

Article

Ag-Cu Synergism-Driven Oxygen Structure Modulation Promotes Low-Temperature NO_x and CO Abatement

Ruoxin Li ¹, Jiuhong Wei ¹, Bin Jia ¹, Jun Liu ^{2,3,*}, Xiaoqing Liu ⁴, Ying Wang ^{1,5}, Yuqiong Zhao ^{1,5} , Guoqiang Li ^{1,5} and Guojie Zhang ^{1,5,*} 

¹ State Key Laboratory of Clean and Efficient Coal Utilization, College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

² College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

³ National Engineering Laboratory for Multi Flue Gas Pollution Control Technology and Equipment, School of Environment, Tsinghua University, Beijing 100084, China

⁴ School of Environment and Safety Engineering, North University of China, Taiyuan 030051, China

⁵ Key Laboratory of Coal Science and Technology, Ministry of Education, Taiyuan University of Technology, Taiyuan 030024, China

* Correspondence: liujun02@tyut.edu.cn (J.L.); zhangguojie@tyut.edu.cn (G.Z.)

Abstract

The efficient simultaneous removal of NO_x and CO from sintering flue gas under low-temperature conditions (110–180 °C) in iron and steel enterprises remains a significant challenge in the field of environmental catalysis. In this study, we present an innovative strategy to enhance the performance of CuSmTi catalysts through silver modification, yielding a bifunctional system capable of oxygen structure regulation and demonstrating superior activity for the combined NH₃-SCR and CO oxidation reactions under low-temperature, oxygen-rich conditions. The modified AgCuSmTi catalyst achieves complete NO conversion at 150 °C, representing a 50 °C reduction compared to the unmodified CuSmTi catalyst (T_{100%} = 200 °C). Moreover, the catalyst exhibits over 90% N₂ selectivity across a broad temperature range of 150–300 °C, while achieving full CO oxidation at 175 °C. A series of characterization techniques, including XRD, Raman spectroscopy, N₂ adsorption, XPS, and O₂-TPD, were employed to elucidate the Ag-Cu interaction. These modifications effectively optimize the surface physical structure, modulate the distribution of acid sites, increase the proportion of Lewis acid sites, and enhance the activity of lattice oxygen species. As a result, they effectively promote the adsorption and activation of reactants, as well as electron transfer between active species, thereby significantly enhancing the low-temperature performance of the catalyst. Furthermore, in situ DRIFTS investigations reveal the reaction mechanisms involved in NH₃-SCR and CO oxidation over the Ag-modified CuSmTi catalyst. The NH₃-SCR process predominantly follows the L-H mechanism, with partial contribution from the E-R mechanism, whereas CO oxidation proceeds via the MvK mechanism. This work demonstrates that Ag modification is an effective approach for enhancing the low-temperature performance of CuSmTi-based catalysts, offering a promising technical solution for the simultaneous control of NO_x and CO emissions in industrial flue gases.



Academic Editor: Zuzeng Qin

Received: 21 June 2025

Revised: 5 July 2025

Accepted: 6 July 2025

Published: 11 July 2025

Citation: Li, R.; Wei, J.; Jia, B.; Liu, J.; Liu, X.; Wang, Y.; Zhao, Y.; Li, G.; Zhang, G. Ag-Cu Synergism-Driven Oxygen Structure Modulation Promotes Low-Temperature NO_x and CO Abatement. *Catalysts* **2025**, *15*, 674. <https://doi.org/10.3390/catal15070674>

Copyright: © 2025 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) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: NH₃-SCR; CO oxidation; Ag-Cu interaction; oxygen structure regulation; bifunctional catalysis; low-temperature flue gas

1. Introduction

Flue gas generated during the fossil fuel sintering process in iron and steel enterprises contains harmful atmospheric pollutants, such as nitrogen oxides (NO_x) and carbon monoxide (CO) [1], which pose serious threats to both environmental quality and human health [2,3]. Among various NO_x removal technologies, ammonia-based selective catalytic reduction (NH_3 -SCR) is widely recognized as the most effective denitrification method [4]. The V_2O_5 - WO_3 / TiO_2 catalyst, known for its excellent catalytic performance, has been extensively applied in industrial NH_3 -SCR processes [5]. However, this catalyst operates optimally within a temperature range of 320–450 °C and involves the use of V_2O_5 , which becomes highly toxic at elevated temperatures [6]. As a result, its application faces significant challenges when treating sintering flue gas at much lower temperatures (110–180 °C) [7]. In light of increasingly stringent environmental regulations, the development of high-performance denitrification catalysts suitable for low-temperature conditions has become an urgent priority. Meanwhile, catalytic CO oxidation, as a well-established technology for CO control, has been widely studied and implemented [8]. Nevertheless, the design and development of a bifunctional catalyst capable of simultaneously removing both NO_x and CO remains a key research focus and challenge in the field of environmental catalysis.

In theory, the selective catalytic reduction of NO_x using CO as a reductant (CO-SCR) offers a promising strategy for addressing the simultaneous removal of NO_x and CO [9]. However, in practical applications, the presence of a large excess of oxygen in flue gas causes CO to preferentially react with O_2 rather than NO_x [10], significantly limiting the effectiveness and applicability of the CO-SCR process. A promising alternative is the development of bifunctional catalysts capable of simultaneously promoting both CO oxidation and NH_3 -SCR reactions under oxygen-rich conditions. These catalysts can utilize the heat generated during CO oxidation to enhance the performance of the NH_3 -SCR reaction, thereby improving overall energy efficiency [11]. This dual-function strategy not only reduces energy consumption and operational costs but also provides a feasible technical pathway for the synergistic control of NO_x and CO emissions in low-temperature flue gas environments.

In recent years, transition metal catalysts such as Cu, Mn, and Fe have demonstrated significant potential in NH_3 -SCR coupled with CO oxidation due to their excellent catalytic activity, superior thermal stability, and relatively low cost [12]. Among these, copper-based catalysts exhibit particular potential, owing to their multiple redox states and strong redox capabilities, which confer significant advantages in both NH_3 -SCR [13] and CO oxidation [14] reactions. To further enhance the catalytic performance of copper-based catalysts, extensive modification and optimization efforts have been undertaken by researchers. Liu et al. [15] introduced phosphorus into a CuCeZr (CCZ) catalyst to achieve a balanced combination of acidity and redox properties, significantly enhancing the catalytic activity of the CCZ-P1 catalyst within the temperature range of 250–350 °C. Shen et al. [16] synthesized a molybdenum-doped CuCeO_x bifunctional catalyst and found that Mo incorporation enhanced the catalyst's reducibility, promoted the adsorption and activation of reactant gases, and enabled the CCM3 catalyst to achieve a NO_x conversion rate of 91.2% at 225 °C, along with complete CO oxidation over a broad temperature window of 150–300 °C. Lv et al. [17] modified a Cu/ TiO_2 catalyst with Sm, constructing asymmetric active sites of Cu^+ - Sm^{3+} - O_v - Ti^{4+} , which effectively facilitated full NO conversion at 200 °C and efficient CO oxidation in the temperature range of 175–300 °C.

Although modified copper-based catalysts such as CuSmTi have exhibited relatively superior low-temperature activity, their performance still does not fully meet the practical requirements for the treatment of sintering flue gas at temperatures below 180 °C. Therefore, further modification strategies are required to enhance their catalytic performance at such

conditions. Liu et al. [18] prepared Ag-modified α - MnO_2 catalysts for efficient benzene oxidation. The Ag modification enriched the variety of oxygen species and increased the quantity and enhanced the reactivity of lattice oxygen, thereby promoting the reaction efficiency. Similarly, Rao et al. [19] reported that the incorporation of Ag could activate a substantial amount of lattice oxygen in CeO_2 nanoparticles. The lattice oxygen activated at the Ag- CeO_2 interface significantly improved the catalytic performance. These studies demonstrate that Ag modification plays a crucial role in regulating the structure and distribution of oxygen species, thereby effectively enhancing the overall catalytic performance of the material.

In this study, an Ag-modified AgCuSmTi bifunctional catalyst was successfully synthesized using the sol-gel method, which facilitated effective oxygen structure regulation. The catalyst exhibits excellent NO and CO conversion efficiencies at low temperatures while maintaining favorable N_2 selectivity. A suite of characterization techniques was employed to investigate the surface structure and internal chemical valence states, revealing pronounced Ag-Cu interactions within the AgCuSmTi catalyst. Further analysis indicated that these Ag-Cu interactions promote the optimization of oxygen structure and modulate the distribution of surface acid sites, thereby enhancing the low-temperature activity of the AgCuSmTi bifunctional catalyst. This study provides new insights into catalytic materials and a theoretical basis for the synergistic removal of multiple pollutants in sintering flue gas.

2. Results and Discussion

2.1. Evaluation of Catalytic Performance

To regulate the performance of the CuSmTi catalyst in the NH_3 -SCR coupled with CO oxidation reaction, Ag species were introduced as dopants, and the influence of varying Ag doping levels on catalytic activity was systematically investigated. The catalytic performance of Ag_xCuSmTi catalysts with different Ag contents ($x = 0.5, 0.8, 1.0, 1.2, 1.5$) was evaluated to determine the optimal doping ratio, where x denotes the molar ratio of AgNO_3 to $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. As shown in Figure S1a, the NO_x conversion at 150°C gradually increases with increasing Ag content, reaching 100% for the $\text{Ag}_{1.2}\text{CuSmTi}$ catalyst. However, further increasing the Ag doping ratio to $x = 1.5$ results in a slight decline in catalytic activity. Figure S1b presents the variation in N_2 selectivity with Ag loading. With increasing Ag content, the N_2 selectivity decreases gradually, and this trend becomes more pronounced at higher doping levels. Nevertheless, the $\text{Ag}_{1.2}\text{CuSmTi}$ catalyst still maintains a N_2 selectivity exceeding 90%, demonstrating a favorable combination of high activity and selectivity. As depicted in Figure S1c, all catalysts achieve complete CO conversion at 175°C . Based on the overall performance analysis, the $\text{Ag}_{1.2}\text{CuSmTi}$ catalyst exhibits the best catalytic performance among the series. For simplicity and consistency in subsequent discussions, the $\text{Ag}_{1.2}\text{CuSmTi}$ catalyst is hereafter referred to as AgCuSmTi.

After determining the optimal silver doping ratio, the effect of Ag modification on catalytic performance was further investigated by comparing the NH_3 -SCR and CO oxidation activities of AgCuSmTi, CuSmTi, and AgSmTi catalysts. Figure 1a presents the NO_x conversion profiles of the three catalysts. The CuSmTi catalyst achieves complete NO_x conversion at 200°C ; however, its activity declines significantly at temperatures above 250°C . Notably, the introduction of Ag markedly enhances low-temperature performance, enabling the AgCuSmTi catalyst to reach 100% NO_x conversion at 150°C ($T_{100\%} = 150^\circ\text{C}$). In contrast, the AgSmTi catalyst, which lacks Cu species, exhibits poor performance, achieving full NO_x conversion only between 225 and 250°C . These results indicate that Ag species strongly interact with CuSmTi and play a crucial role in promoting the NH_3 -SCR reaction. Figure 1b shows the N_2 selectivity of the three catalysts. The AgSmTi catalyst exhibits a sharp de-

crease in N_2 selectivity above 150 °C. Although the addition of Ag slightly lowers the N_2 selectivity compared to CuSmTi, the AgCuSmTi catalyst maintains over 90% selectivity across the entire temperature range of 50–300 °C. This suggests that the interaction between Ag and Cu not only enhances catalytic activity but also contributes to the preservation of high N_2 selectivity. The CO oxidation performance, shown in Figure 1c, further confirms the beneficial effect of Ag modification. Among the three catalysts, AgCuSmTi exhibits the lowest $T_{100\%}$ value. At any given temperature within the tested range, its CO conversion rate is slightly higher than that of CuSmTi, whereas AgSmTi shows relatively poor performance. This indicates that the synergistic interaction between Ag and CuSmTi plays a key role in enhancing CO oxidation activity as well. The TOF values for NO and CO conversion over the AgCuSmTi and CuSmTi catalysts are presented in Figure S2a and Figure S2b, respectively. The results clearly demonstrate that the incorporation of Ag significantly enhances the TOF values associated with the Cu species. Consequently, the AgCuSmTi catalyst exhibits markedly higher catalytic efficiency compared to the CuSmTi catalyst.

