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Electron-Pump Engineering via CuO-Sm₂CuO₄ Heterojunction for Side-on N₂O Activation and Efficient Catalytic Decomposition under O₂-Rich Conditions

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Abstract

Catalytic N₂O decomposition on CuO-based catalysts is limited by poor N-O activation. Interfacial electron engineering can modulate active-site structure, yet its effect on N₂O remains unclear. Here, we have developed a CuO-Sm₂CuO₄ heterostructure, which achieves over 90% N₂O decomposition at 400 °C in 5% O₂. In simulated NO_x-N₂O co-reduction, it retains 96% activity at 450 °C for 168 hours. This performance indicates significant application potential compared to reported catalyst systems. Our study demonstrates that Cu²⁺-O⁻ sites on as-synthesized CuO-based catalysts drive N₂O decomposition via the Mars-van-Krevelen mechanism, generating Cu⁺ species that complete the catalytic cycle through the Langmuir-Hinshelwood pathway. On pure CuO, Cu⁺ adsorbs N₂O end-on and activates it via σ -backdonation. In contrast, the CuO-Sm₂CuO₄ heterojunction forms a dynamic electron-pumping interface where Sm₂CuO₄ donates electrons to stabilize Cu⁺, reverses N₂O's adsorption-configuration to side-on and enables π -backdonation-mediated activation. This work advances understanding of interfacial electron regulation in heterogeneous catalysis and provides a strategy for designing high-performance N₂O decomposition catalysts.

Keywords: N₂O decomposition, CuO-based catalyst, Interfacial electron interaction, Reaction mechanism

1. Introduction

Nitrous oxide (N_2O), a potent greenhouse gas with ~ 300 times the 100-year global warming potential of CO_2 , has emerged as a critical focus for emission reduction.^{1,2} Catalytic decomposition ($\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2$) stands as the dominant industrial technology for N_2O abatement, attributed to its operational simplicity and lack of secondary pollution.^{3,4} However, commercial catalysts (e.g., $\text{Co}_3\text{O}_4/\alpha\text{-Al}_2\text{O}_3/\text{cordierite}$ ⁵) demand elevated operating temperatures, leading to increased energy costs. Flue gas impurities, including O_2 , nitrogen oxide (NO_x , $x=1, 2$), and H_2O , further degrade catalyst performance. Among these, O_2 presents a particularly significant challenge as it impedes the transfer of oxygen species and competes with N_2O for active sites, thereby reducing reaction sustainability.^{6,7} Despite extensive research on noble metals⁸⁻¹⁰, zeolites¹¹⁻¹³, and transition metal oxides¹⁴⁻¹⁶, the development of low-temperature, impurity-resistant catalysts remains a pressing challenge in environmental catalysis, especially for O_2 -rich industrial flue gases.^{3,17}

Based on the electronic configuration of N_2O and the inherent spin-forbidden nature of its decomposition reaction, the process is kinetically hindered even though it is thermodynamically favorable.¹⁸ Overcoming such barriers necessitates the coordination and activation of metal ions.^{18,19} As a weak-field ligand for transition metals, N_2O decomposition depends strongly on the electronic properties of surface-active sites on the catalyst.¹⁹ The reaction mechanism involves electron transfer for N_2O activation and the diffusion, recombination, and desorption of surface oxygen intermediates. The latter often acts as the rate-limiting step.^{3,20} CuO -based catalysts show good efficacy in N_2O decomposition.^{13,21,22} This efficacy comes from the unique dynamic equilibrium of oxygen vacancy generation and annihilation. Inherent $\text{Cu}^{2+}/\text{Cu}^+$ redox couples facilitate efficient electron transfer through their valence-state cycling capability. The moderate Cu-O bond strength gives high mobility and reactivity to surface oxygen species.²²⁻²⁴ In contrast to Co_3O_4 , Fe_2O_3 , Fe_3O_4 , and Mn_3O_4 ,²⁵ CuO readily generates oxygen vacancies under mild conditions while preserving structural integrity. This significantly accelerates O_2 desorption. Other oxides either need harsh conditions for vacancy formation or experience structural collapse after formation,

which impedes sustained catalytic cycles.²⁵ From an electronic configuration perspective, CuO's catalytic superiority comes from orbital symmetry matching between Cu(3d) and N₂O(π^*). In an octahedral crystal field, Cu²⁺ induces Jahn-Teller distortion. This weakens Cu-O bond strength and promotes oxygen vacancy formation and reversible structural reconstruction. The d⁹ "intermediate state" allows easy Cu²⁺/Cu⁺ interconversion. This establishes a rapid electron transfer pathway for N₂O dissociation. Cu⁺ has a d¹⁰ configuration and strong π -backbonding capacity. It injects electrons into N₂O's π^* antibonding orbitals, destabilizing the N-O bond while maintaining structural stability.^{13,26,27} Theoretically, this reduces the activation energy for N₂O adsorption and dissociation. It also enables rapid cleavage and catalytic cycle completion. The synergistic interplay of Cu²⁺/Cu⁺ redox pairs is the cornerstone of CuO-based catalysts' good performance in N₂O abatement. However, CuO-based catalysts face inherent limitations under oxygen-rich conditions. Despite Cu⁺'s potent N₂O activation ability, its high-oxophilicity leads to poor O₂ desorption.^{24,28} In oxidizing atmospheres, Cu⁺ tends to oxidize to Cu²⁺, which disrupts the redox equilibrium. This can trigger O₂ poisoning, leading to diminished or complete loss of catalytic activity.^{6,21}

Modulating the geometric and electronic structures of active sites to shift the rate-determining step from O₂ desorption to N-O activation has been identified as an effective strategy to enhance the N₂O decomposition performance of oxide catalysts under aerobic conditions in our prior studies.²⁹ Therefore, rationally tuning the electronic properties of active copper species holds promising feasibility for promoting the N₂O decomposition activity of CuO-based catalysts in the presence of O₂. For example, constructing heterostructures via interfacial chemical engineering enables efficient modulation of the electronic structure of active sites, thereby enhancing reaction performance, which a strategy widely applied in heterogeneous catalysis research.³⁰⁻³³ In our previous work,^{14,20} we modified the electronic structure of active cobalt species by engineering Co₃O₄ amorphous-crystalline interfaces and δ -MnO₂/Co_{3-x}Mn_xO₄ interfaces, which improved the N₂O decomposition activity of catalysts under O₂-free conditions. In this study, we introduced samarium species into CuO and observed the formation of the Sm₂CuO₄ perovskite³⁴ phase, resulting in an

oxide-perovskite heterostructure that significantly enhanced the N₂O decomposition activity of CuO-based catalysts under oxygen-rich conditions. By integrating advanced spectroscopic techniques, in-situ characterization, and density functional theory calculations, we analyzed the catalyst's microstructure, revealed the catalytic reaction pathway, clarified the mechanism of N₂O adsorption and activation by active copper species, and elucidated the influence of O₂. Consequently, we established the structure-activity relationship of the catalyst for N₂O decomposition under oxygen-rich conditions. This research provides a novel and effective approach for the design and development of high-performance N₂O decomposition catalysts, which is of great significance for environmental protection and the reduction of greenhouse gas emissions.

2. Results and Discussion

2.1 Analysis of catalyst structure

Pure CuO and a series of composite oxides with different Sm:Cu molar ratios (denoted as Sm_n-CuO_x, where n represents the Sm:Cu ratio of n:1) were synthesized by the sol-gel method with employing citric acid as the chelating agent. The textural properties of CuO and Sm-containing catalysts are shown in **Table 1** and **Figure S1-S2**. The CuO sample has a smaller specific surface area and a microporous structure. Introducing Sm changes the pore structure, increasing the specific surface area, pore volume, and average pore size. However, increasing the Sm content does not significantly influence on these three properties. The X-ray diffraction (XRD) patterns of CuO and Sm-modified samples are presented in **Figure 1(a)**. For the pristine CuO catalyst, the dominant diffraction peaks correspond to CuO (PDF#48-1548). The introduction of Sm cations leads to the appearance of diffraction peaks characteristic of the Sm₂CuO₄ perovskite phase. As the Sm molar content increases, the intensity of Sm₂CuO₄ peaks increases and their full width at half maximum (FWHM) narrows. Meanwhile, the intensity of CuO peaks in the 34-40° range weakens and their FWHM broadens. The unchanged position of CuO diffraction peaks after Sm incorporation suggests that Sm cations do not substitute Cu sites in the CuO lattice. **Figure (b)** displays the Raman spectra of these samples. For pure CuO³⁵, the peaks at 288 cm⁻¹ (A_g) and 337, 621 cm⁻¹ (B_g)

correspond to the vibration modes of the Cu-O bond. In the case of the Sm_2CuO_4 perovskite,^{34,36,37} the peaks at 229 and 435 cm^{-1} are assigned to the A_{1g} vibration modes of the Sm-O and Cu-O bonds, respectively. The peak at 384 cm^{-1} corresponds to the asymmetric bending vibration of O-Cu-O in the $[\text{CuO}_2]$ plane of the perovskite phase, while the peak at 547 cm^{-1} results from the shear deformation of the Sm-O bond in the Sm layer. As shown in **Figure 1(b)**, after adding Sm species to CuO, both the A_g and B_g vibration peaks of the Cu-O bond shift to the left and become broader. Meanwhile, the signal of the asymmetric bending vibration of O-Cu-O in the $[\text{CuO}_2]$ plane of the Sm_2CuO_4 perovskite is detected. These phenomena may be attributed to the strong electronic interaction between the Sm_2CuO_4 perovskite phase and the CuO phase,^{34,38} which is induced by the introduction of Sm.

