order: NH₃ adsorbed on Lewis-acid sites (~ 1197 cm⁻¹ and 1238 cm⁻¹), NH₄⁺ on Brønsted-acid sites (~ 1440 cm⁻¹), -NH species (~ 1457 cm⁻¹), -HNO species (1504–1522 cm⁻¹), bidentate nitrate species (1547–1572 cm⁻¹), bridging nitrate species (~ 1620 cm⁻¹), N₂⁻ species (~ 2167 cm⁻¹), N-H stretching vibrations (3211–3411 cm⁻¹), and surface hydroxyl groups (~ 3731 cm⁻¹).
- For Ag/Al₂O₃, NH₃ is preferentially adsorbed on Lewis-acid sites at low temperatures. These bands gradually decay with rising temperature, originating from both NH₃ consumption by reaction and the migration of adsorbed NH₃ toward Brønsted-acid sites. Distinct -NH signals emerge at 150°C and are largely consumed at 175°C. Combined with by-product distribution and previous reports, the imide pathway dominates under these conditions: NH₃ undergoes successive dehydrogenation to form -NH; part of -NH is further oxidized to -HNO; subsequently, -NH couples with -HNO to produce N₂ and H₂O.
- Nevertheless, Ag/Al₂O₃ exhibits strong oxidizing capability, which can over-oxidize excessive -NH into -HNO. When -NH species become insufficient, two -HNO intermediates can react with each other to generate N₂O and H₂O, hence lowering N₂ selectivity. With further temperature elevation, weak N₂⁻ signals are detected, revealing partial transition toward the N₂⁻ pathway. In this route, -NH is further dehydrogenated to yield active N* species; adjacent N* can couple to form N₂ or be over-oxidized into N₂O. As temperature continues to increase, the N₂⁻ band disappears, bridging-nitrate species are consumed, while bidentate nitrates accumulate progressively. This suggests that the reaction gradually shifts toward the i-SCR pathway. Only bridging nitrates can be efficiently reduced under such conditions, whereas accumulated bidentate nitrates tend to decompose at high temperature and generate undesirable NO_x by-products.

- Ag-Cu/Al₂O₃-C shares similar overall evolutionary trends with Ag/Al₂O₃, while several distinctions can still be identified. First, abundant N₂⁻ species are generated over Ag-Cu/Al₂O₃-C already at 150°C, indicating that the N₂⁻ pathway dominates at low temperature with substantial residual -NH. Accordingly, N₂O by-products mainly originate from further oxidation of N₂⁻ under these conditions. Second, the N₂⁻ band begins to decay above 225°C, accompanied by rapid consumption of bridging nitrates, signifying the transition toward the i-SCR pathway. Once the temperature exceeds 250°C, bidentate nitrates start to accumulate and keep growing with rising temperature. These unconsumed nitrate species eventually decompose in large quantities and produce NO₂.
- Although N₂⁻ can also form on Ag-Cu/Al₂O₃-T at low temperatures, its concentration is much lower than that over Ag-Cu/Al₂O₃-C. Before 250°C, -NH is continuously consumed yet always remains partially reserved, revealing weakened oxidation capacity compared with the other two catalysts. Such moderate oxidation strength avoids excessive -HNO formation in the imide pathway and prevents massive oxidation of N₂⁻, which accounts for its intrinsically high N₂ selectivity at low temperature. Above 250°C, bridging nitrates are steadily consumed, whereas massive bidentate nitrate accumulation is absent. It is speculated that the unique surface structure of Ag-Cu/Al₂O₃-T enables partial reduction of bidentate nitrates. This behavior greatly suppresses NO₂ formation at 300°C and maintains superior N₂ selectivity across the whole investigated temperature window.

