

Article

Effect of Mn/Cu Ratio on the Structure–Performance Relationship of Spinel-Type Mn–Cu/Al₂O_x Catalysts for Methanol Steam Reforming

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Abstract

The development of highly active, thermally stable, and low-CO-selective catalysts is critical for practical methanol steam reforming (MSR) to produce high-purity hydrogen for fuel cell applications. In this work, a series of Mn–Cu/Al₂O_x catalysts with varying Mn/Cu/Al molar ratios were synthesized via co-precipitation and systematically investigated to establish the relationship between composition, structure, and catalytic performance. XRD analysis revealed the formation of spinel-type CuAl₂O₄ and MnAl₂O₄ phases, with Mn preferentially occupying octahedral B-sites to form MnAl₂O₄, thereby inducing lattice distortion and inhibiting grain growth. SEM and TEM–EDS mapping confirmed uniform elemental distribution and a porous nanoscale morphology, while H₂-TPR results suggested that increasing the Mn/Cu ratio strengthens Mn–Cu interactions, shifts Cu²⁺ reduction to higher temperatures, and enhances Cu dispersion (up to 26.11 m²/g). XPS analysis indicated that Mn doping enriches Mn³⁺ species and facilitates oxygen vacancy formation, which promotes water–gas shift (WGS) activity and suppresses CO formation. Catalytic testing (240–300 °C) showed that Mn₂Cu₂Al₄O_x achieved the highest methanol conversion while maintaining low CO selectivity; in contrast, reducing the Mn/Cu ratio increased CO selectivity, detrimental to hydrogen purification. Stability tests under continuous steam exposure for 24 h demonstrated minimal activity loss (~2%) and negligible increase in CO selectivity (<1%), confirming excellent hydrothermal stability. The results indicate that tailoring the Mn/Cu ratio optimizes the balance between redox properties and metallic Cu dispersion, offering a promising route to design low-CO, durable catalysts for on-site hydrogen generation via MSR.

Keywords: methanol steam reforming; Mn–Cu/Al₂O_x spinel; Mn/Cu ratio; CO suppression; hydrogen production; hydrothermal stability



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1. Introduction

The growing shift toward low-carbon energy systems has heightened interest in hydrogen as a clean energy carrier. Among the various production routes, methanol steam reforming (SRM: CH₃OH + H₂O → CO₂ + 3H₂) is considered highly promising for on-site hydrogen generation due to methanol's high hydrogen content, easy handling, and mild operation temperatures (200–300 °C) [1]. The core advantages of SRM-based hydrogen production focus on three aspects: (1) the raw material methanol has high hydrogen content and can be efficiently converted into hydrogen, (2) methanol exhibits

stable physical properties, making it easy to store and transport, and (3) the reaction requires a mild operating temperature, only 200–300 °C, which reduces equipment and energy consumption costs [2]. However, the commercialization process of SRM technology is still limited by catalyst performance. The current core challenge lies in the lack of catalysts that simultaneously possess high activity, long-term thermal stability, and ultra-low CO selectivity (<1%). These three properties are exactly the key prerequisites for ensuring the stable operation of fuel cells and preventing CO from poisoning the electrodes, and they directly hinder the practical implementation of SRM technology [3,4].

Copper-based catalysts, particularly Cu/ZnO/Al₂O₃, remain the industrial benchmark for MSR due to their excellent C–H and O–H bond activation capabilities [5,6]. Yet, they are prone to Cu nanoparticle sintering at higher temperatures (>250 °C), structural degradation, and deactivation mechanisms, including carbon deposition [7,8]. Additionally, unwanted CO production via the reverse water–gas shift (RWGS) ($\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$) reaction compromises fuel-cell compatibility [9,10]. D. Hammoud et al. found that 10% Cu/Al-400-500 exhibits the best catalytic activity, with about 75.44% of H₂ yield and 51.87% of methanol conversion at 250 °C [11]. These shortcomings have steered research toward the development of improved supports and doping strategies to enhance performance [12]. Alumina (Al₂O₃) is a commonly employed support, valued for its thermal stability, high surface area, and its ability to form CuAl₂O₄ spinel phases that anchor Cu species, mitigate sintering, and extend catalyst life [13,14]. Spinel structures serve as reservoirs of Cu, facilitating the gradual migration of active species under reducing conditions, effectively stabilizing the catalytic activity [15]. Recent studies highlight that Mn incorporation into Al₂O₃ forms MnAl₂O₄ spinels, fostering stronger Cu–Mn interactions and further inhibiting sintering while enhancing redox behavior [16,17]. For instance, Mn-doped Cu/Al₂O₃ catalysts have shown promise in suppressing CO formation by promoting water–gas shift (WGS) activity through oxygen vacancy generation and improved redox cycling. Mao et al. found that the Cu–Al₂O₃ interface serves as the main active site in methanol steam reforming, guiding the construction of high-performance catalysts [18].

Recently, manganese (Mn) has gained attention as a promoter in Cu-based catalysts. Mn's multi-valent nature (Mn²⁺/Mn³⁺/Mn⁴⁺) enables it to modulate redox behavior, enhance oxygen mobility, and create oxygen vacancies [19,20]. Incorporating Mn into Al₂O₃ can also form MnAl₂O₄ spinels, fostering stronger interaction with Cu and further inhibiting sintering while enhancing redox cycling [21,22]. Experimental studies reveal that Mn doping in Cu/Al₂O_x systems enhances reducibility, modifies surface acidity-basicity, and suppresses CO formation by favoring water–gas shift (WGS) activity [23,24]. Component optimization, support effects, and surface modification strategies synergistically enhance the exposure of active sites, improve the anti-sintering capability, and boost the resistance to carbon deposition in copper-based catalysts for methanol steam reforming [7]. Despite these promising findings, systematic investigations of the effect of different Mn/Cu ratios on catalyst structure and SRM performance remain lacking.

Herein, we prepare Mn-doped Cu/Al₂O_x catalysts via co-precipitation, varying the Mn/Cu ratio. We employ comprehensive characterizations (XRD, BET, TEM-EDS, H₂-TPR, XPS) and assess SRM performance (240–300 °C). The goals are to understand how Mn influences CuAl₂O₄ phase formation, Cu dispersion, redox behavior, and CO suppression—providing rational design strategies for Mn–Cu/Al₂O_x catalysts with enhanced SRM performance.

2. Results and Discussion

2.1. XRD Analysis

The XRD patterns of catalyst samples with different molar ratios are presented in Figure 1.

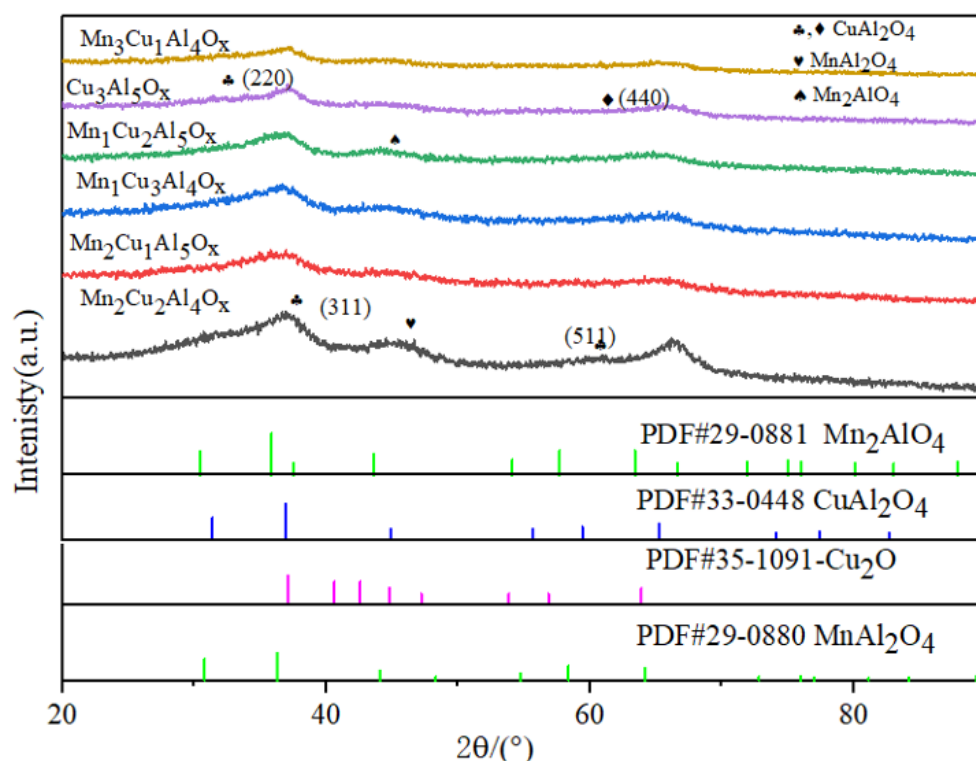


Figure 1. XRD patterns of the Mn/Cu/Al catalysts with different mole ratio.