Moreover, a spherical aberration-corrected high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) was employed to directly observe the crystal structure of the synthesized Cu-based catalysts. Pure CuO presents as irregular nanoparticles (**Figure S3**). Through analysis of the STEM images and simulation of the atomic structure arrangement of the CuO crystal, it was discovered that the atomic arrangement aligns along the $[110]$ zone axis and terminates at the (001), (100), and (010) side planes (**Figure 1(c)** and **Figure S3**). Similarly, the Sm_2CuO_4 perovskite also occurs as irregular nanoparticles (**Figure S4**). At the microscopic level, its atomic arrangement follows the $[010]$ zone axis and terminates at the (100) and (001) side planes (**Figure 1(d)** and **Figure S4**). In the case of the $\text{Sm}_{0.2}\text{-CuO}_x$ composite oxide catalyst (**Figure 1(e₁)** and **Figure S5**), it is clearly observable that the Sm_2CuO_4 perovskite is supported on the surface of the CuO nanoparticles (as Sm atoms are heavier and appear notably brighter than Cu in the HAADF-STEM images), resulting in a supported catalyst akin to $\text{Sm}_2\text{CuO}_4/\text{CuO}$. Additionally, a distinct heterogeneous interface exists between the Sm_2CuO_4 perovskite phase and the CuO phase (**Figure 1(e₂)** and **Figure S5**). Meanwhile, the EDX-Mapping reveals the uniform dispersion of the Sm element, from which the uniformity of this heterogeneous structure can be deduced (**Figure 1(e₃)**). When the Sm content is increased, specifically in the $\text{Sm}_{0.3}\text{-CuO}_x$ catalyst (**Figure S6** and **S7**), it

was found that the size of the Sm_2CuO_4 nanoparticles increases significantly. Although the heterogeneous interface remains well-defined, the proportion of the Sm_2CuO_4 perovskite in this structure rises substantially, resembling the formation of a $\text{CuO}/\text{Sm}_2\text{CuO}_4$ supported catalyst. The present findings provide conclusive evidence that the incorporation of Sm species into CuO does not yield atomically dispersed rare-earth single-atom modified oxides, as observed in our prior research.³⁹ Instead, it results in the creation of an *in-situ* derived perovskite-oxide heterojunction with anchored interface. Furthermore, in $\text{Sm}_n\text{-CuO}_x$ mixed oxide catalysts (**Figure 1(f)**), increasing Sm content facilitates the growth of Sm_2CuO_4 crystallites while promoting the refinement of CuO grains. Ultimately, under stoichiometric conditions, a pure Sm_2CuO_4 perovskite phase is formed.

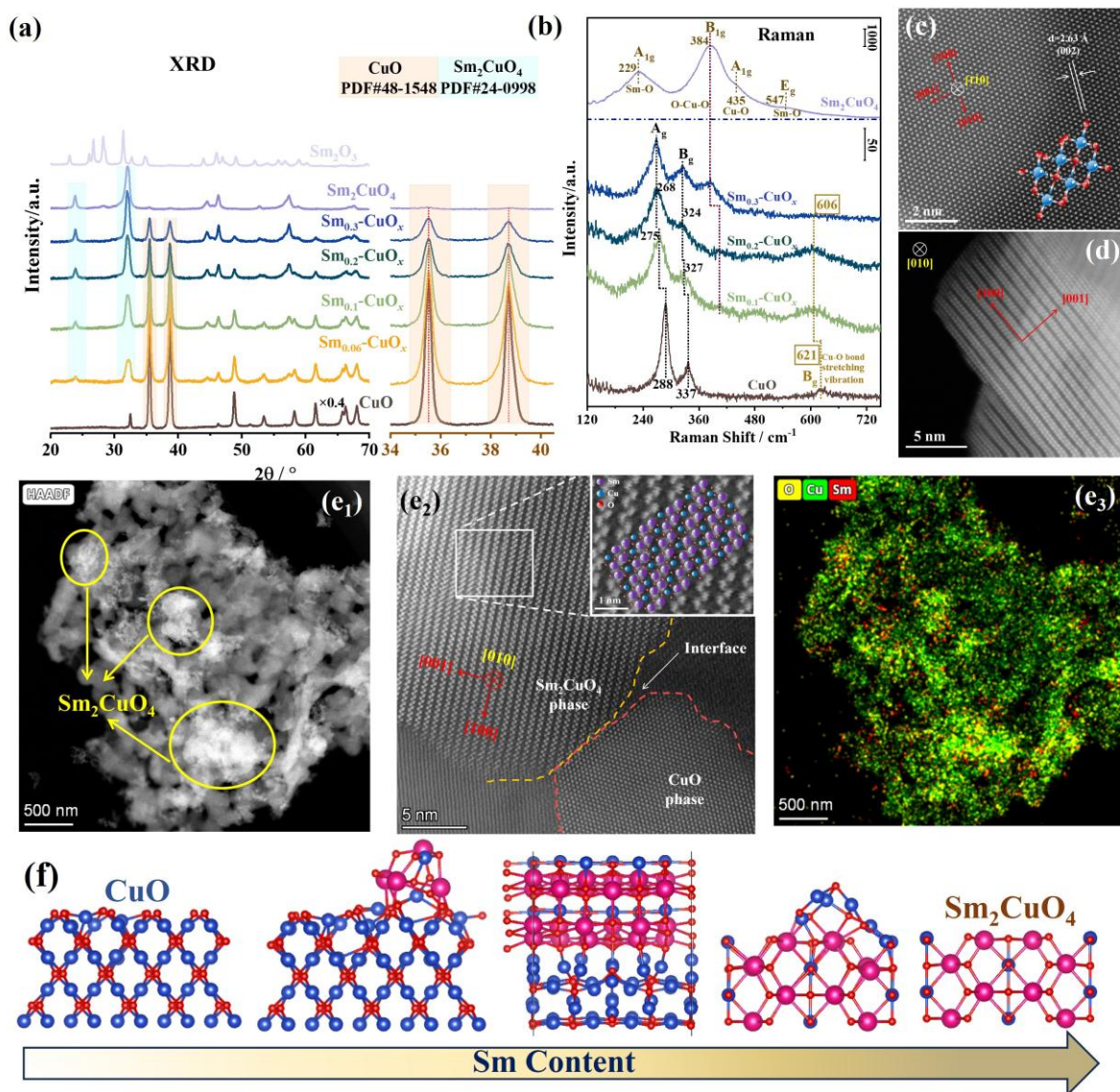


Figure 1. Analysis of catalyst structure. (a) XRD patterns and (b) Raman spectra of the CuO and $\text{Sm}_2\text{-CuO}_x$ composites with various Sm contents. AC-HAADF-STEM images of (c) bare CuO , (d)

Sm₂CuO₄ sample, and (e₁₋₃) Sm_{0.2}-CuO_x catalyst. (f) Schematic diagram of the evolution of Sm₂CuO₄ purity with the Sm content increase introduced into CuO catalysts. (The blue, red, and pink balls represent Cu, O and Sm, respectively.)

2.2 Catalytic Performance

Figure 2(a) depicts the O₂-resistant N₂O decomposition activity of CuO and Sm-containing catalysts as a function of temperature. Bare CuO exhibits low activity, failing to reach 90% conversion even at 550 °C. However, Sm-introducing significantly enhances performance, with Sm_{0.06}-CuO_x reducing the T₉₀ (temperature for 90% conversion) to ~470 °C, and Sm_{0.2}-CuO_x achieving the optimal T₉₀ of ~405 °C, after which excess Sm leads to a decline in activity. In contrast, pure Sm₂CuO₄ perovskite shows poor performance (T₉₀ ~475 °C, ~43% conversion at 550 °C), while Sm₂O₃ displays negligible activity across all test temperatures. Intrinsic activity analysis (**Figure 2(b)**) reveals that Sm_{0.2}-CuO_x has a 4–5 times higher specific surface area-normalized reaction rate (R_s) at 300–325 °C than bare CuO, outperforming other Sm-containing samples. Notably, in O₂-free conditions, all catalysts follow the same activity trend but exhibit better performance, confirming O₂'s inhibitory effect (**Figure S8**). Benchmarking (**Figure 2(c)**) further demonstrates that Sm_{0.2}-CuO_x has considerable potential for N₂O purification compared to recent noble metal-based and transition metal oxide catalysts, leading to its selection as the target catalyst for further investigation.

Adipic acid and nitric acid production exhausts contain coexisting NO_x (a primary precursor of PM_{2.5} and urban ozone)⁴⁰ and N₂O, making their combined reduction critical. As presented in **Figure 2(d)** illustration, this study proposes a single-reactor tandem catalyst design integrating commercial V₂O₅-WO₃/TiO₂ (the catalyst of selective catalytic reduction of NO_x by NH₃) with Sm_{0.2}-CuO_x for simultaneous removal. The upstream V₂O₅-WO₃/TiO₂ leverages its excellent H₂O resistance and mature production technology for efficient NO_x reduction, while the downstream Sm_{0.2}-CuO_x avoids NO_x inhibition of N₂O decomposition. This is a key issue since O₂, NO_x, and H₂O in flue gas typically interfere with N₂O decomposition catalysts, sometimes causing deactivation.^{3,6} Notably, at 450 °C, Sm_{0.2}-CuO_x catalyst exhibits good tolerance to these impurities, and can fully

recovered its initial performance after removing the impurities (**Figure S9**). The performance evaluations (**Figure 2(d)**) display this setup maintains over 96% N₂O decomposition efficiency for ≥ 100 hours (even with flue gas H₂O), keeps outlet NO_x ≤ 60 ppm with near-zero NH₃ slip, and eliminates separate systems to cut costs and resolve space constraints, offering a competitive dual emission abatement solution.

