

Fuel-Rich Ammonia Catalytic Combustion on Gadolinium-Doped Ceria (GDC) Supported Copper Oxide Catalyst

Siqi Wang, Haliru Ibrahim Muhammad, Ziqi Shen, and Mingming Zhu 

Faculty of Engineering and Applied Sciences, Cranfield University, Bedford, UK

ABSTRACT

Ammonia combustion faces challenges such as high ignition temperature, low flame speed, and potential NO_x emissions. Catalytic combustion offers an alternative solution to burn ammonia with high efficiency while minimizing NO_x formation. This study aims to develop a fuel-rich, catalytically stabilized ammonia combustion and study the reactivity and NO_x formation of a novel gadolinium-doped ceria (GDC) supported CuO catalyst (CuO/GDC). The CuO/GDC catalyst was synthesized using the wet impregnation method and characterized using physisorption, X-ray diffraction (XRD), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), and Transmission Electron Microscopy (TEM). Its performance was tested in a fixed-bed reactor and compared to CuO/γ-Al₂O₃, with an equivalence ratio (ER) of 1.5 and temperatures ranging from 100°C to 800°C. The reaction mechanism of ammonia combustion over CuO/GDC was investigated with X-ray photoelectron spectroscopy (XPS) analysis and microkinetic modeling integrated with Density Functional Theory calculations. The CuO/GDC catalyst demonstrated a high NH₃ conversion of 100% with a great N₂ selectivity of over 99% at 800°C and minimal NO_x formation, which was attributed to the strong adsorption of N and O species on its surface and mitigation of nitrogen oxide formation. Apart from altering the overall adsorptive properties of the catalyst, the mixed ionic-electronic conductivity of GDC also facilitates oxygen ion transport on the catalyst surface, promoting redox-driven catalytic activity. These findings highlight the potential of the use of mixed conductor as an effective catalyst support for fuel-rich ammonia catalytic combustion.

ARTICLE HISTORY

Received 24 July 2025
Revised 22 October 2025
Accepted 23 November 2025

KEYWORDS

Ammonia; catalytic combustion; copper oxide catalysts; mixed conductor support

Introduction

Ammonia (NH₃) has gained increasing attention as a carbon-free fuel and a promising hydrogen carrier due to its relatively high energy density, ease of storage and transport, and well-established infrastructure (Jeerh et al. 2021; Lamb et al. 2019; Pinzón et al. 2024). However, the direct combustion of ammonia presents several challenges, including high ignition temperature, low flame speed, and the potential formation of high NO_x (Valera-

CONTACT Mingming Zhu  Mingming.Zhu.152@cranfield.ac.uk  Faculty of Engineering and Applied Sciences, Cranfield University, Bedford MK43 0AL, UK

 Supplemental data for this article can be accessed online at <https://doi.org/10.1080/00102202.2025.2595672>

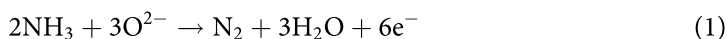
© 2025 The Author(s). Published with license by Taylor & Francis Group, LLC.

This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. The terms on which this article has been published allow the posting of the Accepted Manuscript in a repository by the author(s) or with their consent.

Medina et al. 2021). These challenges require the development of advanced combustion strategies to enhance efficiency while mitigating NO_x emissions.

Catalytic ammonia combustion is an alternative solution to overcome the limitations of conventional ammonia combustion, where ammonia combustion takes place on the surface of a catalyst without a flame. With the properly designed catalysts, ammonia can be selectively oxidized to N_2 to mitigate both thermal and fuel NO_x formation. Among the catalytic combustion technologies, fuel-rich stabilised catalytic combustion, also known as catalytic-rich/gaseous-lean combustion, is a unique technique in catalytic combustion, proving to achieve effective combustion performance for natural gas combustion. It involves two stages: the first stage of fuel-rich catalytic combustion, followed by the second stage of fuel-lean gaseous combustion. The catalyst is primarily employed in the first fuel-rich catalytic combustion stage to promote ammonia oxidation, reduce NO_x formation, and generate intermediate species (such as NH , NH_2 , and unburnt NH_3) for complete combustion in the subsequent, fuel-lean gaseous combustion stage (Karim et al. 2002; Schultze et al. 2013). The fuel-rich catalytic combustion was cooled by a bypass airflow to minimize the catalytic combustion below 800°C , thus mitigating catalyst overheat. With fuel-rich catalytic combustion as the first stage of a two-stage combustion system, it has been successfully demonstrated for methane and syngas catalytic combustion in gas turbines with ultra-low or near-zero NO_x emission using Pd-based catalysts (Eriksson et al. 2006).

Copper oxide-based catalysts were found to be effective in catalytic ammonia combustion. Hinokuma et al. (Hinokuma et al. 2016a, 2018b, 2017a, 2017b) tested a series of different catalysts for ammonia combustion under fuel-lean conditions, including 3d transition metal oxides and noble metal-based catalyst ($\text{Pt}/\text{Al}_2\text{O}_3$). They concluded that a lower oxygen bond energy (defined as the enthalpy of the dissociation of the first metal-oxygen bond) promotes the activity of the catalysts. Among the various materials tested, MnO_2 , Co_3O_4 , and CuO exhibited the highest activity, with CuO achieving the lowest NO_x selectivity. Considering that CuO is a cost-effective and abundant material with promising performance in catalytic ammonia combustion, it was selected as the active metal phase in this work. The NH_3 oxidation rate on copper oxides is largely determined by the amount and mobility of the lattice oxygen (O^{2-}) on the catalyst surface (Hinokuma et al. 2018a). Building on this, it is hypothesized that a catalyst supported on a mixed ionic and electronic conductor with rich oxygen vacancies, which has been widely used in solid oxide fuel cells (SOFCs), may promote ammonia combustion under fuel-rich conditions. To test the hypothesis, a gadolinium-doped ceria (GDC)-supported copper oxide catalyst (CuO/GDC) is conceptualized in this work. CuO/CeO_2 catalysts have been tested for fuel-lean catalytic ammonia combustion and achieved a high NH_3 conversion of 100% and a good N_2 yield of 98% over 6 hours (Kang et al. 2024). The doping of Gd in CeO_2 could further improve its oxygen-ion conductivity (Swathi et al. 2022; Vinchhi et al. 2024), as the substitution of Ce^{4+} by Gd^{3+} creates oxygen vacancies and promotes the reduction of Ce^{4+} to Ce^{3+} for charge compensation (Miura-Stempel et al. 2024), making GDC a promising support material. Additionally, GDC itself also serves as a catalyst for the selective reduction of NO by NH_3 to form N_2 (Vernoux et al. 2013), which helps to decrease NO_x while enhancing NH_3 oxidation.



The aim of this study is to design and test the performance (reactivity and NO_x selectivity) of a novel CuO/GDC catalyst for fuel-rich ammonia combustion and conduct kinetic studies to understand the reaction mechanisms and interactions between metal and support. The performance of the catalyst was assessed in terms of NH₃ conversion and NO_x selectivity using a lab-scale fixed-bed reactor under isothermal conditions. The results were compared to CuO/Al₂O₃ to highlight the advantages of the mixed ionic and electronic conductor support. In addition, XPS analysis and microkinetic modeling combined with Density Functional Theory-based calculations were performed to provide insights into the reaction mechanisms and kinetics.