4 Conclusions

- In this work, a series of Ag-Cu/Al₂O₃ bifunctional catalysts were fabricated via different metal-loading routes and sequences. Catalytic performance together with physicochemical characterizations were systematically compared with the reference Ag/Al₂O₃ sample, and the main conclusions are summarized as follows.
- The monometallic Ag/Al₂O₃ delivers the optimal low-temperature activity. Among Cu-modified catalysts, co-impregnated Ag-Cu/Al₂O₃-C exhibits the highest low-temperature activity yet only a limited improvement in N₂ selectivity. By contrast, sequentially impregnated Ag-Cu/Al₂O₃-T shows relatively inferior low-temperature activity but achieves prominent enhancement of N₂ selectivity; therefore, this preparation strategy is selected for further investigation.
- XPS, H₂-TPR and in-situ Raman results demonstrate that Ag/Al₂O₃ possesses the richest surface active-oxygen species and exhibits outstanding O₂-activation capability at low temperature. Ag-Cu/Al₂O₃-C contains fewer active-oxygen sites but still retains considerable O₂-activation performance. Ag-Cu/Al₂O₃-T suffers from both low content of active oxygen and poor O₂-activation efficiency, which is responsible for its worst low-temperature activity.
- Cu doping hardly alters the intrinsic pore structure of γ-Al₂O₃ support, yet it modulates the dispersion of Ag species. Sequential impregnation occupies more surface hydroxyl sites and induces moderate aggregation of Ag/Ag⁺ while preserving partial dispersion. Co-impregnation aggravates Ag agglomeration and generates large silver-oxide particles, leading to severe deterioration of low-temperature catalytic activity.

- Both Ag-Cu/Al₂O₃-C and Ag-Cu/Al₂O₃-T modify the dominant low-temperature reaction pathway of Ag/Al₂O₃, partially switching the low-selectivity imide pathway to the N₂⁻ pathway. Ag-Cu/Al₂O₃-T presents the most prominent modulation effect and realizes greatly improved N₂ selectivity over the entire temperature range. On Ag-Cu/Al₂O₃-T, the reaction is partially redirected to the N₂⁻ pathway with sufficient – NH reserved at low temperature; meanwhile, partial reduction of otherwise unreducible bidentate nitrates proceeds at high temperature, thus restraining NO₂ generation.

Notes

The authors declare no competing financial interest.

Declarations

Notes

The authors declare no competing financial interest.

Data availability

The data that support the findings of this study are available on request.

Funding Declaration

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Author Contribution

B.G. and L.Z. conceived and designed the research. Z.Q.Z. performed catalyst preparation, experimental tests, material characterizations and in-situ spectroscopic measurements. T.K.Z., S.Y.C., J.L.M., R.W., Q.J.Y., D.X.Y. and Z.H. assisted with experimental setup, data processing and literature collection. B.G., Z.Q.Z. and L.Z. wrote the main manuscript text. Z.Q.Z. prepared all figures and tables. All authors discussed the results, commented on the manuscript, and reviewed the final version of the manuscript.