As shown in Figure 1, characteristic diffraction peaks of the CuAl_2O_4 spinel are observed at 31.3° (220 plane), 36.9° (311 plane), and 65.2° (440 plane) in the sample without manganese. With increasing Mn content in the catalysts, the diffraction peak intensity of the $\text{Mn}_2\text{Al}_2\text{O}_4$ phase (36.1° (311)) significantly enhances [25]. This indicates that Mn preferentially occupies the B-sites of the spinel structure to form MnAl_2O_4 . Concurrently, peak broadening occurs, which may be attributed to lattice distortion induced by Mn^{2+} doping, thereby suppressing crystallite growth. At excessive Mn concentrations, the formation of amorphous MnO_x structures becomes dominant, leading to the weakening of spinel phase peaks. Consistent with findings by Dasireddy et al., Mn doping enhances sintering resistance [19].

When Cu content increases, the CuAl_2O_4 phase becomes predominant, evidenced by the highest intensity of the 36.9° (311) peak and improved crystallinity. Controlled variation in the Mn/Cu ratio reveals that high Mn content promotes MnAl_2O_4 formation, while high Cu content favors CuAl_2O_4 crystallization. At a Mn/Cu/Al molar ratio of 2:2:4, a composite spinel phase of $\text{Mn}_2\text{Cu}_1\text{Al}_4$ forms, where the Mn-Cu synergistic effect balances redox properties and structural stability, potentially yielding superior performance in steam reforming of methanol (SRM). Subsequent characterizations via H_2 -TPR and XPS will be conducted to validate the valence distributions of Mn, Cu, and oxygen species. As Cu serves as the catalytic core for hydrogen production via methanol steam reforming, an optimal Mn/Cu/Al ratio is critical to simultaneously achieve high dispersion, structural stability, and catalytic activity—key factors for realizing efficient hydrogen generation from methanol [26].

2.2. SEM Analysis

The morphologies of MnCuAl catalysts with different molar ratios are depicted in Figure 2. The overall morphology exhibits grain aggregates composed of nanoscale particles, with mesoporous gaps existing between the particles. The molar ratio has an impact on the morphology; specifically, samples with higher Cu content, namely $\text{Mn}_2\text{Cu}_2\text{Al}_4$ and $\text{Mn}_1\text{Cu}_2\text{Al}_5$, exhibit more densely packed blocky structures with smoother surfaces and fewer pores [14]. Samples with higher Mn/Al ratios or elevated Al ($\text{Mn}_2\text{Cu}_1\text{Al}_5\text{O}_x$) proportions exhibit a more loosely packed structure with abundant porosity, facilitating mass diffusion. This observation aligns with the established mechanism that Cu species are more prone to migration and neck growth during thermal treatment, whereas high-valence Mn ions effectively suppress sintering by stabilizing the structural framework. A significant improvement in particle dispersion is observed, which corroborates the XRD-derived conclusion that Mn doping effectively inhibits sintering by stabilizing the crystal lattice when Mn content is ≥ 2 (in atomic/molar ratio) [27]. An appropriate Mn/Cu ratio can enhance the specific surface area and optimize pore connectivity of the catalyst, as Mn^{2+} acts as a “structural directing agent” to suppress self-agglomeration of active components [28].

2.3. H_2 -TPR Analysis

The H_2 -TPR profiles of different catalysts are presented in Figure 3. As shown in Figure 3 (left), the $\text{Cu}_3\text{Al}_5\text{O}_x$ catalyst exhibits the most intense reduction peak in the 220–300 °C range, consistent with its higher Cu content. The $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ catalyst also displays a pronounced reduction peak in this temperature region, albeit with lower intensity compared to $\text{Cu}_3\text{Al}_5\text{O}_x$. These peaks are primarily attributed to the reduction of surface CuO species ($\text{Cu}^{2+} \rightarrow \text{Cu}^0$) [29]. With increasing Mn/Cu ratios, the reduction peaks shift toward higher temperatures, indicating enhanced dispersion of copper species, reduced reducibility, and improved thermal stability. This observation suggests a synergistic interaction between Mn and Cu, likely forming Mn-Cu composite oxides, which aligns with XRD analysis results. Such interactions contribute to superior high-temperature stability and sintering resistance during catalytic reactions [28].

Post- N_2O oxidation and subsequent H_2 -TPR analysis (Figure 3, right) reveal that high-Cu catalysts (Mn:Cu < 1), such as $\text{Cu}_3\text{Al}_5\text{O}_x$, exhibit reduction peaks predominantly in the low-temperature region (~150 °C) with large peak areas, indicating facile reduction of CuO species and weak Cu-O bonding. Mn doping shifts the reduction temperature to higher values and increases reduction difficulty, thereby enhancing the sintering resistance of Cu-based catalysts [30].

The key structural properties derived from H_2 -TPR and BET analyses are summarized in Table 1. Notably, the $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ sample exhibits the highest copper-specific surface area (S_{Cu}) of 26.11 m^2/g . This finding, combined with its high copper dispersion (D_{Cu}), confirms that an optimal Mn/Cu ratio is crucial for achieving superior Cu dispersion and exposing a larger active Cu surface area, which is beneficial for the MSR reaction [31].

Table 1. Structural and surface properties of the prepared Mn-Cu-Al catalysts.

Sample	S_{BET} (m^2/g)	C_Cu (%)	D_Cu (%)	S_{Cu} (m^2/g)	TPR1 (°C)	TPR2 (°C)	H_2 Consumption of TPR1 (mmol/g)	H_2 Consumption of TPR2 (mmol/g)
$\text{Cu}_3\text{Al}_5\text{O}_x$	51.43	0.34	11.71	15.91	287.17	171.22	12.37	0.99
$\text{Mn}_1\text{Cu}_3\text{Al}_4\text{O}_x$	55.87	0.31	18.40	21.65	244.01	171.63	11.35	1.05
$\text{Mn}_1\text{Cu}_2\text{Al}_5\text{O}_x$	57.45	0.26	13.47	17.56	251.51	162.45	8.57	1.26
$\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$	76.44	0.25	24.60	26.11	257.86	144.90	6.34	0.88
$\text{Mn}_2\text{Cu}_1\text{Al}_5\text{O}_x$	71.62	0.16	27.42	19.88	215.23	170.83	14.45	1.97
$\text{Mn}_3\text{Cu}_1\text{Al}_4\text{O}_x$	65.32	0.15	31.25	21.65	277.38	151.66	11.29	1.77