Methodology

Catalysts synthesis

The commercial γ -Al₂O₃ support and all other chemicals used for catalyst preparation in this study were purchased from Thermo Fisher Scientific. The GDC support was synthesized using the co-precipitation method. The appropriate amount of cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6 H₂O, 99.5%, Thermo Scientific Chemicals) and gadolinium (III) nitrate hexahydrate (Gd(NO₃)₃·6 H₂O, 99.9%, Thermo Scientific Chemicals) was dissolved in deionized water. Ammonium carbonate ((NH₄)₂CO₃, ≥30% NH₃ basis, Merck) was dissolved in deionized water and added dropwise to the nitrate solution until pH = 10.5. The pH was maintained at 10.5 for 30 minutes, while the solution was constantly stirred by a magnetic stirrer. The precipitate formed in the solution was washed and filtered three times to ensure that there were no impurities. The precipitate was dried overnight in a static oven at 100°C. The dried precipitate was crushed into powder before being calcined at 900°C for 90 minutes, with a heating rate of 10°C·min⁻¹ (Hapsari et al. 2019). The calcined sample was used as the GDC support for the catalyst.

The CuO/ γ -Al₂O₃ and CuO/GDC catalysts used in this study were synthesized using the wet-impregnation method. The crushed γ -Al₂O₃ and GDC powders were impregnated with copper nitrate hemi-pentahydrate (Cu(NO₃)₂·2.5 H₂O) solution, and the final Cu loading was controlled to 10 wt.%. The beakers containing the solutions were placed in an ultrasonic bath and shaken for 1 hour. The impregnated samples were dried overnight in a static oven at 100°C. The dried samples supported on α -Al₂O₃ and GDC were calcined for 4 hours at 600°C and 8 hours at 650°C, respectively, both with a heating rate of 10°C·min⁻¹. The calcined samples were sieved, and particles within the range of 0.05–0.4 μm were kept and used for the catalytic combustion tests.

Catalytic reactivity tests

A fixed-bed reactor was used for the ammonia oxidation reactivity tests simulating ammonia fuel-rich combustion conditions. A schematic diagram of the experimental setup is shown in Figure 1 Experimental setup for ammonia oxidation.

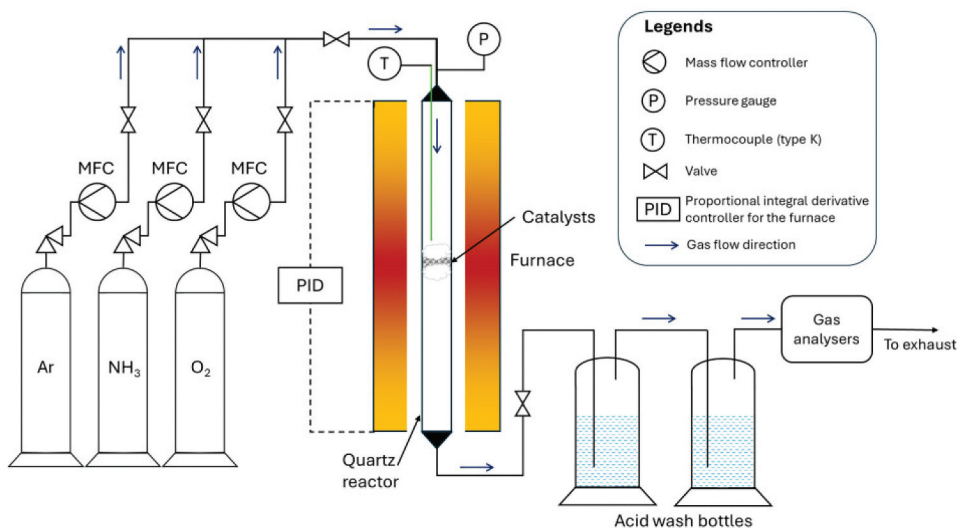


Figure 1. Experimental setup for ammonia oxidation.

Approximately 0.28 g of the catalyst sample was loaded into the quartz liner and fixed into position with two layers of quartz wool. The flow rates of argon, ammonia, and oxygen were regulated by three Mass Flow Controllers (MFC, purchased from Alicat Scientific) and set to 195.5, 3, and 1.5 mL·min⁻¹, respectively, to maintain an Equivalence Ratio (ER) of 1.5, a total flow rate of 200 mL·min⁻¹, and a Weight Hourly Space Velocity (WHSV) of 43 L·h⁻¹·g_{cat}⁻¹. The ER and WHSV were defined by the equations below:

$$ER = \frac{(P_{\text{NH}_3}/P_{\text{O}_2})_{\text{experimental}}}{(P_{\text{NH}_3}/P_{\text{O}_2})_{\text{stoichiometric}}} \quad (3)$$

$$WHSV = \frac{F}{m_{\text{catalyst}}} \quad (4)$$

where $(P_{\text{NH}_3}/P_{\text{O}_2})_{\text{experimental}}$ and $(P_{\text{NH}_3}/P_{\text{O}_2})_{\text{stoichiometric}}$ are the ratio between the partial pressure of NH₃ and O₂ under experimental and stoichiometric conditions, respectively, F is the total flow rate, and m_{catalyst} is the mass of the catalyst used for the reaction.

The temperature of the catalyst bed was monitored using a K-type thermocouple. Once the reaction was stable, the exhaust gas was passed through two acid wash bottles containing 0.4 L of diluted sulfuric acid solution (0.01 M) to capture unreacted ammonia. The amount of unreacted ammonia was measured using the indophenol blue method with UV-vis Spectroquant ammonium cell test kits. N₂O, NO, and NO₂ concentrations were measured using an ABB EL3000 Gas Analyzer and a Horiba VSE-3003 Analyzer. The performance of the catalysts was evaluated based on the NH₃ and O₂ conversion, as well as the N₂ and NO_x selectivities. The equations used to calculate the parameters are summarized in Supplementary Information.

Catalyst characterization

The composition of the samples was confirmed using X-ray diffraction (XRD) analysis. The XRD tests were carried out using a Siemens D5005 X-ray Diffractometer with Cu K α radiation. The samples were crushed into powders and scanned in the 2θ range of 20° – 80° with a step size of 0.02° .

The liquid nitrogen physisorption tests were carried out using the Micromeritics 3Flex instrument. Prior to the tests, the samples were degassed at 400°C for 4 hours with a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. The specific surface area was calculated using the Brunauer – Emmett – Teller (BET) equation. The total pore volume and average pore size were calculated using the Barrett-Joyner-Halenda (BJH) method.

The morphology and elemental distribution of the samples were studied using the TESCAN VEGA 3 Scanning Electron Microscope (SEM) and through Energy-Dispersive X-ray Spectroscopy (EDX).

The Transmission Electron Microscopy (TEM) images were obtained using a JEOL JEM-1400 Electron Microscope with an Accelerating Voltage of 120 kV. The samples were ultrasonically dispersed in ultrapure water and drop-cast onto carbon-coated copper grids before analysis.

X-ray photoelectron spectroscopy (XPS) was measured on an AXIS Supra+ K-Alpha Photoelectron spectrometer (Japan), with an Al K α source being used as the radiation source. All XPS spectra binding energies were calibrated by using the contaminant carbon (C 1s = 284.8 eV) as a reference.