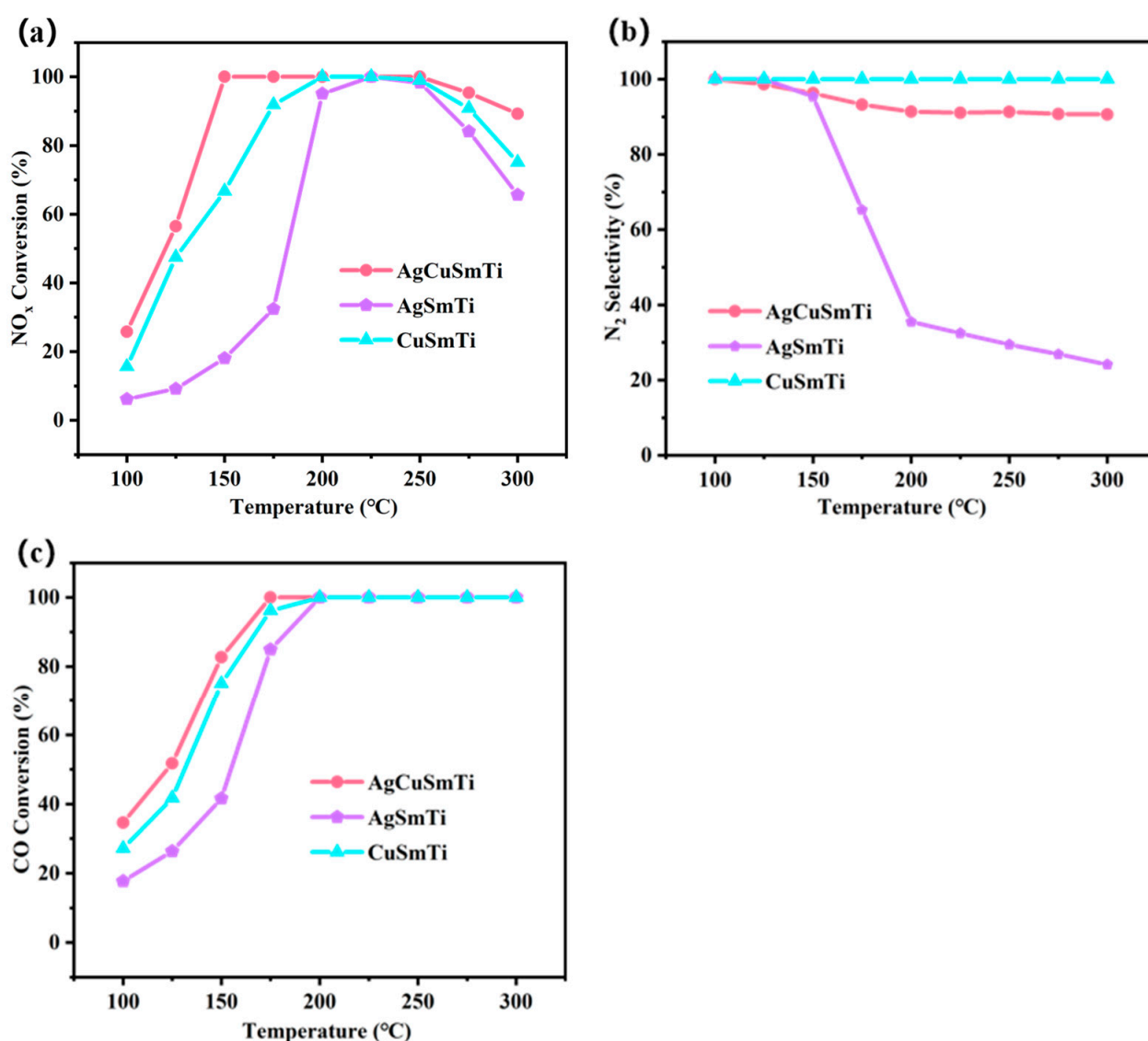


Figure 1. NO_x conversion (a), N₂ selectivity (b), and CO conversion (c) of catalyst. Gas composition: GHSV = 60,000·h⁻¹, [NO_x] = [NH₃] = 500 ppm, [CO] = 1000 ppm, O₂ = 5 vol%, N₂ as balance.

To further highlight the outstanding catalytic performance of the AgCuSmTi catalyst, Table S1 summarizes recent studies on Cu-based catalysts applied in NH₃-SCR coupled

with CO oxidation [15–17,19–24]. As shown, the α -MnO₂-Cu catalyst achieves a NO_x conversion rate of 85% at 150 °C and complete CO conversion at 175 °C [25]. In comparison, the AgCuSmTi catalyst developed in this study exhibits a 100% NO_x conversion rate at the same temperature of 150 °C. Moreover, the NO conversion rate over the CuO_x/ α -MnO₂ catalyst reaches only 81% at 150 °C. Several other well-reported catalysts, such as MnCuCeO_x/ γ -Al₂O₃ [26], CuMgFeO [20], V₂O₅-CuO/TiO₂ [22], CuO/VWTi [11], and CuW/CeZr, exhibit higher temperature requirements for achieving maximum NO and CO conversion. The results demonstrate that the AgCuSmTi catalyst not only exhibits competitive low-temperature catalytic activity compared to traditional systems, but in fact surpasses many of them, highlighting its significant potential for practical applications in low-temperature flue gas treatment.

To evaluate the stability of the AgCuSmTi catalyst, stability tests were carried out at 150 °C and 175 °C over a period of 20 h. The results presented in Figure S3a,b clearly indicate that during the 20 h reaction duration, the conversion rates of NO and CO, as well as the N₂ selectivity, remained relatively constant. This demonstrates that the AgCuSmTi catalyst exhibits excellent stability under reaction conditions. In summary, the synergistic interaction between Ag and CuSmTi significantly enhances the catalytic performance in both the NH₃-SCR and CO oxidation reactions. The AgCuSmTi catalyst displays outstanding low-temperature activity, excellent N₂ selectivity, strong CO conversion capability, and superior stability, highlighting its significant potential for practical applications.

2.2. Structural and Chemical Characterization of the Catalyst

2.2.1. Morphological Characterization of the Catalysts

The SEM images (Figure 2a–f) reveal that both the AgCuSmTi and CuSmTi catalysts exhibit irregular nanoparticle morphologies. The incorporation of Ag effectively suppresses nanoparticle agglomeration and promotes the uniform dispersion of active species, thereby enhancing the overall catalytic performance [27]. The particle size distribution of the AgCuSmTi catalyst is presented in Figure 2g. The results indicate that the particle sizes are predominantly within the range of 14–18 nm and are relatively uniformly distributed. However, the average particle size of AgCuSmTi is 16.77 nm, which is significantly larger than that of CuSmTi (6.22 nm; see Figure S4). This suggests that the introduction of Ag has somewhat altered the particle size characteristics of the catalyst. TEM images (Figure 2h,i) show a clear lattice fringe with an interplanar spacing of approximately 0.35 nm, consistent with the (101) plane of anatase TiO₂ [28]. Notably, no distinct lattice fringes corresponding to Ag, Cu, or Sm species were observed, indicating that these metal dopants are highly dispersed on the catalyst surface rather than forming large crystalline domains or aggregates.

To further investigate the elemental composition and surface distribution characteristics of the AgCuSmTi catalyst, energy-dispersive X-ray spectroscopy (EDX) mapping analysis was conducted. As shown in Figure 2j, elements such as Ag, Cu, Sm, Ti, and O are clearly present and exhibit a uniform spatial distribution, with no signs of agglomeration. This result indicates that all metallic components are highly dispersed on the catalyst surface. This uniform elemental distribution not only confirms the successful integration and dispersion of multiple metal components but also indicates the presence of well-distributed active sites, which are crucial for efficient catalytic performance. Additionally, the high dispersion of various elements suggests that there may be strong synergistic interactions between different active components, which could help enhance catalytic activity.

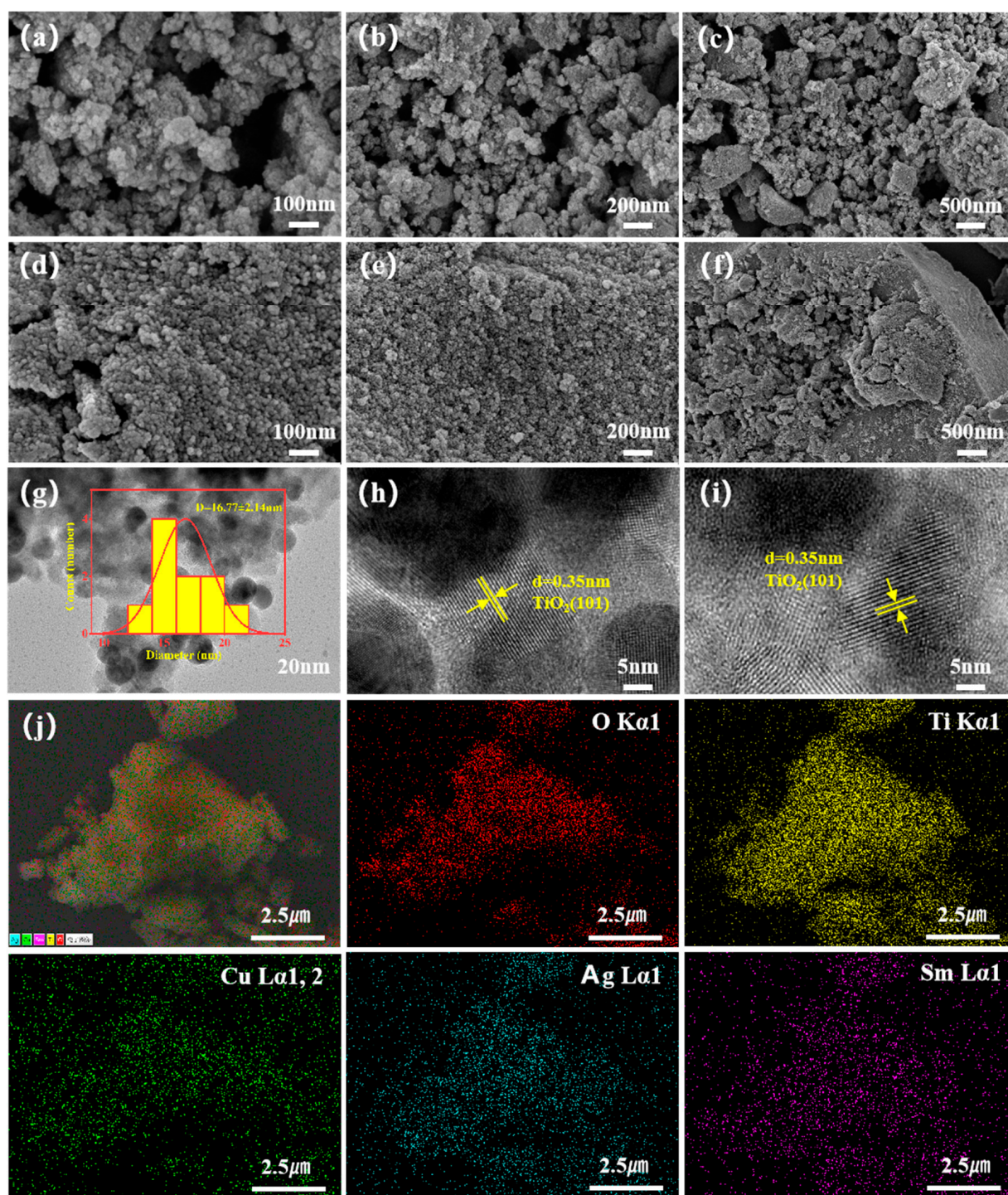


Figure 2. SEM (a–c) spectra of CuSmTi catalyst and SEM (d–f) and TEM (g–i) spectra and EDX mapping (j) of AgCuSmTi catalyst.