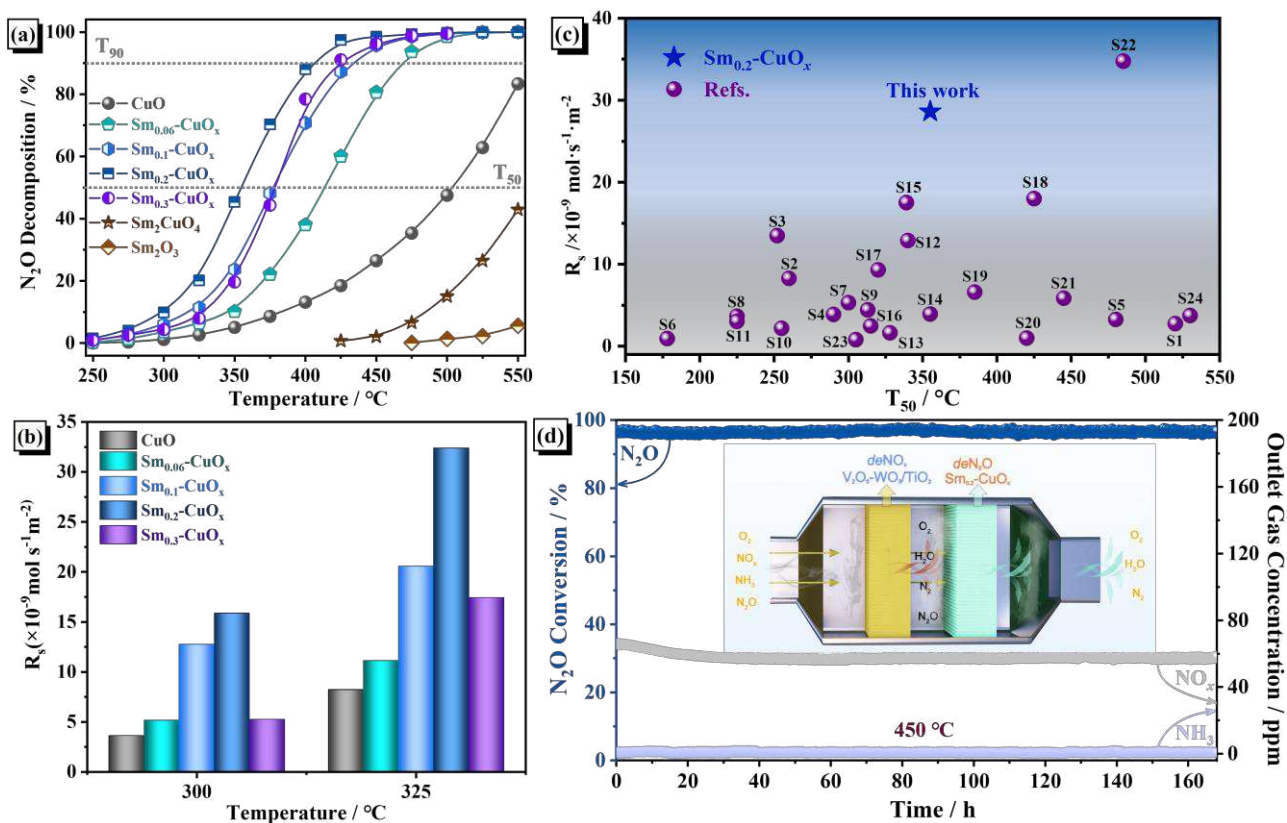


Figure 2. Reaction performance evaluation. (a) N₂O decomposition activity for the CuO and Sm-containing samples ([N₂O]=1000 ppm, 5% O₂, WHSV=30000 mL·g⁻¹·h⁻¹). (b) N₂O decomposition reaction rates are based on the specific surface area of the catalysts. (c) Summary of recent key advances in noble metals and transition metal oxides-based catalysts for N₂O decomposition (relevant references are listed in **Table S2**). (d) Stability test for simultaneous elimination of N₂O and NO_x at 450 °C (Illustration: Schematic diagram of double-layer tandem catalysts device for simultaneous purification of NO_x and N₂O) (Reaction conditions: [NO_x]=[NH₃]=500 ppm, [N₂O]=1000 ppm, [O₂]=[H₂O]=5 %, GHSV=30000 h⁻¹).

2.3 Analysis of Microscopic Properties

The chemical environments of the Cu species in bare CuO, Sm_{0.2}-CuO_x, Sm_{0.3}-CuO_x, and Sm₂CuO₄ are distinct, as determined by extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) measurements. EXAFS data indicate that (**Figure 3(a)**), with Cu foil, Cu₂O, and CuO (reference samples) as references, all the Cu-based catalysts

selected in this study exhibit peaks at 1.5 and 2.4 Å, which are attributed to the first-shell Cu-O bonds and the second-shell Cu-O-Cu bonds, respectively.^{23,41} When Sm species are introduced, up to the stoichiometric Sm₂CuO₄ perovskite, a peak attributed to the Cu-O-Sm structure appears at 2.9 Å and gradually intensifies.³⁶ The wavelet transform (WT) analysis of the EXAFS spectra leads to a two-dimensional representation of EXAFS (**Figure 3(b)**), simultaneously revealing the signal characteristics in both R and k spaces.²⁴ A comparison shows that the first shell peak with the strongest signal in Sm_{0.2}-CuO_x (centered at 4.5 Å⁻¹, 1.47 Å) is higher than the equivalent peak in CuO (centered at 4.4 Å⁻¹, 1.43 Å) but weaker than those in Sm_{0.3}-CuO_x (4.6 Å⁻¹, 1.46 Å) and Sm₂CuO₄ (4.7 Å⁻¹, 1.46 Å). This difference further confirms that the Sm₂CuO₄/CuO structure represented by the Sm_{0.2}-CuO_x catalyst has longer Cu-O bonds than pure CuO, while the chemical environment of the Cu-O bonds in the CuO/Sm₂CuO₄ structure represented by the Sm_{0.3}-CuO_x catalyst is more similar to that of Sm₂CuO₄. Based on the above results, the electronic interaction between the CuO phase and Sm₂CuO₄ was investigated. As displayed in **Figure 3(c)**, for the Cu K-edge of the XANES, the pre-edge absorption around 8988 eV is assigned to the Cu²⁺ dipole-forbidden 1s→3d transition, and the peak around 8998 eV is assigned to the 1s→4p transition of Cu²⁺ with a distorted square-planar or octahedral coordination geometry.^{23,42} The Cu species in Sm_{0.2}-CuO_x, Sm_{0.3}-CuO_x, and Sm₂CuO₄ all exist in the form of Cu²⁺. However, the absorption edge position of Sm_{0.2}-CuO_x is the lowest, suggesting that the Cu cations in this catalyst have a stronger electron density. By calculating the work functions of pure CuO and Sm₂CuO₄ perovskite (**Figure 3(d)**), which are 5.88 and 5.45 eV, respectively, it is indicated that in the composite oxide, Sm₂CuO₄ can act as an electron donor and transfer electrons to the CuO phase. The slab model of CuO, Sm₂CuO₄/CuO, and CuO/Sm₂CuO₄ were constructed through DFT calculations, and the electron localization function (ELF) of the three structures was obtained (**Figure S10** and **Figure 3(e)**). The ELF values range from 0 to 1, where a higher value indicates a higher degree of electron localization, and ELF>0.5 is generally regarded as the criterion for covalent bond formation. As shown in the figure, the ELF values in the Cu-O bond region on the

surfaces of CuO and CuO/Sm₂CuO₄ are both lower than 0.5 (but the value of CuO/Sm₂CuO₄ is higher than that of CuO), indicating a low degree of electron localization and the ionic bond characteristics between Cu and O atoms. In contrast, the degree of electron localization on the Sm₂CuO₄/CuO surface significantly increases, indicating a significant enhancement of the covalent nature of the Cu-O bonds. The underlying reason is that in Sm₂CuO₄/CuO, due to the strong correlated electron characteristics of CuO itself, when Sm₂CuO₄ transfers electrons to the CuO phase, the electrons occupy the antibonding orbitals of Cu(3d)-O(2p), reducing the bond order of the Cu-O bonds, promoting the hybridization between the Cu 3d and O 2p orbitals, and increasing the covalent component.

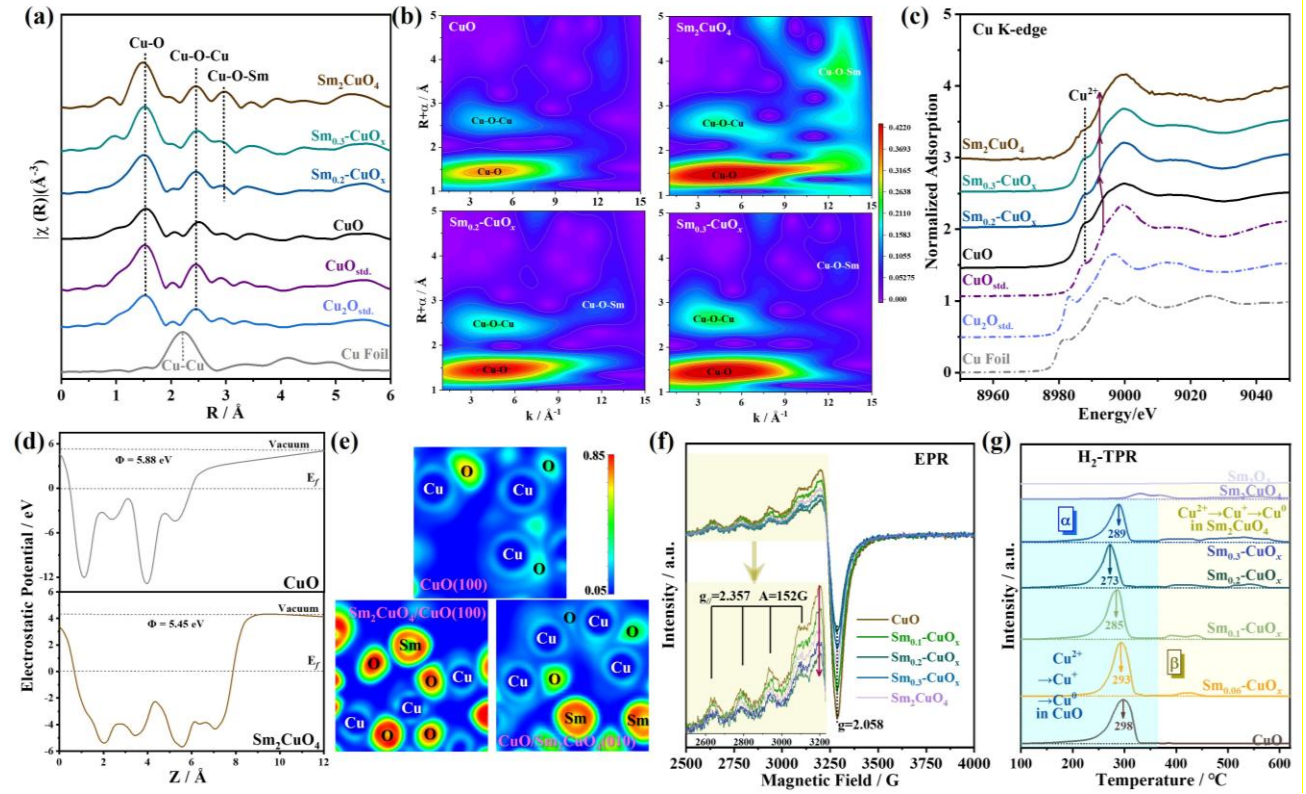


Figure 3. Characterizations of as-synthesized Cu-based catalysts. (a) Fourier transforms (FT) curves and (b) wavelet transforms of Cu K-edge EXAFS. (c) Cu K-edge XANES spectra of CuO, Sm_{0.2}-CuO_x, Sm_{0.3}-CuO_x and Sm₂CuO₄ catalysts. (d) The work functions of CuO and Sm₂CuO₄. (e) Two-dimensional electronic local function (ELF) maps of slab CuO, Sm₂CuO₄/CuO and CuO/Sm₂CuO₄ models. (f) EPR spectra and (g) H₂-TPR curves of the samples.