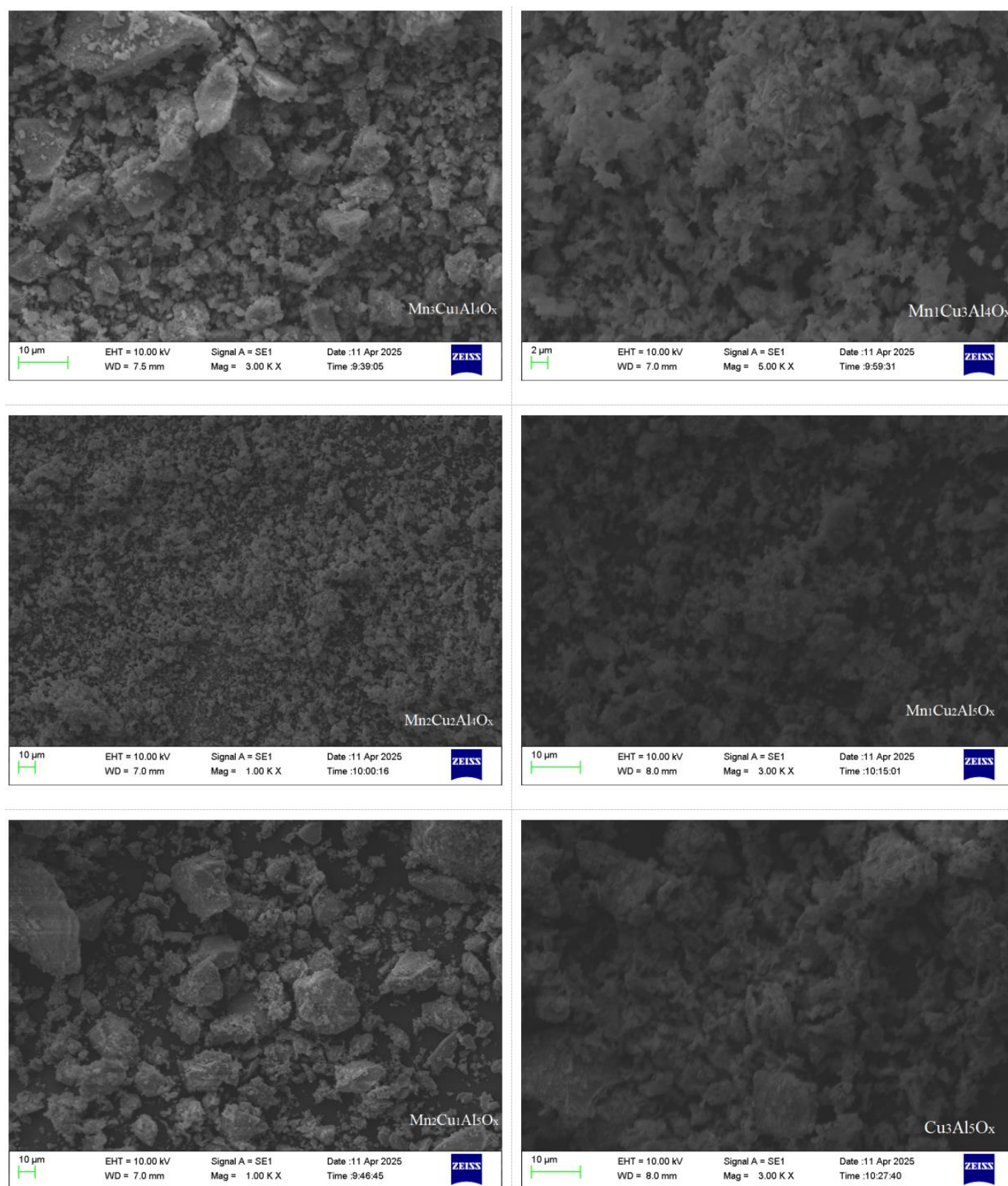


Figure 2. SEM scan of MnCuAl catalyst.

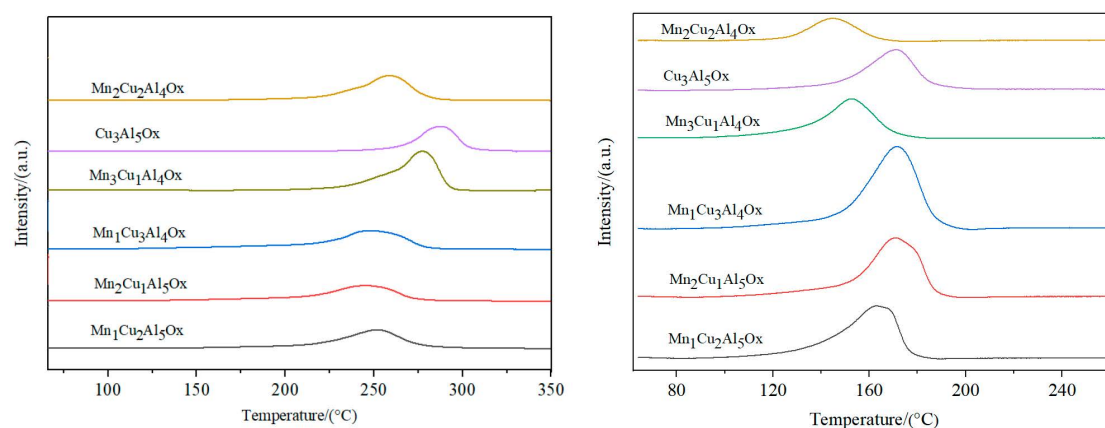


Figure 3. TPR1 (left) and TPR2 (right) spectra of different MnCuAl catalysts.

2.4. BET Analysis

The N₂ physical adsorption/desorption isotherms and key textural properties of the catalysts are presented in Figure 4 and Table 1, respectively. All six catalysts exhibit Type IV isotherms with H3-type hysteresis loops, indicative of mesoporous structures formed by the stacking of plate-like particles [32]. As summarized in Table 1, the Mn doping significantly influences the specific surface area. The non-Mn-doped Cu₃Al₅O_x catalyst shows the smallest specific surface area ($S_{\text{BET}} = 51.43 \text{ m}^2/\text{g}$), whereas the Mn₂Cu₂Al₄O_x sample achieves the highest S_{BET} of $76.44 \text{ m}^2/\text{g}$. This enhancement is attributed to the optimal Mn/Cu ratio promoting better dispersion of active components and inhibiting particle aggregation during calcination. Furthermore, the copper dispersion (D_{Cu}) data in Table 1 reveals a clear trend. The Cu₃Al₅O_x and Mn₁Cu₂Al₅O_x samples exhibit relatively low Cu dispersion values of 11.71% and 13.47%, respectively. In stark contrast, the Mn₂Cu₂Al₄O_x catalyst demonstrates the highest Cu dispersion of 24.6%, unequivocally confirming that appropriate Mn doping is highly effective in improving Cu dispersion and increasing the number of exposed active sites in Cu-based catalysts [33].

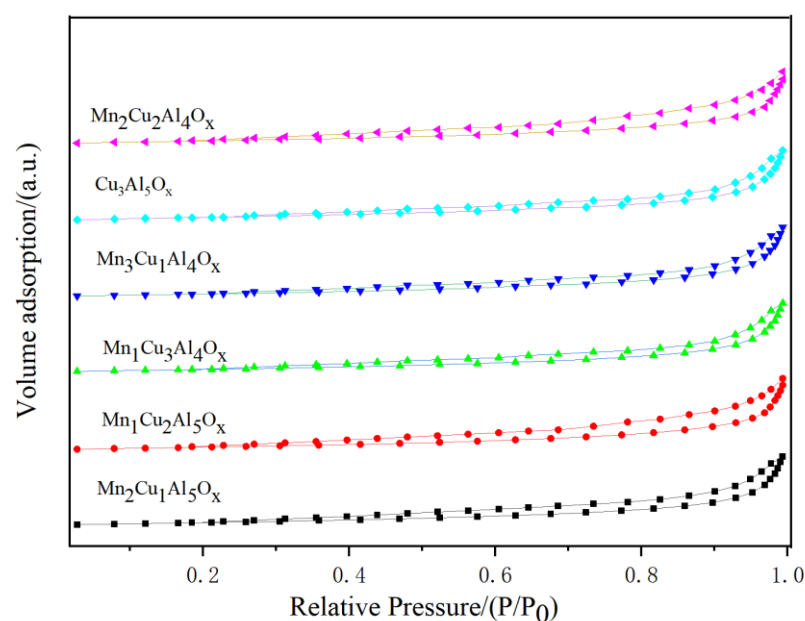


Figure 4. N₂ physical adsorption/desorption isotherms of different catalysts.

2.5. XPS Analysis

To investigate the surface composition and chemical states of spinel catalysts, XPS analysis was performed on the Cu 2p, Mn 2p, and O 1s regions for Mn₂Cu₂Al₄O_x samples

before and after reduction [34], with results presented in Figure 5. As shown in Figure 5a, the pre-reduction Cu 2p_{3/2} spectrum exhibits characteristic peaks of Cu²⁺, attributable to both non-spinel and spinel phases, with distinct satellite peaks observed in the 943–945 eV range [35]. In comparison with the Cu 2p spectrum of CuAl₂O₄ reported in the literature, Mn doping induces a negative binding energy shift in the Mn₂Cu₂Al₄O_x catalyst [36]. Following H₂ reduction, the main Cu 2p peak of Mn₂Cu₂Al₄O_x shifts to lower binding energies (~932–933 eV), accompanied by a significant decrease in satellite peak intensity. These spectral changes indicate partial reduction of Cu²⁺ to Cu⁰/Cu⁺ species [37].