2.2.2. Evidence for Ag-Cu Interaction

To further investigate the structural characteristics of the catalysts, XRD analysis was conducted, and the results are presented in Figure 3a. All samples exhibited diffraction peaks corresponding to the anatase phase of TiO_2 . Notably, no characteristic diffraction peaks associated with Sm, Cu, or Ag species were observed, indicating that these elements are either amorphous or highly dispersed within the matrix [29]. Compared to pure TiO_2 , the intensity of the diffraction peaks in the SmTi sample was significantly reduced, suggesting that Sm doping inhibits the growth of TiO_2 crystallites. Upon further introduction of

Cu to form the CuSmTi catalyst, the peak intensities remained nearly unchanged relative to SmTi. However, upon co-doping with Ag, Cu, and Sm to obtain AgCuSmTi, the diffraction peak intensities decreased further, implying a further reduction in the average grain size of TiO_2 . The smaller grain size facilitates the dispersion of active species, leading to an increased number of active sites and thereby enhancing the catalytic performance [30]. This phenomenon can be attributed to the lattice distortion and increased defect density resulting from the synergistic interaction among Ag, Cu, and Sm species, which collectively suppress the growth of TiO_2 grains.

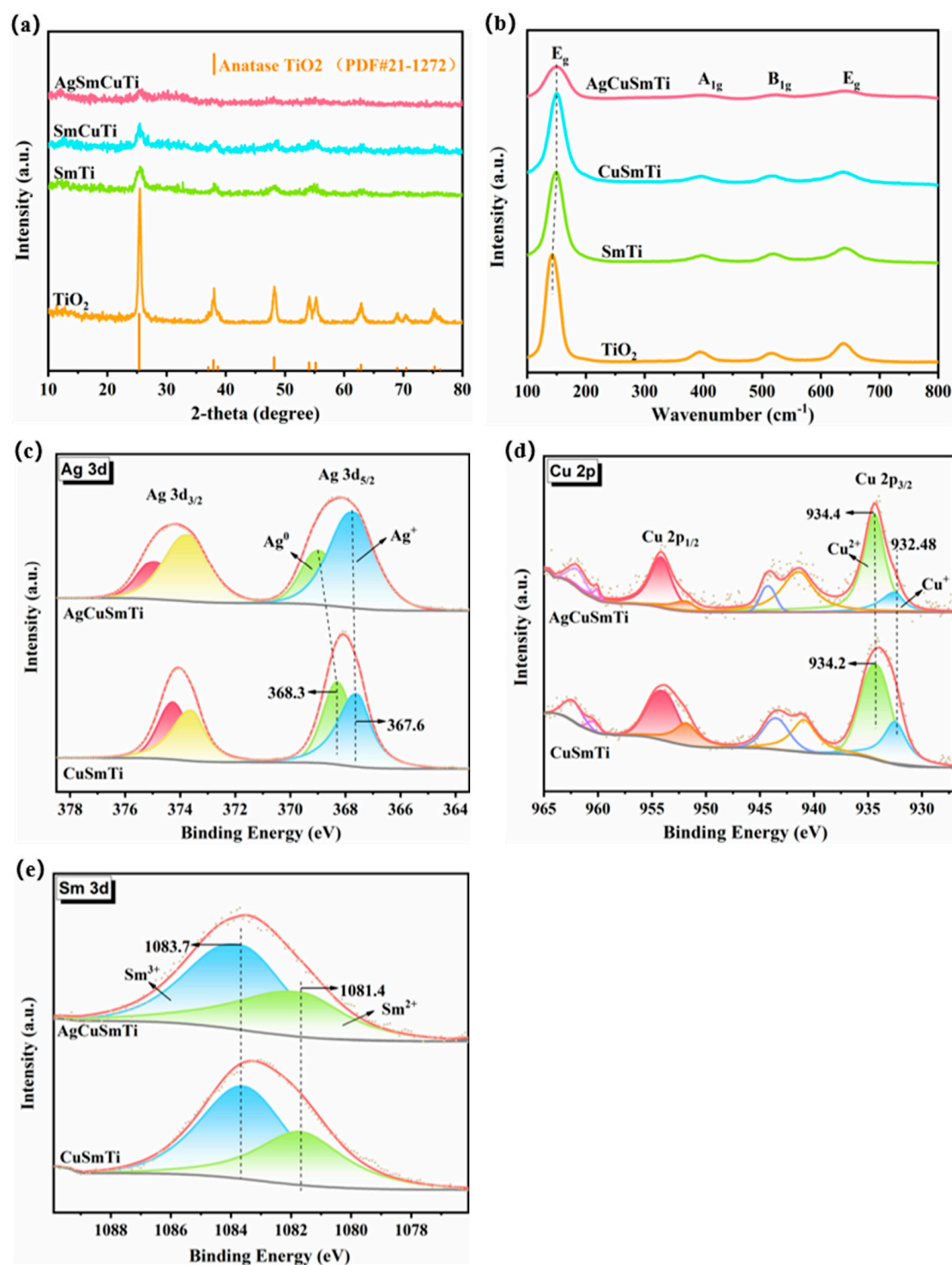


Figure 3. XRD (a), Raman (b), and XPS spectrum of (c) Ag 3d, (d) Cu2p, and (e) Sm 3d for catalysts.

The crystal structures of the samples were further analyzed using Raman spectroscopy. As shown in Figure 3b, all catalysts exhibit the characteristic Raman bands of anatase TiO₂ at approximately 143 cm⁻¹ (E_g), 396 cm⁻¹ (B_{1g}), 515 cm⁻¹ (A_{1g}), and 638 cm⁻¹ (E_g) [31]. These results confirm that doping does not induce any phase transformation of TiO₂ or lead to the formation of detectable secondary oxide phases, consistent with the XRD findings. However, after doping with Sm, Cu, and Ag, the E_g mode of TiO₂ undergoes noticeable blue shifts, exhibits reduced peak intensity, and shows an increased full width at half maximum (FWHM), reflecting enhanced local lattice distortions and internal stress within the TiO₂ lattice [32]. Further analysis of the changes in the E_g peak position, intensity, and FWHM reveals that the degree of lattice disturbance follows the order TiO₂ > SmTi > CuSmTi > AgCuSmTi. This trend indicates that the co-doping of Ag and Cu introduces the most significant structural perturbation. This effect is likely due to the large differences in ionic radii between Cu²⁺ (0.73 Å) and Ag⁺ (1.26 Å) compared to Ti⁴⁺ (0.64 Å), which generate considerable lattice strain when incorporated into the TiO₂ structure [33]. Moreover, Cu doping tends to create localized stress fields, while the addition of Ag further weakens the Ti-O bond strength, thereby suppressing and broadening the Raman-active vibrational modes [33,34]. In particular, the most pronounced E_g peak broadening is observed for the AgCuSmTi sample. Therefore, the combined interaction of Ag, Cu, and Sm significantly disturbs the TiO₂ lattice, resulting in blue shifting of the E_g peak, reduced intensity, and increased peak width. These structural modifications provide a fundamental basis for the enhanced catalytic performance observed in the AgCuSmTi catalyst.

Figure S5 presents the nitrogen adsorption–desorption isotherms and corresponding pore size distribution curves of the samples. As shown in Figure S5a, all catalysts display IV-type nitrogen adsorption isotherms accompanied by H₂-type hysteresis loops, indicating that they possess typical mesoporous structural characteristics. The pore size distributions calculated from the desorption branches further support this conclusion [35]. As illustrated in Figure S5b, the pore size distribution of the SmTi catalyst is only slightly affected by Cu modification. However, upon co-doping with Ag and Cu, a noticeable change in the pore size distribution is observed. The data summarized in Table S2 indicate that the incorporation of Ag and Cu leads to an increase in average pore size and a broader pore size distribution. This suggests that the synergistic interaction among Ag, Cu, and Sm alters the aggregation behavior of the particles, thereby influencing both the pore structure and specific surface area. Moreover, by comparing the catalytic performance with the specific surface area data, it can be inferred that the specific surface area is not the dominant factor affecting catalytic performance.

To further investigate the chemical states of the elements in the AgCuSmTi catalyst and its reference samples, XPS analysis was carried out. As shown in Figure 3c, the Ag 3d spectrum exhibits two main peaks corresponding to the Ag 3d_{3/2} and Ag 3d_{5/2} spin–orbit components. The binding energies at 368.3 eV and 367.6 eV are assigned to metallic Ag⁰ and oxidized Ag⁺ species in the Ag 3d_{3/2} orbital, respectively [36]. According to the atomic ratio calculations presented in Table S3, the Ag⁺/(Ag⁰ + Ag⁺) ratio in the AgCuSmTi catalyst is higher than that in the AgSmTi catalyst upon Cu doping. Moreover, the binding energy of Ag⁺ in the AgCuSmTi sample shifts toward a higher value compared to that in AgSmTi. These observations suggest that the introduction of Cu promotes the oxidation of Ag⁰ to Ag⁺, indicating possible electron transfer interactions among Ag, Cu, and Sm, which may enhance the electronic affinity of Ag.

The Cu 2p spectrum is displayed in Figure 3d. The peaks at 934.2 eV and 932.5 eV correspond to Cu²⁺ and Cu⁺ species in the Cu 2p_{3/2} orbital, respectively [36,37]. Compared with the CuSmTi catalyst, the proportion of Cu²⁺ in the AgCuSmTi catalyst is significantly increased, as summarized in Table 1. This indicates that the incorporation of Ag improves

the stability of the Cu in its respective oxidation states, further supporting the presence of synergistic electronic interactions between Ag, Cu, and Sm.

Table 1. Surface elemental composition of the catalyst as determined by XPS analysis.

Sample	Surface Atomic Concentration (%)					Relative Concentration Ratio (%)		
	Ag	Cu	Sm	Ti	O	$\text{Cu}^{2+}/(\text{Cu}^+ + \text{Cu}^{2+})$	$\text{Sm}^{3+}/(\text{Sm}^{2+} + \text{Sm}^{3+})$	$\text{O}_\beta/(\text{O}_\alpha + \text{O}_\beta)$
AgCuSmTi	8.79	2.61	5.50	24.63	58.46	82.51	60.98	77.77
CuSmTi	-	2.90	4.99	27.67	64.44	68.35	61.05	64.77

As shown in the Sm 3d spectrum (Figure 3e), all catalysts exhibit two fitted peaks at 1083.7 eV and 1081.4 eV, corresponding to Sm^{3+} and Sm^{2+} species, respectively [38]. Compared to the CuSmTi catalyst, the $\text{Sm}^{3+}/(\text{Sm}^{2+} + \text{Sm}^{3+})$ ratio in the AgCuSmTi catalyst remains nearly unchanged. This result suggests that the incorporation of Ag has little influence on the oxidation state of Sm, implying the absence of a strong direct interaction between Ag and Sm. Instead, the primary effect of Ag doping appears to be on its interaction with Cu species, rather than forming a direct synergistic relationship with Sm.

2.2.3. Structural Regulation of Oxygen

To gain deeper insight into the regulation of surface oxygen species and their role in catalytic performance, a comprehensive analysis of the oxygen structure in the catalyst was conducted. First, O 1s XPS was employed to qualitatively and quantitatively distinguish between lattice oxygen (O_{latt}) and surface-adsorbed oxygen (O_{ads}). As shown in Figure 4a, the O 1s spectrum can be deconvoluted into two characteristic peaks at 529.7–529.9 eV and 531.3–531.5 eV, corresponding to lattice oxygen (O_β) and surface-adsorbed oxygen (O_α), respectively [38]. The quantitative results summarized in Table 1 reveal that the AgCuSmTi catalyst exhibits a higher proportion of lattice oxygen compared to the CuSmTi catalyst. This enhancement may be attributed to the electronic synergy between Ag and Cu, which strengthens metal–oxygen bonding and increases the content of lattice oxygen within the crystal structure. The increased lattice oxygen content suggests that the AgCuSmTi catalyst possesses a greater reservoir of active oxygen species available during the initial reaction stage. This facilitates the rapid oxidation of reactant molecules and enhances the overall reaction rate. Concurrently, the consumption of lattice oxygen leads to the formation of oxygen vacancies, which can be readily replenished by gaseous oxygen, thereby sustaining efficient and continuous catalytic cycles [29].

Subsequently, O_2 -TPD analysis was carried out on both the CuSmTi and AgCuSmTi catalysts to evaluate the mobility and desorption behavior of surface oxygen species, reflecting their potential involvement in oxidation reactions. As presented in Figure 4b, both catalysts exhibit two distinct desorption peaks: one in the low-temperature region ($<300^\circ\text{C}$), assigned to surface-adsorbed oxygen (O_α), and another in the medium-to-high temperature range ($300\text{--}600^\circ\text{C}$), corresponding to lattice oxygen (O_β) [20]. Notably, the AgCuSmTi catalyst shows a significant increase in lattice oxygen content, from 33.48% in CuSmTi to 48.25% after the introduction of Ag, indicating that Ag promotes the enrichment of lattice oxygen (Table S4). Therefore, the incorporation of Ag likely activates lattice oxygen through electronic interactions with Cu, enhancing both the reaction rate and stability of the catalyst.

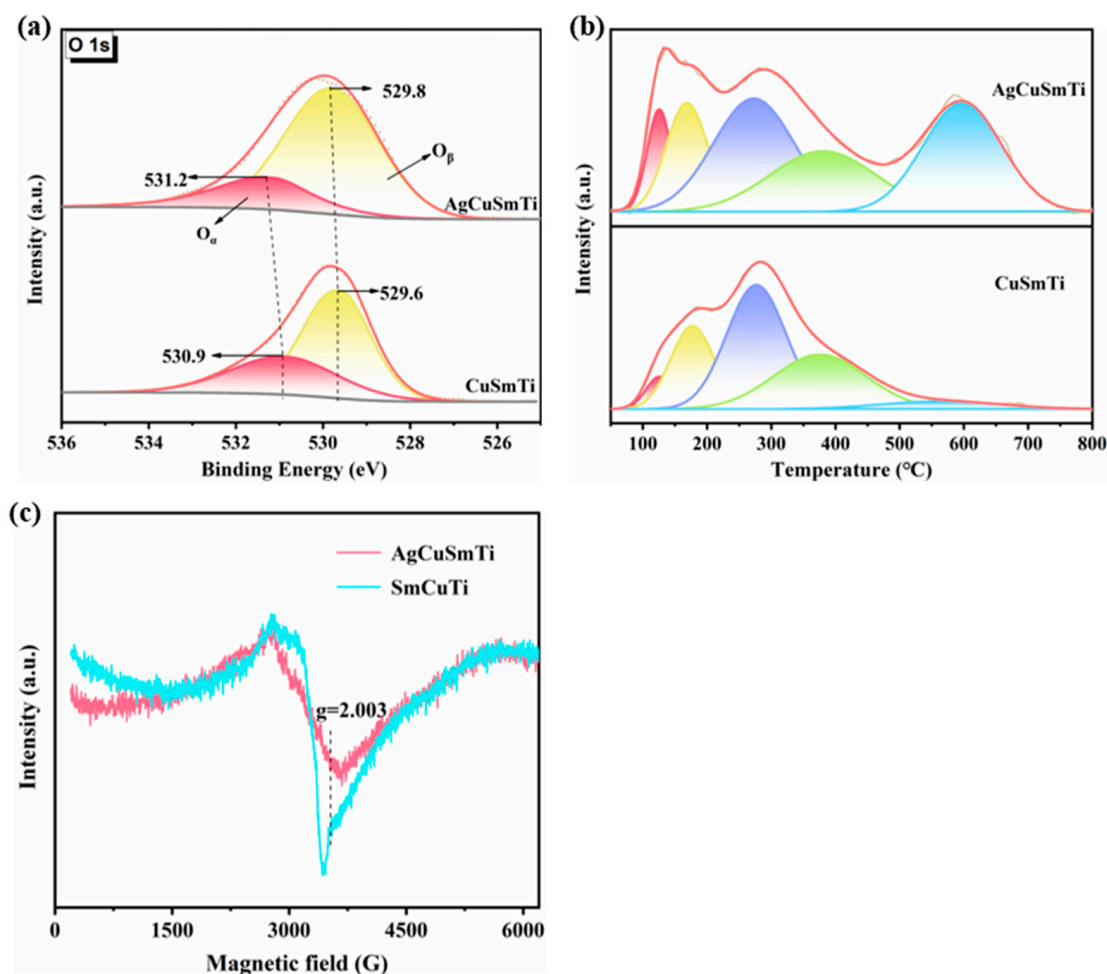


Figure 4. XPS (a), O₂-TPD (b), and EPR (c) spectrum of catalysts.

To further validate changes in oxygen vacancy concentration, EPR spectroscopy was employed for sample analysis. As illustrated in Figure 4c, all catalysts display a distinct EPR signal at $g = 2.003$, which is characteristic of oxygen vacancies [39]. Among them, the CuSmTi catalyst exhibits the strongest signal intensity, indicating a high concentration of oxygen vacancies on its surface. In contrast, the AgCuSmTi catalyst shows a significantly weakened EPR signal, suggesting a reduction in oxygen vacancy density. It can be inferred that the interaction between Ag and Cu contributes to the suppression of oxygen defects while simultaneously facilitating the mobilization and enrichment of lattice oxygen.

In summary, the synergistic effect between Ag and Cu drives the structural regulation of oxygen species, not only creating favorable conditions for oxygen migration and release but also improving the accessibility and utilization efficiency of reactive oxygen species during the reaction. These effects collectively enhance the catalytic activity of the AgCuSmTi system in low-temperature NH₃-SCR processes.

2.2.4. Redox Properties and Surface Acidity Characterization

To further investigate the influence of active species on the catalyst surface and their reduction behavior in relation to catalytic performance, H₂-TPR characterization was carried out on all catalysts, with the results presented in Figure 5a. The reduction profile of the CuSmTi catalyst can be divided into three distinct stages: the low-temperature peak (131 °C) corresponds to the reduction of Cu²⁺ to Cu⁺; the medium-temperature peak (149 °C) is attributed to the reduction of Cu⁺ to Cu⁰; and the high-temperature peak (178 °C) is associated with the reduction of CuO clusters [40]. These findings indicate that

Cu species exist in multiple oxidation states and undergo progressive reduction to the metallic state through sequential electron transfer processes. Upon Ag doping, all three reduction peaks in the AgCuSmTi catalyst shift toward lower temperatures, suggesting a notable enhancement in the reducibility of Cu species. This improvement can be attributed to the synergistic interaction between Ag and Cu, which facilitates electron transfer and promotes the activation of oxygen species. Consequently, Cu^{2+} becomes more readily reduced to Cu^+ and ultimately to Cu^0 . Additionally, a new reduction peak appears at approximately 228 °C for the AgCuSmTi catalyst, which is assigned to the reduction of Ag_2O to metallic Ag^0 [41]. The enhanced Ag–Cu interaction accelerates the redox reaction kinetics at lower temperatures, thereby improving the overall redox activity of the catalyst.

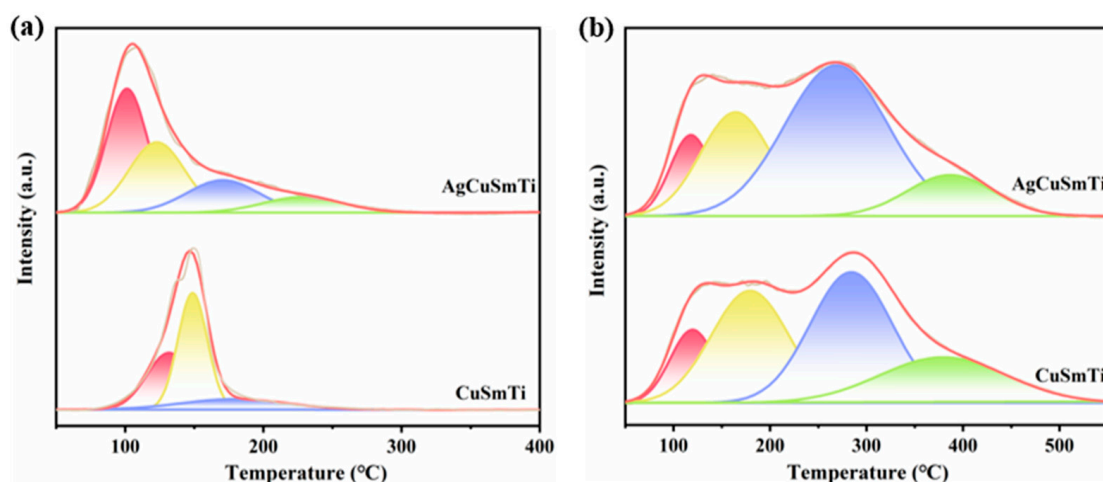


Figure 5. H_2 -TPR (a) and NH_3 -TPD (b) spectrum of catalysts.

The acid characteristics of the catalyst surfaces were investigated using NH_3 -TPD analysis for the AgCuSmTi and CuSmTi samples. The results are shown in Figure 5b, with the desorption peak areas quantitatively analyzed and summarized in Table 2. Both catalysts exhibit three distinct NH_3 desorption peaks: the α peak (100–150 °C) corresponds to weak Lewis acid sites; the β peak (150–300 °C) represents strong Lewis acid sites; and the γ peak (>300 °C) is associated with Brønsted acid sites [42]. Comparative analysis reveals a significant increase in the proportion of the β peak in the AgCuSmTi catalyst, from 68.15% in CuSmTi to 76.86%, indicating that Ag incorporation substantially enhances the density of strong Lewis acid sites. This facilitates NH_3 adsorption and activation, providing abundant active sites for subsequent surface reactions. In contrast, the proportion of the γ peak decreases in AgCuSmTi, reflecting a reduction in Brønsted acidity. These observations suggest that the Ag–Cu interaction plays a crucial role in modulating the surface acidic structure, favoring the formation of strong Lewis acid sites that are more conducive to the NH_3 -SCR reaction mechanism [43]. As a result, the catalytic performance is significantly improved.