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Figures

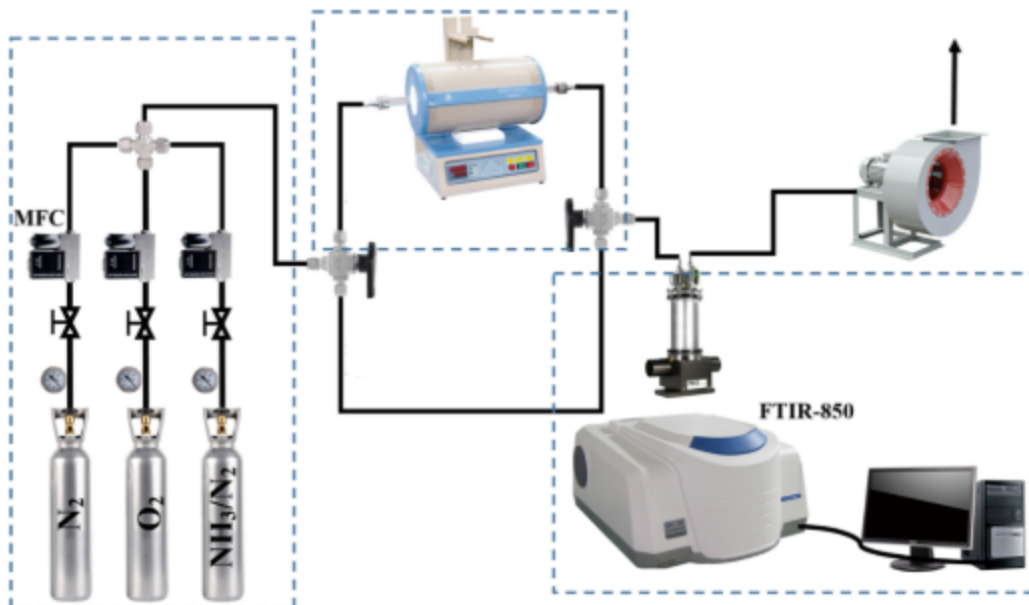


Figure 1

Schematic diagram of the reaction performance testing system structure

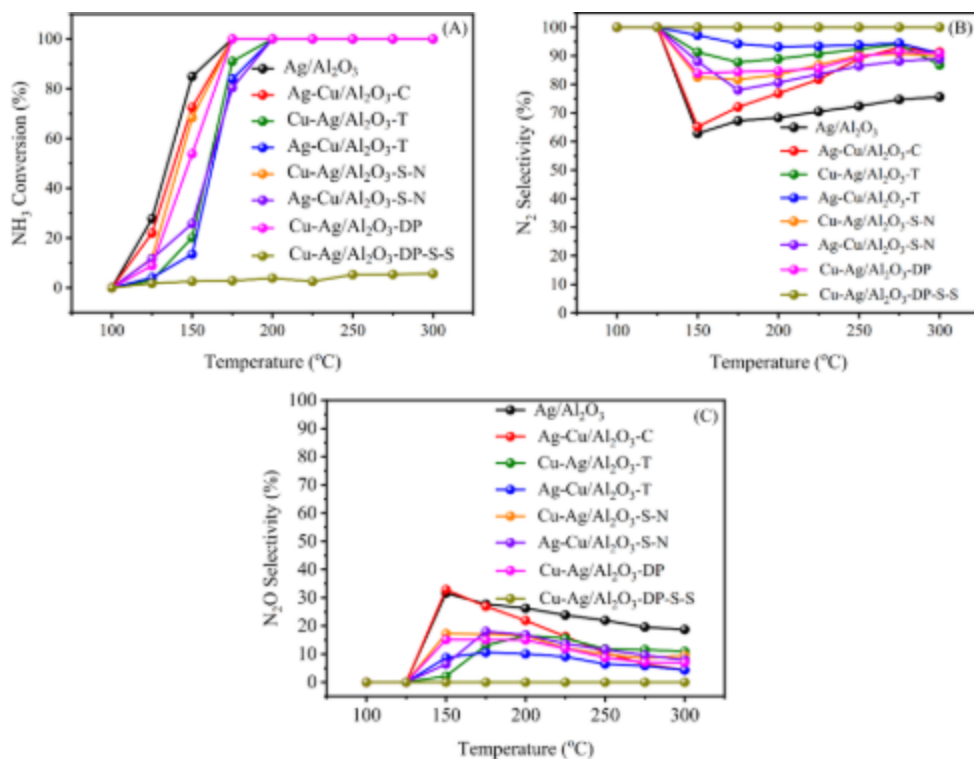


Figure 2

Conversion rate of NH₃ (A), selectivity to N₂ (B), and selectivity to N₂O (C) of Ag-Cu/Al₂O₃ catalysts prepared by different methods and loading sequences as a function of temperature. Reaction conditions: 500 ppm NH₃, 10 vol.% O₂, N₂ as balance gas. Space velocity = 60,000 mL·g⁻¹·h⁻¹