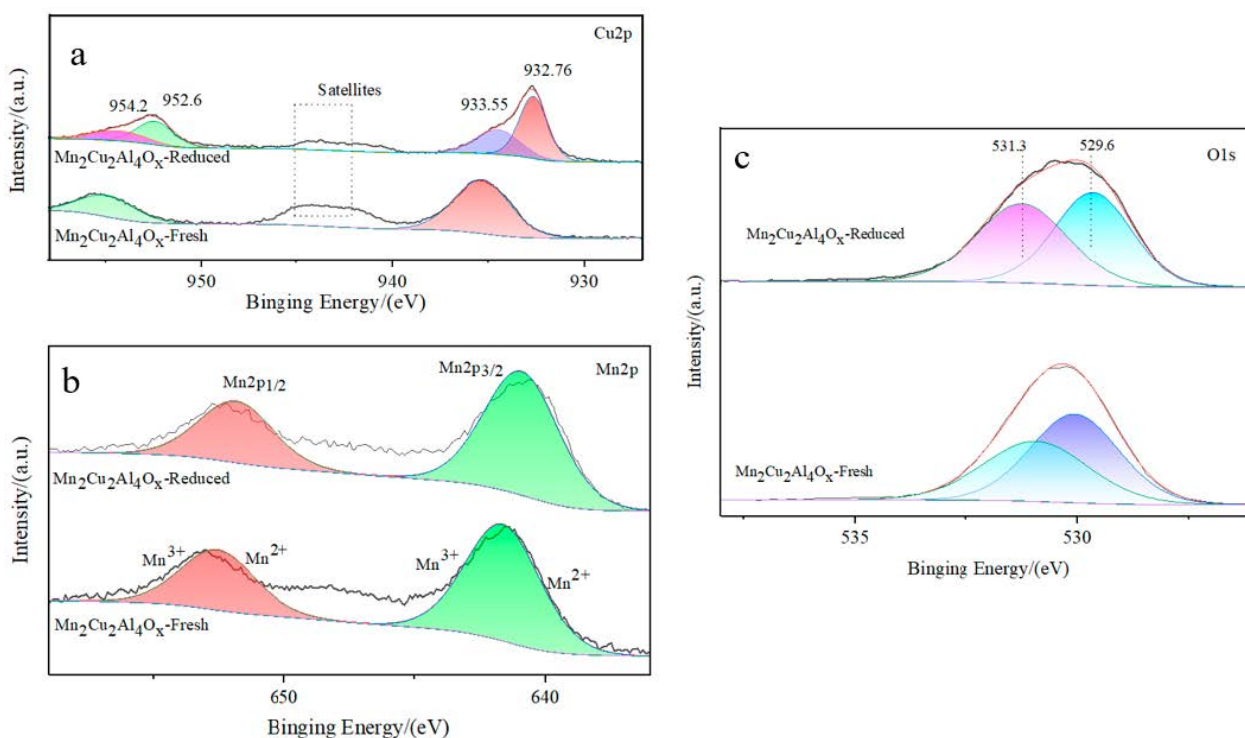


Figure 5. Cu 2p XPS spectra (a), Mn 2p XPS spectra (b), and O 1s XPS spectra (c) of the Mn₂Cu₂Al₄O_x catalyst before and after reduction.

As shown in Figure 5b, the Mn 2p_{3/2} spectrum can be deconvoluted into multiple components, indicating the coexistence of multiple Mn oxidation states (Mn²⁺, Mn³⁺, Mn⁴⁺) [38]. Notably, the as-prepared Mn₂Cu₂Al₄O_x catalyst exhibits a high proportion of Mn³⁺ (binding energy ~641 eV) [39]. After reduction, the Mn⁴⁺/Mn³⁺ ratio decreases while the Mn²⁺ content increases. In methanol steam reforming for hydrogen production, the Mn⁴⁺/Mn³⁺ redox couple facilitates CO oxidation to CO₂, thereby reducing CO selectivity [40].

As depicted in Figure 5c, the O 1s spectrum can be deconvoluted into two distinct components: lattice oxygen (~529.6 eV) and surface-adsorbed oxygen (~531.3 eV) [41]. Notably, the Mn 2p_{3/2} peak also shifts to lower binding energies after reduction. Concurrently, the lattice oxygen peak intensity decreases while the surface-adsorbed oxygen peak intensity increases with a high-energy shift in its position. These spectral changes indicate the formation of oxygen vacancies and an increase in surface hydroxyl groups during reduction. The enhanced presence of chemically adsorbed oxygen species facilitates CO oxidation to CO₂, thereby reducing CO selectivity and improving the catalyst's CO₂ selectivity [42]. It is noteworthy that surface-adsorbed oxygen is considered one of the key factors influencing the reaction rate of methanol steam reforming (MSR), as it can regulate the redox reaction rate and facilitate the dissociative adsorption of methanol [43].

2.6. TEM Characterization

TEM image of fresh and reduced $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ sample was shown in Figure 6. As shown in Figure 6A, the fresh $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ catalyst is composed of highly dispersed nanoparticles with an average particle size of 15.53 nm. After reduction with hydrogen, the active metal particles undergo significant sintering, resulting in a notable increase in the average particle size to 22.58 nm.

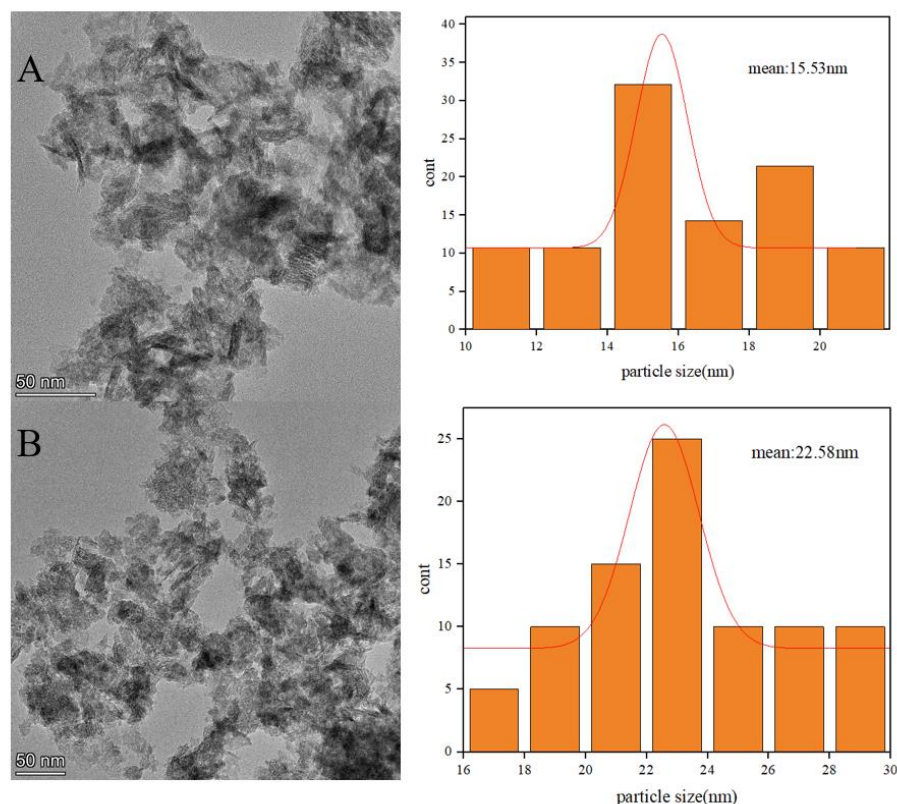


Figure 6. TEM images of the spinels: images of $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$: (A) Fresh catalyst; (B) The catalyst after reduction.