Based on this, further verification was carried out through electron paramagnetic resonance (EPR) experiments, and the results are shown in **Figure 3(f)**. The hyperfine-split signals with spin Hamiltonian parameters of $g_{\parallel} = 2.357$ and $A = 152$ G are associated with Cu²⁺ cations on the

sample.^{43,44} With the introduction of Sm species, this signal gradually decreases, and Sm_{0.2}-CuO_x exhibits the lowest EPR signal. However, as the Sm content further increases, the EPR signal shows an increasing trend. The decrease in the EPR signal indicates that due to the electron filling from the Sm₂CuO₄ phase to the CuO phase, the spin density of the unpaired electrons in the Cu²⁺ species is dispersed, resulting in the broadening and weakening of the g-factor signal.^{45,46} The results of the H₂ temperature-programmed reduction (H₂-TPR) experiments also confirm that the electron filling from the Sm₂CuO₄ phase to the CuO phase increases the electron density at the Cu sites, leading to the lowest Cu²⁺ reduction peak (peak α)²⁸ for Sm_{0.2}-CuO_x catalyst (**Figure 3(g)**).

2.4 Investigation on the N₂O Decomposition Reaction Mechanism

The decomposition of N₂O proceeds via distinct mechanisms (e.g., Mars-van Krevelen (MvK), Eley-Rideal (ER), Langmuir-Hinshelwood (LH)) depending on the catalyst system.^{3,13,14,47} To elucidate the N₂O decomposition mechanism over Cu-based catalysts herein, we first performed ¹⁶O¹⁸O isotope exchange experiments to determine the origin of oxygen in the O₂ product and identify reaction intermediates: the catalyst surface was treated with ¹⁸O₂ at 550 °C to replace surface lattice oxygen (¹⁶O) with ¹⁸O, and using pure CuO and Sm_{0.2}-CuO_x as target-catalysts, temperature-programmed N₂O decomposition was conducted after He purging, with mass-to-charge ratios (m/z) of 32, 34, and 36 monitored in the effluent, where m/z = 32 (¹⁶O¹⁶O) originated from the recombination of ¹⁶O derived from N₂O decomposition on the surface (indicative of the LH pathway), m/z = 34 (¹⁶O¹⁸O) arose from the reaction between ¹⁶O (from N₂O decomposition) and surface lattice oxygen (¹⁸O) (consistent with the MvK mechanism), and m/z = 36 (¹⁸O¹⁸O) was attributed to the recombination of lattice oxygen itself. As demonstrated in **Figure 4(a)**, pure CuO primarily produced ¹⁶O¹⁶O, although a transient peak of ¹⁶O¹⁸O was observed at 417 °C, indicating that while the MvK pathway contributed in the initial stage, the LH pathway dominated the overall reaction; in contrast, Sm_{0.2}-CuO_x (**Figure 4(b)**) exhibited dramatically lower peaks for both ¹⁶O¹⁸O and ¹⁶O¹⁶O, a dual observation that confirms two key findings that Sm_{0.2}-CuO_x has higher N₂O decomposition activity (lower peak intensity implies faster consumption of labeled oxygen species)

and shares the same N₂O decomposition mechanism as pure CuO.

In-situ Raman spectroscopy was employed to track the structural evolution of the catalyst during N₂O decomposition. For CuO (**Figure 4(c)**), in the N₂O decomposition reaction, the vibration mode of the [Cu²⁺-O] bond remained stable with increasing temperature, as observed for the Sm₂CuO₄ perovskite (**Figure S11**). However, but upon N₂O introduction into the Sm_{0.2}-CuO_x catalyst (**Figure 4(d)**), new peaks attributed to [Cu⁺-O] emerge at 156 and 195 cm⁻¹.^{48,49} By comparison and inference, it is likely that these peaks originate from the evolution of the CuO phase in the catalyst. Based on this, we further study the changes in the electronic states of each element during the reaction using *in-situ* near-ambient-pressure X-ray photoelectron spectroscopy (NAP-XPS). **Figures 4(e) and (f)** illustrate the evolution of the O 1s and Cu 2p XPS spectra of the CuO catalyst with temperature under the reaction gas conditions. For the O 1s, lattice oxygen (O_α, low binding energy) and surface chemisorbed oxygen (O_β, high binding energy) were identified, with O_β content remaining unchanged after N₂O introduction while O_α shifted 0.4 eV to higher binding energy, and at elevated temperatures, O_β content increased (due to N₂O decomposition derived oxygen) but O_α position was unchanged. In addition, in an Ar atmosphere at 300 °C, the Cu 2p spectrum has two satellite peaks in the range of 945-940 eV, which are attributed to the unoccupied Cu 3d⁹ shell, a characteristic of Cu²⁺ cations. The peak at 933.5 eV corresponds to Cu 2p_{3/2}, confirming that the copper species in CuO are mainly Cu²⁺. When the Ar is replaced with a N₂O/Ar mixed gas, the full width at half maximum (FWHM) of the Cu 2p_{3/2} peak narrows, the peak shifts 1.4 eV towards the low binding energy direction, and the intensity of the satellite peaks weakens. This indicates that in the N₂O atmosphere, the copper species on the surface of the CuO catalyst gradually transform into Cu⁺ cations. As the reaction temperature further increases, the 2p_{3/2} peak shifts back to 932.2 eV, and the satellite peaks disappear, suggesting that Cu⁺ is the active species for the catalytic decomposition of N₂O on the CuO catalyst. However, when the N₂O supply is shut off at 500 °C, the satellite peaks representing Cu²⁺ reappear, and the 2p_{3/2} peak shifts back to 932.7 eV. This may be due to the oxidation of Cu⁺ to Cu²⁺ by the residual O₂ in the XPS instrument

chamber after the decomposition of N_2O . For the $\text{Sm}_{0.2}\text{-CuO}_x$ catalyst, its O 1s XPS (**Figure 4(g)**) displays a peculiar phenomenon. After introducing N_2O at 300 °C, an O_γ peak attributed to superoxide species (O_2^-) appears at ~532 eV,^{50,51} which is regarded as a sign of the recombination of the O species left after the N-O bond breakage of N_2O .³⁹ Moreover, as the reaction temperature increases, its content increases, signaling the acceleration of the N_2O decomposition. For the Cu 2p (**Figure 4(h)**), under the Ar condition at 300 °C, satellite peaks indicating Cu^{2+} appear in the range of 945-940 eV. However, the position of Cu 2p_{3/2} is 0.4 eV lower than that observed in CuO, suggesting that the formation of the heterostructure between CuO and Sm_2CuO_4 in $\text{Sm}_{0.2}\text{-CuO}_x$ facilitates the formation of an electron-rich CuO phase, which is consistent with the results of EPR and H_2 -TPR et al. When 20% N_2O is introduced, almost all the copper species on the catalyst surface transform into Cu^+ . Notably, at 300 °C, for $\text{Sm}_{0.2}\text{-CuO}_x$, the shift of the Cu 2p XPS caused by the introduction of N_2O is 1.3 eV, while it is 0.6 eV for pure CuO, indicating that Sm_2CuO_4 may donate electrons to the CuO phase during the N_2O decomposition. When the N_2O supply is shut off at 500 °C, the Cu 2p XPS spectrum of $\text{Sm}_{0.2}\text{-CuO}_x$ returns to the initial state, similar to that of CuO. Furthermore, the Cu 2p XPS of the pure Sm_2CuO_4 perovskite (**Figure 4(i)**) remains unchanged throughout the experiment, reflecting the inertness of the Cu species in this sample during the N_2O decomposition reaction. **Figure 4(j)** shows the evolution of the Sm 3d XPS of the $\text{Sm}_{0.2}\text{-CuO}_x$ catalyst during the N_2O decomposition reaction. Under the Ar condition at 300 °C, the Sm 3d XPS spectrum can be deconvoluted into four peaks, where the green and pink peaks correspond to Sm^{2+} and Sm^{3+} species, respectively. After introducing N_2O gas, the Sm 3d_{5/2} and 3d_{3/2} peaks shift 0.3 eV towards the higher binding energy direction, and the content of Sm^{2+} decreases from about 25% to about 22% (**Figure 4(l)**), indicating that the Sm species lose electrons during the reaction. As the temperature increases from 300 °C to 400 °C, the Sm 3d_{5/2} and 3d_{3/2} peaks continue to shift, and the content of Sm^{2+} gradually decreases until it stabilizes above 400 °C. For the pure Sm_2CuO_4 perovskite (**Figure 4(k)**), the position of the Sm 3d XPS peaks and the content of Sm^{2+} (**Figure 4(l)**) remain unchanged throughout the process, reflecting its inertness.

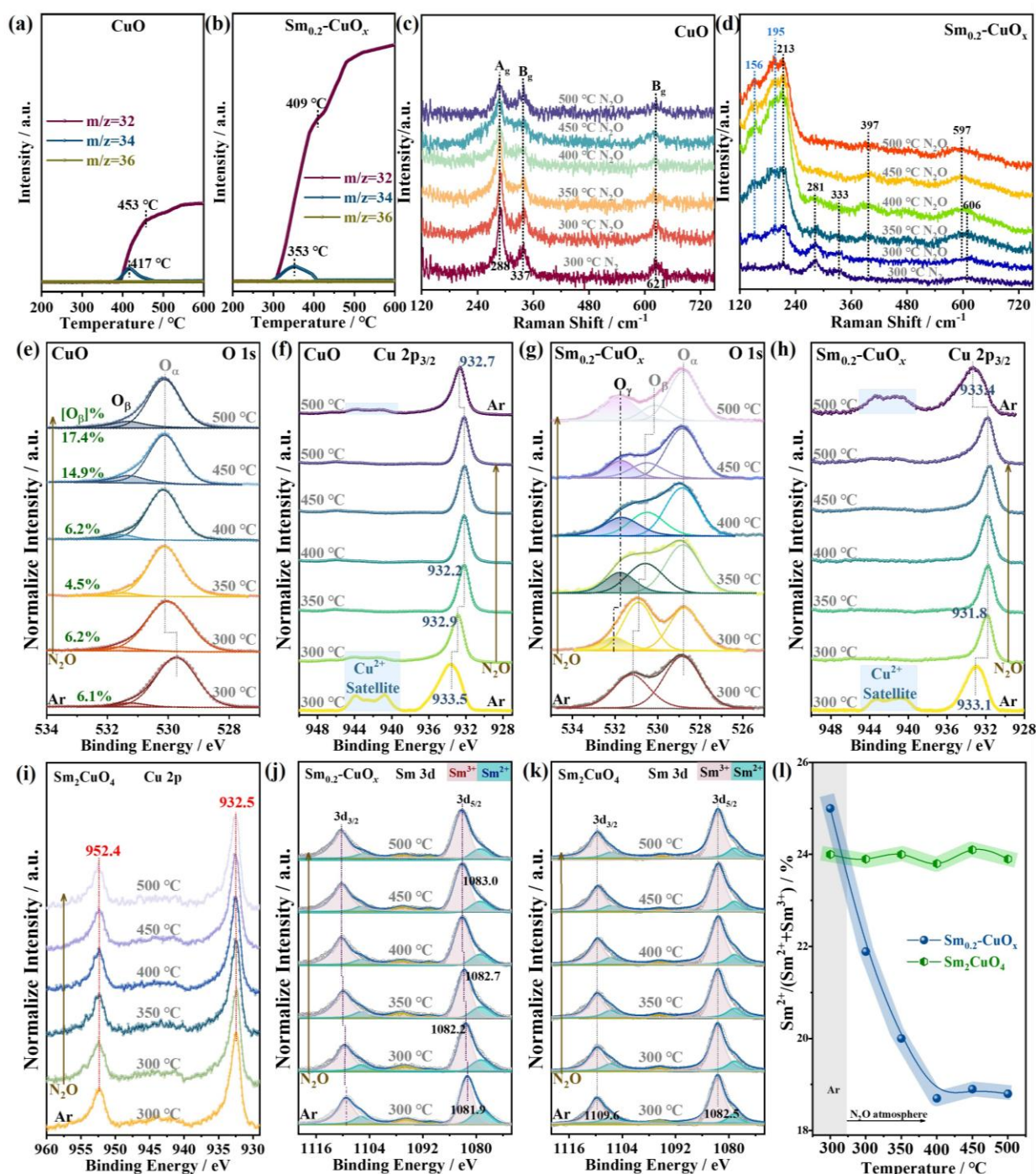
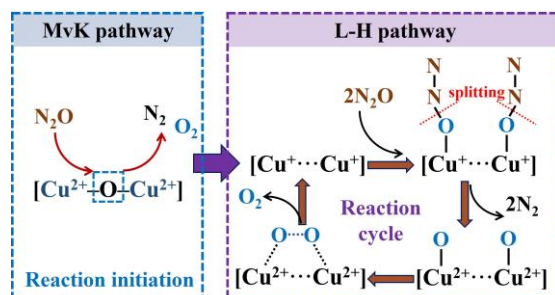
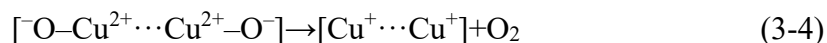
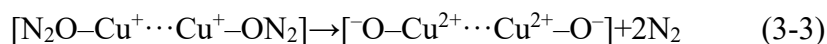
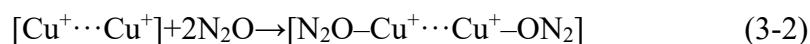
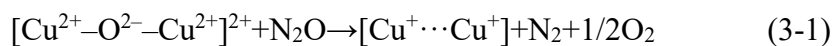


Figure 4. *In situ* investigation of surface species evolution during reaction. Temperature-programmed N_2O decomposition on the isotope exchange (a) CuO and (b) $\text{Sm}_{0.2}\text{-CuO}_x$ catalysts. *In-situ* Raman spectra of the N_2O decomposition reaction over the (c) CuO, and (d) $\text{Sm}_{0.2}\text{-CuO}_x$ samples as a function of temperature. (Reaction conditions: $[\text{N}_2\text{O}] = 20$ vol.%, N_2 balance). *In situ* NAP-XPS spectra results of (e, g) O 1s, (f, h, i) Cu 2p and (j, k, l) Sm 3d for CuO, $\text{Sm}_{0.2}\text{-CuO}_x$ and Sm_2CuO_4 samples in 20 vol.% N_2O (Ar balance) airflow as a function of temperature.

Based on the above experimental results, we have preliminarily revealed the mechanism of the N_2O decomposition reaction catalyzed by the CuO and $\text{Sm}_{0.2}\text{-CuO}_x$ catalysts studied in this work. It is found that the CuO species is the reactive species for the reaction. Although the addition of Sm

induces the formation of the CuO-Sm₂CuO₄ heterostructure, it does not change the reaction pathway of N₂O decomposition. Combining with previous reports,^{13,22,27} as shown in **Scheme 1**, the reaction starts with the divalent copper sites ([Cu²⁺-O²⁻-Cu²⁺]²⁺) catalyzing the decomposition of N₂O through the MvK mechanism, forming [Cu⁺···Cu⁺] sites and releasing O₂ molecules (eq. 3-1). Then, the [Cu⁺···Cu⁺] unit adsorbs two N₂O molecules (eq. 3-2). Among them, the Cu⁺ species transfers electrons to the lowest unoccupied antibonding orbital of the N₂O molecule, activating and breaking the N-O bond to release N₂ molecules (eq. 3-3). Finally, the remaining oxygen anions pair up and desorb (eq. 3-4), completing the reaction cycle centered around the [Cu⁺···Cu⁺] sites and following the L-H mechanism.



Scheme 1. The main pathways for catalytic N₂O decomposition over the Cu-based catalysts.

To gain deeper mechanistic understanding of N₂O decomposition over catalysts, density functional theory (DFT) calculations were systematically performed. First, leveraging the intrinsic properties of metal oxides,^{52,53} the oxygen vacancy (O_{vac}) formation energies of CuO, Sm₂CuO₄/CuO, and Sm₂CuO₄ were computed. The results revealed that CuO exhibits intrinsic O_{vac}. (**Figure S12**, denoted as CuO-O_{vac}.), while O_{vac}. are most readily generated at Cu-O-Cu sites within the CuO phase at the two-phase interface of the Sm₂CuO₄/CuO configuration (**Figure S13**, denoted as Sm₂CuO₄/CuO-O_{vac}.). In contrast, pure Sm₂CuO₄ perovskite shows negligible O_{vac}. formation tendency (**Figure S14**). Building on these findings, the N₂O adsorption energy (*E*_{ads}), charge density

difference, Bader charge analysis, and crystal orbital Hamilton population (COHP) results for N₂O molecules adsorbed on CuO-O_{vac.}, Sm₂CuO₄/CuO-O_{vac.}, and Sm₂CuO₄ were obtained, as presented in **Figure 5 (a-c)**. Compared to the CuO-O_{vac.} configuration, Sm₂CuO₄/CuO-O_{vac.} displays a more negative E_{ads} , facilitating greater electron injection into N₂O molecules and resulting in a lower -IpCOHP value for the N-O bond. For Sm₂CuO₄, despite its high N₂O adsorption energy, its electron-donating capacity to N₂O molecules is limited. These computational observations are further corroborated by N₂O temperature-programmed desorption coupled with mass spectrometry experiments (N₂O-TPD-MS, **Figure S15**). **Figure 5 (d)** illustrated the detailed reaction pathways of N₂O decomposition on the CuO-O_{vac.} and Sm₂CuO₄/CuO-O_{vac.} surfaces. For the Sm₂CuO₄/CuO-O_{vac.} catalyst, gaseous N₂O molecule first adsorbs onto the surface, interacting with Sm atom at the N-terminal while the O-terminal interacts with the surface Cu-O_{vac}-Cu site (**IM1**), with an adsorption energy of -0.28 eV. Subsequently, the first O-N bond cleavage occurs, overcoming an energy barrier of 2.04 eV (**TS1**), forming an adsorbed O* radical and N₂ molecule (**IM2**). Then, the N₂ molecule desorbs from the surface, which is endothermic by 0.30 eV. Meanwhile, the O* radical interacts with a surface lattice O atom to form an adsorbed O₂ molecule (**IM3**). Afterward, the O₂ molecule desorbs and creates a new oxygen vacancy on the catalyst surface (**IM4**), the system is endothermic with an energy of 0.74 eV. Next, another gaseous N₂O molecule adsorbs onto the catalyst surface, interacting with Sm atom via its N-terminal and with the newly formed Cu-O_{vac}-Cu site via its O-terminal (**IM5**). This step releases an energy of -0.72 eV with a barrier of 0.81 eV (**TS2**), resulting in the second O-N bond cleavage and the formation of a new O* radical and N₂ molecule (**IM6**). Finally, the N₂ molecule desorbs by absorbing 0.16 eV of energy, while the O* radical fills the surface vacancy (**FS**), restoring the catalyst surface and completing the catalytic cycle. Additionally, a similar MvK mechanism was observed on the CuO-O_{vac.} surface. After binding to the surface O_{vac.} with an adsorption energy of -0.11 eV, N₂O molecule must overcome a 2.88 eV energy barrier (**TS1'**) to complete the first step of O-N bond cleavage. Subsequently, N₂ and O₂ molecules desorb, and the second step of O-N bond cleavage

occurs near the newly formed vacancy, requiring an energy barrier of 0.94 eV (TS2'). Overall, on both catalyst surfaces, the rate-determining step is the initial O-N bond cleavage. This calculation is further validated by kinetic studies of N₂O decomposition (**Figure S16**), where both CuO and Sm_{0.2}-CuO_x catalysts exhibit first-order reaction kinetics for N₂O decomposition, confirming that the rate-determining step involves N-O bond splitting rather than O₂ desorption.^{54,55}

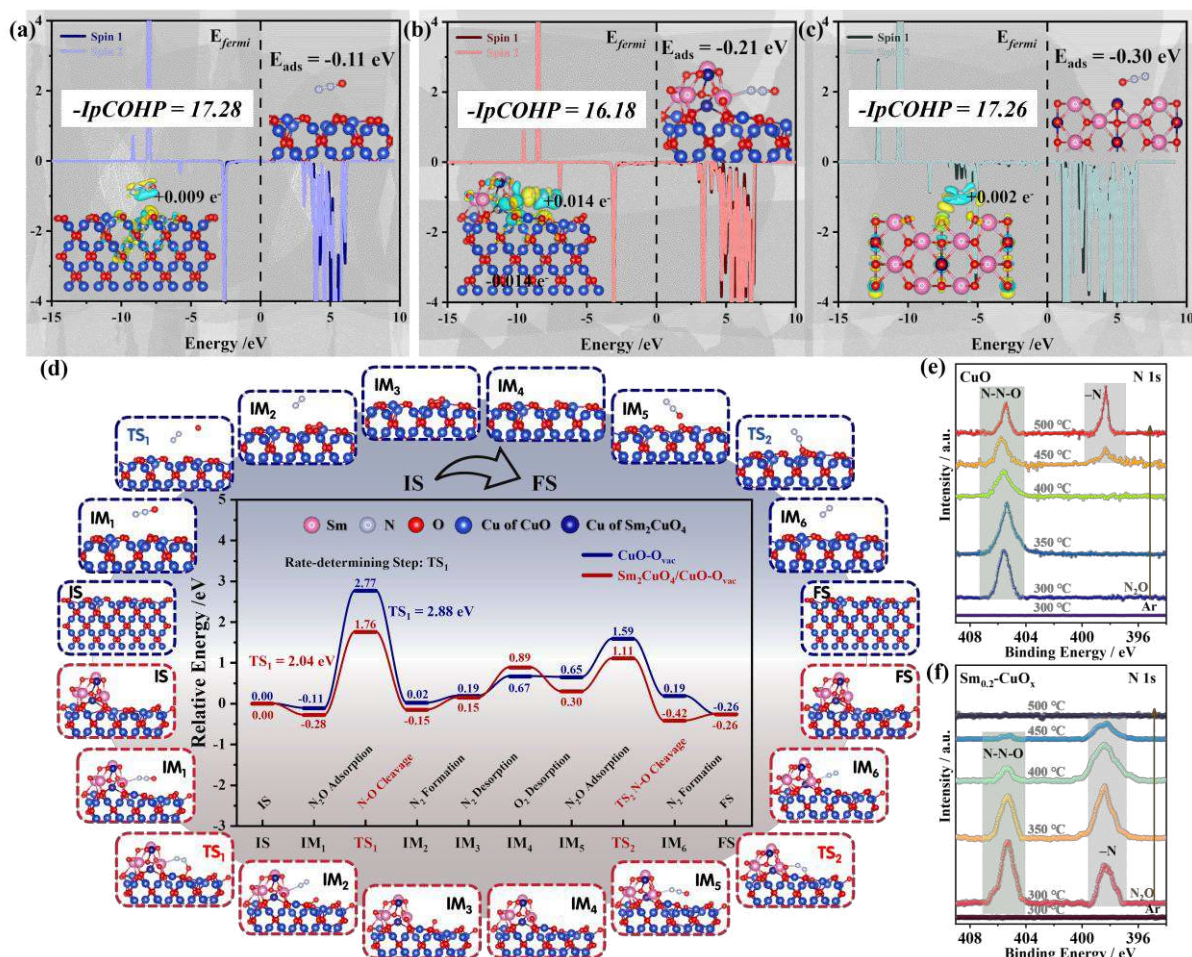


Figure 5. Mechanistic study on N₂O decomposition. DFT calculations of N₂O-adsorbed (a) CuO-O_{vac}, (b) Sm₂CuO₄/CuO-O_{vac}, and (c) Sm₂CuO₄ configurations with N₂O adsorption energy, charge difference, bader charge, and pCOHP analyses. (d) Free-energy diagram of the reaction pathways for N₂O decomposition over the slab CuO-O_{vac} and Sm₂CuO₄/CuO-O_{vac} model surface. *In situ* NAP-XPS spectra of N 1s for (e) bare CuO and (f) Sm_{0.2}-CuO_x catalysts during the N₂O decomposition process.

Furthermore, NAP-XPS was employed to systematically probe the adsorption and transformation behaviors of N₂O molecules on the surfaces of CuO and Sm_{0.2}-CuO_x catalysts. For the pristine CuO catalyst (**Figure 5 (e)**), only the characteristic signal of physico/chemical-adsorbed N₂O molecules was captured upon exposure to N₂O at 300 °C. Upon elevating the temperature to 450 °C, a transient -N intermediate was detected⁵⁶, which was attributed to the cleavage of the N-O

bond in the adsorbed N₂O species. In contrast, for the Sm_{0.2}-CuO_x catalyst (**Figure 5 (f)**), the -N intermediate was immediately observed after N₂O introduction at 300 °C. As the temperature continued to increase, the peak intensity corresponding to this intermediate first increased and then decreased, with complete disappearance at 500 °C. These observations collectively indicate that during N₂O decomposition, the electron-donating effect of Sm₂CuO₄ in Sm_{0.2}-CuO_x catalyst facilitates the activation of N₂O molecules and accelerates the migration of reaction intermediates over the CuO phase.

Based on the above findings, we have clarified the key steps of N₂O decomposition over the Cu-based catalyst studied in this work. How do active Cu⁺ species effectively activate adsorbed N₂O? From the perspective of frontier molecular orbital theory, N₂O is a linear molecule with the electron configuration (1σ)²(2σ)²(3σ)²(4σ)²(5σ)²(6σ)²(1π)⁴(7σ)²(2π)⁴(3π)⁰.¹⁸ Its lowest unoccupied molecular orbital (LUMO) is the antibonding 3π orbital (3π*), composed of the p_x and p_y orbitals of the terminal N atom (**Figure S17**), which exhibits π symmetry and better matches the symmetry of the metal t_{2g} orbital to enable efficient electron transfer.^{16,18,57} For Cu⁺, the electron configuration is [Ar]3d¹⁰, representing a closed-shell structure. However, if coordinated with N₂O, the 3d orbitals of Cu⁺ could be split into t_{2g} (d_{xy}, d_{xz}, d_{yz}) and e_g (d_{x²-y²}, d_{z²}) orbitals under the ligand field. Theoretically, the e_g orbitals have higher energy but extend primarily along the axial direction, leading to stronger σ interactions with the end-on coordination mode of N₂O (via the terminal N atom) while contributing weakly to electron filling of the π* orbital (LUMO) of N₂O. In contrast, the t_{2g} orbitals typically have lower energy and spatial orientation more favorable for lateral overlap with the linear N₂O molecule, facilitating electron injection into the 3π* orbital of N₂O, weakening the N-O bond, and thus promoting N₂O activation. This process resembles the classic "π-backdonation" mechanism,^{58,59} where metal d electrons are donated back to the π orbital of the ligand, and the t_{2g} orbitals serve as the primary electron source for such backdonation interactions.

A comparison of the d-orbital projected density of states (PDOS) of Cu⁺ species before

(**Figure 6 (a)**) and after (**Figure 6 (b)**) N_2O adsorption on $\text{CuO-O}_{\text{vac}}$, reveals a significant decrease in e_g orbital electrons and an increase in t_{2g} electrons. This is particularly notable for the d_{yz} orbital following N_2O adsorption. In contrast to free N_2O molecules (**Figure S18**), the empty orbital intensity of the terminal N atom (N_2) in adsorbed N_2O weakens (**Figure 6 (c)**). The electron occupancy of the p_z orbitals of both N atoms also diminishes. This phenomenon seemingly contradicts the " π -backdonation" mechanism. DFT calculations demonstrate that on $\text{CuO-O}_{\text{vac}}$ surfaces featuring $\text{Cu}^+\text{-O}_{\text{vac}}\text{-Cu}^+$ sites, N_2O molecules preferentially adopt an end-on adsorption mode. The terminal N atom directly coordinates to the Cu^+ site in this configuration. The d_{z^2} orbital of Cu^+ , an e_g orbital, spatially overlaps with the p_z orbital of the terminal N atom of N_2O , a σ orbital. This forms σ - σ overlap. Electrons transfer exclusively through this σ channel. When e_g electrons of Cu^+ fill the p_z orbital of N_2O , the N_2O molecule bends as shown in **TS1** of **Figure 5(d)**. The N-O bond weakens in this process. This constitutes σ -backdonation rather than π -backdonation. It indicates that σ -backdonation dominates N_2O activation on pure $\text{CuO-O}_{\text{vac}}$, as shown in **Figure 6 (d)**.

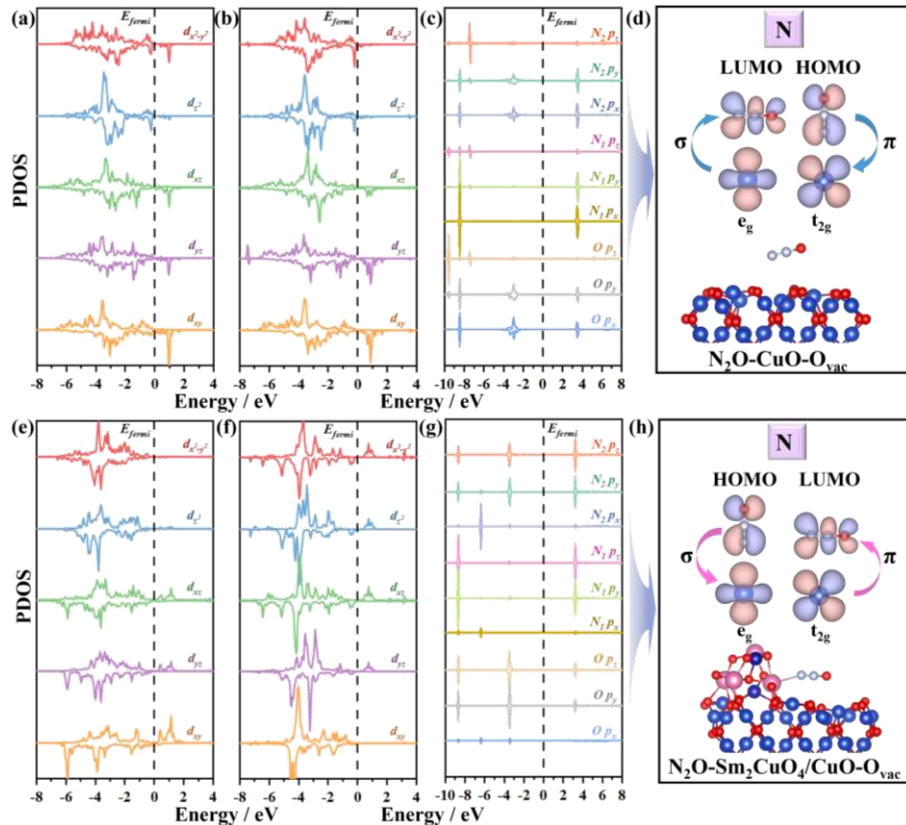


Figure 6. Interaction of orbitals of the adsorbed- N_2O molecule and active Cu site. The PDOS