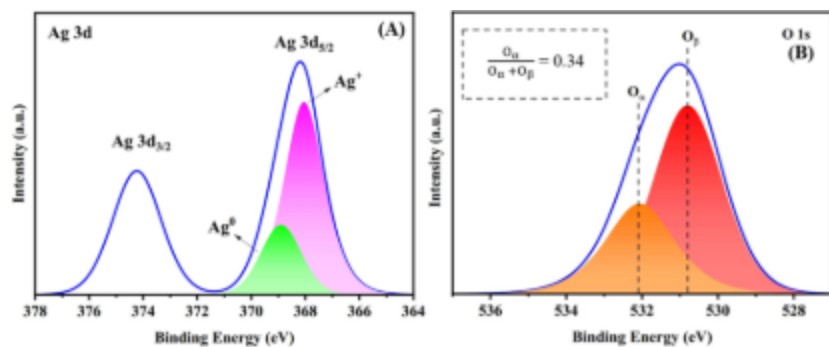


Figure 3

XPS spectra of Ag/Al₂O₃ catalyst (A) Ag 3d (B) O 1s

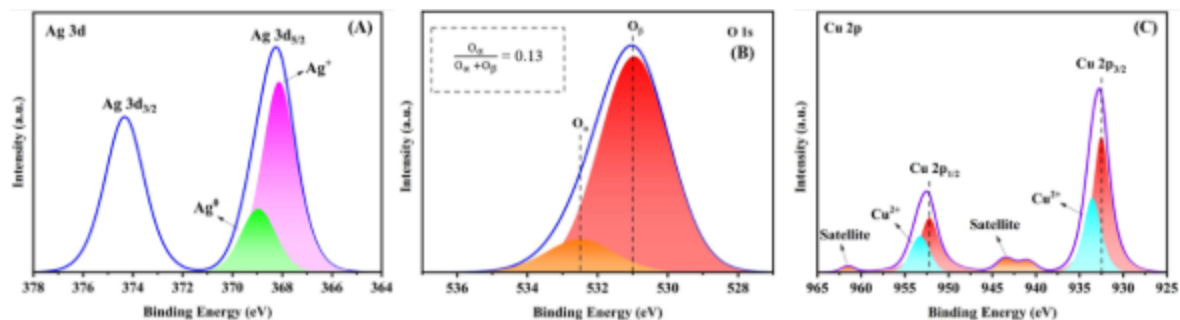


Figure 4

XPS spectra of Ag-Cu/Al₂O₃-C catalyst (A) Ag 3d (B) O 1s (C) Cu 2p

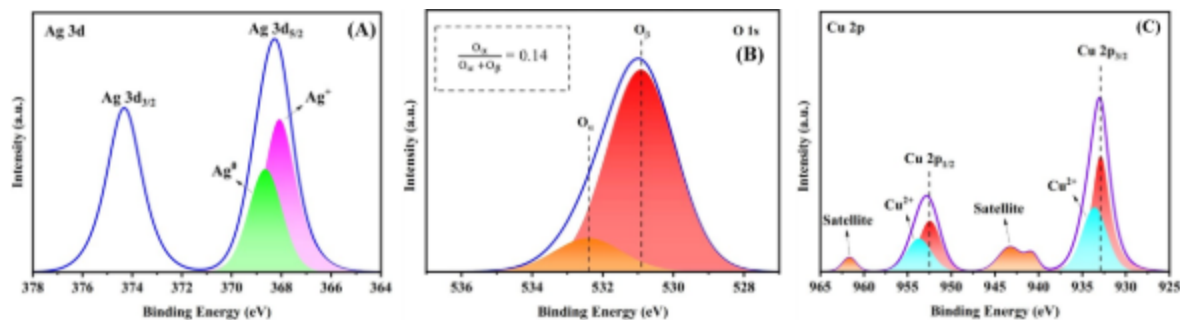


Figure 5