HRTEM and STEM of fresh and reduced $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ sample was shown in Figure 7. As displayed in Figure 7A, the fresh $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ catalyst exhibits two distinct lattice spacings of 0.14 nm and 0.16 nm. The 0.14 nm spacing can be assigned to the (440) crystal plane of the spinel-type structure, whereas the 0.16 nm spacing likely corresponds to the (111) plane of CuO, suggesting the formation of a composite oxide with well-intermixed phases in the as-prepared catalyst [44]. After H_2 reduction, the observed lattice spacings become 0.14 nm and 0.18 nm. The persistence of the 0.14 nm spacing indicates that the spinel framework remains structurally stable under reductive conditions. In contrast, the expansion from 0.16 nm to 0.18 nm suggests lattice relaxation, which can be attributed to the creation of oxygen vacancies and the reduction of metal cations, most likely arising from the transformations of Cu^{2+} to Cu^+/Cu^0 and Mn^{4+} to $\text{Mn}^{3+}/\text{Mn}^{2+}$ [45]. Similar lattice expansions upon reduction have been reported for transition metal oxides, where removal of lattice oxygen and partial reduction of metal ions lead to weakened metal–oxygen bonds, increased inter-planar distances, and defect-mediated structural relaxation. The formation of oxygen vacancies not only modifies the local coordination environment but also enhances the mobility of surface oxygen species, as corroborated by the O 1s XPS results (Figure 5c), thereby potentially contributing to the improved CO_2 selectivity observed during methanol steam reforming [19].

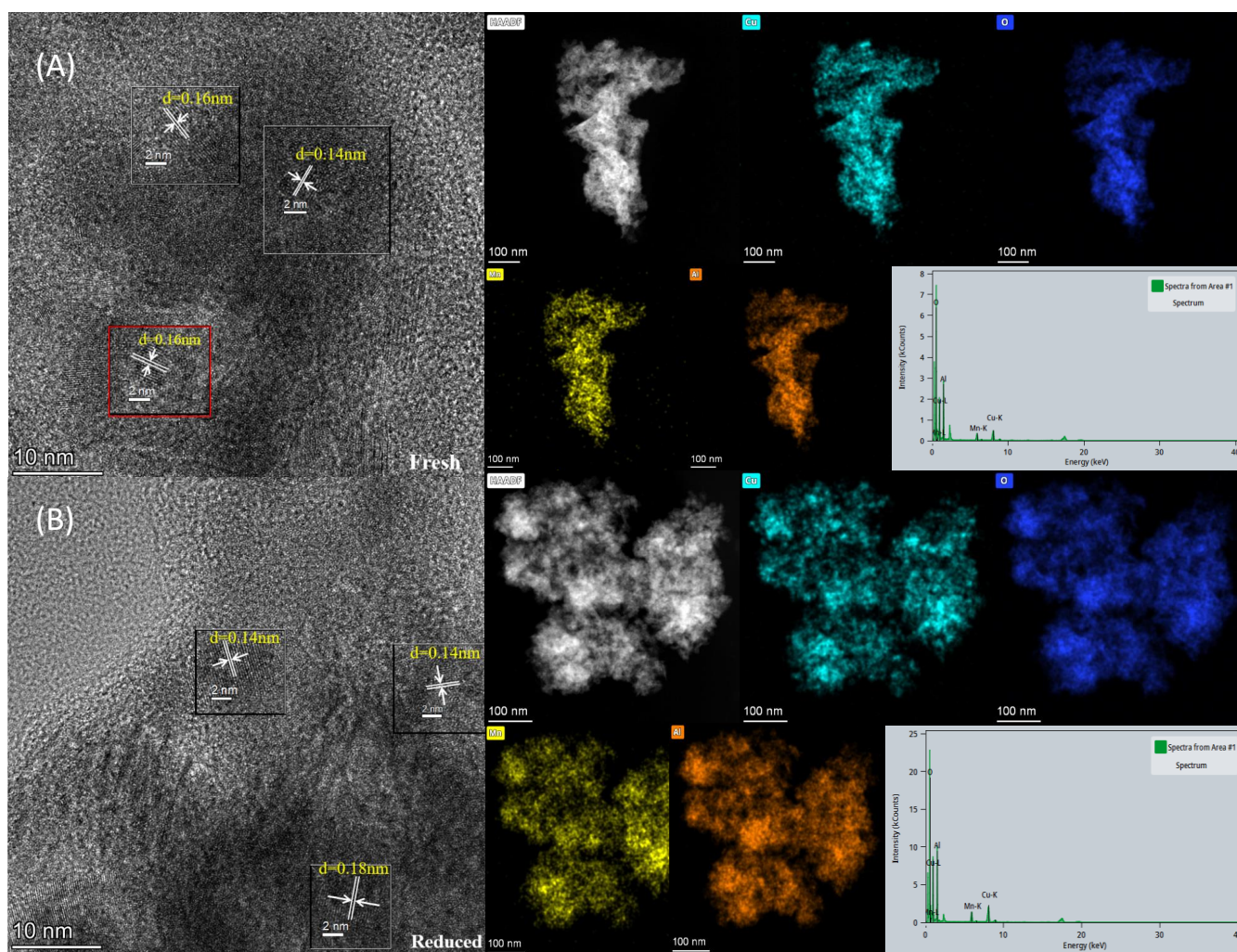


Figure 7. HRTEM and STEM mapping images of $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$: (A) Fresh catalyst; (B) The catalyst after reduction.

Elemental mapping of the fresh $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ sample shows that Mn (yellow), Cu (cyan), Al (orange), and O (blue) are homogeneously distributed, indicating that the co-precipitation method effectively achieved uniform mixing of the constituent elements without noticeable elemental segregation [19]. This uniform elemental distribution is consistent with the particle morphology observed in the TEM images, suggesting the formation of a homogeneous multi-component composite oxide. After H_2 reduction, the overall elemental distribution remains relatively uniform; however, slight aggregation of Cu is observed, implying element migration during the reduction process. This phenomenon is likely due to the reduction of CuO to metallic Cu. The Al distribution remains highly stable, indicating that the spinel framework is preserved under the reductive conditions [46].

The elemental content of $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ samples before and after reduction was shown in Table 2. As shown in Table 2, after H_2 reduction, the Cu content in the $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ sample increases by approximately 31%, while the Mn content increases by about 40%, accompanied by a decrease of around 15% in oxygen content. The Al content remains nearly unchanged, indicating that the spinel framework is highly stable during the reduction process.

TEM-mapping analysis further reveals that the $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ catalyst prepared by the co-precipitation method undergoes notable structural and surface compositional changes upon reduction. The observed lattice expansion—in particular, the increase in the inter-planar spacing from 0.16 nm to 0.18 nm—suggests the formation of oxygen vacancies.

Meanwhile, elemental distribution analysis shows that, despite the structural changes, the overall distribution of elements remains relatively homogeneous after reduction. However, the surface concentration of metallic species increases, which is favorable for the catalytic reaction.

Table 2. Elemental Composition Changes in $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ Samples Before and After Reduction.

Element	Composition Before Reduction (%)	Composition After Reduction (%)	Numerical Change (%)
Mn	10.21	14.32	+40.3
Cu	11.86	15.56	+31.2
Al	18.20	19.37	+6.4
O	59.73	50.75	−15.0

2.7. Assessment of Catalytic Activity and Selectivity

Figure 8 compares the methanol conversion (solid lines) and CO selectivity (dashed lines) of the catalysts with different Mn/Cu/Al molar ratios in the temperature range of 240–300 °C. For all samples, methanol conversion increases markedly with temperature, reflecting the endothermic nature of the methanol steam reforming (MSR) reaction. The variation in the Mn/Cu/Al ratio has a pronounced influence on catalytic activity. Notably, the $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ catalyst consistently demonstrates the highest methanol conversion across the entire temperature range, reaching over 95% at 300 °C, which correlates well with its high specific surface area and optimal Cu dispersion as shown in Table 1.