Table 2. Acidic site distribution of catalysis.

Sample	α	β	γ
AgCuSmTi	11.25%	76.86%	11.89%
CuSmTi	11.5%	68.15%	20.35%

2.3. Proposed Reaction Mechanism Investigation

2.3.1. Proposed Reaction Mechanism of CO Oxidation

To elucidate the intermediate species and reaction mechanisms involved in CO oxidation over the AgCuSmTi composite metal oxide catalyst, in situ DRIFTS experiments were carried out under CO + O₂ co-adsorption conditions at various temperatures. The results are presented in Figure 6a. Upon exposure to CO and O₂, two main carbonate species formed via interactions between CO and surface oxygen species were observed: monodentate carbonate (1329 cm⁻¹ and 1463 cm⁻¹) [16,44] and bidentate carbonate (1042 cm⁻¹ and 1581 cm⁻¹) [45,46]. A distinct peak at 2113 cm⁻¹ was assigned to Cu⁺-CO, whose intensity decreased with increasing temperature and vanished entirely above 150 °C. A peak at 2163 cm⁻¹ was attributed to Cu²⁺-CO [47,48]. Additionally, broad bands in the range of 2285–2390 cm⁻¹ corresponded to CO₂ molecules, indicating the formation of gaseous CO₂ as a result of CO oxidation [49]. As shown in the spectra, the band at 1581 cm⁻¹, associated with bidentate carbonate, along with the peak at 1329 cm⁻¹, representing monodentate carbonate, both diminished significantly with rising temperature. However, these features remained detectable even at 300 °C. In contrast, the peaks at 1463 cm⁻¹ and 1042 cm⁻¹ exhibited an opposite trend, showing increased intensity at higher temperatures. Considering the evolution of CO₂ and Cu⁺-CO signals, it can be inferred that the thermal decomposition of carbonate species contributes significantly to the oxidation of CO at elevated temperatures.

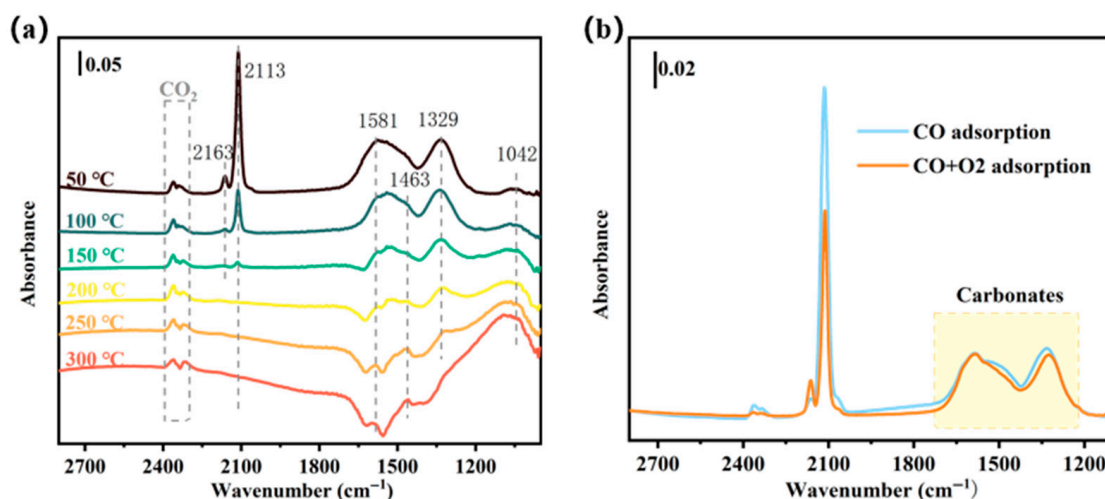


Figure 6. In situ DRIFTS analysis of the AgCuSmTi catalyst under different gas atmospheres: CO + O₂ adsorption across a temperature range of 50 to 300 °C (a) and CO adsorption alone versus co-adsorption with O₂ at 50 °C (b).

The involvement of molecular oxygen in the CO oxidation mechanism was examined by comparing DRIFTS spectra obtained at 50 °C under conditions with and without O₂, as shown in Figure 6b. Notably, the intensity of the Cu⁺-CO peak at 2113 cm⁻¹ is significantly lower under CO + O₂ co-adsorption compared to CO-only adsorption, suggesting that O₂ partially occupies the active sites responsible for CO adsorption. Meanwhile, the spectral region between 1200 and 1700 cm⁻¹, which includes the carbonate-related peaks, remains largely unchanged regardless of O₂ presence. This indicates that O₂ does not directly influence the formation of carbonate species [15]. Notably, without molecular oxygen present, CO reacts with lattice oxygen, resulting in the production of carbonate intermediates. Based on the above observations, the CO oxidation reaction over the AgCuSmTi catalyst proceeds primarily through the Mars–van Krevelen (MvK) mechanism.

2.3.2. Proposed Reaction Mechanism of NH_3 -SCR

To investigate the acid sites and intermediate species formed on the catalyst upon incorporation of Ag species, NH_3 adsorption–desorption DRIFTS measurements were carried out at various temperatures. Figure 7a presents the in situ DRIFTS spectra of NH_3 adsorption on the AgCuSmTi catalyst as a function of surface temperature from 50 to 300 °C. The broad band observed in the range of 3000–3400 cm^{-1} is attributed to the N–H stretching of adsorbed NH_3 [50,51]. Additionally, two distinct peaks at 1668 cm^{-1} and 1479 cm^{-1} are assigned to NH_4^+ species formed via NH_3 protonation on Brønsted acid sites [52], whereas the bands at 1195 cm^{-1} and 1606 cm^{-1} correspond to NH_3 coordinated to Lewis acid sites [50,53]. It is evident that the intensity of the Lewis acid site-related peaks is significantly higher than that of the Brønsted acid site peaks, indicating the dominant role of Lewis acidity in NH_3 adsorption on the AgCuSmTi catalyst. As the temperature increases, the intensities of these NH_3 adsorption features gradually decrease, suggesting progressive desorption and activation of NH_3 . Notably, the spectral at 1308 cm^{-1} and 1520 cm^{-1} can be assigned to the formation of $-\text{NH}_2$ species generated via dehydrogenation of NH_3 [54,55]. Furthermore, as the temperature increases, a new band emerges at 1429 cm^{-1} in the DRIFTS spectrum of the AgCuSmTi catalyst (Figure 7a), which is absent in the CuSmTi catalyst (Figure S6). This spectral feature can be attributed to the formation of $-\text{NH}$ species on the Ag-doped catalyst surface [56]. $-\text{NH}$ intermediates are likely involved in subsequent redox reactions with NO molecules, potentially leading to the formation of N_2O . This observation provides a plausible explanation for the reduced N_2 selectivity observed upon Ag doping.

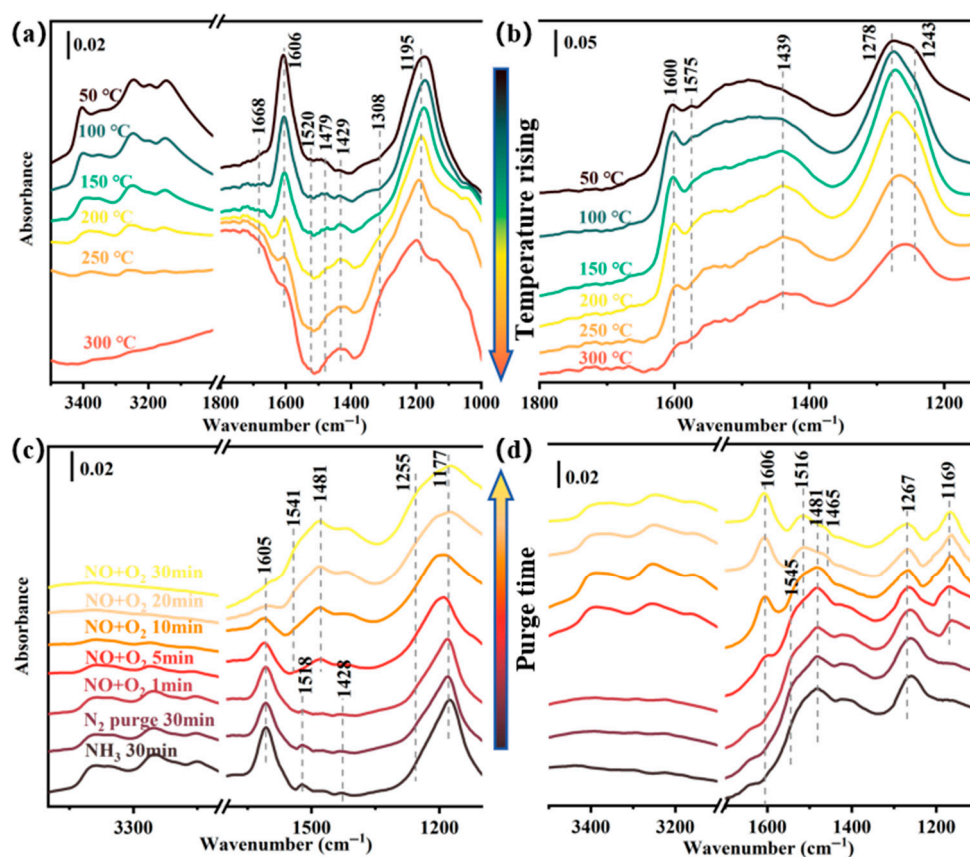


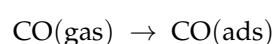
Figure 7. In situ DRIFTS spectra of AgCuSmTi catalyst under various reaction conditions: NH_3 adsorption (a) and $\text{NO} + \text{O}_2$ adsorption at temperatures ranging from 50 to 300 °C (b). Reaction between pre-adsorbed NH_3 species and $\text{NO} + \text{O}_2$ at 150 °C for 30 min (c) and reaction of NH_3 with pre-adsorbed NO_x species at 150 °C for 30 min (d). Gas composition: $[\text{NH}_3] = [\text{NO}] = 500$ ppm (when used), 5 vol% O_2 (when used), and N_2 as balance.

To further explore the interaction between NO and O₂ on the catalyst surface, in situ DRIFTS analysis of NO + O₂ adsorption was also conducted under the same temperature conditions. The results are shown in Figure 7b. Several nitrate species were identified based on their characteristic vibrational frequencies. The bands at 1600 cm^{−1} and 1243 cm^{−1} are attributed to bridged nitrate species [57,58], while the peak at 1575 cm^{−1} corresponds to bidentate nitrates [59]. The signals at 1439 cm^{−1} and 1278 cm^{−1} are associated with monodentate nitrate species [15,60]. As clearly observed in the spectra, the intensity of the monodentate nitrate peaks is significantly higher compared to that of bridged and bidentate nitrates. According to previous studies, the preferential formation of monodentate nitrates is beneficial for enhancing low-temperature NH₃-SCR performance [61,62]. This finding supports the conclusion that the AgCuSmTi catalyst exhibits excellent catalytic activity at low temperatures.

To elucidate the reaction mechanism of NH₃-SCR over the AgCuSmTi catalyst, in situ DRIFTS transient experiments were carried out. In the first set of experiments, NO + O₂ was introduced after NH₃ had been pre-adsorbed on the catalyst surface. The results are presented in Figure 7c. Following NH₃ pre-adsorption on the AgCuSmTi catalyst, characteristic peaks corresponding to Lewis acid sites (L-acid) were observed at 1177 cm^{−1} and 1605 cm^{−1}, along with a peak at 1518 cm^{−1} attributed to -NH₂ species and another at 1428 cm^{−1} assigned to -NH species. After 30 min of N₂ purging, the intensities of the L-acid-related peaks slightly decreased, indicating that weakly physisorbed NH₃ was partially desorbed. Upon introduction of NO + O₂ for 1 min, slight decreases in the intensities of the L-acid and -NH₃ peaks were observed, suggesting that gaseous NO and O₂ reacted with adsorbed NH₃ species, consistent with an Eley–Rideal (E-R) reaction mechanism. At 5 min after NO + O₂ exposure, new spectral features emerged corresponding to nitrate species, bridged nitrate (1255 cm^{−1}), monodentate nitrate (1481 cm^{−1}), and bidentate nitrate (1541 cm^{−1}), confirming successful adsorption of NO on the catalyst surface [16]. As the reaction time increased, the intensities of these nitrate-related peaks continued to rise, while the peak at 1605 cm^{−1} (attributed to L-acid sites) gradually diminished and eventually disappeared after 30 min. The reaction occurring 5 min after NO + O₂ introduction can be interpreted as the interaction between adsorbed NH₃ and adsorbed NO species, indicating that a Langmuir–Hinshelwood (L-H) mechanism also operates on the catalyst surface. In summary, the AgCuSmTi catalyst exhibits both the E-R and L-H mechanisms during the NH₃-SCR process.

To further validate the above findings, a second set of experiments was conducted with a reversed reactant introduction order, where NH₃ was introduced after NO + O₂ had been pre-adsorbed on the catalyst. The results are shown in Figure 7d. Following 30 min of NO + O₂ pre-adsorption, characteristic peaks corresponding to bidentate nitrate (1545 cm^{−1}) and monodentate nitrate (1481 cm^{−1} and 1267 cm^{−1}) were clearly observed. After introducing NH₃ for 1 min, a new peak at 1169 cm^{−1} appeared, which is associated with L-acid centers. By 5 min, the intensities of the nitrate-related bands began to decrease, while signals corresponding to -NH₂ species and Brønsted acid (B-acid) centers emerged. This evolution indicates that the adsorbed NO species interacted with the incoming NH₃ via the L-H mechanism.

Figure 8 presents the proposed reaction pathway for the AgCuSmTi catalyst during the simultaneous removal of NO and CO. During the CO oxidation process, CO molecules adsorbed on the catalyst surface react with lattice oxygen to form either CO₂ or carbonate species. Upon desorption of CO₂, oxygen vacancies are generated, which are subsequently replenished by molecular oxygen, thereby facilitating continuous CO oxidation through lattice oxygen migration [63]. The detailed reaction mechanism is summarized as follows:



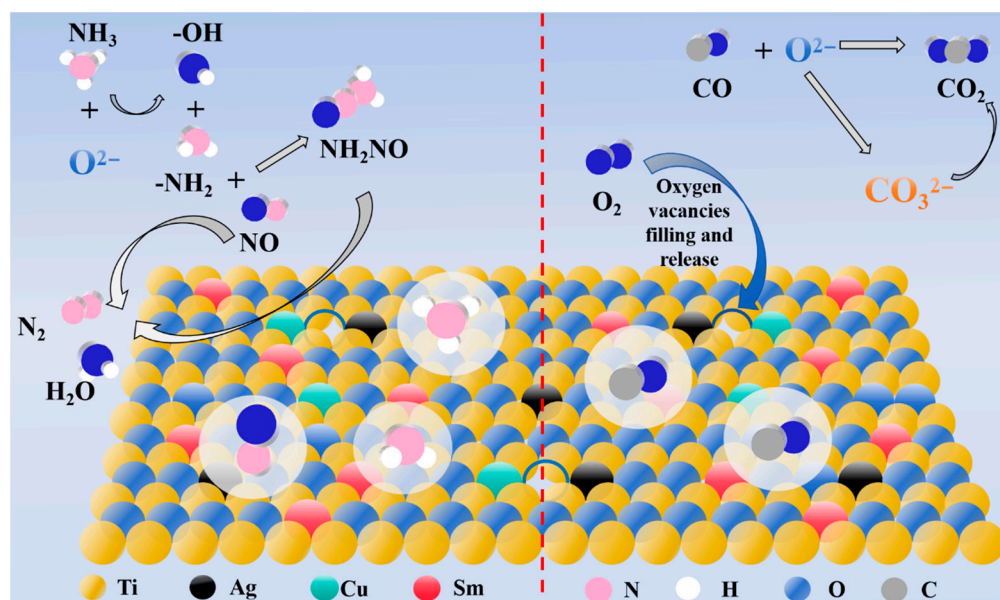
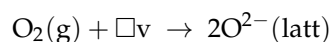
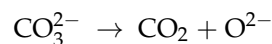
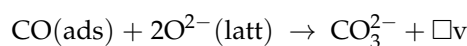
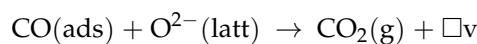
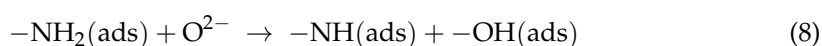
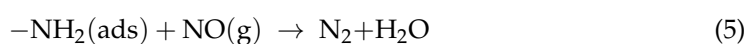
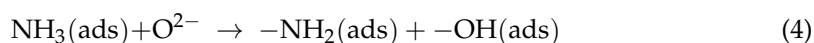


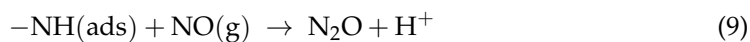
Figure 8. Schematic illustration of the NH_3 -SCR and CO oxidation mechanisms occurring on the AgCuSmTi catalytic system.

Here, “ $\square\text{v}$ ” represents an oxygen vacancy.

The NH_3 -SCR reaction mechanism over the AgCuSmTi catalyst is predominantly governed by the L-H mechanism, with the E-R mechanism playing a secondary role. In this process, gaseous NH_3 is adsorbed and activated on the catalyst surface to form $-\text{NH}_2$ intermediates (Equations (1)–(4)). Activated lattice oxygen facilitates the generation of $-\text{NH}_2$ species and enhances the redox cycling during the reaction. Subsequently, the $-\text{NH}_2$ intermediate reacts with either gaseous NO (Equation (5)) or adsorbed nitrate species (Equations (6) and (7)) to yield N_2 and H_2O . During the reaction, the $-\text{NH}_2$ species can undergo further dehydrogenation to form $-\text{NH}$ intermediates, which then react with NO species to produce N_2O (Equations (8) and (9)). The formation of N_2O reduces the overall N_2 selectivity of the catalyst.

The detailed reaction mechanism is summarized as follows:





3. Experimental Section

3.1. Catalyst Preparation

All catalysts were synthesized using the sol–gel method. In a typical procedure, 25.2 mL of n-butanol and 2.8 mL of glacial acetic acid were first mixed uniformly, followed by the gradual addition of 2.4 mL of deionized water under continuous stirring for 30 min to obtain solution A. Subsequently, 1.88 g of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.68 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and a precisely weighed amount of AgNO_3 were added to solution A. The mixture was stirred continuously until complete dissolution of all components. Then, 9.6 mL of titanium tetrabutyltitanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) was slowly introduced into the homogeneous solution, which was further stirred at room temperature for 3 h to obtain a viscous gel-like solution. The obtained sol was then aged at ambient temperature until gelation occurred. Afterward, the gel was transferred to an oven and dried at 110 °C overnight. Finally, the dried precursor was calcined in a muffle furnace at 500 °C for 4 h to obtain the Ag_xCuSmTi composite metal oxide catalysts with different Ag loadings ($x = 0.5, 0.8, 1.0, 1.2, 1.5$).

For comparative analysis, other catalytic systems were prepared following similar procedures. In one case, 9.6 mL of $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ was added directly to solution A without incorporating any metal nitrates. The mixture was then dried and calcined under the same conditions to yield pure TiO_2 . Additionally, three reference catalysts, SmTi , CuSmTi , and AgSmTi , were synthesized by sequentially adding the following combinations to solution A: (1) 1.88 g of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, (2) 1.88 g of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.68 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and (3) 1.88 g of $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and a certain amount of AgNO_3 . Each mixture was processed through the same drying and calcination steps as described above.

3.2. Catalyst Activity Test

The catalytic performance was evaluated using a fixed-bed reactor system. Detailed descriptions of the experimental setup, operating procedures, test conditions, and conversion rate calculations are provided in the Supporting Information.

3.3. Reagents and Gases

The reagents used in the preparation of the catalysts and the gases employed in the evaluation of their catalytic performance are listed in the Supporting Information.

3.4. Catalyst Characterization

The physical properties of the catalyst were investigated using a range of characterization techniques, including X-ray diffraction (XRD), N_2 adsorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. Furthermore, the redox properties and acidic characteristics of the catalyst were systematically analyzed using X-ray photoelectron spectroscopy (XPS), H_2 temperature-programmed reduction (H_2 -TPR), O_2 temperature-programmed desorption (O_2 -TPD), NH_3 temperature-programmed desorption (NH_3 -TPD), electron paramagnetic resonance (EPR), and in situ DRIFTS. Additional experimental details are provided in the Supporting Information.

4. Conclusions

This study presents an innovative approach in which Ag is introduced to modify the CuSmTi catalyst, resulting in the successful development of a dual-functional AgCuSmTi catalyst capable of effectively regulating oxygen structure. A combination of characterization techniques, including XRD, N_2 adsorption, and XPS, revealed a pronounced synergistic interaction between Ag and Cu, which plays a critical role in enhancing the

catalyst's low-temperature activity. Firstly, the Ag-Cu synergy significantly improves the physical properties of the catalyst by optimizing the dispersion of active sites, thereby establishing a structural foundation for its superior performance. Secondly, this synergistic effect markedly enhances the mobility of lattice oxygen. The highly active lattice oxygen not only facilitates redox cycling during the reaction but also accelerates electron transfer between metal species. Furthermore, the Ag-Cu interaction effectively modulates the acidic properties of the catalyst surface, increasing the density of Lewis acid sites, which are particularly favorable for the NH_3 -SCR reaction. This enhancement promotes the adsorption and activation of reactant molecules, contributing to improved catalytic performance. These structural and chemical modifications significantly enhanced the performance of the AgCuSmTi catalyst, enabling complete conversion of NO and CO at temperatures as low as 150 °C and 175 °C, respectively, along with excellent N_2 selectivity. To further elucidate the underlying reaction mechanisms, in situ DRIFTS studies were conducted for both the NH_3 -SCR and CO oxidation reactions. The results indicate that the NH_3 -SCR process predominantly follows the L-H mechanism, with the E-R mechanism also playing a secondary role. Meanwhile, the CO oxidation reaction proceeds via the MvK mechanism. Overall, the results presented herein offer both a fundamental understanding and a promising theoretical foundation for the simultaneous elimination of nitrogen oxides and carbon monoxide from low-temperature industrial flue gases.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal15070674/s1>, Figure S1: NO_x conversion, N_2 selectivity, and CO conversion of catalysts with different proportions; Figure S2: TOF values for NO and CO conversions of the catalyst; Figure S3: Stability test (20 h) of AgCuSmTi catalyst at 150 °C and 175 °C; Figure S4: TEM spectrum of CuSmTi catalyst; Figure S5: N_2 adsorption and desorption isotherms and pore size distribution curves of catalysts; Figure S6: In situ DRIFTS on CuSmTi catalyst: changes in the NH_3 surface reaction with temperature when NH_3 is continuously introduced; Table S1: Summary of preparation methods, operating reaction conditions, catalytic performance metrics, and reaction mechanism for Cu-based catalysts in NO_x and CO abatement processes [11,15–17,21–26,38,64]; Table S2: Physical properties of catalysts; Table S3: Chemical state of Ag species on catalyst surface; Table S4: Distribution of desorbed oxygen species of catalyst.

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

Funding: This work was supported by the Key Technologies Research and Development Program, China (No. 2022YFC3701900) and Applied Basic Research Project of Shanxi Province (Nos. 202203021211178, 202303021211032, 202303021211034, and 202403021211217).

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

Conflicts of Interest: The authors declare no competing financial interest.

References

1. Li, C.; Han, Q.; Zhu, T.; Xu, W. Catalytic NO Reduction by CO over Ca-Fe Oxides in the Presence of O_2 with Sintering Flue Gas Circulation. *Ind. Eng. Chem. Res.* **2020**, *59*, 20624–20629. [[CrossRef](#)]
2. Gan, L.; Shi, W.; Li, K.; Chen, J.; Peng, Y.; Li, J. Synergistic Promotion Effect between NO_x and Chlorobenzene Removal on MnO_x - CeO_2 Catalyst. *ACS Appl. Mater. Interfaces* **2018**, *10*, 30426–30432. [[CrossRef](#)]

3. Qiao, B.; Wang, A.; Yang, X.; Allard, L.F.; Jiang, Z.; Cui, Y.; Liu, J.; Li, J.; Zhang, T. Single-atom catalysis of CO oxidation using Pt1/FeO_x. *Nat. Chem.* **2011**, *3*, 634–641. [\[CrossRef\]](#)
4. Jiang, L.; Xu, Y.; Jiang, W.; Pu, Y.; Yang, L.; Dai, Z.; Yao, L. The promotion of NH₃-SCR performance by AC addition on Mn-Fe/Z catalyst. *Sep. Purif. Technol.* **2023**, *322*, 124274. [\[CrossRef\]](#)
5. Zhu, M.; Lai, J.-K.; Tumuluri, U.; Wu, Z.; Wachs, I.E. Nature of Active Sites and Surface Intermediates during SCR of NO with NH₃ by Supported V₂O₅-WO₃/TiO₂ Catalysts. *J. Am. Chem. Soc.* **2017**, *139*, 15624–15627. [\[CrossRef\]](#)
6. Choi, J.-H.; Kim, J.-H.; Bak, Y.-C.; Amal, R.; Scott, J. Pt-V₂O₅-WO₃/TiO₂ catalysts supported on SiC filter for NO reduction at low temperature. *Korean J. Chem. Eng.* **2005**, *22*, 844–851. [\[CrossRef\]](#)
7. Wang, Y.-Z.; Zhang, J.-L.; Liu, Z.-J.; Du, C.-B. Recent Advances and Research Status in Energy Conservation of Iron Ore Sintering in China. *JOM* **2017**, *69*, 2404–2411. [\[CrossRef\]](#)
8. Dey, S.; Dhal, G.C.; Mohan, D.; Prasad, R. Advances in transition metal oxide catalysts for carbon monoxide oxidation: A review. *Adv. Compos. Hybrid. Mater.* **2019**, *2*, 626–656. [\[CrossRef\]](#)
9. Li, X.; Ren, S.; Jiang, Y.; Chen, Z.; Wang, L.; Liu, M.; Chen, T. In situ IR spectroscopy study of NO removal over CuCe catalyst for CO-SCR reaction at different temperature. *Catal. Today* **2023**, *418*, 114082. [\[CrossRef\]](#)
10. Hamada, H.; Haneda, M. A review of selective catalytic reduction of nitrogen oxides with hydrogen and carbon monoxide. *Appl. Catal. A Gen.* **2012**, *421–422*, 1–13. [\[CrossRef\]](#)
11. Zeng, Y.; Rong, W.; Zhang, S.; Wang, Y.; Zhong, Q. Promoting NH₃-SCR denitration via CO oxidation over CuO promoted V₂O₅-WO₃/TiO₂ catalysts under oxygen-rich conditions. *Fuel* **2022**, *323*, 124357. [\[CrossRef\]](#)
12. Zhang, X.; Zhang, G.; Liu, J.; Li, G.; Zhao, Y.; Wang, Y.; Lv, Y. Effects of defective structure originating from N incorporation-evaporation of Co-based biomass carbon catalysts on methane dry reforming. *Fuel* **2024**, *357*, 129752. [\[CrossRef\]](#)
13. Wang, X.; Sun, Y.; Han, F.; Zhao, Y. Effect of Fe addition on the structure and SCR reactivity of one-pot synthesized Cu-SSZ-13. *J. Environ. Chem. Eng.* **2022**, *10*, 107888. [\[CrossRef\]](#)
14. Shen, Z.; Xing, X.; She, Y.; Wang, S.; Lv, M.; Li, J.; Li, H. Revealing of K and SO₂ poisoning mechanism on CuCeO_x catalyst for low-temperature CO oxidation. *Chem. Eng. J.* **2024**, *485*, 149373. [\[CrossRef\]](#)
15. Liu, Q.; Mi, J.; Chen, X.; Wang, S.; Chen, J.; Li, J. Effects of phosphorus modification on the catalytic properties and performance of CuCeZr mixed metal catalyst for simultaneous removal of CO and NO_x. *Chem. Eng. J.* **2021**, *423*, 130228. [\[CrossRef\]](#)
16. Shen, Z.; Xing, X.; She, Y.; Guo, P.; Ren, S.; Niu, W.; Li, J.; Li, H.; Meng, H. Unveiling the promoting mechanism of Mo on the performance of CuCeO_x catalyst for simultaneously NH₃-SCR denitration and CO oxidation under oxygen-rich conditions. *Sep. Purif. Technol.* **2025**, *355*, 129561. [\[CrossRef\]](#)
17. Lv, D.; Liu, J.; Zhang, G.; Wang, Y.; Zhao, Y.; Li, G. Novel insights for simultaneous NO_x and CO Removal: Cu⁺-Sm³⁺-Ov-Ti⁴⁺ asymmetric active site promoting NH₃-SCR coupled with CO oxidation reaction. *Chem. Eng. J.* **2024**, *481*, 148534. [\[CrossRef\]](#)
18. Liu, Y.; Zhou, X.; Zhan, J.; Zhang, X.; Lian, H.-Y.; Zhou, H.; Yi, X.; Yang, H.-H.; Shan, J. Enhancing water resistance of α-MnO₂ catalyst for efficient airborne benzene oxidation at mild temperatures via facile Ag incorporation. *J. Environ. Chem. Eng.* **2023**, *11*, 110725. [\[CrossRef\]](#)
19. Rao, R.; Liang, H.; Hu, C.; Dong, H.; Dong, X.; Tang, Y.; Fang, S.; Ling, Q. A melamine-assisted pyrolytic synthesis of Ag-CeO₂ nanoassemblies for CO oxidation: Activation of Ag-CeO₂ interfacial lattice oxygen. *Appl. Surf. Sci.* **2022**, *571*, 151283. [\[CrossRef\]](#)
20. Md Saad, S.K.; Ali Umar, A.; Ali Umar, M.I.; Tomitori, M.; Abd Rahman, M.Y.; Mat Salleh, M.; Oyama, M. Two-Dimensional, Hierarchical Ag-Doped TiO₂ Nanocatalysts: Effect of the Metal Oxidation State on the Photocatalytic Properties. *ACS Omega* **2018**, *3*, 2579–2587. [\[CrossRef\]](#)
21. Ren, S.; Li, X.; He, C.; Chen, L.; Wang, L.; Li, F. Surface tailoring on bifunctional CuO_x/MnO₂ catalyst to promote the selective catalytic reduction of NO with NH₃ and oxidation of CO with O₂. *Sep. Purif. Technol.* **2024**, *346*, 127471. [\[CrossRef\]](#)
22. Li, X.; Lai, C.; Zhang, Y.; Wang, S.; Ding, S. Bifunctional catalysts V-Cu/TiO₂ for selective catalytic reduction of NO_x and CO oxidation under oxygen-rich conditions. *Mol. Catal.* **2024**, *569*, 114574. [\[CrossRef\]](#)
23. Gui, R.; Xiao, J.; Gao, Y.; Li, Y.; Zhu, T.; Wang, Q. Simultaneously achieving selective catalytic reduction of NO_x with NH₃ and catalytic oxidation of CO with O₂ over one finely optimized bifunctional catalyst Mn₂Cu₁Al₁O_x at low temperatures. *Appl. Catal. B Environ.* **2022**, *306*, 121104. [\[CrossRef\]](#)
24. Li, Z.; Cheng, H.; Zhang, X.; Ji, M.; Wang, S.; Wang, S. CuW/CeZr Catalysts: A Dual-Function Catalyst for Selective Catalytic Reduction of NO and CO Oxidation Under Oxygen-Rich Conditions. *Catal. Lett.* **2021**, *151*, 3361–3371. [\[CrossRef\]](#)
25. Wang, L.; Wang, B.; Guo, Y.; Zheng, Y.; Zhu, T. Interactions between CO oxidation and selective catalytic reduction of NO with NH₃ over Mn-based catalysts. *Catal. Sci. Technol.* **2022**, *12*, 4776–4788. [\[CrossRef\]](#)
26. Wang, J.; Xing, Y.; Su, W.; Li, K.; Zhang, W. Bifunctional Mn-Cu-CeO_x/γ-Al₂O₃ catalysts for low-temperature simultaneous removal of NO_x and CO. *Fuel* **2022**, *321*, 124050. [\[CrossRef\]](#)
27. Resitoglu, I.A.; Keskin, A. Hydrogen applications in selective catalytic reduction of NO_x emissions from diesel engines. *Int. J. Hydrog. Energy* **2017**, *42*, 23389–23394. [\[CrossRef\]](#)

28. Gao, C.; Shi, J.-W.; Fan, Z.; Wang, B.; Wang, Y.; He, C.; Wang, X.; Li, J.; Niu, C. “Fast SCR” reaction over Sm-modified $\text{MnO}_x\text{-TiO}_2$ for promoting reduction of NO_x with NH_3 . *Appl. Catal. A Gen.* **2018**, *564*, 102–112. [\[CrossRef\]](#)
29. Wang, B.; Wang, M.; Han, L.; Hou, Y.; Bao, W.; Zhang, C.; Feng, G.; Chang, L.; Huang, Z.; Wang, J. Improved Activity and SO_2 Resistance by Sm-Modulated Redox of MnCeSmTiO_x Mesoporous Amorphous Oxides for Low-Temperature NH_3 -SCR of NO. *ACS Catal.* **2020**, *10*, 9034–9045. [\[CrossRef\]](#)
30. Sun, H.; Wang, H.; Qu, Z. Construction of CuO/CeO_2 Catalysts via the Ceria Shape Effect for Selective Catalytic Oxidation of Ammonia. *ACS Catal.* **2023**, *13*, 1077–1088. [\[CrossRef\]](#)
31. Djaoued, Y.; Badilescu, S.; Ashrit, P.V.; Bersani, D.; Lottici, P.P.; Robichaud, J. Study of Anatase to Rutile Phase Transition in Nanocrystalline Titania Films. *J. Sol-Gel Sci. Technol.* **2002**, *24*, 255–264. [\[CrossRef\]](#)
32. Alhomoudi, I.A.; Newaz, G. Residual stresses and Raman shift relation in anatase TiO_2 thin film. *Thin Solid. Film.* **2009**, *517*, 4372–4378. [\[CrossRef\]](#)
33. Choudhury, B.; Dey, M.; Choudhury, A. Defect generation, d-d transition, and band gap reduction in Cu-doped TiO_2 nanoparticles. *Int. Nano Lett.* **2013**, *3*, 25. [\[CrossRef\]](#)
34. Liu, H.; Fan, Z.; Sun, C.; Yu, S.; Feng, S.; Chen, W.; Chen, D.; Tang, C.; Gao, F.; Dong, L. Improved activity and significant SO_2 tolerance of samarium modified $\text{CeO}_2\text{-TiO}_2$ catalyst for NO selective catalytic reduction with NH_3 . *Appl. Catal. B Environ.* **2019**, *244*, 671–683. [\[CrossRef\]](#)
35. Guo, X.; Lin, F.; Gao, M.; Dai, Q.; Zhan, W.; Wang, L.; Guo, Y.; Wang, A.; Guo, Y. Enhanced catalytic performance and N_2 yield of Ag/CeO_2 catalyst by Cu modification for NVOCs removal. *Chem. Eng. J.* **2024**, *488*, 151117. [\[CrossRef\]](#)
36. Chen, C.; Cao, Y.; Liu, S.; Chen, J.; Jia, W. SCR catalyst doped with copper for synergistic removal of slip ammonia and elemental mercury. *Fuel Process. Technol.* **2018**, *181*, 268–278. [\[CrossRef\]](#)
37. Wang, M.; Ren, S.; Jiang, Y.; Su, B.; Chen, Z.; Liu, W.; Yang, J.; Chen, L. Insights into co-doping effect of Sm and Fe on anti-Pb poisoning of Mn-Ce/AC catalyst for low-temperature SCR of NO with NH_3 . *Fuel* **2022**, *319*, 123763. [\[CrossRef\]](#)
38. Zang, P.; Liu, J.; He, Y.; Zhang, G.; Li, G.; Wang, Y.; Lv, Y. LDH-derived preparation of CuMgFe layered double oxides for NH_3 -SCR and CO oxidation reactions: Performance study and synergistic mechanism. *Chem. Eng. J.* **2022**, *446*, 137414. [\[CrossRef\]](#)
39. Liu, S.; Xue, W.; Ji, Y.; Xu, W.; Chen, W.; Jia, L.; Zhu, T.; Zhong, Z.; Xu, G.; Mei, D.; et al. Interfacial oxygen vacancies at $\text{Co}_3\text{O}_4\text{-CeO}_2$ heterointerfaces boost the catalytic reduction of NO by CO in the presence of O_2 . *Appl. Catal. B: Environ.* **2023**, *323*, 122151. [\[CrossRef\]](#)
40. Yao, X.; Zhang, L.; Li, L.; Liu, L.; Cao, Y.; Dong, X.; Gao, F.; Deng, Y.; Tang, C.; Chen, Z.; et al. Investigation of the structure, acidity, and catalytic performance of $\text{CuO/Ti}_{0.95}\text{Ce}_{0.05}\text{O}_2$ catalyst for the selective catalytic reduction of NO by NH_3 at low temperature. *Appl. Catal. B Environ.* **2014**, *150–151*, 315–329. [\[CrossRef\]](#)
41. Qu, Z.; Wang, Z.; Quan, X.; Wang, H.; Shu, Y. Selective catalytic oxidation of ammonia to N_2 over wire-mesh honeycomb catalyst in simulated synthetic ammonia stream. *Chem. Eng. J.* **2013**, *233*, 233–241. [\[CrossRef\]](#)
42. Wang, X.; Qin, M.; Xu, Y.; Li, Q. Improvement of Cu-SAPO-34 hydrothermal stability by tuning P/Al ratio for selective catalytic reduction of NO by NH_3 . *J. Colloid. Interface Sci.* **2023**, *638*, 686–694. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Yang, B.; Li, Z.; Huang, Q.; Chen, M.; Xu, L.; Shen, Y.; Zhu, S. Synergetic removal of elemental mercury and NO over $\text{TiCe}_{0.25}\text{Sn}_{0.25}\text{O}_x$ catalysts from flue gas: Performance and mechanism study. *Chem. Eng. J.* **2019**, *360*, 990–1002. [\[CrossRef\]](#)
44. Kang, R.; Wei, X.; Bin, F.; Wang, Z.; Hao, Q.; Dou, B. Reaction mechanism and kinetics of CO oxidation over a $\text{CuO/Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2\text{-}\delta$ catalyst. *Appl. Catal. A Gen.* **2018**, *565*, 46–58. [\[CrossRef\]](#)
45. Qi, L.; Yu, Q.; Dai, Y.; Tang, C.; Liu, L.; Zhang, H.; Gao, F.; Dong, L.; Chen, Y. Influence of cerium precursors on the structure and reducibility of mesoporous CuO-CeO_2 catalysts for CO oxidation. *Appl. Catal. B Environ.* **2012**, *119–120*, 308–320. [\[CrossRef\]](#)
46. Davó-Quinónero, A.; Bailón-García, E.; López-Rodríguez, S.; Juan-Juan, J.; Lozano-Castelló, D.; García-Melchor, M.; Herrera, F.C.; Pellegrin, E.; Escudero, C.; Bueno-López, A. Insights into the Oxygen Vacancy Filling Mechanism in CuO/CeO_2 Catalysts: A Key Step Toward High Selectivity in Preferential CO Oxidation. *ACS Catal.* **2020**, *10*, 6532–6545. [\[CrossRef\]](#)
47. Lu, J.; Wang, J.; Zou, Q.; He, D.; Zhang, L.; Xu, Z.; He, S.; Luo, Y. Unravelling the Nature of the Active Species as well as the Doping Effect over Cu/Ce-Based Catalyst for Carbon Monoxide Preferential Oxidation. *ACS Catal.* **2019**, *9*, 2177–2195. [\[CrossRef\]](#)
48. Ma, Y.; Li, Y.; Liang, P.; Min, X.; Sun, T. SnO_2 -modified CuMnO_x catalysts for humid CO oxidation at low temperature. *J. Ind. Eng. Chem.* **2024**, *138*, 300–310. [\[CrossRef\]](#)
49. Sasmaz, E.; Wang, C.; Lance, M.J.; Lauterbach, J. In situ spectroscopic investigation of a Pd local structure over Pd/CeO_2 and $\text{Pd/MnO}_x\text{-CeO}_2$ during CO oxidation. *J. Mater. Chem. A* **2017**, *5*, 12998–13008. [\[CrossRef\]](#)
50. Dann, E.K.; Gibson, E.K.; Blackmore, R.H.; Catlow, C.R.A.; Collier, P.; Chutia, A.; Erden, T.E.; Hardacre, C.; Kroner, A.; Nachttegaal, M.; et al. Structural selectivity of supported Pd nanoparticles for catalytic NH_3 oxidation resolved using combined operando spectroscopy. *Nat. Catal.* **2019**, *2*, 157–163. [\[CrossRef\]](#)
51. Chen, Y.; Yan, H.; Teng, W.; Li, J.; Liu, W.; Ren, S.; Yang, J.; Liu, Q. Comparative study on N_2O formation pathways over bulk MoO_3 and MoO_{3-x} nanosheets decorated Fe_2O_3 -containing solid waste NH_3 -SCR catalysts. *Fuel* **2023**, *337*, 127210. [\[CrossRef\]](#)

52. Zhang, Z.; Li, R.; Wang, M.; Li, Y.; Tong, Y.; Yang, P.; Zhu, Y. Two steps synthesis of CeTiO_x oxides nanotube catalyst: Enhanced activity, resistance of SO₂ and H₂O for low temperature NH₃-SCR of NO_x. *Appl. Catal. B Environ.* **2021**, *282*, 119542. [[CrossRef](#)]
53. Hao, Z.; Jiao, Y.; Shi, Q.; Zhang, H.; Zhan, S. Improvement of NH₃-SCR performance and SO₂ resistance over Sn modified CeMoO_x electrospun fibers at low temperature. *Catal. Today* **2019**, *327*, 37–46. [[CrossRef](#)]
54. Wang, X.; Peng, J.; Wang, Y.; Guo, N.; Li, T.; Li, H.; Ren, D.; Gui, K. Poisoning mechanism of different Cd precursors on Fe-Ce/TiO₂ catalyst for selective catalytic reduction of NO_x with NH₃. *J. Environ. Chem. Eng.* **2023**, *11*, 109625. [[CrossRef](#)]
55. Jia, B.; Liu, J.; Kang, J.; Zhang, G.; Lv, D.; Wang, Y. Investigating NH₃-SCR coupled with CO oxidation reaction mechanisms on titanium nanotube-loaded CuMnFe composite metal catalysts. *Appl. Surf. Sci.* **2024**, *652*, 159299. [[CrossRef](#)]
56. Liu, Y.; Gu, T.; Weng, X.; Wang, Y.; Wu, Z.; Wang, H. DRIFT Studies on the Selectivity Promotion Mechanism of Ca-Modified Ce-Mn/TiO₂ Catalysts for Low-Temperature NO Reduction with NH₃. *J. Phys. Chem. C* **2012**, *116*, 16582–16592. [[CrossRef](#)]
57. Yao, W.; Wang, X.; Liu, Y.; Wu, Z. CeOP material supported CeO₂ catalysts: A novel catalyst for selective catalytic reduction of NO with NH₃ at low temperature. *Appl. Surf. Sci.* **2019**, *467–468*, 439–445. [[CrossRef](#)]
58. Liu, F.; He, H.; Zhang, C.; Shan, W.; Shi, X. Mechanism of the selective catalytic reduction of NO_x with NH₃ over environmental-friendly iron titanate catalyst. *Catal. Today* **2011**, *175*, 18–25. [[CrossRef](#)]
59. Wu, Z.; Jiang, B.; Liu, Y.; Wang, H.; Jin, R. DRIFT Study of Manganese/Titania-Based Catalysts for Low-Temperature Selective Catalytic Reduction of NO with NH₃. *Environ. Sci. Technol.* **2007**, *41*, 5812–5817. [[CrossRef](#)]
60. Chen, L.; Li, J.; Ge, M. DRIFT Study on Cerium–Tungsten/Titania Catalyst for Selective Catalytic Reduction of NO_x with NH₃. *Environ. Sci. Technol.* **2010**, *44*, 9590–9596. [[CrossRef](#)]
61. Chen, Z.; Ren, S.; Wang, M.; Yang, J.; Chen, L.; Liu, W.; Liu, Q.; Su, B. Insights into samarium doping effects on catalytic activity and SO₂ tolerance of MnFeO_x catalyst for low-temperature NH₃-SCR reaction. *Fuel* **2022**, *321*, 124113. [[CrossRef](#)]
62. Han, L.; Cai, S.; Gao, M.; Hasegawa, J.Y.; Wang, P.; Zhang, J.; Shi, L.; Zhang, D. Selective Catalytic Reduction of NO_x with NH₃ by Using Novel Catalysts: State of the Art and Future Prospects. *Chem. Rev.* **2019**, *119*, 10916–10976. [[CrossRef](#)] [[PubMed](#)]
63. Ye, Z.; Liu, Y.; Nikiforov, A.; Ji, J.; Zhao, B.; Wang, J. The research on CO oxidation over Ce–Mn oxides: The preparation method effects and oxidation mechanism. *Chemosphere* **2023**, *336*, 139130. [[CrossRef](#)] [[PubMed](#)]
64. Li, X.; Ren, S.; Chen, Z.; Chen, L.; Wang, M.; Wang, L.; Wang, A. Promoting mechanism of CuO on catalytic performance of CeFe catalyst for simultaneous removal of NO_x and CO. *Fuel* **2023**, *347*, 128435. [[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.