Density Functional Theory

The Density Functional Theory (DFT) calculations were performed using the Quantum Espresso software package (Giannozzi et al. 2009). The Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was used to describe the exchange correlation (Perdew et al. 1996). The ultrasoft pseudopotential was used to describe the electron–ion interactions. The DFT+U correction was used to deal with the strong electron correlations of the Cu 3d, Ce 4f, and Gd 4f orbitals, with the Hubbard U parameters set to 7, 5, and 5 eV, respectively (Han et al. 2020; Zheng and Zhao 2021). A four-layer CuO(111) slab was constructed based on a fully optimized CuO unit cell, with the two bottom layers fixed and a vacuum layer of 12 Å. The CuO(111) facet was chosen as it is generally considered as the most dominant and stable facet in CuO-based catalysts (Maimaiti et al. 2014), which was also evidenced by the XRD patterns of the synthesized samples (Figure 2). The CuO/ γ -Al $_2$ O $_3$ slab was constructed by creating a γ -Al $_2$ O $_3$ (110) slab and adding a Cu atom to the top layer. Similarly, a four-layer GDC slab was constructed by creating a CeO $_2$ slab and substituting the Ce atom with Gd to achieve the desired Ce:Gd ratio. A Cu atom is then added to the top layer of the GDC(111) slab to simulate the CuO/GDC catalyst. Figures of the three slab models used in this study can be found in Supplementary Information. For all models, the plane wave cutoff energy was set to 25 Ry, and the convergence criteria for force and energy were set to $0.03\text{ eV}/\text{\AA}$ and 10^{-5} eV , respectively. A Monkhorst-

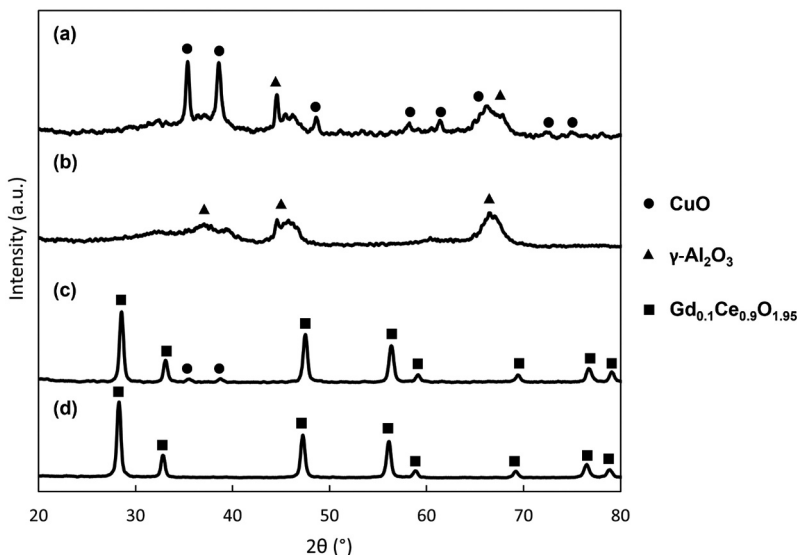


Figure 2. XRD patterns of (a) CuO/ γ -Al₂O₃, (b) γ -Al₂O₃, (c) CuO/GDC, and (d) GDC.

Pack k-point grid of $3 \times 3 \times 1$ was set for the slab models. The N and O adsorption energies on the catalyst surface were calculated using the equation below:

$$E_{ads} = E_{ads*slab} - E_{adsorbate} - E_{slab} \quad (5)$$

where E_{ads} is the adsorption energy, $E_{ads*slab}$ is the total energy of the slab with the adsorbate, $E_{adsorbate}$ is the energy of the adsorbate in the isolated form, and E_{slab} is the energy of the clean slab. The isolated adsorbates, which are N and O atoms in this study, were modeled by placing the atoms in a cube ($a = 20 \text{ \AA}$, $b = 20.5 \text{ \AA}$, and $c = 21 \text{ \AA}$) using a Monkhorst-Pack k-point grid of $1 \times 1 \times 1$.

Microkinetic modeling

A Microkinetic Model (MKM) was developed to simulate the catalytic ammonia combustion reaction using the descriptor-based analysis package, CatMAP (Medford et al. 2015). Based on previous studies (Ma and Schneider 2019; Su X, Gao X, et al. 2024), 15 elementary reactions were selected to simulate the reaction between NH₃ and O₂ to produce N₂, H₂O, N₂O, and NO. A list of the elementary reactions considered in the model can be found in Supplementary Information. The DFT-calculated adsorption energies obtained (Density functional theory) were converted into their corresponding “formation energies” and integrated into the MKM using a “formation energy approach (Medford et al. 2015). The formation energies and vibrational frequencies of the gas-phase, intermediate, and transition-state species used to develop the MKM were extracted from the work by Su et al. (Su X, Gao X, et al. 2024).

Table 1. Results from the liquid nitrogen physisorption analysis.

Material	BET surface area ($\text{m}^2\cdot\text{g}^{-1}$)	Pore volume ($\text{cm}^3\cdot\text{g}^{-1}$)	Average pore diameter (nm)
$\gamma\text{-Al}_2\text{O}_3$	188.7	0.79	16.2
$\text{CuO}/\gamma\text{-Al}_2\text{O}_3$	181.9	0.64	13.0
GDC	17.3	0.10	22.2
CuO/GDC	20.2	0.15	26.2

Results and discussion

Catalyst characterization

The XRD analysis was carried out to confirm the composition and crystalline structures of the support materials and the catalysts synthesized (Figure 2). The XRD pattern of the commercial $\gamma\text{-Al}_2\text{O}_3$ support (Figure 2(b)) shows three broad peaks at 38° , 46° , and 67° , corresponding to the (311), (400), and (440) surfaces, respectively (COD #96–101-0462). These broad and low-intensity peaks were due to the partial amorphous structure or surface disorder, which are common for commercial $\gamma\text{-Al}_2\text{O}_3$ (Rozita et al. 2010; Zhu et al. 2020). The $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst showed additional peaks at 35.5° , 38.7° , 48.8° , 58.4° , 61.5° , 66.3° , 72.3° , and 75.3° , which aligns with the various surfaces of tenorite (COD #96–901-5925). Based on Figure 2(d), the composition of the synthesized GDC support was confirmed to be $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (COD #96–154-1473). The presence of CuO in the CuO/GDC catalyst was confirmed by the peaks at 35.5° and 38.7° (Figure 2(c)).

Results from the physisorption tests are summarized in Table 1. The as-synthesized GDC support has a surface area of $17.3 \text{ m}^2\cdot\text{g}^{-1}$, which is significantly lower than the commercial $\gamma\text{-Al}_2\text{O}_3$ support with a surface area of $188.7 \text{ m}^2\cdot\text{g}^{-1}$. The $\gamma\text{-Al}_2\text{O}_3$ -supported CuO catalyst also showed a more porous structure with a larger total pore volume of $0.64 \text{ cm}^3\cdot\text{g}^{-1}$, formed by smaller pores with an average diameter of 13 nm. The loading of Cu on the $\gamma\text{-Al}_2\text{O}_3$ support decreased the surface area and the pore volume of the bare support. This is a common observation for catalysts supported on highly porous alumina materials, where the metal oxide particles block the fine pores of alumina during the impregnation process (Wang et al. 2024). On the other hand, the loading of Cu did not significantly alter the overall morphology of the GDC support, the average pore size remained in the mesoporous range ($\sim 20 \text{ nm}$) with a total pore volume of $0.10\text{--}0.15 \text{ cm}^3\cdot\text{g}^{-1}$.

The SEM images and the EDX elemental mapping of the fresh $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ and CuO/GDC catalysts are presented in Figure 3. Spherical CuO nanoparticles were found to deposit on the surface of the supports. On the $\gamma\text{-Al}_2\text{O}_3$ support, Cu is evenly dispersed with an average loading of 12.9 wt.%. On the GDC support, the average Cu loading was 12.3 wt.%.

The successful synthesis of CuO nanoparticles was evidenced by the TEM images of the CuO/GDC catalyst, shown in Figure 4. A uniform distribution of nanoscale particles can be observed, with an average particle size in the range of 10–50 nm.

Catalytic combustion performance

The performance of the catalysts for fuel-rich catalytic ammonia combustion was tested for temperatures ranging from 100°C to 800°C , and the results are presented in Figure 5.

The $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst was found to be inactive below 250°C with a light-off temperature (T_{10} , the temperature at which 10% NH_3 conversion is reached) of 300°C . The GDC

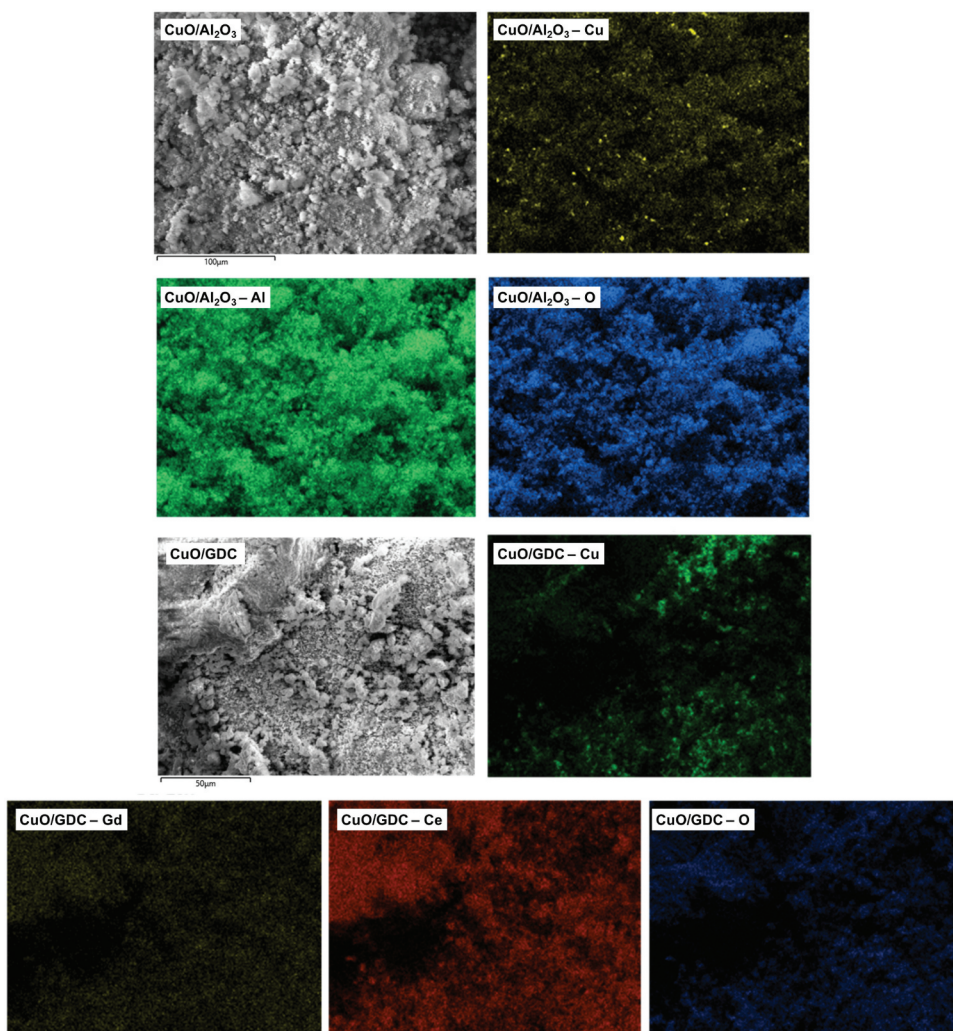


Figure 3. SEM images and EDX elemental mapping of CuO/γ-Al₂O₃ (top) and CuO/GDC (bottom).

support significantly improved the overall performance of the catalyst. The T_{10} of CuO/GDC was 180°C, showing the easy onset of the catalytic combustion reaction with the mixed conductor-supported catalyst. At a high reaction temperature of 800°C, CuO/γ-Al₂O₃ only reached an NH₃ conversion of 73%, whereas CuO/GDC achieved 100% conversion. Although the GDC-supported catalyst has a significantly lower surface area and pore volume with fewer fine pores and, therefore, available active sites compared to the conventional high-surface area alumina support, a good catalytic activity was still achieved by CuO/GDC. This is potentially due to the unique conductive properties of the mixed conductor support, which facilitates oxygen and electron transfer to the available active sites. Table 2 summarizes the catalytic activity and product selectivity of CuO/GDC compared to existing CuO- and noble metal-based catalysts under both ammonia catalytic combustion and selective reduction conditions. As can be seen from the table, CuO/GDC showed superior performance compared to the catalysts tested in previous studies. A higher equivalence ratio generally decreases NH₃

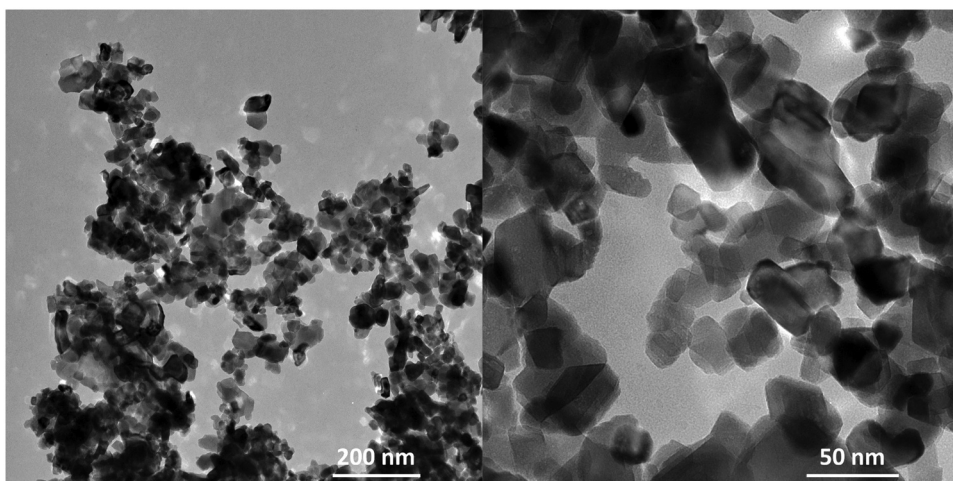


Figure 4. TEM images of the CuO/GDC catalyst.

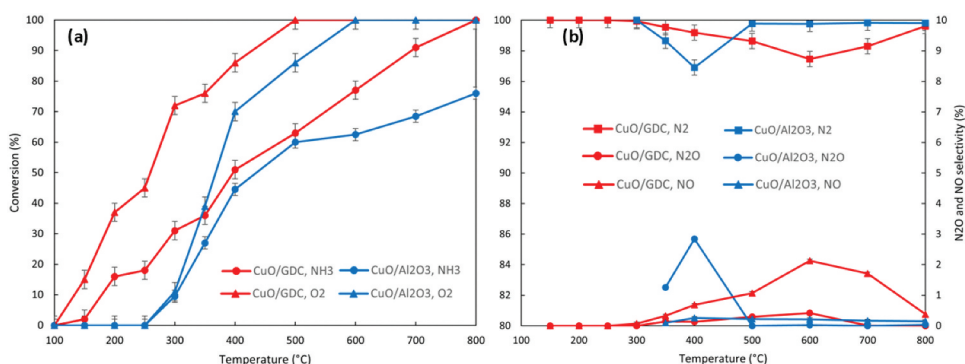


Figure 5. (a) NH₃ and O₂ conversion, and (b) N₂, N₂O, and NO selectivity as a function of temperature for CuO/ γ -Al₂O₃ and CuO/GDC, with an ER of 1.5 and WHSV of 43 L·h⁻¹·g_{cat}⁻¹.

conversion in fuel-rich combustion. However, CuO/GDC achieved a NH₃ conversion of 75% at 600°C with an ER of 1.5, comparable to the CuO/CeO_x catalysts tested by Su et al. (Su et al. 2024), which achieved the same conversion with a lower ER of 1.1. The effect of GDC support on the reduction of light-off temperature is also significant – the light-off temperature of CuO/GDC is lower than the other CuO-based catalysts (Kang et al. 2024; Su et al. 2024) and noble metal-based catalysts (Gang et al. 2000; Hinokuma et al. 2016b; Shin et al. 2020).

Apart from exhibiting excellent catalytic activity, CuO/GDC also shows good product selectivity. Both catalysts exhibited negligible selectivity toward NO₂ (< 0.01%), with only trace amounts detected at the ppm level. CuO/GDC maintained over 97% N₂ selectivity across all temperatures. For CuO/GDC, the peak N₂O selectivity occurred within the temperature range of 500–650°C, reaching a maximum of 0.41%. Consistent with previous observations (Hinokuma et al. 2018a), NO selectivity slightly increased with temperature and reached its peak value of 2.13% at 600°C. CuO/ γ -Al₂O₃ also exhibited excellent product selectivities, with over 96% N₂ selectivity.

Table 2. Comparison of catalytic activity and product selectivity of CuO/GDC with existing CuO- and noble metal-based catalysts.

Catalyst	ER	T ₁₀ (°C)	T ₅₀ (°C)	T ₉₀ (°C)	N ₂ selectivity (%) at T ₉₀	N ₂ O selectivity (%) at T ₉₀	NO selectivity (%) at T ₉₀	NO ₂ selectivity (%) at T ₉₀	Reference
CuO/Al ₂ O ₃	1.5	300	430	>800	T ₉₀ not reached	T ₉₀ not reached	T ₉₀ not reached	T ₉₀ not reached	This work
CuO/GDC	1.5	180	400	690	98	0.1	1.9	0	This work
CuO/CeO _x	1.1	240	280	>700	T ₉₀ not reached	Not reported	Not reported	Not reported	Su et al. (2024)
CuO/CeO ₂	0.36	190–320	200–350	220–411	98	0.2	1.8	0	Kang et al. (2024)
Pt/Al ₂ O ₃	0.04	280	300	360	53	27	11	9	Hinokuma et al. (2016b)
Pd/Al ₂ O ₃	0.1	100% reach at 300°C			98	Not reported	Not reported	Not reported	Gang et al. (2000)
Ru/TiO ₂	0.0015	206	230	256	70.1	9.6	10.7	9.6	Shin et al. (2020)

In conclusion, the mixed conductor support significantly enhanced the catalytic activity of the CuO catalyst, achieving a 10–30% higher NH₃ conversion compared to CuO supported on an inert material. Additionally, the light-off temperature was lowered by 120°C, allowing for an easier reaction initiation. The mixed conductor-supported catalyst also demonstrated optimal product selectivity, maintaining over 97% N₂ selectivity even at a high reaction temperature of 800°C.

Microkinetic modeling and spectroscopic analysis

The reaction mechanism of fuel-rich catalytic ammonia combustion over the CuO/GDC catalyst was investigated using XPS analysis and microkinetic modeling. Results from the XPS analysis provide insights into the surface composition, while the MKM helps identify key reaction descriptors influencing catalytic performance.

XPS analysis was carried out for the CuO/GDC catalyst before and after the combustion test. The XPS spectra of Cu 2*p*, Gd 3*d*, and Ce 3*d* are presented in Figure 6 and no significant changes were observed before and after the reaction. The presence of Cu²⁺ species in the sample was confirmed by the peaks at 934.5 (2*p*_{3/2}) and 954.8 eV (2*p*_{1/2}), along with their corresponding satellite peaks at 943 and 963.5 eV, observed in the Cu 2*p* spectra (Deng et al. 2022). The presence of Gd³⁺ species was confirmed by the peaks at 1187.6 (3*d*_{3/2}) and 1220 (3*d*_{5/2}) eV, observed in the Gd 3*d* spectra (Haunsbhavi et al. 2022). In the Ce 3*d* spectra, the intense U''' and V''' peaks (916.3 and 897.9 eV, respectively), together with the U'', V'', U, and V peaks (908, 888, 901.4, and 882.5 eV, respectively), are identified as the three spin-orbit doublets of Ce⁴⁺ species (Li et al. 2018).

The O 1*s* spectra of the fresh and used samples are presented in Figure 7. The concentration of each oxygen species was determined based on the area of its corresponding peak. The spectrum of the fresh CuO/GDC sample was fitted with three peaks (Binding Energy = 528.8, 530.1, and 532.0 eV), corresponding to lattice oxygen (O_{lattice}), oxidative O₂²⁻/O⁻ species, and chemisorbed oxygen (O_{adsorbed}) (Huang et al. 2023). The peak at 530.1 eV was assigned to O₂²⁻/O⁻ species and potentially hydroxyl groups on the surface of the

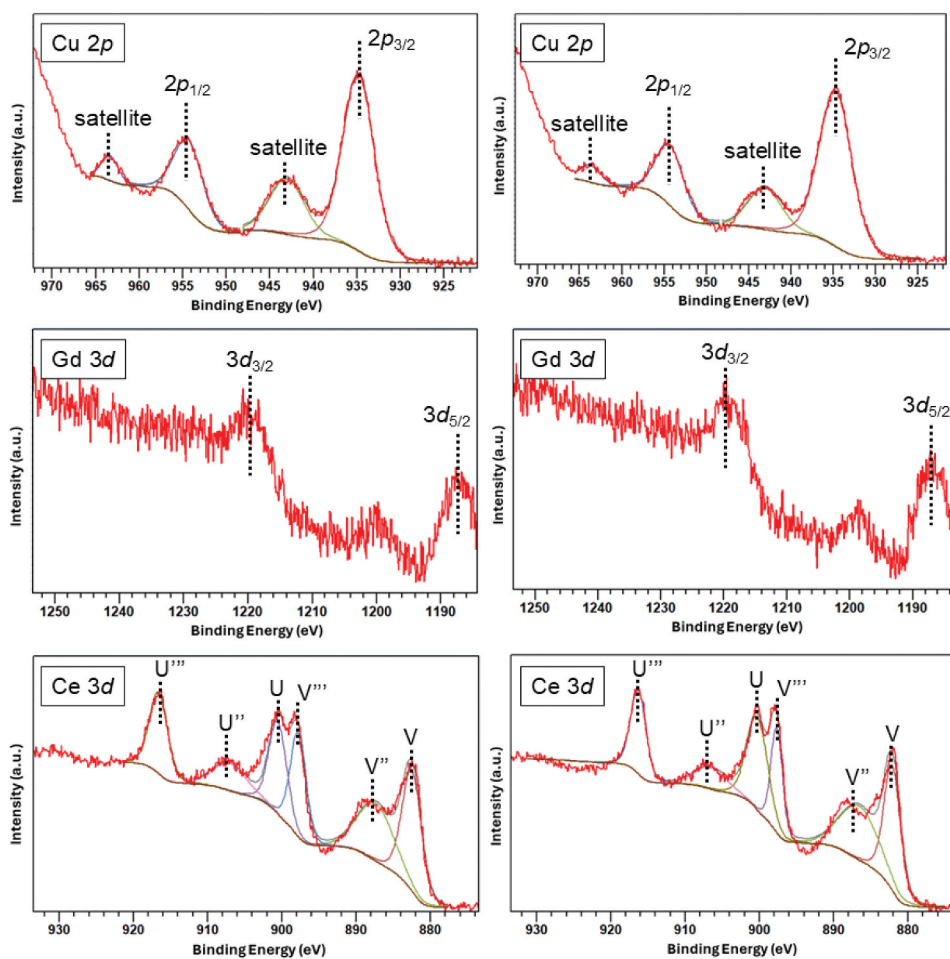


Figure 6. XPS Cu 2p, Gd 3d, and Ce 3d spectra of the fresh (left) and used (right) CuO/GDC catalyst.

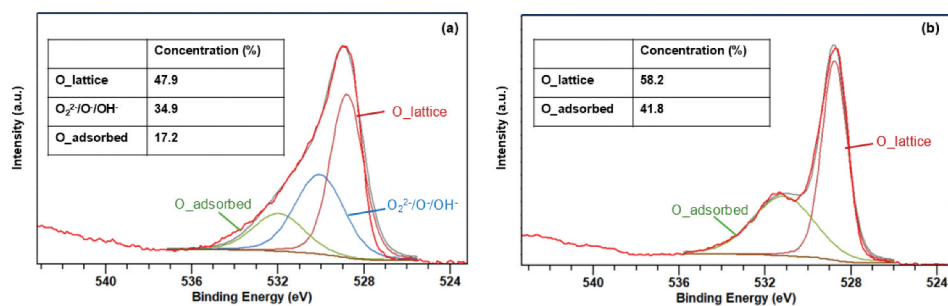


Figure 7. XPS O 1s spectra of the (a) fresh and (b) used CuO/GDC catalyst.

sample due to the oxidation of oxygen vacancy sites by moisture (Idriss 2021; Vinchhi et al. 2024). The peak at the highest binding energy level was assigned to chemisorbed oxygen on the surface. By comparing the O 1s spectra of the fresh and used samples, an increase in the content of adsorbed oxygen and a decrease in the oxidative species and hydroxyl group can be observed. This indicates the participation of the GDC support in the catalytic ammonia combustion reaction. As evidenced by previous research (Miura-Stempel et al. 2024), the doping of Gd^{3+} improves the surface reactivity of CeO_2 by enriching its oxygen vacancies. In the oxidative environment where the catalytic ammonia combustion reaction takes place, oxygen from the moisture content, which previously filled the surface oxygen vacancies of GDC, was replaced by gaseous O_2 chemisorbed on the surface. The chemisorbed O atoms then participate in the oxidation of NH_3 at the adjacent active sites. This greatly improved the NH_3 conversion over CuO/GDC compared to CuO supported on the inert support, $\gamma\text{-Al}_2\text{O}_3$, which exhibits low surface oxygen-ion mobility.

The results from the microkinetic modeling of the catalytic ammonia combustion reaction are presented in the form of a “volcano plot” (Figure 8), with the color contour representing the logarithm of the turnover frequency ($\log(\text{TOF})$). The $\log(\text{TOF})$ of the reaction products is presented as a function of N and O formation energies, and the central area colored in red represents the highest reactivity. As shown in the volcano plot, the highest activity is achieved when the N and O formation energies are equal to 1.9 and -0.7 eV, respectively. At this point, the

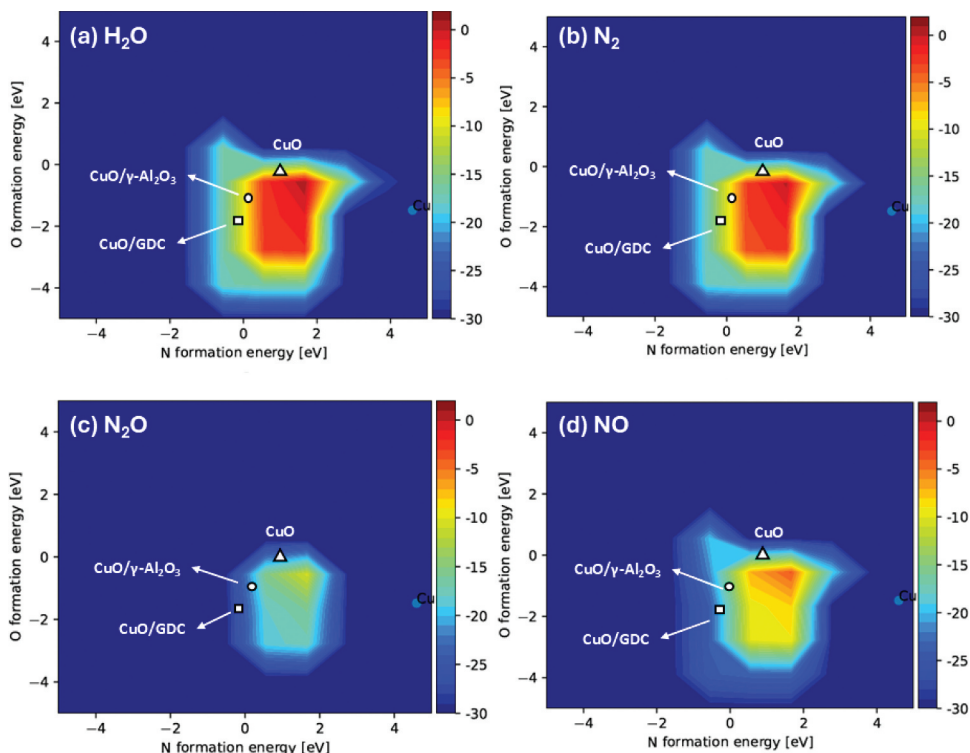


Figure 8. Volcano plot showing $\log(\text{TOF})$ in s^{-1} of (a) H_2O , (b) N_2 , (c) N_2O , and (d) NO production as a function of N and O adsorption energies. $\log(\text{TOF})$ is represented by the color scale.

TOF of H_2O and N_2 are equal to 100 and 30 s^{-1} , corresponding to their stoichiometric ratio in the ammonia oxidation reaction (Eq.(1)). TOF of NO and N_2O are 10^{-4} and 10^{-9} s^{-1} . This is consistent with the experimental observation that at 500°C , selectivity toward NO is higher than N_2O . Four Cu-based catalysts, including Cu, CuO, CuO/ $\gamma\text{-Al}_2\text{O}_3$, and CuO/GDC, were plotted against the volcano plot based on their N and O formation energies. Detailed calculations of the formation energies are included in Supplementary Information. It can be observed that the copper oxide species show stronger N adsorption affinity compared to metallic Cu, which contributes to their higher activity toward the ammonia oxidation reaction. All three CuO-based materials showed similar catalytic activity with an N_2 TOF of $10^{-8} - 10^{-11} \text{ s}^{-1}$. This TOF value is relatively low considering that a 60% NH_3 conversion was achieved based on the experimental results, which may be due to simplified assumptions used in the model, including the single-site surface model and the exclusion of potential defect-mediated reactions. Consistent with the experimental observations, CuO/GDC showed almost zero selectivity toward N_2O (10^{-27} s^{-1}) and lower NO selectivity (10^{-22} s^{-1}) compared to CuO/ $\gamma\text{-Al}_2\text{O}_3$. This may be attributed to the stronger adsorption of N and O atoms on the CuO/GDC surface, which mitigates the formation and desorption of nitrogen oxide compounds.

Limitations and future work

One limitation of the CuO/GDC catalyst tested in this work is the relatively low surface area of the GDC support, which may restrict the number of accessible active sites. Future work will explore alternative synthesis routes, optimization of Ce:Gd ratio, and calcination conditions to enhance surface area and oxygen vacancy concentration. In addition, the microkinetic model employed in this work included simplified assumptions to reduce computational time and resources. Future modeling will consider defect-mediated reaction pathways for more accurate predictions.

This work serves as a proof-of-concept demonstration of the potential of mixed conductor-supported catalysts for low-NO_x ammonia fuel-rich stabilized catalytic combustion. Future studies will include long-term stability test of the catalyst, comparison with alternative mixed conductor materials, and a techno-economic analysis to evaluate the scalability and economic viability of the proposed catalysts.

Conclusions

This study investigated the catalytic performance and reaction mechanism of CuO/GDC catalysts for fuel-rich ammonia combustion. Experimental results demonstrated that CuO/GDC effectively catalyzes NH_3 oxidation, achieving a high NH_3 conversion of 100% at 800°C and a high N_2 selectivity of over 99%. The improved performance of CuO/GDC over CuO/ $\gamma\text{-Al}_2\text{O}_3$ was attributed to the active participation of the mixed conductor support (GDC) in ammonia oxidation, in which surface-adsorbed oxygen replaces moisture-derived species at oxygen vacancies and promotes ammonia oxidation at adjacent Cu sites. DFT calculations and microkinetic modeling provide further insights into the reaction mechanism. The strong adsorption of N and O atoms on the CuO/GDC surface due to the electronic interaction between the mixed conductor support and the active metal mitigates

the formation and release of nitrogen oxide species, contributing to its high N₂ selectivity. Future work, including analysis of the samples using additional characterization techniques (operando XANES, *in-situ* Raman, *in-situ* XPS, EXAFS, and H₂-TPR), will provide more information on the reaction mechanisms. Overall, the findings from the experimental and numerical analyses demonstrated the potential of mixed conductor-supported catalysts for ammonia combustion applications, providing a pathway toward efficient and low-emission NH₃ utilization.

Acknowledgements

This research was funded by the EPSRC (EP/X03593X/1). The authors gratefully acknowledge Dr Jiaojiao Zheng from Aston University for her assistance with the XPS analysis. The authors also acknowledge the support from Dr Igor Kraev and Dr Elena Shishkova from Open University for their assistance with the TEM analysis.

Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding

The work was supported by the Engineering and Physical Sciences Research Council [EP/X03593X/1].

ORCID

Mingming Zhu  <http://orcid.org/0000-0002-3643-1799>

References

- Deng S, Tu Y, Fu L, Liu J, Jia L. 2022. A label-free biosensor for selective detection of Gram-negative bacteria based on the oxidase-like activity of cupric oxide nanoparticles. *Microchim Acta*. 189 (12):471. <https://doi.org/10.1007/s00604-022-05571-4>
- Eriksson S et al. 2006. Fuel-rich catalytic combustion of methane in zero emissions power generation processes. *Catal Today*. 117(4):447–453. <https://doi.org/10.1016/j.cattod.2006.06.010>
- Gang L, Anderson BG, van Grondelle J, van Santen RA. 2000. Nh₃ oxidation to nitrogen and water at low temperatures using supported transition metal catalysts. *Catal Today*. 61(1–4):179–185. [https://doi.org/10.1016/S0920-5861\(00\)00375-8](https://doi.org/10.1016/S0920-5861(00)00375-8)
- Giannozzi P et al. 2009. Quantum espresso: a modular and open-source software project for quantum simulations of materials. *J Phys Condens Matter*. 21(39):395502. <https://doi.org/10.1088/0953-8984/21/39/395502>
- Han X, Amrane N, Zhang Z, Benkraouda M. 2020. Interplay between Gd and oxygen vacancy on the electronic properties and defect chemistry of Gd-doped CeO₂: A DFT + U study. *Chem Phys*. 534:110741. <https://doi.org/10.1016/j.chemphys.2020.110741>
- Hapsari AU et al. 2019. Synthesis and characterization of gadolinium doped cerium (Ce_{0.9}Gd_{0.1}O_{1.95}) by using various carbonates as a precipitant. *IOP Conf Ser Mater Sci Eng*. 622(1):012011. <https://doi.org/10.1088/1757-899X/622/1/012011>
- Haunsbhavi K et al. 2022. The effect of rare-earth element (Gd, Nd, La) doping of NiO films on UV photodetector. *Phys Scr*. 97(5):055815. <https://doi.org/10.1088/1402-4896/ac64d4>

- Hinokuma S et al. 2017b. *Operando* XAFS studies of supported copper oxides for catalytic ammonia combustion. *J Ceram Soc Jpn*. 125(10):770–772. <https://doi.org/10.2109/jcersj2.17075>
- Hinokuma S et al. 2016a. Copper oxides supported on aluminum oxide borates for catalytic ammonia combustion. *J Phys Chem C*. 120(43):24734–24742. <https://doi.org/10.1021/acs.jpcc.6b07157>
- Hinokuma S et al. 2016b. Catalytic activity and selectivities of metal oxides and Pt/Al₂O₃ for NH₃ combustion. *Chem Lett*. 45(2):179–181. <https://doi.org/10.1246/cl.151031>
- Hinokuma S et al. 2017a. Local structures and catalytic ammonia combustion properties of copper oxides and silver supported on aluminum oxides. *J Phys Chem C*. 121(8):4188–4196. <https://doi.org/10.1021/acs.jpcc.6b13024>
- Hinokuma S et al. 2018a. Catalytic ammonia combustion properties and operando characterization of copper oxides supported on aluminum silicates and silicon oxides. *J Catal*. 361:267–277. <https://doi.org/10.1016/j.jcat.2018.03.008>
- Hinokuma S et al. 2018b. Supported and unsupported manganese oxides for catalytic ammonia combustion. *Catalysis Commun*. 105:48–51. <https://doi.org/10.1016/j.catcom.2017.11.009>
- Huang M et al. 2023. Performance enhancement of Cu decorated LSCM-GDC composite cathode for CO₂ electroreduction. *Solid State Ionics*. 402:116357. <https://doi.org/10.1016/j.ssi.2023.116357>
- Idriss H. 2021. On the wrong assignment of the XPS O1s signal at 531–532 eV attributed to oxygen vacancies in photo- and electro-catalysts for water splitting and other materials applications. *Surf Sci*. 712:121894. <https://doi.org/10.1016/j.susc.2021.121894>
- Jeerh G, Zhang M, Tao S. 2021. Recent progress in ammonia fuel cells and their potential applications. *J Mater Chem A*. 9(2):727–752. <https://doi.org/10.1039/D0TA08810B>
- Kang R et al. 2024. Distinct structure-activity relationship and reaction mechanism over CuO/CeO₂ catalysts for NH₃ self-sustained combustion. *Proc Combust Inst*. 40(1–4):105647. <https://doi.org/10.1016/j.proci.2024.105647>
- Karim H et al. 2002. Advanced catalytic pilot for low NO_x industrial gas turbines. Volume 1 Turbo Expo. 2002:483–490. <https://doi.org/10.1115/GT2002-30083>
- Lamb KE, Dolan MD, Kennedy DF. 2019. Ammonia for hydrogen storage; a review of catalytic ammonia decomposition and hydrogen separation and purification. *Int J Multiling Hydrogen Energy*. 44(7):3580–3593. <https://doi.org/10.1016/j.ijhydene.2018.12.024>
- Li S et al. 2018. Preferential oxidation of CO in H₂-rich stream over Au/CeO₂–NiO catalysts: effect of the preparation method. *Catal Lett*. 148(1):328–340. <https://doi.org/10.1007/s10562-017-2231-1>
- Ma H, Schneider WF. 2019. Structure- and temperature-dependence of Pt-catalyzed ammonia oxidation rates and selectivities. *ACS Catal*. 9(3):2407–2414. <https://doi.org/10.1021/acscatal.8b04251>
- Maimaiti Y, Nolan M, Elliott SD. 2014. Reduction mechanisms of the CuO(111) surface through surface oxygen vacancy formation and hydrogen adsorption. *Phys Chem Chem Phys*. 16(7):3036. <https://doi.org/10.1039/c3cp53991a>
- Medford AJ et al. 2015. CatMAP: A software package for descriptor-based microkinetic mapping of catalytic trends. *Catal Lett*. 145(3):794–807. <https://doi.org/10.1007/s10562-015-1495-6>
- Miura-Stempel E et al. 2024. CeO₂ nanoparticle doping as a probe of active site speciation in the catalytic hydrolysis of organophosphates. *ACS Appl Nano Mater*. 7(13):15498–15507. <https://doi.org/10.1021/acsanm.4c02410>
- Perdew JP, Burke K, Ernzerhof M. 1996. Generalized gradient approximation made simple. *Phys Rev Lett*. 77(18):3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>
- Pinzón M et al. 2024. Ammonia as a hydrogen carrier: an energy approach. *Energy Convers Manag*. 321:321. <https://doi.org/10.1016/j.enconman.2024.118998>
- Rozita Y, Brydson R, Scott AJ. 2010. An investigation of commercial gamma-Al₂O₃ nanoparticles. *J Phys Conf Ser*. 241: 012096. <https://doi.org/10.1088/1742-6596/241/1/012096>
- Schultze M, Mantzaras J, Bombach R, Boulouchos K. 2013. An experimental and numerical investigation of the hetero-/homogeneous combustion of fuel-rich hydrogen/air mixtures over platinum. *Proc Combust Inst*. 34(2):2269–2277. <https://doi.org/10.1016/j.proci.2012.05.029>
- Shin JH, Kim GJ, Hong SC. 2020. Reaction properties of ruthenium over Ru/TiO₂ for selective catalytic oxidation of ammonia to nitrogen. *Appl Surf Sci*. 506:144906. <https://doi.org/10.1016/j.apsusc.2019.144906>

- Su X et al. 2024. Performance of ammonia catalytic combustion over Cu-CeO_x catalyst and the impact of oxygen concentration. *Mol Catal.* 562:114224. <https://doi.org/10.1016/j.mcat.2024.114224>
- Su X, Gao X, Yu X-Y, Chang C-R, Huang Z-Q. 2024. Design of Cu-based bimetals for ammonia catalytic combustion via DFT-based microkinetic modeling. *J Catal.* 429:115264. <https://doi.org/10.1016/j.jcat.2023.115264>
- Swathi S et al. 2022. Gadolinium doped CeO₂ for efficient oxygen and hydrogen evolution reaction. *Fuel.* 310:122319. <https://doi.org/10.1016/j.fuel.2021.122319>
- Valera-Medina A et al. 2021. Review on ammonia as a potential fuel: From synthesis to economics. *Energy Fuels.* 35(9):6964–7029. <https://doi.org/10.1021/acs.energyfuels.0c03685>
- Vernoux P et al. 2013. Ionically conducting ceramics as active catalyst supports. *Chem Rev.* 113(10):8192–8260. <https://doi.org/10.1021/cr4000336>
- Vinchhi P, Ray A, Mallik K, Pati R. 2024. Gd-doped ceria with extraordinary oxygen-ion conductivity for low temperature solid oxide fuel cells. *Sci Rep.* 14(1):19010. <https://doi.org/10.1038/s41598-024-59030-6>
- Wang S, Shen Z, Osatiashtiani A, Nabavi SA, Clough PT. 2024. Ni-based bimetallic catalysts for hydrogen production via (sorption-enhanced) steam methane reforming. *Chem Eng J.* 486:150170. <https://doi.org/10.1016/j.cej.2024.150170>
- Zheng C, Zhao H. 2021. The microscopic oxidation mechanism of NH₃ on CuO(111): A first-principles study. *Fuel Process Technol.* 213:106712. <https://doi.org/10.1016/j.fuproc.2020.106712>
- Zhu X et al. 2020. Ammonia synthesis over γ -Al₂O₃ pellets in a packed-bed dielectric barrier discharge reactor. *J Phys D Appl Phys.* 53(16):164002. <https://doi.org/10.1088/1361-6463/ab6cd1>



DSPACE

<https://dspace.org/>

Fuel-rich ammonia catalytic combustion on gadolinium-doped ceria (GDC) supported copper oxide catalyst

Wang, Siqi; Ibrahim Muhammad, Haliru; Shen, Ziqi; Zhu, Mingming

2025-11-28

Taylor & Francis

<https://doi.org/10.1080/00102202.2025.2595672>

Wang S, Ibrahim Muhammad H, Shen Z, Zhu M. (2025) Fuel-rich ammonia catalytic combustion on gadolinium-doped ceria (GDC) supported copper oxide catalyst. Combustion Science and Technology, Available online 28 November 2025