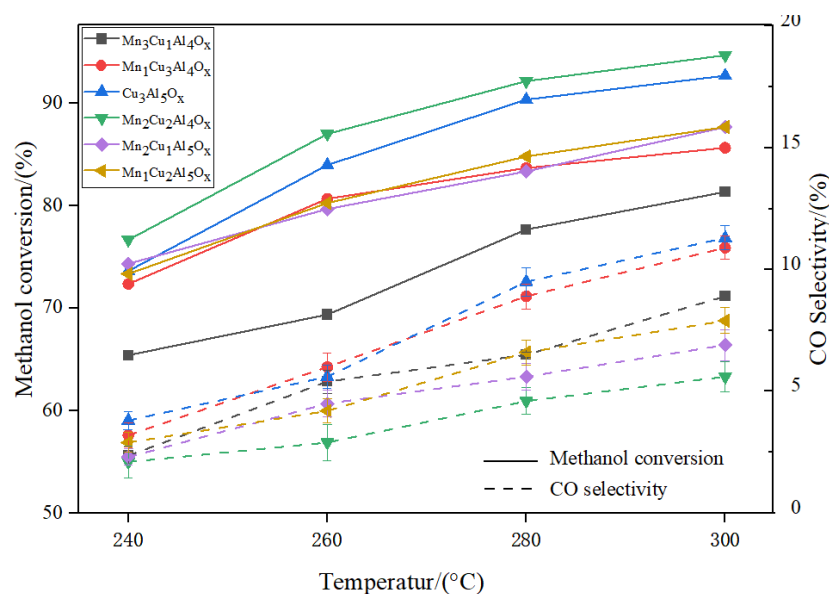


Figure 8. Effect of Mn/Cu/Al molar ratio on methanol conversion and CO selectivity. (The solid lines represent methanol conversion, and the dashed lines denote CO selectivity. Error bars represent the standard deviation from three independent experiments.).

Regarding CO selectivity, the differences among the catalysts are relatively small and largely within the margin of experimental error at lower temperatures (240 and 260 °C). However, as the temperature increases to 280 °C and 300 °C, where side reactions such as methanol decomposition and reverse water-gas shift (RWGS) become more significant [47], clear and statistically meaningful trends emerge.

Specifically, at 300 °C, catalysts with a lower Mn/Cu ratio, such as $\text{Mn}_1\text{Cu}_3\text{Al}_4\text{O}_x$, exhibit a significantly higher CO selectivity of approximately 9–10%. In contrast, the catalysts with a balanced or high Mn/Cu ratio, particularly our optimal $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$,

effectively maintain a lower CO selectivity (around 6%). This trend strongly suggests that a sufficient amount of manganese plays a crucial role in suppressing CO formation under more demanding reaction conditions. This is consistent with our XPS analysis, which indicates that Mn doping enriches Mn^{3+} species and facilitates oxygen vacancy formation, thereby promoting the water-gas shift (WGS) reaction that consumes CO [48]. While this effect is less discernible at lower temperatures, the data at higher temperatures clearly validates that catalysts with an insufficient Mn content are more prone to undesirable CO production. Therefore, catalysts with balanced Mn and Cu contents, like $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$, offer the best compromise between achieving high conversion and maintaining low CO selectivity.

Figure 9 illustrates the temporal evolution of methanol conversion and CO selectivity for the optimal $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ catalyst during a 24 h stability test at 240 °C. The catalyst shows an initial steady-state methanol conversion of approximately 90%. It is noted that this conversion is higher than the ~76% reported in the activity test (Figure 8) at the same temperature. This is attributed to a catalyst ‘break-in’ period, where the catalyst reaches a more stable and highly active state after being held on stream at a constant temperature. Over the 24 h period, the conversion only experiences a slight decline, demonstrating the catalyst’s high structural and catalytic stability under prolonged hydrothermal conditions. Simultaneously, the CO selectivity remains consistently low (~1.1%) with only a marginal change (<0.3% absolute), confirming its excellent resistance to side reactions like methanol decomposition.

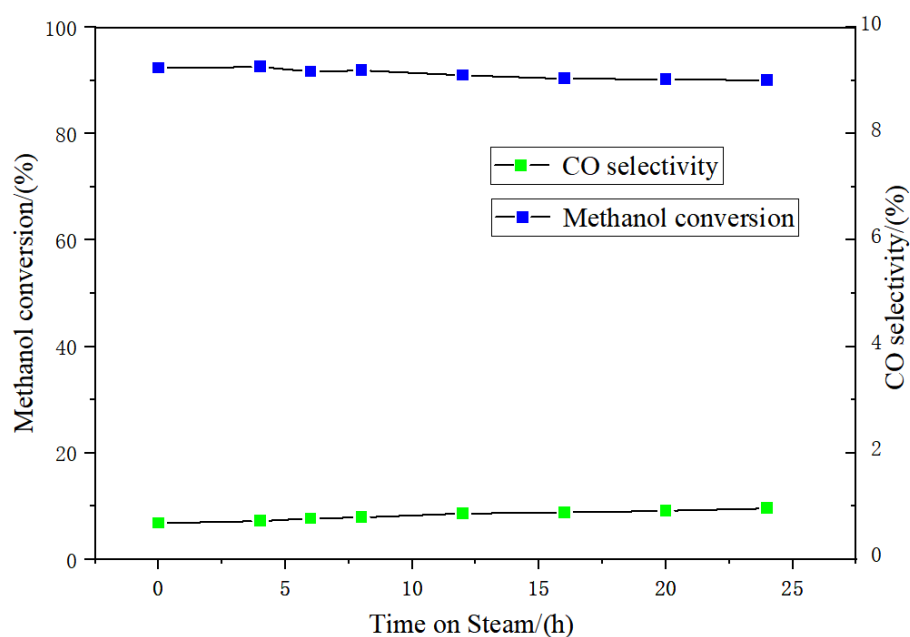


Figure 9. Operational Stability of $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ Catalyst.

Varying the Mn:Cu:Al molar ratio tunes the balance between redox properties and metallic copper dispersion, thereby controlling both methanol conversion efficiency and CO selectivity. Mn-rich spinel-type catalysts (for instance $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$) offer higher conversions with no apparent penalty in CO selectivity, making them promising candidates for low-CO hydrogen production via MSR.

To further contextualize the performance of our optimized catalyst, Table 3 provides a comparison of the catalytic activity of the $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ catalyst with other recently reported Cu-based catalysts for methanol steam reforming.

Table 3. Comparison of catalytic performance for methanol steam reforming over the $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ catalyst and other reported Cu-based catalysts.

Catalyst Composition	Temperature (°C)	MeOH Conv. (%)	CO Sel. (%)	Stability/Notes	Reference
$\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$	300	>95	6	Excellent stability (>88% conv. after 24h)	This work
$\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$	260	87	3		This work
10% Cu/Al-400-500	250	51.9	N/A		[11]
Cu/ZnO/Al ₂ O ₃	250	>90	~3–5	Prone to sintering and deactivation	[5,6]
5%Mn-15%Cu/Al ₂ O ₃	300	~90	12.0		[18]
4.25Cu/Cu(Al)O _x	270	~92.3	N/A	Good performance, complex structure	[23]
Cu/ZnO/Al ₂ O ₃	280	~75	~15	Lower activity, higher CO selectivity	[14]

As shown in Table 3, our optimal $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ catalyst demonstrates outstanding performance. Compared to the simple Cu/Al₂O₃ catalyst reported by Hammoud et al. [11], our catalyst achieves significantly higher methanol conversion at similar temperatures. While the commercial Cu/ZnO/Al₂O₃ catalyst shows high initial activity, it is known to suffer from poor thermal stability, an issue our spinel-based catalyst effectively overcomes, as evidenced by the 24 h stability test.

More importantly, when benchmarked against other Mn-promoted systems, the $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ catalyst remains highly competitive. For instance, compared to a reported Mn-doped Cu/Al₂O₃ catalyst, our system achieves higher conversion and lower CO selectivity at 300 °C. Although catalysts derived from LDH precursors show excellent results [23], our spinel-based catalyst prepared by a straightforward co-precipitation method offers a comparable high-performance profile. The superior activity and significantly suppressed CO formation compared to the pure CuAl₂O₄ spinel [14] unequivocally highlight the critical synergistic effect of incorporating an optimal amount of manganese.

In summary, this comparison validates that tailoring the Mn/Cu ratio to form a $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ spinel structure is a highly effective strategy, yielding a catalyst that not only surpasses many existing systems in activity but also provides the crucial durability and low-CO selectivity required for practical hydrogen production applications.