XPS spectra of Ag-Cu/Al₂O₃-T catalyst (A) Ag 3d (B) O 1s (C) Cu 2p

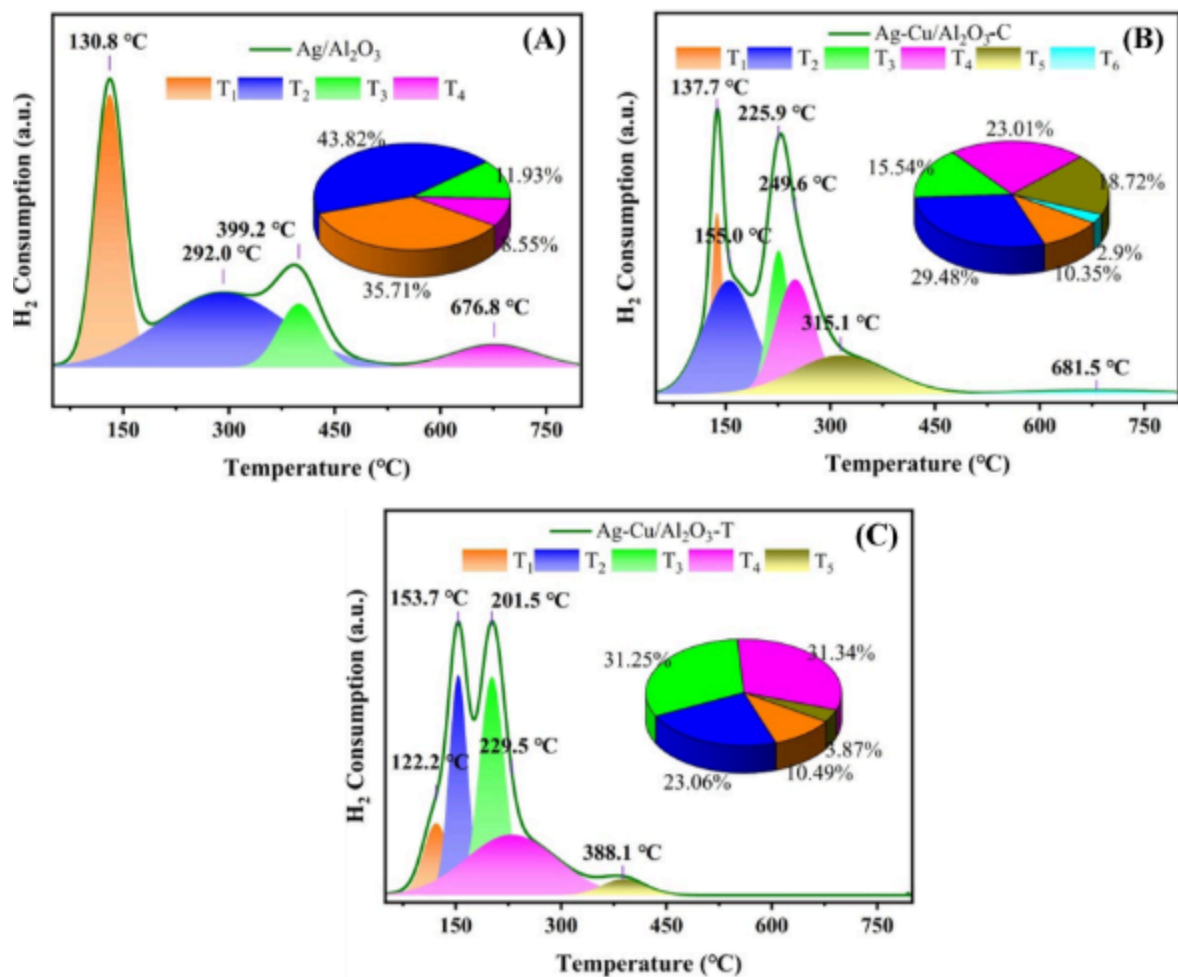


Figure 6

Hydrogen Temperature-Programmed Reduction (H₂-TPR) results of Ag-based catalysts supported on Al₂O₃ (A) Ag/Al₂O₃ (B) Ag-Cu/Al₂O₃-C (C) Ag-Cu/Al₂O₃-T

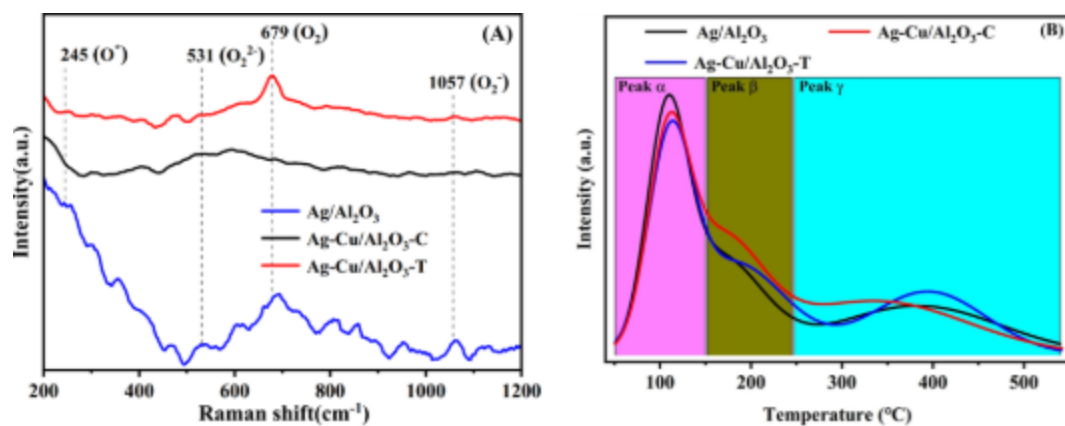


Figure 7

In-situ Raman spectra of Ag/Al₂O₃, Ag-Cu/Al₂O₃-C, and Ag-Cu/Al₂O₃-T samples (Test conditions: 175°C, 10 vol.% O₂ in N₂) (A) and peak fitting results of NH₃-TPD tests (B)

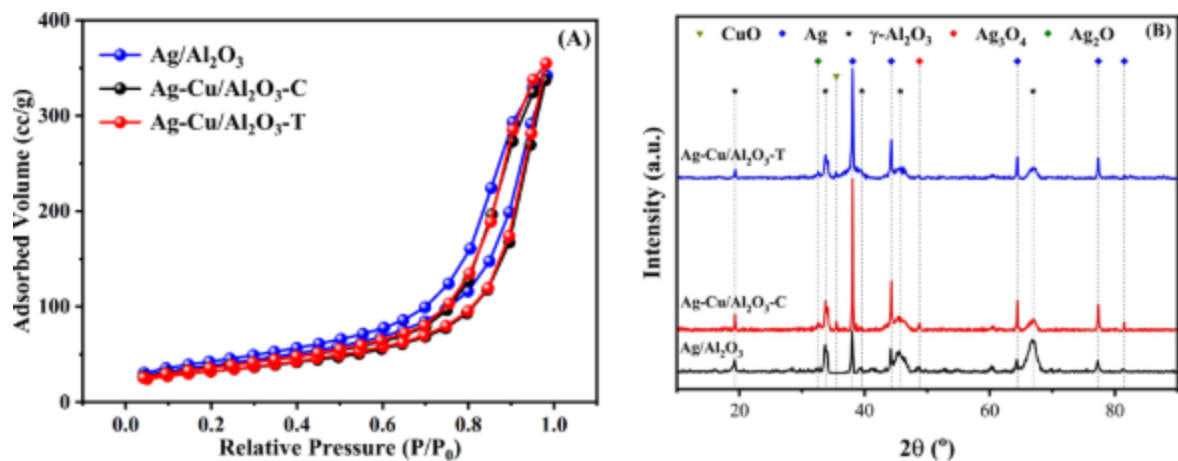


Figure 8

BET adsorption-desorption curves and XRD test spectra of Ag/Al₂O₃, Ag-Cu/Al₂O₃-C, and Ag-Cu/Al₂O₃-T

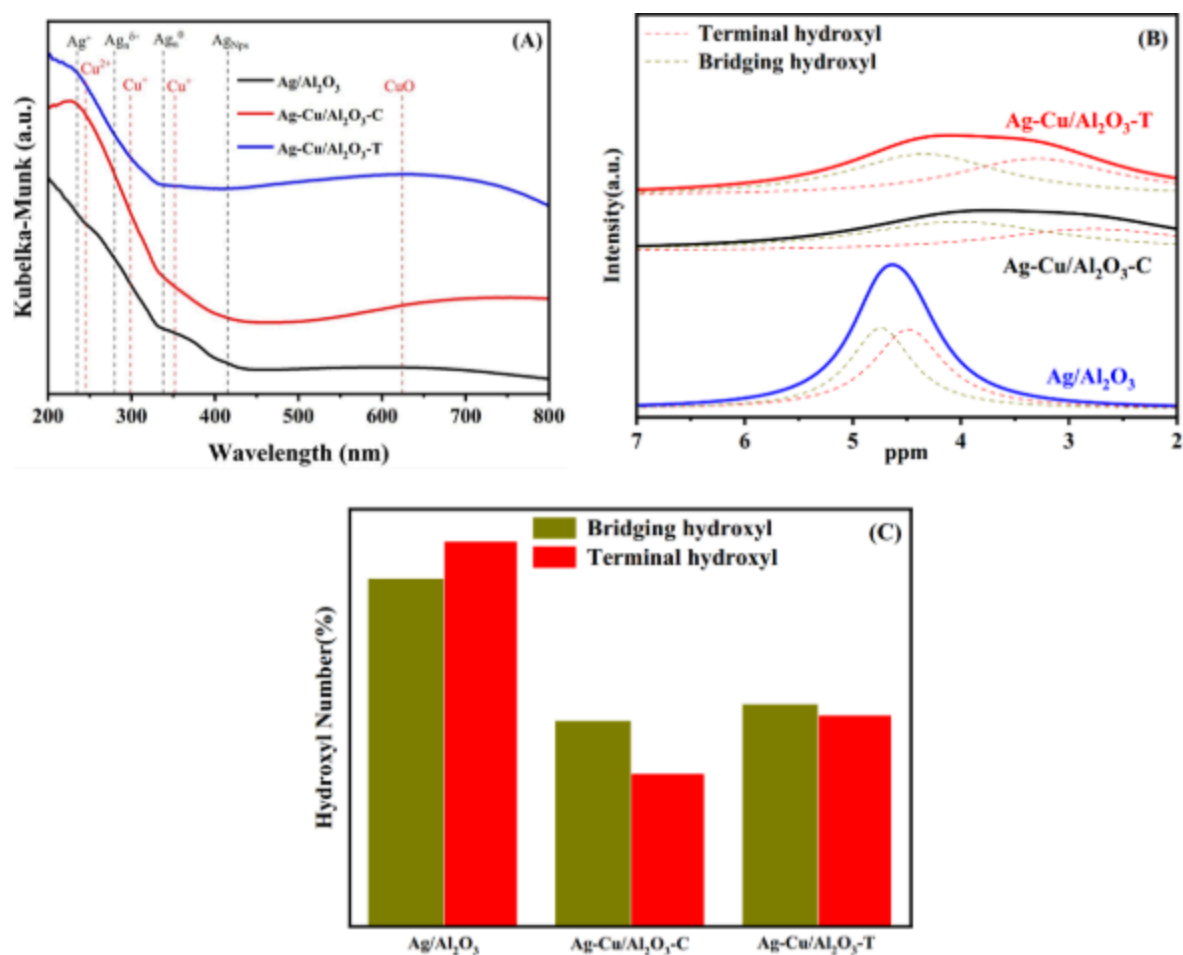


Figure 9

UV-vis spectra (A), ¹H MAS NMR spectra (B), and statistical results of ¹H MAS NMR (C) for Ag/Al₂O₃, Ag-Cu/Al₂O₃-C, and Ag-Cu/Al₂O₃-T

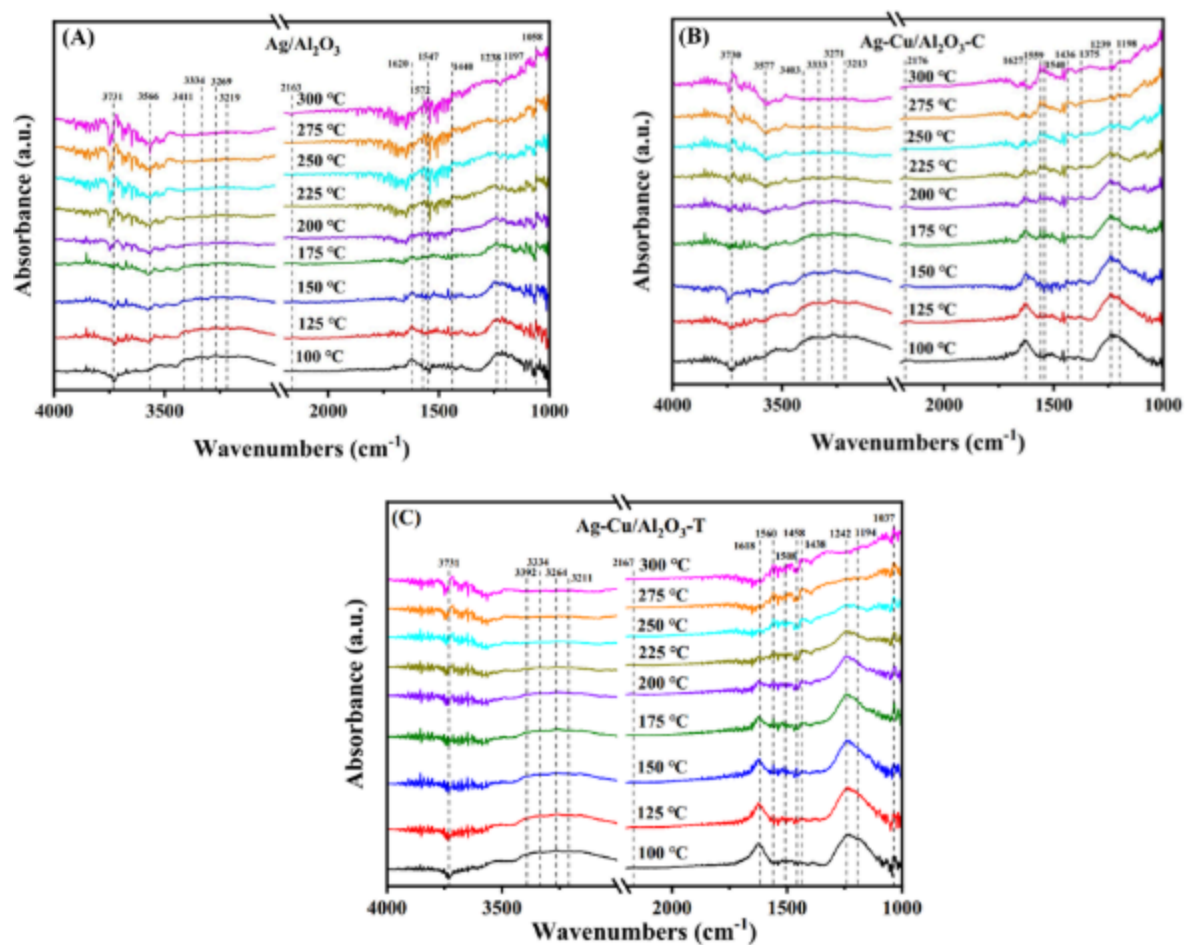


Figure 10

In situ DRIFTS spectra of the main samples in this chapter at different temperatures (A) Ag/Al₂O₃, (B) Ag-Cu/Al₂O₃-C, and (C) Ag-Cu/Al₂O₃-T