of (a) Cu d orbitals in CuO-O_{vac} configurations, (b) Cu d and (c) N/O p orbitals in N₂O adsorbed-CuO-O_{vac} configurations (N₂O: N2-N1-O). (d) CuO-O_{vac} surface: reactant-active-site interactions involve σ - and π -interactions of the Cu 3d orbitals with the highest occupied (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the N₂O molecule. The PDOS of (e) Cu d orbitals (CuO phase) in Sm₂CuO₄/CuO-O_{vac} configurations, (f) Cu d and (g) N/O p orbitals in N₂O adsorbed-Sm₂CuO₄/CuO-O_{vac} configurations (N₂O: N2-N1-O). (d) Sm₂CuO₄/CuO-O_{vac} surface: reactant-active-site interactions involve σ - and π -interactions of the Cu 3d orbitals with the HOMO and the LUMO of the N₂O molecule.

In stark contrast, the Sm₂CuO₄/CuO-O_{vac} configuration exhibits unique behavior. Compared with **Figure 6 (e) and (f)**, following N₂O adsorption, Cu⁺ shows a decrease in t_{2g} orbital electrons. This is especially true for d_{xy} and d_{yz} orbitals. An increase in e_g orbital electrons also occurs. Concurrently, the unoccupied and occupied state intensities of the p_x orbitals of the O atom and all N atoms in N₂O weaken (**Figure 6 (g)**). This partially aligns with the " π -backdonation" mechanism. Structural characterization confirms that Sm doping into CuO induces the formation of the Sm₂CuO₄ perovskite phase. This creates a heterostructure with CuO. Previous studies have shown that in analogous oxide-perovskite heterojunctions, electrons migrate from electron-rich perovskite phases to electron-poor oxide surfaces.^{60,61} Here, advanced spectroscopy, *in situ* experiments, and DFT calculations demonstrate that in the Sm_{0.2}-CuO_x catalyst, an "electron pumping heterojunction" forms between Sm₂CuO₄ and CuO, where Sm₂CuO₄ acts as an "electron pump" during N₂O decomposition by continuously injecting electrons into the CuO phase (the "reaction cell") to stabilize Cu⁺. DFT results as shown in **Figure 6 (h)** show that N₂O molecules prefer side-on adsorption at Cu⁺ sites. The 3 π^* orbital of N₂O, composed of p_x and p_y orbitals of the terminal N, perfectly matches the symmetry of Cu⁺'s t_{2g} orbitals (d_{xy} and d_{yz}). This maximizes the overlap integral. This π -backdonation mechanism enables multi-center electron transfer from Cu⁺'s d orbitals to Cu⁺'s π^* orbitals. This is far more efficient than the single-center σ -backdonation in end-on adsorption. It thus becomes the dominant N₂O activation mode.

In essence, the "electron pumping heterojunction" allows Sm₂CuO₄ phase to "charge" the CuO-O_{vac} phase by pumping electrons. This enhances Cu⁺ activity. To "discharge" efficiently, which means activating N₂O, the system favors the "high-speed channel" of side-on adsorption via " π -backdonation" mechanism. It does not prefer the "unconventionally path" of end-on adsorption

on pure CuO-O_{vac.} surface.

To elucidate the mechanism by which O₂ modulates the catalytic decomposition of N₂O, a combination of reaction kinetics tests and DFT calculations was employed. Reaction kinetics results confirmed that the N₂O decomposition reaction remained first-order for both CuO (**Figure 7 (a)**) and Sm_{0.2}-CuO_x (**Figure 7 (b)**) catalysts in the presence of 5% O₂. This result indicates that O₂ does not alter the fundamental reaction pathway of N₂O decomposition over these catalysts. However, comparative analysis of reaction rates at identical temperatures with and without O₂ (**Figure S16**) revealed a pronounced inhibitory effect of O₂ on CuO's N₂O decomposition performance. In contrast, its impact on Sm_{0.2}-CuO_x was minimal, which suggests distinct interactions between O₂ and the two catalyst systems. DFT calculations further resolved the divergent effects of O₂ on N₂O adsorption and activation by unveiling configuration-specific mechanisms. For the CuO-O_{vac.} configuration (**Figure 7 (c)**), N₂O molecules still interacted with Cu⁺ sites via their terminal N atoms. However, O₂ molecules chemisorbed at the oxygen vacancy of the Cu⁺-O_{vac.}-Cu⁺ structure. This led to competitive adsorption with N₂O, which weakened N₂O adsorption energy and elevated the -IpCOHP value of the N-O bond. Both factors are indicative of reduced N₂O activation. In contrast, for the Sm₂CuO₄/CuO-O_{vac.} configuration (**Figure 7 (d)**), O₂ exerted negligible influence on N₂O adsorption properties, including adsorption energy, charge transfer, and the -IpCOHP value of the N-O bond. This is because O₂ molecules preferentially bonded to Sm species in the Sm₂CuO₄ perovskite phase. This behavior is consistent with the oxygen affinity of rare-earth perovskites.⁶²⁻⁶⁴ It thus eliminates competitive adsorption with N₂O and preserves the catalyst's activity toward N₂O decomposition. This mechanistic distinction highlights the critical role of structural design in mitigating O₂ inhibition. The Sm₂CuO₄ phase in Sm_{0.2}-CuO_x effectively sequesters O₂ through preferential bonding to Sm species. This prevents O₂ from interfering with N₂O adsorption and activation on the active Cu⁺ sites.

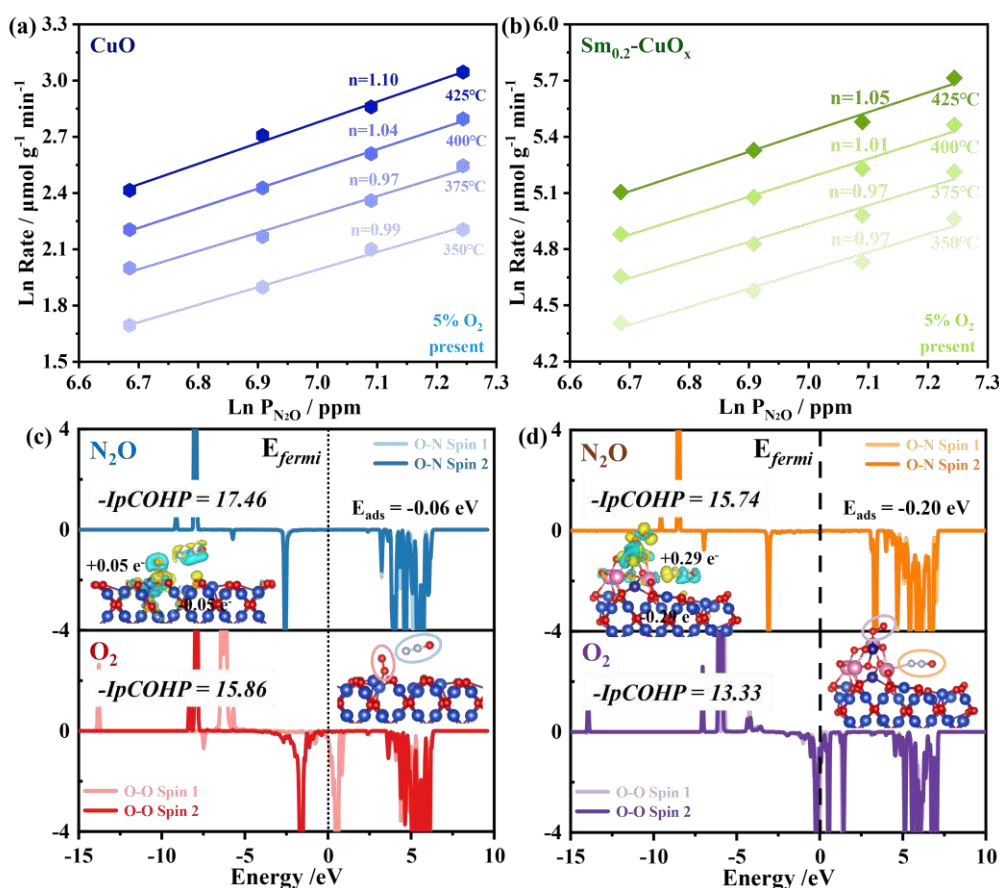


Figure 7. Mechanistic investigation of O_2 influence on N_2O Decomposition over catalysts. Dependences of the N_2O decomposition rate on N_2O concentration in 5% O_2 conditions at 350, 375, 400 and 425 °C of (a) bare CuO and (b) $\text{Sm}_{0.2}\text{-CuO}_x$ catalysts. DFT calculations of $\text{N}_2\text{O}+\text{O}_2$ co-adsorbed (c) $\text{CuO-O}_{\text{vac}}$. and (d) $\text{Sm}_2\text{CuO}_4/\text{CuO-O}_{\text{vac}}$ configurations with N_2O adsorption energy, charge difference, bader charge, and pCOHP analyses.

3 Conclusion

In this work, we designed and synthesized a samarium-modified CuO -based composite oxide catalyst system using a citric acid-assisted sol-gel method. The catalyst with a $\text{Sm}:\text{Cu}$ molar ratio of 0.2:1 ($\text{Sm}_{0.2}\text{-CuO}_x$) exhibited excellent N_2O decomposition reaction activity in the presence of O_2 and showed good reaction activity and stability in the simultaneous elimination process of N_2O and NO_x under simulated real operating conditions. Combining the results of XRD, Raman, HADDF-STEM and EXAFS confirmed that the introduction of Sm would induce the formation of the Sm_2CuO_4 perovskite phase, which forms a tight heterostructure with the CuO phase. The results of XAFS, H_2 -TPR, EPR and DFT calculations certified that the Sm_2CuO_4 perovskite phase in the $\text{Sm}_{0.2}\text{-CuO}_x$ catalyst can fill electrons into the CuO phase, making the CuO phase in an electron-rich state. Isotope labeling experiments, *in situ* Raman and NAP-XPS results confirmed that for both the

pure CuO and Sm_{0.2}-CuO_x catalysts, the reaction starts with the MvK mechanism to form Cu⁺ sites. On this basis, the reaction cycle is completed through the LH pathway, that is, the Cu⁺ species are the active species for the N₂O decomposition reaction. Meanwhile, it was also clear that the rate-determining step of the N₂O decomposition reaction is the N-O activation and cleavage, rather than the recombination and desorption process of oxygen species.

The intrinsic reason for the poor N₂O decomposition activity of pristine CuO lies in the preferential binding of N₂O molecules to Cu⁺ sites via their terminal N atoms (i.e., forming a Cu⁺-N-NO configuration), with N₂O activation proceeding through a non-classical "σ-backdonation" mechanism. Additionally, O₂ inhibits N₂O adsorption and activation on CuO via competitive adsorption. For the Sm_{0.2}-CuO_x catalyst, the heterostructure formed between Sm₂CuO₄ and CuO acts as a dynamic "electron-pumping heterojunction" during N₂O decomposition. Here, Sm₂CuO₄ functions as an "electron pump", continuously and actively transferring electrons to the CuO phase to stabilize Cu⁺ species. Concomitantly, this heterostructure reverses the adsorption and activation mode of N₂O on active Cu⁺ sites, enabling N₂O to adsorb in a side-on configuration and activate via a "π-backdonation" mechanism. Notably, O₂ does not interfere with N₂O adsorption and activation on Sm_{0.2}-CuO_x, as O₂ preferentially adsorbs on Sm sites within the Sm₂CuO₄ phase, eliminating competitive adsorption with N₂O.

This study not only provides a fundamental understanding of the structure-activity relationship in Sm-modified CuO catalysts but also offers a promising strategy for the rational design of high-performance catalysts for N₂O abatement with potential applications in industrial flue gas treatment and environmentally green chemical technologies.

4 Method

Catalyst Preparation

The catalysts were prepared by sol-gel method, employing citric acid as the complexing agent. Typically, copper nitrate (Cu(NO₃)₂·3H₂O, 99%, Macklin) and samarium nitrate (Sm(NO₃)₃·6H₂O, ≥99.9%, Aladdin) are used as precursor salts. They are dissolved in deionized water, followed by

the addition of citric acid ($\geq 99.5\%$ (T), Macklin), and the mixture is stirred thoroughly. The molar ratio of metal cations to citric acid to H_2O is set at 1:2:100. The solution is then heated in a 90 °C oil bath until it forms a gel. The resulting colloid is transferred to a drying oven at 110 °C for 36 hours. Finally, the samples are calcined in a muffle furnace, first holding at 250 °C for 1 hour, then heating to 550 °C for 4 hours at a rate of 2 °C·min⁻¹. The samples are labeled as CuO and Sm_z-CuO_x, where z denotes the molar ratio of Sm to Cu.

Low-Temperature N₂ Adsorption-Desorption

The low-temperature N₂ adsorption-desorption experiment was performed on a Micromeritics Asp-2020 instrument, where an appropriate amount of catalyst was added to a pre-weighed empty sample tube, followed by vacuum degassing at 300 °C for 2 h to remove surface impurities, post-cooling to room temperature, N₂ backfilling completed pre-treatment, the tube with catalyst was re-weighed and transferred to the instrument for isotherm measurement at 77 K (liquid nitrogen temperature), and specific surface area was calculated via Brunauer-Emmett-Teller (BET) method while pore size distribution was derived using Barret-Joyner-Halenda (BJH) model.

X-Ray Diffraction (XRD), Raman Spectroscopy and X-ray absorption structure (XAS)

XRD patterns were acquired using a Bruker D8 Advance diffractometer (Germany) with Cu K α radiation. Scans were performed at a rate of 2°·min⁻¹ over a 2 θ range of 10–90°. Raman spectra were recorded on a Horiba LabRAM Aramis laser Raman spectrometer (Japan) using a 532 nm Ar⁺ laser (10 mW power). Spectral data were collected over the range of 100–1000 cm⁻¹. XAFS and extended X-ray absorption fine structure (EXAFS) experiments were carried out at the TableXAFS-500 at the Speccreation Instruments Co., Ltd.

Scanning Transmission Electron Microscopy (STEM)

High-angle annular dark-field (HAADF) STEM images with Z-contrast were obtained using a FEI Titan 80-300 spherical-aberration corrected electron microscope (SAC-STEM, USA), which featured an energy resolution of ≤ 0.7 eV.

Hydrogen Temperature-Programmed Reduction (H₂-TPR)

H₂-TPR experiments were carried out on a Micromeritics ChemBET Pular chemical adsorption analyzer (USA). Approximately 50 mg of catalyst powder was loaded into a U-tube reactor and heated to 300 °C under He to remove impurities. After cooling to 40 °C, the gas stream was switched to 5 vol.% H₂/95 vol.% He (100 mL·min⁻¹ flow rate), and the temperature was ramped to 900 °C at 10 °C·min⁻¹.

Electron paramagnetic resonance (EPR)

The EPR signals of Cu²⁺ species were recorded at 150 K on an EMXPLUS10/12 ESR spectrometer (Bruker Company, Karlsruhe, Germany) in the region of 2200–3800 G. Before the test, the quality of each test sample was ensured to be identical.

***In Situ* Near-Ambient Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS)**

In situ NAP-XPS measurements were performed on a SPECS NAP-XPS system. Al K α radiation (1486.6 eV) from a SPECS XR-50 aluminum anode (50 W power) was used for excitation. A differential pumping system isolated the SPECS Phoibos NAP-150 electron analyzer from the reaction zone, where pressure was maintained at 1 mbar via a pressure-reducing valve. The reactant gas consisted of 20 vol.% N₂O balanced with Ar.

Density functional theory (DFT) calculations

All the spin-polarized density functional theory calculations were performed using the Vienna ab initio simulation package (VASP). The generalized gradient approximation (GGA) method was employed, along with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. The interaction between ions and electrons was described using the Projector Augmented Wave (PAW) method. Kinetic energy cutoff value of the plane wave was set to 500 eV. In order to accurately describe highly localized orbitals and solve the strong electron correlation problem in transition metal atoms and their oxide systems, the DFT+U method (Cu, U_{eff} = 4.0 eV, Sm, U_{eff} = 8.0 eV) was used to correct the on-site coulomb interaction of localized electrons. Based on the results of HR-TEM and AC-HAADF-STEM, the CuO(100) and Sm₂CuO₄(010) surfaces were selected for calculation, and then the Sm₂CuO₄ and CuO species were loaded on the surface, respectively.

Electron smearing was employed through the Gaussian smearing method with a smearing width of 0.05 eV, and the Brillouin zone was sampled at the $1 \times 1 \times 1$ k-point mesh. The self-consistent field tolerance was 1×10^{-5} eV, and the optimized structures were obtained by minimizing the forces on each atom until they were below $0.03 \text{ eV} \cdot \text{\AA}^{-1}$.

The adsorption energy of species (ΔE_{ads}) was calculated as:

$$\Delta E_{\text{ads}} = E_{\text{surface + adsorbate}} - E_{\text{surface}} - E_{\text{adsorbate}}$$

where $E_{\text{surface + adsorbate}}$, E_{surface} , and $E_{\text{adsorbate}}$ are the total energies of surface with adsorbate, surface, and gas-phase adsorbate, respectively. A climbing image nudged elastic band (CI-NEB) method⁶⁵ and DIMER method⁶⁶ were employed to locate the transition state (TS). Each transition state was confirmed by a single imaginary frequency.

Catalytic performance test

The catalyst is placed on a packed-bed reactor, the gas flow rate is $100 \text{ mL} \cdot \text{min}^{-1}$ (2000 ppm N_2O , 5 vol.% O_2 (when used), 500 ppm NO_x (when used), 5 vol. % H_2O (when used), N_2 balance). The N_2O concentration at the outlet was monitored online by a Fourier transform infrared continuous gas analyzer (GASMET DX-4000). The decomposition activity was characterized by N_2O conversion:

$$\text{N}_2\text{O decomposition conversion \%} = \frac{[\text{N}_2\text{O}]_{\text{in}} - [\text{N}_2\text{O}]_{\text{out}}}{[\text{N}_2\text{O}]_{\text{in}}} * 100\%$$

Based on specific surface area (S_{BET}) normalized reaction rates (R_s , $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) were calculated by the following formula:

$$R_s (\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}) = \frac{C_{\text{inlet}} \cdot F}{m_{\text{cat}} \cdot S_{\text{BET}}} \cdot \ln(1 - X_{\text{N}_2\text{O}})$$

where C_{inlet} refers to the N_2O concentration in the inlet gas, F ($\text{mol} \cdot \text{s}^{-1}$) is the flow rate, m_{cat} (g) is the mass of catalyst, S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$) is the specific surface area obtained by low-temperature N_2 adsorption-desorption technology, $X_{\text{N}_2\text{O}}$ is N_2O decomposition efficiency.

Steady-state kinetic experiments for N₂O decomposition were performed on selected catalyst samples in simulated flue gas containing N₂O at concentrations of 800, 1000, 1200, and 1400 ppm, respectively, at three reaction temperatures: 350 , 375 , 400 , and 340 °C. An extremely high weight hourly space velocity (WHSV) was adopted in the experiments to strictly control the N₂O conversion within the range of 5-20%, thereby effectively eliminating the influence of internal and external diffusion mass transfer limitations.

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Competing interests

The authors declare no conflict of interest.

Author contributions

H. Liu and C. Z. Sun proposed idea. H. Liu and X .Q. Liu wrote the manuscript and performed DFT simulation. Y. P. Long, J. J. Chen and J. H. Li modified the manuscript. C. Z. Sun. and J. H. Li supervised the whole work. X .Q. Liu and F. Huang performed all the experiments. All the authors discussed the results and commented on the manuscript.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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