3. Experimental Section

3.1. Materials

The chemical reagents and experimental water used in this experiment are as follows: Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), manganese nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium hydroxide (NaOH), and Graphite: All are of Analytical Reagent (AR) grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methanol (CH_3OH): Of Guaranteed Reagent (GR) grade, purchased from Shanghai Macklin Biochemical Technology Co. (Shanghai, China), Ltd. Ammonia solution: With a mass fraction of 5%, purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH): Of Analytical Reagent (AR) grade, provided by Aladdin Reagents (Shanghai) Co., Ltd. (Shanghai, China). Graphite (C_{60}): Provided by Aladdin Reagents Co., Ltd. (Shanghai, China).

3.2. Instruments

The catalytic performance in the methanol steam reforming (MSR) reaction was evaluated using a gas–solid fixed-bed reactor (Tianjin Honghua Technology Co., Ltd., Tianjin, China). The crystalline phase structures were characterized by an X-ray powder diffractome-

ter (Bruker Corporation, Karlsruhe, Germany). The product compositions were analyzed using a gas chromatograph (Shimadzu Corporation, Kyoto, Japan). Surface properties were investigated using a dynamic chemical adsorption analyzer (Beijing JWGB Sci. & Tech. Co., Ltd., Beijing, China), while morphological observations were conducted via a scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany). The elemental composition was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Fisher Scientific Inc., Waltham, MA, USA). The calcination process was carried out in a muffle furnace (Qixin, Shanghai, China). Textural properties were measured using a BSDPM2 surface area and micropore analyzer (Beishide Instrument Technology (Beijing) Co., Ltd., Beijing, China). X-ray photoelectron spectroscopy (XPS) analyses were performed using a Nexsa system (Thermo Fisher Scientific Inc., Waltham, MA, USA), and transmission electron microscopy (TEM) tests were conducted with a Talos F200X G2 instrument (Thermo Fisher Scientific Inc., Waltham, MA, USA).

3.3. Catalyst Preparation

Mn–Cu/Al₂O₄ catalysts were synthesized via a co-precipitation method using copper(II) nitrate trihydrate, manganese nitrate, and aluminum nitrate as the respective precursors of Cu, Mn, and Al. Catalysts with varying Mn:Cu:Al molar ratios (0:2:5, 1:2:5, 2:2:4, 1:3:4, 2:1:5, and 3:1:4) were prepared. The calculated amounts of metal salts were dissolved in 80 mL of deionized water, followed by the addition of five drops of 0.1 M nitric acid to obtain solution A. The mixture was maintained at 30 °C in an oil bath under constant stirring for 30 min. A 1 wt% NH₃·H₂O solution was then introduced dropwise at a rate of 1 mL/min under magnetic stirring (200 rpm). After complete addition, the pH of the suspension was adjusted to 9.0, and the slurry was aged for 2 h with continuous stirring. The resulting precipitate was filtered, washed three times with deionized water and ethanol, and subsequently dried in a vacuum oven at 80 °C (0.08 MPa) for 12 h. The dried solid was ground into fine precursor powders, which were finally calcined in air at 400 °C for 4 h in a tubular furnace (heating rate: 5 °C/min). The obtained catalysts with different molar ratios were denoted as MnCuAlO_x. The sample preparation process is shown in Figure 10.

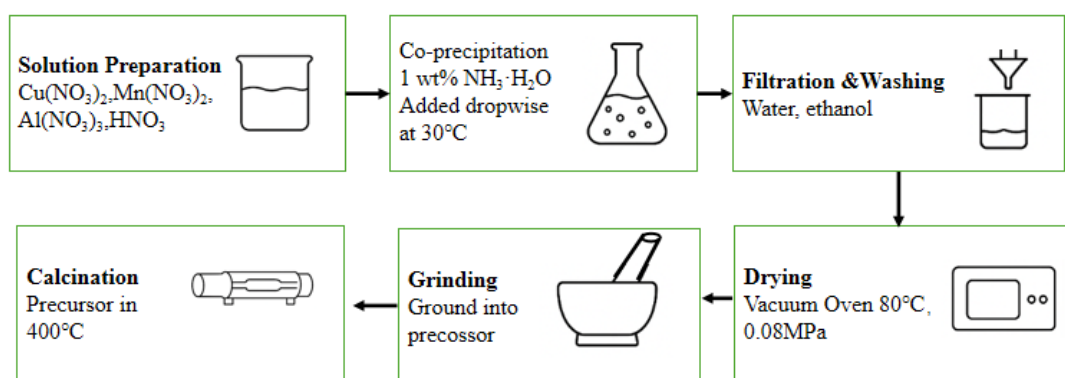


Figure 10. Sample Preparation Flowchart.

3.4. Characterization of Catalysts

3.4.1. X-Ray Diffraction (XRD)

The crystalline phases of the catalysts were analyzed using a Bruker D8 Advance X-ray diffractometer (Bruker Corporation, Karlsruhe, Germany) equipped with Cu K α radiation ($\lambda = 0.154$ nm). The instrument was operated at a tube voltage of 40 kV and a tube current of 40 mA. Diffraction patterns were collected over a 2θ range of 10–90° with a step size of 0.02° and a scan rate of 2°/min. For sample preparation, catalyst powder was uniformly packed into a standard sample holder and flattened with a glass slide to ensure a planar

surface coplanar with the holder edge. Phase identification and crystallite size analysis were performed using MDI Jade software (version 6.5) by matching diffraction peaks to reference patterns in the ICDD PDF-4+ database.

3.4.2. Scanning Electron Microscopy (SEM)

Surface morphology and elemental composition were examined using a Zeiss Evo 18 scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. Samples were prepared by affixing double-sided conductive carbon tape to an aluminum stub. Catalyst powder was dispersed onto the tape using a capillary tube, and loose particles were removed with compressed air. To enhance conductivity, samples were sputter-coated with a 5 nm gold layer using a Quorum Q150R ES sputter coater (Quorum Technologies Ltd., Ramsgate, Kent, UK). Imaging was performed under high-vacuum conditions at accelerating voltages of 0.2–30 kV, with a working distance of 8–10 mm. Secondary electron images were acquired at various magnifications (500–50,000 $\times$), while EDS analysis was conducted at 20 kV to quantify elemental distribution (Mn, Cu, Al, O) with an acquisition time of 60 s per spectrum.

3.4.3. H₂-TPR Characterization

The dispersion and specific surface area of Cu in the catalysts were determined using a JW-DTP1009 chemisorption analyzer (Beijing JWGB Sci. & Tech. Co., Ltd., Beijing, China). The reduction of the catalyst samples with hydrogen, followed by dynamic adsorption, was employed to reveal the distribution characteristics and variation trends of copper under different reaction conditions.

Approximately 30 mg of the prepared catalyst sample was placed into a U-shaped quartz tube packed with asbestos, with an additional asbestos layer used for fixation. The tube was then mounted on the chemisorption analyzer. The reducibility of the catalysts was investigated under a 10% H₂/Ar mixed atmosphere in the temperature range of 30–350 °C, referred to as TPR1. After reduction, the sample was titrated with N₂O, followed by a second reduction in a 10% H₂/Ar mixture at 50–300 °C, designated as TPR2. The copper dispersion (D_{Cu}) and S-Cu data of Mn/Cu/Al catalyst samples were calculated by Equations (1) and (2) as following:

$$D_{Cu} = 2n_2/n_1 \times 100\% \quad (1)$$

$$S_{Cu} = 2n_2 N_A / (n_1 M_{Cu} N_{Cu}) \quad (2)$$

where n_1 is the amount of H₂ consumed during TPR1 (mol), n_2 is the amount of H₂ consumed during the reaction in Equation (2) (mol), N_A is Avogadro's constant ($6.02 \times 10^{23} \text{ mol}^{-1}$), M_{Cu} is the atomic weight of Cu (63.55 g/mol), ρ_{Cu} is the density of Cu (8.92 g/cm³), and N_{Cu} is the number of copper atoms per unit surface area ($1.4 \times 10^{19} \text{ atoms/m}^2$).

3.4.4. Determination of Elemental Content by ICP

The Perkin-Elmer Optima 8000 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Thermo Fisher Scientific Inc., Waltham, MA, USA) was used to analyze the content of various metal elements in the catalyst. Prior to sample loading and analysis, the samples were digested using nitric acid and hydrofluoric acid.

3.4.5. N₂ Physisorption Analysis

Surface area and porosity measurements were conducted on a BSD-PM2 automated analyzer (Beijing JWGB Sci. & Tech. Co., Ltd., Beijing, China) equipped with a high-precision pressure transducer ($\pm 0.15\%$ reading accuracy). Specific surface areas were

calculated via multi-point BET analysis ($P/P_0 = 0.05\text{--}0.30$), and pore volume distributions were determined using the BJH model applied to the desorption isotherms.

3.4.6. XPS and TEM Analysis

X-ray photoelectron spectroscopy (XPS) was performed on a Nexsa system (Thermo Fisher Scientific Inc., Waltham, MA, USA), and transmission electron microscopy (TEM) was carried out using a Talos F200X G2 microscope (Thermo Fisher Scientific Inc., Waltham, MA, USA).

3.5. Catalyst Evaluation

The catalytic performance for methanol steam reforming was evaluated in a conventional gas–solid fixed-bed reactor [48]. Methanol conversion and carbon monoxide selectivity were used as the primary indicators.

A total of 2.0 g of catalyst mixed with graphite at a 93:7 weight ratio (catalyst:graphite) to facilitate pelletization was loaded into the reactor for testing. A mixed gas of H_2 (15 mL/min) and N_2 (75 mL/min) was introduced, and the sample was pretreated at $30\text{ }^\circ\text{C}$ for 30 min. The temperature was then increased to $260\text{ }^\circ\text{C}$ at a heating rate of $3\text{ }^\circ\text{C}/\text{min}$, and the catalyst was reduced for 3 h. After reduction, the reactor was cooled directly to $240\text{ }^\circ\text{C}$.

Subsequently, a water–methanol mixture (mass ratio 1.2:1) was fed into the reactor at a flow rate of 0.2 mL/min using a micro-liquid pump. The catalyst bed temperature was controlled in the range of $240\text{--}300\text{ }^\circ\text{C}$, with a heating rate of $1\text{ }^\circ\text{C}/\text{min}$. Catalyst stability tests were carried out at $240\text{ }^\circ\text{C}$ for 24 h under identical reaction conditions.

The gas-phase products were analyzed using a Shimadzu GC-2014PLUS gas chromatograph (Shimadzu Corporation, Kyoto, Japan). Methanol conversion was determined by collecting and analyzing the condensed liquid. The methanol concentration in the condensate was calculated by the area normalization method, from which the methanol conversion was obtained according to the following Equation:

$$\alpha_{\text{Methanol conversion}} = \left(1 - \frac{V_{\text{effluent}} \times \rho_{\text{effluent}} \times \omega_{\text{methanol content of effluent}}}{0.2 \times t \times \rho_{\text{methanol content of feed}} \times 0.4} \right) \quad (3)$$

$$S_{\text{CO}} = \frac{F_{\text{CO}}}{F_{\text{CO}} + F_{\text{CO}_2} + F_{\text{CH}_4}} \times 100\% \quad (4)$$

where F_i represents the flow rate of CO , CO_2 , CH_4 . The molar flow rates were obtained from the concentrations measured by GC and the total volumetric flow rate of the dry gas effluent.

The carbon balance was calculated for each data point by comparing the total moles of carbon in the outlet gas stream (CO , CO_2 , and unreacted CH_3OH in the condensate) to the moles of carbon fed into the reactor. For all reported catalytic tests, the carbon balance was maintained in the range of 97–102%, confirming the reliability of the collected data and indicating that the formation of other carbonaceous byproducts, such as coke, was negligible under these reaction conditions.

4. Conclusions

This study demonstrates that precise tuning of the Mn/Cu ratio in spinel-type Mn–Cu/ Al_2O_3 catalysts is an effective strategy to optimize structural stability, active phase dispersion, and CO suppression in methanol steam reforming. Higher Mn content promotes MnAl_2O_4 spinel formation, induces lattice distortion, and inhibits Cu crystallite growth, while balanced Mn–Cu compositions yield dual-spinels that combine Mn–O redox cycles with well-dispersed metallic Cu sites. H_2 -TPR, BET, and XPS analyses confirm that

Mn doping enhances Cu dispersion (up to 24.6%), enriches Mn^{3+} species, and generates abundant oxygen vacancies, which collectively facilitate CH_3OH activation and water–gas shift coupling while suppressing methanol decomposition routes to CO. Catalytic tests reveal that $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ achieves near-complete methanol conversion at 300 °C with CO selectivity below 10% and maintains >88% conversion with negligible CO increase during 24 h hydrothermal stability trials. These findings establish $\text{Mn}_2\text{Cu}_2\text{Al}_4\text{O}_x$ as a promising, durable, and low-CO catalyst for on-site hydrogen production in fuel-cell-powered energy systems.

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References

1. Tiba, S.; Omri, A. Literature survey on the relationships between energy, environment and economic growth. *Renew. Sustain. Energy Rev.* **2017**, *69*, 1129–1146. [[CrossRef](#)]
2. Ramasubramanian, B.; Sundarajan, S.; Rao, R.P.; Reddy, M.; Chellappan, V.; Ramakrishna, S. Novel low-carbon energy solutions for powering emerging wearables, smart textiles, and medical devices. *Energy Environ. Sci.* **2022**, *15*, 4928–4981. [[CrossRef](#)]
3. Ranjekar, A.M.; Yadav, G.D. Steam reforming of methanol for hydrogen production: A critical analysis of catalysis, processes, and scope. *Ind. Eng. Chem. Res.* **2021**, *60*, 89–113. [[CrossRef](#)]
4. Rostami, M.; Farajollahi, A.H.; Amirkhani, R.; Farshchi, M.E. A review study on methanol steam reforming catalysts: Evaluation of the catalytic performance, characterizations, and operational parameters. *AIP Adv.* **2023**, *13*, 030701. [[CrossRef](#)]
5. Jiang, L.; Yuan, S.; Ma, J.; Deng, S.; Fang, X.; Xu, X.; Meng, H.; Wang, X. Enhancing the Reactivity of $\text{Cu}/\text{Al}_2\text{O}_3$ for Methanol Steam Reforming through adding CrO_x : Unraveling Reaction Pathways and the Mechanism for Improvement. *ACS Catal.* **2025**, *15*, 7138–7152. [[CrossRef](#)]
6. Shahmohammadi, N.; Rezaei, M.; Alavi, S.M.; Akbari, E. Methanol steam reforming over highly efficient $\text{CuO}-\text{Al}_2\text{O}_3$ nanocatalysts synthesized by the solid-state mechanochemical method. *Int. J. Hydrogen Energy* **2023**, *48*, 13139–13150. [[CrossRef](#)]
7. Pang, S.; Dou, X.; Zhao, W.; Bai, S.; Wan, B.; Wang, T.; Yang, J.H. A Review on the Design Strategies of Copper-Based Catalysts for Enhanced Activity and Stability in Methanol Reforming to Hydrogen. *Nanomaterials* **2025**, *15*, 1118. [[CrossRef](#)]
8. Kamsuwan, T.; Guntida, A.; Praserttham, P.; Jongsomjit, B. Differences in Deterioration Behaviors of $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ Catalysts with Different Cu Contents toward Hydrogenation of CO and CO_2 . *ACS Omega* **2022**, *7*, 25783–25797. [[CrossRef](#)]
9. Zamel, N.; Groos, U. Hydrogen Energy Recovery— H_2 -Based Fuel Cells. *Adv. Energy Storage Latest Dev. RD Mark.* **2022**, 559–588.
10. Jambur, S.R. *Techno-Economic Assessment of High-Temperature $\text{H}_2\text{O}/\text{CO}_2$: Co-Electrolysis in Solid Oxide Electrolysers for Syngas Production*; Technical University of Denmark/DTU: Kongens Lyngby, Denmark, 2022.

11. Hammoud, D.; Gennequin, C.; Aboukaïs, A.; Aad, E.A. Steam reforming of methanol over x% Cu/Zn–Al 400 500 based catalysts for production of hydrogen: Preparation by adopting memory effect of hydrotalcite and behavior evaluation. *Int. J. Hydrogen Energy* **2015**, *40*, 1283–1297. [\[CrossRef\]](#)
12. Shan, J.; Zheng, Y.; Shi, B.; Davey, K.; