

Article

High-Entropy Oxide-Stabilized Pt-Cu Dual Sites for Hydrothermally Durable and N₂-Selective NH₃-SCO

Zhongqiang Bao ^{1,†}, Yiwei Zhang ^{1,†}, Zhenhua Ji ¹, Zhenguo Li ^{1,2,*}, Peng Zhang ¹, Ding Luo ¹, Zhanming Chen ¹, Han Gao ³, Lei Zhu ³ and Hao Chen ^{1,*}

¹ Shaanxi Provincial Key Laboratory of New Transportation Energy and Automotive Energy Saving, School of Energy and Electrical Engineering, Chang'an University, Xi'an 710018, China;

baozhongqiang@chd.edu.cn (Z.B.); 2024138012@chd.edu.cn (Y.Z.); jizhenhua0525@126.com (Z.J.); zproc@chd.edu.cn (P.Z.); luoding@chd.edu.cn (D.L.); ZM_Chen@chd.edu.cn (Z.C.)

² China Automotive Technology & Research Center Co., Ltd., Tianjin 300300, China

³ China Coal Energy Research Institute Co., Ltd., Xi'an 710054, China; gaohan1986@126.com (H.G.); zhulei@chinacoal.com (L.Z.)

* Correspondence: lizhenguo@catarc.ac.cn (Z.L.); chenhao@chd.edu.cn or colen7680@126.com (H.C.)

† These authors contributed equally to this work.

Abstract

Supported Pt catalysts are highly active for the selective catalytic oxidation of ammonia (NH₃-SCO), but their practical use is limited by poor N₂ selectivity and insufficient hydrothermal durability under high-temperature exhaust conditions. Herein, we report a composition-regulated high-entropy oxide interface strategy to stabilize Pt–Cu dual sites and steer NH₃ oxidation toward selective N₂ formation. A series of fluorite-type Ce-based high-entropy oxides, including CeZrLaPrYO_x, CeSmLaPrYO_x, and CeSnLaPrYO_x, were constructed as thermally robust supports for Pt and Cu loading. Among them, PtCu/HEO-Zr calcined at 1000 °C exhibits the best NH₃-SCO performance, achieving 90% NH₃ conversion at 260 °C while maintaining N₂ selectivity above 80% over a broad temperature window of 100–300 °C under a high weight hourly space velocity of 100,000 mL·g^{−1}·h^{−1}. More importantly, after harsh hydrothermal aging at 800 °C with 10 vol% H₂O for 12 h, the catalyst shows negligible activity loss and nearly unchanged N₂ selectivity, demonstrating exceptional structural and catalytic robustness. Structural and surface analyses reveal that Zr incorporation optimizes the fluorite high-entropy lattice, increases oxygen vacancy concentration, promotes lattice oxygen mobility, strengthens surface acidity, and enriches active Cu²⁺ species, thereby enhancing the interfacial cooperation between NH₃ activation and oxygen-assisted intermediate conversion. In situ DRIFTS further reveals that PtCu/HEO-Zr favors an O_{lat}-assisted internal selective catalytic reduction pathway, in which adsorbed NH₃ is activated to -NH₂ species and subsequently reacts with lattice oxygen-derived intermediates to form N₂O₂^{2−}-like species that decompose into N₂ and H₂O. Meanwhile, the formation of nonselective NO_x and N₂O products is suppressed. This work highlights high-entropy oxide-supported Pt–Cu interfaces as a promising platform for designing hydrothermally durable and N₂-selective NH₃-SCO catalysts.

Keywords: high entropy materials; NH₃-SCO; ASC supported catalysts; hydrothermal durability



Academic Editors: Dmitry Yu. Murzin and Nataliya D. Shcherban

Received: 7 July 2026

Revised: 24 July 2026

Accepted: 27 July 2026

Published: 29 July 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

Climate change has become one of the most pressing issues in the world today, prompting countries to establish ambitious emission reduction targets and related laws and regula-

tions. A case in point is the European Commission's target of slashing net greenhouse gas emissions by no less than 55% by 2030, followed by the attainment of net-zero emissions in 2050 [1]. Over 25% of all greenhouse gas emissions are attributable to the transportation sector [2]. Therefore, to reduce emissions, strategies promoting low-emission vehicles have been introduced. This category covers two main types: electric or hybrid vehicles, and vehicles that retain conventional internal combustion engines but operate on low-carbon fuels [3]. Among them, natural gas, which consists primarily of CH_4 , is considered a highly promising clean fuel alternative to traditional gasoline or diesel and has been widely used in the transportation sector, particularly in heavy-duty vehicles and marine applications [4]. It is worth noting that although methane has the highest hydrogen-to-carbon ratio among all hydrocarbons, which significantly reduces CO_2 emissions, increasingly stringent emission regulations still require the use of aftertreatment systems to reduce conventional pollutants such as CO, hydrocarbons (HC), and NO_x . Most natural gas engines today are operated stoichiometrically and are equipped with three-way catalysts (TWCs) to abate CO, HC, and NO_x emissions in the exhaust [5,6]. However, while TWCs control conventional pollutant emissions, they are often accompanied by increased ammonia emissions [7]. Therefore, it is necessary to combine TWCs with ammonia slip catalysts (ASCs) to achieve maximum clean emissions. However, compared with diesel engines, natural gas engines have higher thermal loads, higher exhaust temperatures, and significantly different exhaust compositions and concentrations [8]. Existing diesel ASC systems cannot be directly transplanted into natural gas engine aftertreatment systems, necessitating the development of dedicated ammonia removal catalyst solutions for natural gas engines.

Researchers have developed a range of catalyst types for ASC, such as noble metal-based catalysts [9], non-noble metal oxides [10], modified zeolites [11], and bifunctional catalysts [12]. While Pt-based noble metal catalysts demonstrate excellent low-temperature activity for ammonia oxidation, they are both costly and prone to over-oxidizing NH_3 to NO_x and N_2O , which significantly reduces N_2 selectivity [13,14]. In contrast to noble metals, Cu-based transition metal catalysts are inexpensive and earth-abundant. While they typically cannot achieve complete NH_3 conversion at low temperatures, they deliver excellent N_2 selectivity during the NH_3 -SCR process [15,16]. Bifunctional catalysts pair noble metal components with modified zeolites to boost selectivity via internal selective catalytic reduction (i-SCR). Although this design improves selectivity, it usually sacrifices low-temperature activity. Furthermore, achieving a promotional effect requires precisely tuning the component ratio within a narrow temperature window [17,18], which poses a challenge for meeting emission reduction targets across all vehicle operating conditions. Consequently, a novel strategy rooted in surface atomic engineering has been introduced to tailor the NH_3 -SCR reaction pathway. This approach relies on the construction of dual sites for surface NH_3 activation and subsequent NO_x -SCR. For example, Liu et al. [19] constructed dual active sites of Pt and Cu on Al_2O_3 . By introducing Cu, they enabled NH_3 dehydrogenation assisted by lattice oxygen and surface active oxygen, achieving an effective balance between high activity and high N_2 selectivity at relatively low temperatures. It is worth noting that although the authors tested the long-term stability of the catalyst, they neglected the catalyst performance after hydrothermal aging. Whether the catalyst is suitable for the high-temperature, high-water-content exhaust conditions of natural gas engines remains debatable. Building on this strategy, An et al. [20] confined PtCu bimetallic clusters within a zeolite to construct a polarized $\text{Cu}(\delta^+)$ - $\text{Pt}(\delta^-)$ interface, synergistically enhancing NH_3 adsorption and O_2 activation and thereby markedly improving low-temperature NH_3 -SCO activity and N_2 selectivity. Liu et al. [21] adopted a heteroatom-ensemble design strategy to construct a Cu-Pt₁-Cu heteroatom ensemble, substantially increasing the turnover frequency (TOF) of the reaction.

To suppress the aggregation of noble metals at high temperatures and enhance the thermal stability of catalysts, loading noble metals onto high-entropy oxides has attracted significant attention from researchers in recent years. In a study by Dai et al. [22], Pt was deposited onto a NiCuZnCoO_x support. This approach effectively suppressed the sintering of Pt at elevated temperatures and simultaneously boosted the catalytic performance. The resulting catalyst still exhibited considerable activity after being subjected to heat treatment at 900 °C. Xu et al. [23] further explored this concept by anchoring single atoms onto high-entropy oxides (HEOs). Their investigation revealed that, while the pristine HEO support showed minimal oxidation activity, the introduction of just 1 wt% Pd into the high-entropy lattice led to a dramatic enhancement in catalysis. This effect is credited to the maximal configurational entropy, which benefits both the structural stability and the catalytic function of the material. For context, HEOs are formally defined as oxides comprising five or more metal cations in roughly equimolar proportions [24]. As documented in the literature, the catalytic benefits of HEOs can be ascribed to their unique architecture and multiple high-entropy effects (i.e., the high-entropy, sluggish diffusion, severe lattice distortion, and cocktail effects [25]). These materials not only lower activation barriers and create more surface defects and unsaturated coordination sites, but also impart structural stability. As a result, reactant adsorption–desorption and charge transfer are significantly improved [26,27]. Therefore, high-entropy materials are regarded as highly promising catalysts for the future.

In summary, to address the issues of high-water content and high temperature in natural gas engine exhaust, this work constructed catalysts based on surface atomic engineering and entropy-driven strategies, using high-entropy metal oxides as supports with co-loaded Pt and Cu. The catalytic activity of the prepared catalysts for the NH₃-SCO reaction was evaluated. Furthermore, by tuning the elemental composition of the high-entropy metal oxides and optimizing the crystalline phase structure (via calcination temperature), the low-temperature activity and hydrothermal aging resistance of the catalysts were improved. In addition, various characterization techniques were employed to thoroughly investigate the effects of different elements and crystalline phases of the high-entropy metal oxides on the structural and surface chemical properties of the catalysts. The reaction pathways in the NH₃-SCO reaction over the catalysts were explored using in situ characterization. The experimental results provide new insights for the development of natural gas engine aftertreatment systems and high-entropy catalysts, demonstrating high application value.

2. Results and Discussion

2.1. Structural Characteristics

To ensure the successful preparation of the catalysts, the chemical composition and crystal structure were first characterized by XRD, as shown in Figure 1A. The XRD patterns in Figure 1A reveal that every catalyst sample consists of a cubic fluorite structure, evidenced by prominent diffraction peaks at (111), (200), (220), and (311), with negligible peaks attributable to impurities. This indicates that the five metal cations form a homogeneous single-phase cubic fluorite structure high-entropy solid solution. It is also observed that the diffraction peaks of PtCu/HEO-Sn are slightly shifted to the right, which is due to the substitution of Sn⁴⁺ (with a radius smaller than those of Zr and Sm), causing a systematic shift. Conversely, PtCu/HEO-Sm, composed of Sm with a larger atomic radius, shows a slight leftward shift in the diffraction peaks, indicating lattice expansion [28], further confirming the flexible tunability of the high-entropy structure. With an increase in calcination temperature, the diffraction peaks of the samples become progressively sharper and the full width at half maximum (FWHM) decreases, reflecting enhanced crystallinity when compared to the PtCu/HEO-Zr calcined at 1000 °C. Moreover, a slight but insignificant

leftward shift in the peaks is observed, attributed to lattice expansion caused by the increase in temperature [29]. It is worth noting that no distinct diffraction peaks of Pt and Cu are clearly found in any of the samples, suggesting that Pt and Cu are likely anchored on the support surface as highly dispersed nanoclusters or in an amorphous state. To investigate the molecular vibrations within the catalysts, Raman characterization was performed. As shown in Figure 1B, although the catalysts exhibit a clear cubic fluorite structure in XRD, none of the samples show an obvious F_{2g} symmetric vibration mode peak at $\sim 450\text{ cm}^{-1}$, which is characteristic of the fluorite structure [30]. The observed changes in the peak shape and position can be attributed to the creation of oxygen vacancies and variations in the original Ce–O bond distance. Therefore, the severe lattice distortion of the high-entropy oxide formed by multiple cations leads to a red shift and broadening of this peak, causing it to become submerged. An increase in calcination temperature from $750\text{ }^{\circ}\text{C}$ to $1000\text{ }^{\circ}\text{C}$ leads to a gradual loss of peak intensity and a more pronounced asymmetry. This behavior is driven by symmetry breaking, manifested as severe lattice distortion, which originates from the disordered solid solution of Ce, La, Pr, Sm, and Y cations and the associated changes in phase stability [31]. In addition, broad peaks corresponding to the defect-induced mode (D) and the second-order longitudinal optical mode (2LO) are observed in the regions $500\text{--}800\text{ cm}^{-1}$ and $920\text{--}1200\text{ cm}^{-1}$, respectively. The defect-induced mode (D) is attributed to the defect vibration mode induced by oxygen vacancies, indicating that the high-entropy oxide support is rich in oxygen vacancies, while the second-order longitudinal optical mode (2LO) originates from charge compensation and bonding between $\text{Ce}^{3+}/\text{Ce}^{4+}$ cations and oxygen vacancies [32,33]. Comparing samples calcined at different temperatures, PtCu/HEO-Zr-MT and PtCu/HEO-Zr-LT show broader F_{2g} peaks and more pronounced D peaks, whereas the peaks of PtCu/HEO-Zr become sharper, indicating that high-temperature treatment reduces defect concentration but improves crystallinity. However, the broadening and asymmetry of the peaks further reflect changes in interatomic forces and inhomogeneity in the distribution of oxygen vacancies. The above Raman results clearly reveal the fluorite structure, severe lattice distortion, abundant oxygen vacancies, and multi-cation disordered occupation characteristics of the HEO.

To further determine the structure and elemental distribution of the catalysts, TEM characterization was performed. Figure 1C–E illustrate that all three catalysts exhibit irregular block-like morphologies. Among them, PtCu/HEO-Zr displays irregular pores on its surface, PtCu/HEO-Sm appears relatively intact, and PtCu/HEO-Sn shows an aggregated morphology composed of multiple blocks. The selected area electron diffraction (SAED) pattern of PtCu/HEO-Zr, shown in Figure 1C, exhibits well-defined diffraction rings that can be indexed to the (111), (200), (220), and (311) planes of a cubic fluorite phase. This observation agrees with the XRD data. Notably, the measured interplanar spacing of the (111) plane is 0.3389 nm , which is larger than that of the standard fluorite structure. The crystal planes distances of the remaining planes likewise exceed the reference values, suggesting an expansion of the lattice due to the incorporation of larger cations (La^{3+} , Sm^{3+} , and Y^{3+}) into Ce^{4+} sites. This finding agrees well with the XRD and Raman observations. Furthermore, Figure 1C–E displays the elemental distribution of the catalyst. It can be seen that the Ce, Zr, La, Pr, and Y elements are uniformly distributed without any phase separation. Meanwhile, Pt and Cu are also homogeneously distributed on the catalyst, indicating that Pt and Cu have been successfully loaded without significant agglomeration. Given the similar atomic number and morphology of Pt and Cu, individual Pt and Cu clusters cannot be reliably distinguished by HRTEM/HAADF imaging alone; the EDS mapping therefore provides the primary evidence for their spatial distribution. Combined with the XRD results discussed above—where the characteristic diffraction peaks of Pt and Cu remain weak or undetectable across all five catalysts—Pt and Cu are inferred to

maintain a consistently high degree of dispersion throughout the series, with no substantial variation among the samples.

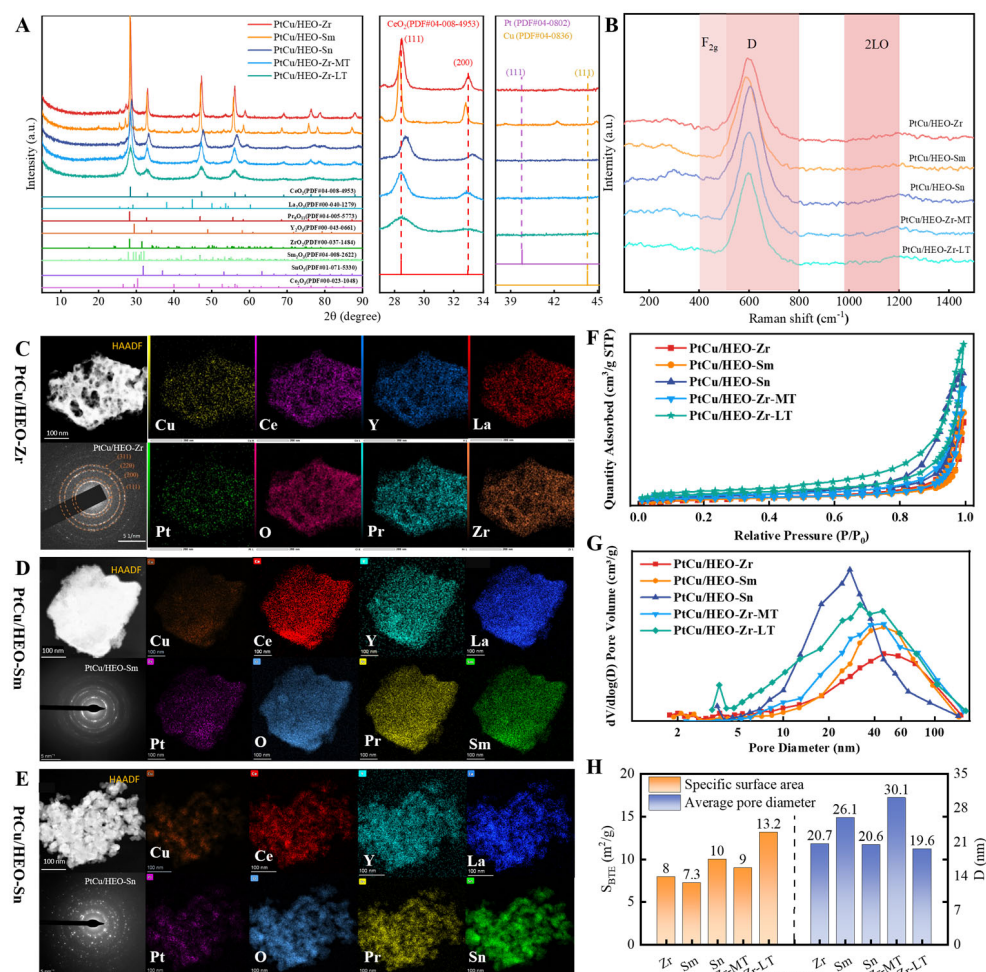


Figure 1. (A) XRD pattern, (B) Raman spectra, (C–E) TEM images, SAED pattern and element mapping of catalysts, (F) N₂ adsorption–desorption isotherms, (G) Average pore size distributions (H) Summary of specific surface area and average pore size.

The N₂ adsorption–desorption isotherms of the five catalysts, as well as their derived pore size distributions, are displayed in Figure 1F,G. All the catalysts are seen to produce typical type IV isotherms with H3-type hysteresis loops, suggesting that the high-entropy oxide materials contain micropores [34,35]. The pore size distributions also reveal that all catalyst samples contain micropores, mesopores, and macropores, but are dominated by mesopores and macropores. Figure 1H lists the pore characteristics and specific surface areas of all samples. Among the catalysts doped with various elements, PtCu/HEO-Sn stands out, delivering the highest specific surface area (10 m²/g), the largest total pore volume (0.065 cm³/g), and the smallest average pore diameter (20.6 nm). This suggests that the introduction of Sn⁴⁺ may inhibit grain agglomeration, thereby maintaining a higher pore volume and possessing smaller sized mesopores. Conversely, PtCu/HEO-Sm exhibited the smallest specific surface area (7.3 m²/g), whereas its average pore diameter was the largest among the samples (26.1 nm). Its total pore volume remained at a moderate level of 0.046 cm³/g. The reason is that the larger ionic radius of Sm³⁺ enhances lattice expansion, leading to an increase in pore size while also promoting grain growth, thus reducing the specific surface area. Furthermore, comparing the catalysts prepared at different calcination temperatures, it can be seen that as the calcination temperature increases from 750 °C to

1000 °C, the specific surface area decreases from 13.2 m²/g to 8 m²/g, indicating that high temperature causes grain sintering and particle growth. Meanwhile, the total pore volume decreases accordingly from 0.079 cm³/g at 750 °C to 0.041 cm³/g at 1000 °C, suggesting pore collapse or blockage. The average pore diameter first increases and then decreases; this may be because some small pores merge into mesopores as the temperature rises, but a further increase in temperature induces sintering, leading to the collapse or blockage of large pore structures [36,37].

2.2. Catalytic Performance

Figure 2 shows the catalytic activity for NH₃ and the N₂ selectivity of the catalysts. Additionally, the activity of the catalysts after hydrothermal aging was also tested. Figure 2A,B show that the NH₃ conversion of catalysts prepared from high-entropy oxides with different elemental compositions exhibits small differences before low temperature (175 °C) and after high temperature (above 250 °C), with the main differences concentrated in the intermediate temperature range. The N₂ selectivity is also relatively close below 175 °C, but the differences gradually increase with rising temperature. Unlike the NH₃ conversion, which increases with temperature, the N₂ selectivity gradually decreases with increasing temperature but remains above 80% throughout. Among them, PtCu/HEO-Zr shows the highest activity, achieving 90% NH₃ conversion and approximately 84% N₂ selectivity at around 260 °C. Compared with other catalysts in Table 1, the catalysts using high-entropy oxides as supports exhibit superior catalytic activity, especially in maintaining high N₂ selectivity. This may be attributed to the multi-element synergy that provides abundant electron donors and acceptors, moderately modifying the d-band center of Pt and inhibiting the excessive dissociation and activation of O₂ on Pt. Meanwhile, the oxygen vacancy defects generated by severe lattice distortion tend to produce N₂ via the hydrazine mechanism or the lattice-oxygen-assisted mechanism, rather than generating NO_x via the imide mechanism. Furthermore, comparing the NH₃ conversion of the other two elemental compositions indicates that doping with Zr is more favorable for enhancing the catalytic activity. Moreover, the three CeZrLaPrY catalytic samples all maintain better N₂ selectivity, even though PtCu/HEO-Zr-LT shows the poorest activity. This is because a higher calcination temperature achieves a true single-phase high-entropy fluorite structure, which is a prerequisite for exerting the high-entropy effect (especially lattice distortion and electronic regulation). This is supported by the XRD and Raman results (Figure 1A,B): the low-temperature calcined samples (PtCu/HEO-Zr-LT and PtCu/HEO-Zr-MT) exhibit broadened diffraction peaks with a larger FWHM, as well as broader Raman F_{2g} peaks and a more pronounced defect-induced (D) mode, indicating incomplete cation homogenization and lower crystallinity relative to PtCu/HEO-Zr. Such a structure approximates a ‘pseudo-high-entropy’ state with insufficient lattice distortion and electronic regulation, resulting in poorer catalytic activity.

Table 1. The physicochemical parameters of samples.

Catalysts	NH ₃ Concentration (ppm)	Oxygen Concentration (%)	T ₉₀ (°C)	N ₂ Sel. (%)	Reference
1.00 wt%Pt/Al ₂ O ₃	200	8	247	50	[18]
Pt/ZSM-5	180	8	250	75	[38]
Pt-Cu/ZSM-5	180	8	245	77	[18]
2.00 wt%Pt/Al ₂ O ₃	600	10	223	74	[19]
1.1 wt%Pt/Nb ₂ O ₅	50	20	250	100	[39]
PtCu/HEO-Zr	500	10	260	84	This work

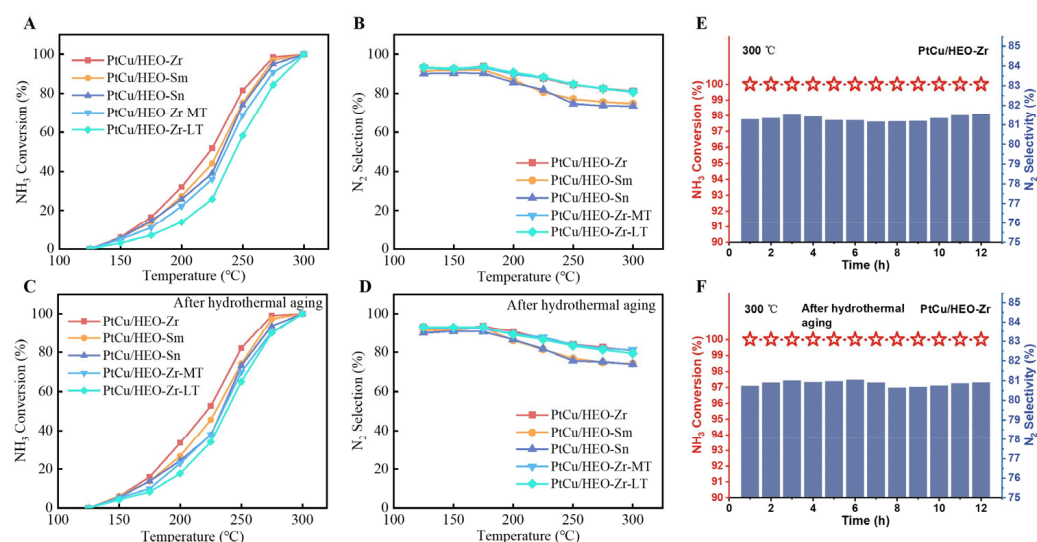


Figure 2. (A) NH₃ conversion and (B) N₂ selectivity of the fresh catalyst, and (C) NH₃ conversion and (D) N₂ selectivity after hydrothermal aging. Test conditions: 500 ppm NH₃, 10 vol% O₂, balanced with N₂, WHSV = 100,000 mL·g^{−1}·h^{−1}. Aging conditions: 800 °C, 10% H₂O, 12 h. Durability testing of PtCu/HEO Zr catalyst in (E) fresh state and (F) after hydrothermal aging.

The aging resistance of the catalysts was further evaluated. As shown in Figure 2C,D, after hydrothermal aging, the catalytic activity is almost unaffected, with only a slight decrease in N₂ selectivity of about 1%. This indicates that the use of high-entropy oxides as supports can significantly improve the stability of the catalysts, which is beneficial for application in real exhaust conditions. And from the durability tests in Figure 2E,F, it can be found that both the catalyst in fresh state and after hydrothermal aging showed excellent performance in the 12 h durability test. The conversion rate of NH₃ was almost maintained at 100% throughout the process, and the selectivity of N₂ changed very little, with the fresh state remaining above 81.2% and the sample after hydrothermal aging also maintaining above 80.7%. The above results indicate that the high entropy oxide supported Pt-Cu catalyst has excellent aging resistance and stability.

2.3. Chemical State Characterization

To further investigate the mechanism influencing catalyst performance, the surface chemical states of the catalysts were characterized. Figure 3A displays the H₂-TPR patterns of the samples. All catalysts display a prominent reduction feature in the 200–300 °C region, attributable to the consumption of surface oxygen [40]. Among them, PtCu/HEO-Zr (doped with Zr) shows the lowest reduction temperature, indicating that it possesses the largest amount of chemisorbed oxygen species and that the generation of active oxygen species on the PtCu/HEO-Zr surface is easier than on the other samples. Furthermore, a relatively distinct reduction peak appears below 200 °C specifically in the three Zr-containing catalysts, but not in PtCu/HEO-Sm or PtCu/HEO-Sn, despite comparable Pt loading across all samples. We attribute this to Pt-support synergy: spillover hydrogen from Pt sites reduces the more mobile lattice oxygen near the Zr-doped supports, consistent with their lower O₂-TPD desorption temperatures (Figure 3B) relative to the Sm- and Sn-doped samples. Platinum migration/redispersion, an alternative mechanism reported in the literature, cannot be entirely ruled out [41].

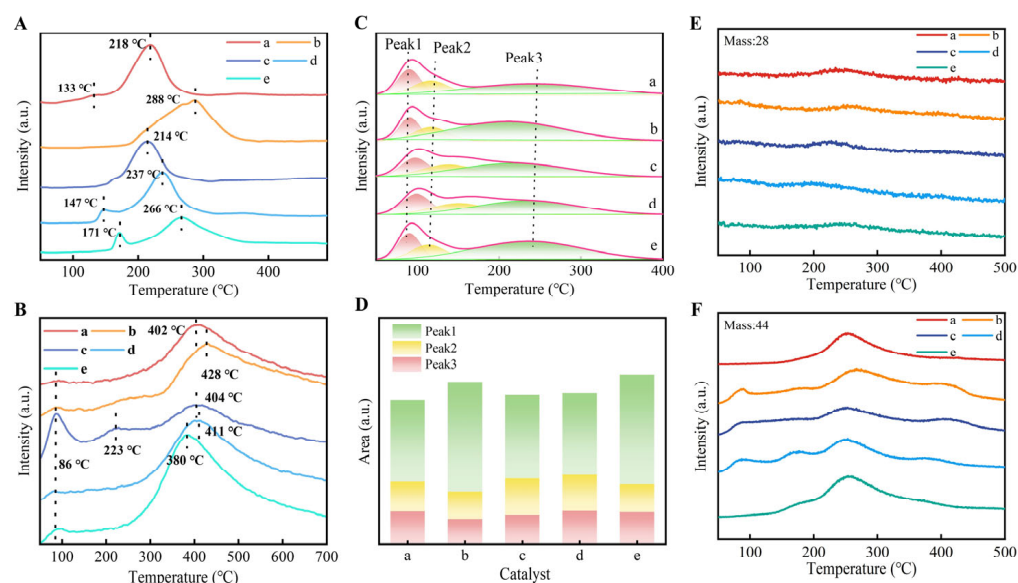


Figure 3. (A) H_2 -TPR, (B) O_2 -TPD, (C) NH_3 -TPD, (D) The proportion of each fitted peak in NH_3 -TPD, (E) The desorption curve of N_2 in NH_3 -TPD, (F) The desorption curve of N_2O in NH_3 -TPD. (a. PtCu/HEO-Zr, b. PtCu/HEO-Sm, c. PtCu/HEO-Sn, d. PtCu/HEO-Zr-MT, e. PtCu/HEO-Zr-LT.).

The O_2 -TPD profiles of the catalysts are presented in Figure 3B. The peak appearing below $300\text{ }^\circ\text{C}$ is assignable to the desorption of weakly bound oxygen (O_2 , O_2^-), whereas the signal located between 300 and $600\text{ }^\circ\text{C}$ corresponds to the release of chemisorbed oxygen species (O^-) [42]. The figure shows that the desorption curves of all catalysts in the range of 100 – $300\text{ }^\circ\text{C}$ are similar, except that PtCu/HEO-Sn exhibits a relatively distinct peak at around $223\text{ }^\circ\text{C}$, which may be related to the active oxygen generated at the Pt-HEO interface and its larger specific surface area [43]. In the range of 300 – $600\text{ }^\circ\text{C}$, compared with the other two catalysts, the three catalysts doped with Zr ions show lower desorption peak temperatures, indicating that their active oxygen species have higher mobility, and this enhanced activity of surface lattice oxygen may be the reason for their higher N_2 selectivity. Moreover, the desorption peak area expanded markedly with rising calcination temperature. This expansion is attributed to the enhanced structural stability of the high-entropy oxide [44], which in turn suppresses the release of lattice oxygen.

Figure 3C shows the NH_3 -TPD results of the catalysts. It can be seen from the figure that the NH_3 desorption peaks can be roughly divided into two parts: the peak at around $200\text{ }^\circ\text{C}$ can be attributed to the desorption of physically adsorbed NH_3 and weakly adsorbed NH_3 , while the peak in the range of 200 – $400\text{ }^\circ\text{C}$ can be attributed to the desorption of strongly adsorbed NH_3 . Generally, catalysts with more NH_3 adsorption sites and a greater proportion of weakly adsorbed NH_3 exhibit higher activity in low-temperature SCR reactions, and this also applies to NH_3 -SCO. Therefore, to more intuitively compare the content of NH_3 adsorption sites in each catalyst, the desorption peaks were fitted and the areas of the fitted peaks were compared, as shown in Figure 3D [45]. PtCu/HEO-Zr-LT exhibited the poorest catalytic performance among the samples. However, it contained the most abundant NH_3 adsorption sites overall, although the relative amount of weakly adsorbed NH_3 was the smallest. PtCu/HEO-Zr, which shows the highest activity, has the lowest total content of NH_3 adsorption sites but a relatively higher proportion of weakly adsorbed NH_3 and a lower desorption temperature for this species. PtCu/HEO-Zr-MT has the highest proportion of weakly adsorbed NH_3 , but its desorption temperature is relatively higher. Furthermore, among the three catalysts doped with Zr ions, the desorption peak temperature of strongly adsorbed NH_3 is higher than that of the other two high-entropy oxides. This indicates that in the NH_3 -SCO reaction, with an appropriate

ratio of weakly adsorbed NH_3 to strongly adsorbed NH_3 , a lower desorption temperature for the weakly adsorbed species and a moderately high desorption temperature (250–350 °C) for the strongly adsorbed species are most conducive to the high-selectivity conversion of NH_3 to N_2 . Furthermore, the desorption curves of N_2 and N_2O in the NH_3 -TPD are shown in Figure 3E,F. It can be observed that the N_2 desorption peak area of PtCu/HEO-Zr is significantly larger than those of the other catalysts, indicating that more adsorbed NH_3 is selectively converted into N_2 during the temperature-programmed process. This directly reflects the higher catalytic activity and selectivity of this catalyst for the oxidation of NH_3 to N_2 . Additionally, a distinct desorption peak of N_2O appears below 200 °C. Since N_2O is a typical byproduct of NH_3 oxidation, usually originating from incomplete oxidation or incomplete conversion of intermediates, this result demonstrates that PtCu/HEO-Zr can selectively convert NH_3 to N_2 with little involvement of the N_2O byproduct pathway, highlighting its excellent low-temperature reaction pathway control capability and high N_2 selectivity.

To determine the surface chemical states of Ce, O, La, Y and Pt, XPS analysis was conducted, and the results are presented in Figure 4. Figure 4J summarizes the relative amounts of the different chemical species. From Figure 4A, it is evident that the Ce 3d spectra of the catalysts exhibit ten peaks corresponding to the Ce 3d_{5/2} and Ce 3d_{3/2} levels. Among them, two spin-orbit doublets labeled u', v' and u₀, v₀ are assigned to Ce³⁺, while the other two doublets labeled u''', v''', u'', v'', and u, v are assigned to Ce⁴⁺ [46]. It can be seen that Ce⁴⁺ is the dominant oxidation state in the catalysts. From Figure 4J, it is found that PtCu/HEO-Zr has the highest proportion of Ce³⁺ (17.0%), while the Ce³⁺ proportions in the other catalysts are similar. This difference may be related to the formation of oxygen vacancies and electron transfer between the noble metal Pt and the Ce species. Figure 4B shows the O 1s spectra, which were also fitted with three peaks. The peak labeled O_{lat} corresponds to lattice oxygen in CeO₂, the peak labeled O_{ads} corresponds to surface adsorbed oxygen, and the peak labeled O_{OH} is assigned to adsorbed molecular water or surface hydroxyl (OH) species [47]. Figure 4J summarizes the O_{ads}/O_{lat} ratio for each catalyst. PtCu/HEO-Zr exhibits the highest O_{ads}/O_{lat} ratio, which is more favorable for low-temperature NH_3 oxidation, while PtCu/HEO-Zr-LT shows the smallest O_{ads}/O_{lat} ratio, consistent with the O₂-TPD results. Figure 4C shows the XPS spectrum of Y 3d, in which two peaks corresponding to 3d_{5/2} and 3d_{3/2} are clearly observed. This spin-orbit coupling of Y³⁺ indicates the successful incorporation of Y element [48]. Figure 4D displays the XPS spectrum of La 3d, where clearly separated spin-orbit splitting peaks can be observed, corresponding to the 3d_{5/2} and 3d_{3/2} spin-orbit components, respectively, indicating the formation of La-O bonds on the catalyst surface [49].

Figure 4E shows the Pt 4d spectra, where three fitted peaks correspond to Pt⁴⁺, Pt²⁺, and Pt⁰ [19], respectively, indicating that Pt exists mainly as metallic Pt as well as Pt²⁺ and Pt⁴⁺ species on the catalysts. Figure 4J shows that the PtCu/HEO-Zr catalyst has the lowest Pt⁰/Pt_{sum} ratio, while the PtCu/HEO-Zr-LT catalyst has the highest Pt⁰/Pt_{sum} ratio; this ratio decreases with increasing calcination temperature. However, the Pt⁰/Pt_{sum} ratio of the PtCu/HEO-Sm catalyst still reaches 57.0%. It should be noted that the NH_3 -SCO reaction is governed by a complex interplay of multiple factors—including surface defect concentration, oxygen adsorption/dissociation, NH_3 adsorption, and dehydrogenation/activation behavior—of which the Pt oxidation state is only one contributing factor rather than the sole determinant. Indeed, the Pt⁰/Pt_{sum} ratio of PtCu/HEO-Zr, although the lowest among the catalysts, remains around 50%, a relatively high proportion capable of providing substantial catalytic promotion in its own right. Ce is also known to play a major role in Pt-group-metal-containing systems, sometimes comparable to or interacting with the effect of Pt oxidation state [50]. PtCu/HEO-Zr possesses the highest Ce³⁺ proportion

among the five catalysts, which, combined with the higher lattice oxygen mobility of the Zr-doped catalysts established from the O₂-TPD results above, may act synergistically to promote activity alongside the contribution from Pt oxidation state.

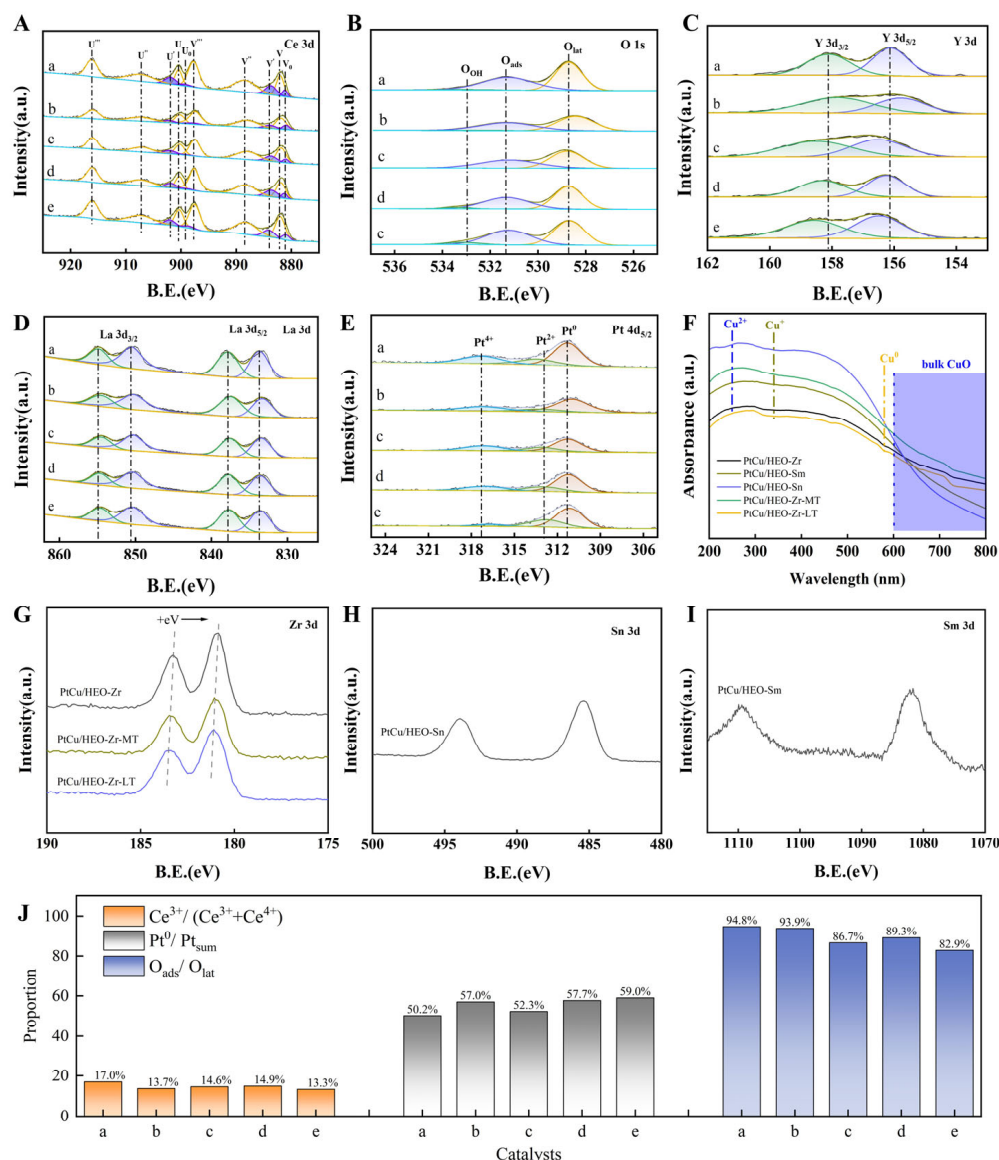


Figure 4. (A) Ce 3d, (B) O 1s, (C) Y 3d, (D) La 3d, (E) Pt 4d results of catalysts: a. PtCu/HEO-Zr, b. PtCu/HEO-Sm, c. PtCu/HEO-Sn, d. PtCu/HEO-Zr-MT, e. PtCu/HEO-Zr-LT, and (F) DR-UV-vis spectra of the catalysts, (G) Zr 3d, (H) Sn 3d, (I) Sm 3d results of catalysts, (J) The percentage content of the different chemical species.

Since the Cu XPS signals overlap with the Pr 3d signals, DR-UV-Vis spectroscopy was employed as an alternative technique for Cu species identification, and the obtained spectra are displayed in Figure 4F. The band at 240 nm corresponds to the ligand-to-metal charge transfer of Cu²⁺ ions, while the broad absorption in the 600–800 nm region originates from d–d transitions of Cu²⁺ in bulk CuO. The peak around 580 nm is assigned to Cu⁰. Moreover, an interband absorption band of Cu⁺ in the range of 300–400 nm is also detected [51,52], which is attributed to electron transfer with CeO₂. It is also found that the content of bulk CuO on the Zr-doped high-entropy oxide is relatively high, which may be the reason for its higher N₂ selectivity. In Figure 4, the Zr, Sm, and Sn species on the catalysts were also measured. Zr mainly exists in an oxidized state, and with increasing calcination temperature, the binding energy of Zr 3d in the PtCu/HEO-Zr catalyst gradually decreases.

This can be ascribed to high temperature promotes the formation of a uniform single-phase high-entropy fluorite structure. Meanwhile, the high-temperature treatment induces an optimized distribution of oxygen vacancies and boosts the electronic interaction between the PtCu alloy and the support, both of which contribute to a higher electron density around the Zr atoms [44]. This corroborates the structural evolution and electronic property regulation of the high-entropy support at high temperatures.

2.4. Catalytic Mechanism

To probe the reaction pathways and intermediates of NH_3 -SCO, in situ DRIFTS experiments were performed on the catalysts, as presented in Figure 5. On all three catalysts at 125 °C, signals corresponding to gaseous NH_3 ($\sim 3334\text{ cm}^{-1}$) and coordinated NH_3 on Lewis acid sites ($\sim 1282\text{ cm}^{-1}$ and a broad $3000\text{--}3600\text{ cm}^{-1}$ band) [53] [19] are observed, yet they are less intense than the bands of Brønsted-acid-bound NH_4^+ ($\sim 1622\text{ cm}^{-1}$ and 1434 cm^{-1}) [54,55]. Moreover, all these peaks are the highest on the PtCu/HEO-Zr catalyst, indicating that PtCu/HEO-Zr possesses the most abundant surface acid sites (especially Brønsted acid sites), which favor the stable adsorption of NH_3 as NH_4^+ . Meanwhile, a peak attributed to $-\text{NH}_2$ species (1560 cm^{-1}) [45,56] appears on all three catalysts, and again it is highest on PtCu/HEO-Zr, suggesting that $-\text{NH}_2$ is a key intermediate in NH_3 dehydrogenation and that PtCu/HEO-Zr exhibits the strongest dehydrogenation activity. A peak corresponding to the $\text{N}_2\text{O}_2^{2-}$ species (1363 cm^{-1}) [19], related to peroxyxynitrite or dioxygen anion intermediates, is observed only on PtCu/HEO-Zr and PtCu/HEO-Sn, and it is weak. According to the literature, $\text{N}_2\text{O}_2^{2-}$ is the core intermediate for the selective conversion of NH_3 to N_2 . Combined with the catalytic activity results, it is likely that PtCu/HEO-Zr already possesses such high reaction activity at low temperatures that the generated $\text{N}_2\text{O}_2^{2-}$ is rapidly consumed and converted into N_2 , resulting in a very low steady-state concentration. In addition, no peaks attributable to partially positively charged NO_2 species (2232 cm^{-1}) or adsorbed N_2O species (2200 cm^{-1}) [51,57] are observed on any of the three catalysts. However, a peak due to NO species (1725 cm^{-1}) [58] is present on all three catalysts with similar intensities.

As the temperature gradually increases, the peak intensity of gaseous NH_3 changes little. The peak at approximately 1282 cm^{-1} , assigned to coordinated NH_3 on Lewis acid sites, gradually decreases. The broad band at $3000\text{--}3600\text{ cm}^{-1}$ on PtCu/HEO-Zr increases with temperature, whereas on the other two catalysts it gradually decreases, especially on PtCu/HEO-Sn. This is likely because PtCu/HEO-Zr possesses the highest Ce^{3+} proportion and oxygen vacancy concentration, allowing water generated from the reaction to dissociate at oxygen vacancies to form $-\text{OH}$ groups. The peaks of ionic NH_4^+ associated with Brønsted acid sites on the three catalysts gradually decrease with temperature. The peak attributed to $-\text{NH}_2$ species decreases with temperature on PtCu/HEO-Zr and PtCu/HEO-Sm, but on PtCu/HEO-Sn it first increases and then decreases. This may be due to slower initial dehydrogenation on PtCu/HEO-Sn, leading to accumulation of $-\text{NH}_2$; as the temperature rises, the reaction accelerates and the peak then begins to decline. The peak assigned to $\text{N}_2\text{O}_2^{2-}$ species (1363 cm^{-1}), related to peroxyxynitrite or dioxygen anion intermediates, appears on PtCu/HEO-Zr after the temperature increases and then gradually increases on all three catalysts. Meanwhile, the peaks assigned to partially positively charged NO_2 species (2232 cm^{-1}) and adsorbed N_2O species (2200 cm^{-1}) gradually increase with temperature on all three catalysts. The peak assigned to NO species (1725 cm^{-1}) shows little difference over the entire temperature range.

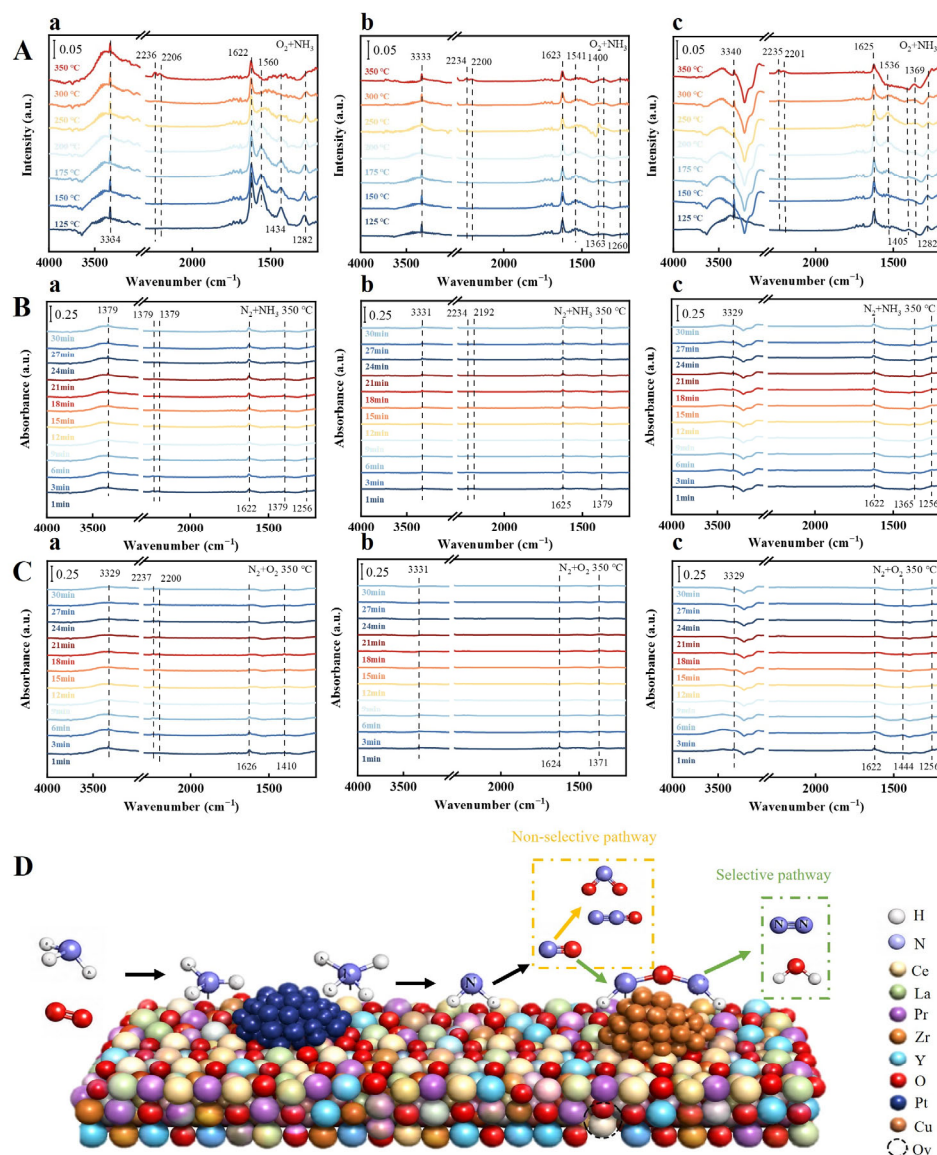


Figure 5. In situ DRIFTS results of (A) reaction between NH_3 and O_2 , (B) NH_3 adsorption at 350°C , (C) Pre-adsorbed NH_3 and O_2 react at 350°C and (D) Schematic diagram of NH_3 -SCO reaction pathway. (a) PtCu/HEO-Zr, (b) PtCu/HEO-Sm and (c) PtCu/HEO-Sn catalysts.

Figure 5B shows the in situ DRIFTS results of the three catalysts at 350°C under only NH_3 flow. All three catalysts exhibit adsorption of gaseous NH_3 and coordinated NH_3 , as well as peaks of NH_4^+ bound to Brønsted acid sites. Among them, the peak of gaseous NH_3 is the highest, and its intensity is even higher on the surface of PtCu/HEO-Zr, indicating that PtCu/HEO-Zr is more favorable for the adsorption of NH_3 species, thereby promoting the reaction. As time increases, these peaks show little change, suggesting that at relatively high temperatures, chemically adsorbed NH_3 species can hardly exist stably on the catalyst surface. In addition, the presence of $\text{N}_2\text{O}_2^{2-}$ species is observed, indicating that $\text{N}_2\text{O}_2^{2-}$ can still be formed even under the action of lattice oxygen. Upon introduction of O_2 , the adsorbed NH_3 and NH_4^+ species gradually convert to N_2 via $\text{N}_2\text{O}_2^{2-}$, or are further oxidized to N_2O and NO_2 via $-\text{NH}_2$ intermediates, as shown in Figure 5C. However, no obvious peak of $-\text{NH}_2$ species is observed in the spectra, which may be due to its rapid conversion rate, making it unstable on the catalyst surface.

The above analysis indicates that the NH_3 -SCO reaction over the PtCu/HEO catalysts follows the lattice oxygen (O_{lat})-assisted i-SCR mechanism, which mainly proceeds via two pathways, as shown in Figure 5D. The first is the selective pathway: NH_3 is first adsorbed

on Lewis or Brønsted acid sites and partially dehydrogenated to form $-\text{NH}_2$ species; these then combine with adjacent lattice oxygen (O_{lat}) or reactive oxygen species to generate $\text{N}_2\text{O}_2^{2-}$, which further decomposes into N_2 and H_2O , simultaneously creating oxygen vacancies. The second is the non-selective pathway: NH_3 or reaction intermediates are over-oxidized by strongly oxidizing adsorbed oxygen to form by-products such as NO , NO_2 , and N_2O . As the temperature increases, the contribution of the non-selective pathway gradually rises, leading to a slow decrease in N_2 selectivity. The doping of Zr optimizes the oxygen vacancy concentration, lattice oxygen mobility, surface acidity, and the abundance of Cu^{2+} sites. As a result, NH_3 is rapidly adsorbed and dehydrogenated to $-\text{NH}_2$ at low temperatures, which is subsequently converted efficiently into the $\text{N}_2\text{O}_2^{2-}$ intermediate, achieving both high activity and high N_2 selectivity.

3. Materials and Methods

3.1. Catalyst Preparation

All chemical reagents were used as received without further purification. Citric acid (anhydrous), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99.5\%$), $\text{ZrO}(\text{NO}_3)_2$ ($\geq 99.5\%$), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99.9\%$), $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99.9\%$), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99.5\%$), $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\geq 99.9\%$), SnCl_4 ($\geq 99\%$), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ($\geq 99\%$), and $\text{Pt}(\text{NO}_3)_4$ (Pt, 18.02 wt%) were purchased from Aladdin company (Shanghai, China). Deionized water was prepared in-house and used throughout the experiments.

Figure 6A shows the preparation process of the catalyst. The preparation process mainly consists of two steps. Firstly, the preparation of HEO support, and finally, the loading of Pt and Cu. Preparation of high-entropy oxides: First, 57.636 g of citric acid was dissolved in 86.454 g of deionized water to prepare a 40 wt% citric acid aqueous solution. Then, 0.02 mol of each metal precursor, namely $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, were mixed at a metal-to-citric acid molar ratio of 1:4. After mixing the solution, ammonia water was added dropwise to adjust the pH to 4–5 (<60 mL). The mixture was continuously stirred at room temperature until a transparent sol formed. The solution was then transferred to a water bath at 60–80 °C, heated, and stirred to evaporate the solvent until a viscous gel (with no flowing liquid) formed. The gel was dried in an oven at 120 °C for 24 h to obtain a xerogel. The xerogel was successively calcined at 400 °C for 2 h and then at 1000 °C for 2 h, followed by grinding to obtain CeZrLaPrYO_x powder. In addition, to compare the effects of different crystalline phase structures on catalyst performance, CeZrLaPrYO_x powder was also prepared by calcining at 900 °C and 750 °C instead of 1000 °C. The preparation methods for CeSmLaPrYO_x and CeSnLaPrYO_x were similar to the above, except that $\text{ZrO}(\text{NO}_3)_2$ was replaced with $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and SnCl_4 , respectively.

Loading of Pt and Cu: The incipient wetness impregnation method was used to load Pt and Cu. First, a certain amount of $\text{Pt}(\text{NO}_3)_4$ (0.7 wt%) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.7 wt%) was dissolved in deionized water. After mixing uniformly, a certain amount of high-entropy oxide powder was impregnated into this solution. After impregnation for 12 h, the support was placed in a drying oven at 80 °C for drying. Subsequently, it was calcined in a muffle furnace at 700 °C for 7 h to obtain the corresponding catalyst.

The catalysts prepared by loading Pt and Cu onto different high-entropy oxides, namely CeZrLaPrYO_x , CeSmLaPrYO_x , and CeSnLaPrYO_x , are denoted as PtCu/HEO-Zr, PtCu/HEO-Sm, and PtCu/HEO-Sn, respectively. The catalysts prepared by loading Pt and Cu onto CeZrLaPrYO_x calcined at 900 °C and 750 °C are denoted as PtCu/HEO-Zr-MT and PtCu/HEO-Zr-LT, respectively.

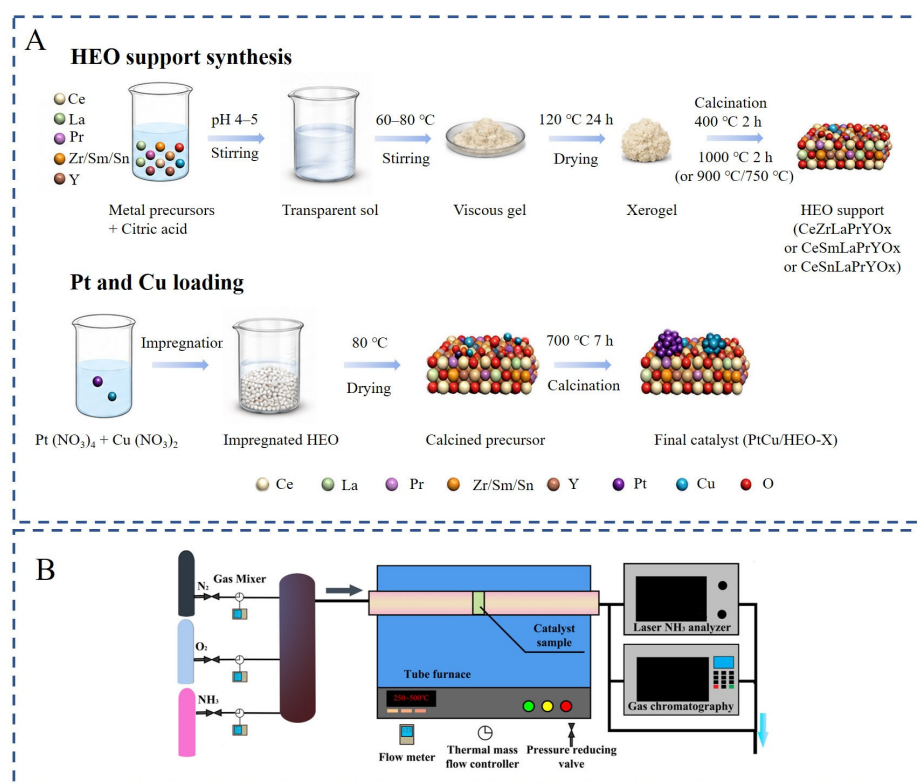


Figure 6. (A) Schematic diagram of catalyst preparation process and (B) ASC catalyst NH₃-SCO performance evaluation device.

3.2. Catalyst Characterizations

The structure and chemical state of the catalyst were systematically characterized using various techniques. Please refer to the Supplementary Materials for detailed procedures.

3.3. Catalytic Performance Evaluation

The continuous NH₃-SCO performance of the catalyst was assessed using a custom-built evaluation apparatus. As illustrated in Figure 6B, the apparatus comprised a gas distribution unit, a reaction unit, and a gas analysis unit. For each test, 0.24 g of the catalyst sample (sieved to 40–60 mesh) was loaded into the reactor. A feed gas containing 500 ppm NH₃ and 10 vol% O₂ balanced with N₂ was introduced at a total flow rate of 400 mL/min, corresponding to a WHSV of 100,000 mL·g^{−1}·h^{−1}. Prior to data collection, the catalyst was activated at 200 °C for 30 min under the reaction atmosphere to remove surface-adsorbed species and establish a stable catalytic state. During the reaction, the effluent gas was allowed to stabilize at each target temperature for 20 min before being analyzed with a laser NH₃ analyzer and an Agilent gas chromatograph (GC). The ammonia conversion and N₂ selectivity were calculated according to the equations below:

$$\text{Con}_{\text{NH}_3} = \frac{C(\text{NH}_3\text{--In}) - C(\text{NH}_3\text{--Out})}{C(\text{NH}_3\text{--In})} \times 100\% \quad (1)$$

$$\text{S}_{\text{N}_2} = \frac{2C(\text{N}_2)}{C(\text{NH}_3\text{--In}) - C(\text{NH}_3\text{--Out})} \times 100\% \quad (2)$$

where $C(\text{NH}_3\text{--In})$ is the NH₃ concentration at the reactor inlet, $C(\text{NH}_3\text{--Out})$ is the NH₃ concentration at the reactor outlet, $C(\text{N}_2)$ is the N₂ concentration difference at the inlet and outlet of the reactor.

In addition, to simulate the atmospheric conditions of high temperature and high-water vapor content in actual natural gas engine exhaust, the fresh catalyst was aged for 7 h in an atmosphere with 10 vol% H₂O/N₂ water content at 800 °C.

4. Conclusions

In this study, high-entropy oxides doped with different elements were successfully prepared by a sol–gel method, and Pt and Cu were successfully loaded onto them. Benefiting from the synergistic effect of Pt and Cu as well as the unique structure and high-entropy effect of the high-entropy oxides, the catalysts not only achieved high activity in the NH₃-SCO reaction but also consistently maintained a N₂ selectivity above 80%. Moreover, they exhibited excellent hydrothermal aging resistance, providing a natural advantage for adapting to natural gas engine aftertreatment systems. Among the prepared high-entropy oxides, compared with Sm and Sn doping, Zr doping optimized the oxygen vacancy concentration, lattice oxygen mobility, surface acidity, and Cu²⁺ sites, thus leading to higher catalytic activity. In situ DRIFTS analysis revealed that the reaction over the PtCu/HEO catalysts proceeds mainly via two pathways. One is the selective pathway: NH₃ is first adsorbed on Lewis or Brønsted acid sites and partially dehydrogenated to form –NH₂ species, which then combine with adjacent lattice oxygen (O_{lat}) or reactive oxygen species to generate N₂O₂² species. Subsequently, the N₂O₂² intermediates undergo further transformation involving lattice oxygen species, leading to N₂ formation while simultaneously creating oxygen vacancies. The other is the non-selective pathway: NH₃ or intermediates are over-oxidized by strongly oxidizing adsorbed oxygen to form by-products such as NO, NO₂, and N₂O.

In summary, this study reports that the high-entropy-oxide-supported noble metal catalyst PtCu/HEO-Zr can significantly enhance the N₂ selectivity of NH₃-SCO and exhibits good hydrothermal aging resistance, providing a new strategy for ASCs aimed at efficiently reducing NH₃ emissions from natural gas engines.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16080689/s1>. Experimental details (XRD, TEM, N₂ adsorption desorption, XPS, UV–vis, H₂-TPR O₂-TPD, NH₃-TPD, Raman spectra, in situ DRIFTS).

Author Contributions: Conceptualization, H.C. and Z.J.; methodology, Z.B., Y.Z. and H.C.; software, Z.B. and Y.Z.; validation, P.Z., D.L. and H.G.; formal analysis, P.Z., L.Z. and H.G.; investigation, H.C., Z.B. and Z.L.; resources, H.C., P.Z. and Z.L.; data curation, Z.B. and Y.Z.; writing—original draft preparation, Z.B., Y.Z. and H.C.; writing—review and editing, Z.J., Z.C. and L.Z.; supervision, D.L., Z.C. and H.G.; funding acquisition, H.C., P.Z. and Z.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by (1) National Natural Science Foundation of China (Program No. 22272010); (2) Ningbo Key Research and Development Program (2024Z250).

Data Availability Statement: Our data can only be obtained by contacting us by email.

Conflicts of Interest: Author Zhenguo Li was employed by China Automotive Technology & Research Center Co., Ltd. Authors Han Gao and Lei Zhu were employed by China Coal Energy Research Institute Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Publications Office of the European Union. *The European Parliament and the Council of the European Union: Regulation (EU) No 2019/63*; Publications Office of the European Union: Luxembourg, 2019.
2. International Energy Agency. *Greenhouse Gas Emissions from Energy: Overview*; International Energy Agency: Paris, France, 2021.

3. Prati, M.V.; Costagliola, M.A. Real driving emissions of Euro 6 electric/gasoline hybrid and natural gas vehicles. *Transp. Res. Part D. Transp. Environ.* **2022**, *113*, 103509. [\[CrossRef\]](#)
4. Sharafian, A.; Blomerus, P.; Mérida, W. Natural gas as a ship fuel: Assessment of greenhouse gas and air pollutant reduction potential. *Energy Policy* **2019**, *131*, 332–346. [\[CrossRef\]](#)
5. Lott, P.; Deutschmann, O. Lean-Burn Natural Gas Engines: Challenges and Concepts for an Efficient Exhaust Gas Aftertreatment System. *Emiss. Control Sci. Technol.* **2021**, *7*, 1–6. [\[CrossRef\]](#)
6. Schmitt, S.; Schwarz, S.; Ruwe, L.; Horstmann, J.; Sabath, F.; Maier, L.; Deutschmann, O.; Kohse-Höinghaus, K. Homogeneous conversion of NO_x and NH₃ with CH₄, CO, and C₂H₄ at the diluted conditions of exhaust-gases of lean operated natural gas engines. *Int. J. Chem. Kinet.* **2021**, *53*, 213–229. [\[CrossRef\]](#)
7. Wang, C.; Tan, J.; Harle, G.; Gong, H.; Xia, W.; Zheng, T.; Yang, D.; Ge, Y.; Zhao, Y. Ammonia Formation over Pd/Rh Three-Way Catalysts during Lean-to-Rich Fluctuations: The Effect of the Catalyst Aging, Exhaust Temperature, Lambda, and Duration in Rich Conditions. *Environ. Sci. Technol.* **2019**, *53*, 12621–12628. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Liu, K.; Pei, Z.; Deng, B.; Yang, J.; Li, Y. Experimental study on transient emissions characteristics of a heavy duty natural gas engine under world harmonized transient cycle. *Case Stud. Therm. Eng.* **2022**, *38*, 102377. [\[CrossRef\]](#)
9. Ji, Z.; Xie, S.; Chen, H.; Zhang, P.; Luo, D.; Chai, Y.; Wang, Z. Study on improving NH₃ oxidation reaction performance of Pt/Al₂O₃ supported catalysts through optimization of porous structures. *Appl. Catal. A Gen.* **2026**, *709*, 120663. [\[CrossRef\]](#)
10. Tian, Y.; Han, Z.; Wu, X.; Zhao, H.; Zeng, Q.; Li, Y.; Ma, D. Sn modulation function on active intermediate species for enhancing NH₃-SCO performance of Cu/Ce_{0.3}TiO_x catalyst. *J. Energy Inst.* **2025**, *119*, 101976. [\[CrossRef\]](#)
11. Wang, H.; Zhang, R.; Liu, Y.; Li, P.; Chen, H.; Wang, F.R.; Teoh, W.Y. Selective catalytic oxidation of ammonia over nano Cu/zeolites with different topologies. *Environ. Sci. Nano* **2020**, *7*, 1399–1414. [\[CrossRef\]](#)
12. Wang, H.; Lin, M.; Murayama, T.; Feng, S.; Haruta, M.; Miura, H.; Shishido, T. Selective catalytic oxidation of ammonia to nitrogen over zeolite-supported Pt-Au catalysts: Effects of alloy formation and acid sites. *J. Catal.* **2021**, *402*, 101–113. [\[CrossRef\]](#)
13. Ma, H.; Schneider, W.F. DFT and microkinetic comparison of Pt, Pd and Rh-catalyzed ammonia oxidation. *J. Catal.* **2020**, *383*, 322–330. [\[CrossRef\]](#)
14. Ghosh, R.S.; Dhillon, P.S.; Harold, M.P.; Wang, D. Kinetics of NH₃ oxidation on Pt/Al₂O₃: Rate enhancement and NH₃ inhibition. *Chem. Eng. J.* **2021**, *417*, 128273. [\[CrossRef\]](#)
15. Jabłońska, M.; Palkovits, R. Copper based catalysts for the selective ammonia oxidation into nitrogen and water vapour—Recent trends and open challenges. *Appl. Catal. B Environ.* **2016**, *181*, 332–351. [\[CrossRef\]](#)
16. Liu, L.; Su, S.; Chen, D.; Shu, T.; Zheng, X.; Yu, J.; Feng, Y.; Wang, Y.; Hu, S.; Xiang, J. Highly efficient NH₃-SCR of NO_x over MnFeW/Ti catalyst at low temperature: SO₂ tolerance and reaction mechanism. *Fuel* **2022**, *307*, 121805. [\[CrossRef\]](#)
17. Shrestha, S.; Harold, M.P.; Kamasamudram, K.; Yezerets, A. Selective oxidation of ammonia on mixed and dual-layer Fe-ZSM-5+Pt/Al₂O₃ monolithic catalysts. *Catal. Today* **2014**, *231*, 105–115. [\[CrossRef\]](#)
18. Sun, M.; Wang, S.; Li, Y.; Wang, Q.; Xu, H.; Chen, Y. Promotion of catalytic performance by adding Cu into Pt/ZSM-5 catalyst for selective catalytic oxidation of ammonia. *J. Taiwan Inst. Chem. Eng.* **2017**, *78*, 401–408. [\[CrossRef\]](#)
19. Liu, Y.; Liu, Z.; Wang, C.; Xu, J.; Ai, J.; Liu, X.; Zhang, A.; Zhao, Y.; Du, C.; Shan, B. Unraveling the Lattice O Assisted Internal Selective Catalytic Reduction Mechanism on High N₂ Selectivity of CuO_x/PtCu Catalysts in NH₃-SCO. *ACS Catal.* **2023**, *13*, 7178–7188. [\[CrossRef\]](#)
20. Wang, H.; Xu, R.; Jin, Y.; Zhang, R. Zeolite structure effects on Cu active center, SCR performance and stability of Cu-zeolite catalysts. *Catal. Today* **2019**, *327*, 295–307. [\[CrossRef\]](#)
21. Liu, Y.-F.; Liu, Z.; Yu, Y.; Du, C.; Xu, J.; Dun, Y.; Wang, C.; Zhao, Y.; Zhang, A.; Liu, F.; et al. Unlocking the Potential of Isolated Pt Atoms for NH₃-SCO Reactions via Modulating Orbital Coupling in Heteroatom Ensembles. *ACS Catal.* **2025**, *15*, 10531–10541. [\[CrossRef\]](#)
22. Chen, H.; Fu, J.; Zhang, P.; Peng, H.; Abney, C.W.; Jie, K.; Liu, X.; Chi, M.; Dai, S. Entropy-stabilized metal oxide solid solutions as CO oxidation catalysts with high-temperature stability. *J. Mater. Chem. A* **2018**, *6*, 11129–11133. [\[CrossRef\]](#)
23. Xu, H.; Zhang, Z.; Liu, J.; Do-Thanh, C.-L.; Chen, H.; Xu, S.; Lin, Q.; Jiao, Y.; Wang, J.; Wang, Y.; et al. Entropy-stabilized single-atom Pd catalysts via high-entropy fluorite oxide supports. *Nat. Commun.* **2020**, *11*, 3908. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Gao, Y.; Liu, Y.; Yu, H.; Zou, D. High-entropy oxides for catalysis: Status and perspectives. *Appl. Catal. A Gen.* **2022**, *631*, 118478. [\[CrossRef\]](#)
25. Deng, C.; Wang, T.; Wu, P.; Zhu, W.; Dai, S. High entropy materials for catalysis: A critical review of fundamental concepts and applications. *Nano Energy* **2024**, *120*, 109153. [\[CrossRef\]](#)
26. Jin, T.; Sang, X.; Unocic, R.; Kinch, R.; Liu, X.; Hu, J.; Liu, H.; Dai, S. Mechanochemical-Assisted Synthesis of High-Entropy Metal Nitride via a Soft Urea Strategy. *Adv. Mater.* **2018**, *30*, 1707512. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Sarkar, A.; Qingsong, W.; Schiele, A.; Chellali, M.; Bhattacharya, S.; Wang, D.; Brezesinski, T.; Hahn, H.; Velasco Estrada, L.; Breitung, B. High-Entropy Oxides: Fundamental Aspects and Electrochemical Properties. *Adv. Mater.* **2019**, *31*, 1806236. [\[CrossRef\]](#) [\[PubMed\]](#)

28. Zhao, J.; Li, C.; Liu, X.; Li, S.; Zhu, Y.; Huang, L.; Yang, K.; Zhang, Z.; Zhang, Y.; Hu, M.; et al. Effect of A-site cation doping on the catalytic oxidation of toluene over mullite catalyst GdMn_2O_5 . *Sep. Purif. Technol.* **2025**, *355*, 129687. [\[CrossRef\]](#)
29. Teng, Z.; Tan, Y.; Zeng, S.; Meng, Y.; Chen, C.; Han, X.; Zhang, H. Preparation and phase evolution of high-entropy oxides $\text{A}_2\text{B}_2\text{O}_7$ with multiple elements at A and B sites. *J. Eur. Ceram. Soc.* **2021**, *41*, 3614–3620. [\[CrossRef\]](#)
30. Loridant, S. Raman spectroscopy as a powerful tool to characterize ceria-based catalysts. *Catal. Today* **2021**, *373*, 98–111. [\[CrossRef\]](#)
31. Sarkar, A.; Loho, C.; Velasco, L.; Thomas, T.; Bhattacharya, S.S.; Hahn, H.; Djenadic, R. Multicomponent equiatomic rare earth oxides with a narrow band gap and associated praseodymium multivalency. *Dalton Trans.* **2017**, *46*, 12167–12176. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Guo, T.; Du, J.; Li, J. The effects of ceria morphology on the properties of Pd/ceria catalyst for catalytic oxidation of low-concentration methane. *J. Mater. Sci.* **2016**, *51*, 10917–10925. [\[CrossRef\]](#)
33. Sarkar, A.; Eggert, B.; Velasco, L.; Mu, X.; Lill, J.; Ollefs, K.; Bhattacharya, S.S.; Wende, H.; Kruk, R.; Brand, R.A.; et al. Role of intermediate 4f states in tuning the band structure of high entropy oxides. *APL Mater.* **2020**, *8*, 051111. [\[CrossRef\]](#)
34. Wang, Y.; Wang, R.; Lin, N.; Wang, Y.; Zhang, X. Highly efficient microwave-assisted Fenton degradation bisphenol A using iron oxide modified double perovskite intercalated montmorillonite composite nanomaterial as catalyst. *J. Colloid Interface Sci.* **2021**, *594*, 446–459. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Sun, H.; Wang, C.; Zhao, R.; Wang, Z.; Zhao, H. Cobalt Supported on Ce-MOF-Derived CeO_2 as a Catalyst for the Efficient Epoxidation of Styrene Under Aerobic Conditions. *Catal. Lett.* **2024**, *154*, 4649–4662. [\[CrossRef\]](#)
36. Shen, W.; Dong, X.; Zhu, Y.; Chen, H.; Shi, J. Mesoporous CeO_2 and CuO-loaded mesoporous CeO_2 : Synthesis, characterization, and CO catalytic oxidation property. *Microporous Mesoporous Mater.* **2005**, *85*, 157–162. [\[CrossRef\]](#)
37. Nakano, M.; Fujiwara, T.; Koga, N. Thermal Decomposition of Silver Acetate: Physico-Geometrical Kinetic Features and Formation of Silver Nanoparticles. *J. Phys. Chem. C* **2016**, *120*, 8841–8854. [\[CrossRef\]](#)
38. Chen, X.; Yang, J.; Liu, Z.; Wen, Y.; Chen, R.; Chang, S.; Zhang, A.; Du, C.; Shan, B. Origin of Ammonia Selective Oxidation Activity of SmMn_2O_5 Mullite: A First-Principles-Based Microkinetic Study. *ACS Appl. Mater. Interfaces* **2023**, *15*, 736–750. [\[CrossRef\]](#) [\[PubMed\]](#)
39. Lin, M.; An, B.; Takei, T.; Shishido, T.; Ishida, T.; Haruta, M.; Murayama, T. Features of Nb_2O_5 as a metal oxide support of Pt and Pd catalysts for selective catalytic oxidation of NH_3 with high N_2 selectivity. *J. Catal.* **2020**, *389*, 366–374. [\[CrossRef\]](#)
40. Ma, Y.; Zhang, Y.; Jian, Y.; Jiang, Z.; Chai, S.; Li, L.; Xia, L.; He, C. High-entropy $(\text{CoCrFeMnNi})_3\text{O}_4$ catalysts for propane catalytic destruction: Effect of the precipitation agent. *Fuel* **2023**, *353*, 129171. [\[CrossRef\]](#)
41. Dong, F.; Meng, Y.; Ling, W.; Han, W.; Han, W.; Li, X.; Tang, Z. Single atomic Pt confined into lattice defect sites for low-temperature catalytic oxidation of VOCs. *Appl. Catal. B Environ. Energy* **2024**, *346*, 123779. [\[CrossRef\]](#)
42. Lv, Y.; Yan, H.; Liu, T.; Xu, J.; Xu, X.; Fang, X.; Wang, X. Manufacturing AAl_2O_4 (A=Cu, Co, Ni, Zn) Spinel Catalysts for Toluene Combustion: Elucidating the A-site Replacement Effect on the Reactivity. *ChemCatChem* **2024**, *16*, e202301264. [\[CrossRef\]](#)
43. Anpo, M.; Costentin, G.; Giamello, E.; Laumon-Pernot, H.; Sojka, Z. Characterisation and reactivity of oxygen species at the surface of metal oxides. *J. Catal.* **2021**, *393*, 259–280. [\[CrossRef\]](#)
44. Zhang, W.; Zhang, W.; Yan, J.; Li, Z.; Kang, S.; Ren, S.; Lei, Z.; Wang, Z.; Shui, H. High-entropy CeZrCoMnNi oxide catalysts with defect-engineered synergy: Simultaneous boosting of activity, stability, and poisoning resistance for propane combustion. *J. Environ. Chem. Eng.* **2025**, *13*, 118450. [\[CrossRef\]](#)
45. Cha, B.J.; Choi, J.Y.; Kim, S.H.; Zhao, S.; Khan, S.A.; Jeong, B.; Kim, Y.D. In Situ Spectroscopic Studies of NH_3 Oxidation of Fe-Oxide/ Al_2O_3 . *ACS Omega* **2023**, *8*, 18064–18073. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Chauhan, A.; Frickel, A.; Papakollu, K.; Begand, S.; Herrmann, M.; Bernardo, E.; Galusek, D. Polymorphic transitions and phase stability of $\text{CeO}_2\cdot\delta\cdot(\text{Dy,La,Sm,Y})_2\text{O}_3$ high-entropy oxides consolidated by spark plasma sintering. *J. Eur. Ceram. Soc.* **2025**, *45*, 117552. [\[CrossRef\]](#)
47. Xie, S.; Tan, W.; Xu, Y.; Wang, C.; Feng, Y.; Ye, K.; Ma, L.; Ehrlich, S.N.; Li, Y.; Zhang, Y.; et al. Pd- CeO_2 catalyst facilely derived from one-pot generated Pd@Ce-BTC for low temperature CO oxidation. *J. Hazard. Mater.* **2024**, *466*, 133632. [\[CrossRef\]](#) [\[PubMed\]](#)
48. Zhang, H.; Guo, H.; Zhang, F.; Zhang, J.; Cheng, Y.; Ma, Y.; Ma, L.; Qi, L. Cascade electrocatalysis via integration of ruthenium clusters and yttrium single atoms for a boosted alkaline hydrogen evolution reaction. *Energy Environ. Sci.* **2025**, *18*, 6141–6153. [\[CrossRef\]](#)
49. Zhang, C.; Jiang, L.; Sun, Z.; Tang, Z.; Lu, K.; Zhu, Q.; Zhang, X.; Ge, H.; Zhao, Z.; Chen, W.; et al. Ligand-Free Pt-Ln Nanoclusters Synthesized by Femtosecond Lasers for Electrocatalytic Methanol Oxidation. *Adv. Funct. Mater.* **2026**, *36*, e18043. [\[CrossRef\]](#)
50. Khivantsev, K.; Pham, H.; Engelhard, M.H.; Aleksandrov, H.A.; Kovarik, L.; Bowden, M.; Li, X.S.; Tian, J.; Koleva, I.Z.; Song, I.; et al. Transforming ceria into 2D clusters enhances catalytic activity. *Nature* **2025**, *640*, 947–953. [\[CrossRef\]](#) [\[PubMed\]](#)
51. Lan, T.; Deng, J.; Zhang, X.; Wang, F.; Liu, X.; Cheng, D.; Zhang, D. Unraveling the Promotion Effects of Dynamically Constructed $\text{CuO}_x\text{-OH}$ Interfacial Sites in the Selective Catalytic Oxidation of Ammonia. *ACS Catal.* **2022**, *12*, 3955–3964. [\[CrossRef\]](#)

52. Qiu, X.; Miyauchi, M.; Sunada, K.; Minoshima, M.; Liu, M.; Lu, Y.; Li, D.; Shimodaira, Y.; Hosogi, Y.; Kuroda, Y.; et al. Hybrid $\text{Cu}_x\text{O}/\text{TiO}_2$ Nanocomposites As Risk-Reduction Materials in Indoor Environments. *ACS Nano* **2012**, *6*, 1609–1618. [[CrossRef](#)] [[PubMed](#)]
53. Leewis, C.M.; Kessels, W.M.M.; van de Sanden, M.C.M.; Niemantsverdriet, J.W. Ammonia adsorption and decomposition on silica supported Rh nanoparticles observed by in situ attenuated total reflection infrared spectroscopy. *Appl. Surf. Sci.* **2006**, *253*, 572–580. [[CrossRef](#)]
54. Lin, Q.-J.; Pei, M.-M.; Yao, P.; Xu, S.; Xu, S.-H.; Liu, S.; Xu, H.-D.; Dan, Y.; Chen, Y.-Q. Determining hydrothermal deactivation mechanisms on Cu/SAPO-34 NH_3 -SCR catalysts at low- and high-reaction regions: Establishing roles of different reaction sites. *Rare Met.* **2022**, *41*, 1899–1910. [[CrossRef](#)]
55. Chen, L.; Guan, X.; Fei, Z.; Asakura, H.; Zhang, L.; Wang, Z.; Su, X.; Yao, Z.; Keenan, L.L.; Hayama, S.; et al. Tuning the selectivity of NH_3 oxidation via cooperative electronic interactions between platinum and copper sites. *Nat. Commun.* **2025**, *16*, 26. [[CrossRef](#)] [[PubMed](#)]
56. Zhang, L.; He, H. Mechanism of selective catalytic oxidation of ammonia to nitrogen over Ag/ Al_2O_3 . *J. Catal.* **2009**, *268*, 18–25. [[CrossRef](#)]
57. Wang, F.; Ma, J.; He, G.; Chen, M.; Zhang, C.; He, H. Nanosize Effect of Al_2O_3 in Ag/ Al_2O_3 Catalyst for the Selective Catalytic Oxidation of Ammonia. *ACS Catal.* **2018**, *8*, 2670–2682. [[CrossRef](#)]
58. Belopukhov, E.A.; Paukshtis, E.A.; Shkurenok, V.A.; Smolikov, M.D.; Belyi, A.S. Investigation of the Pt/MOR- Al_2O_3 Catalysts by IR Spectroscopy. *Procedia Eng.* **2015**, *113*, 19–25. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.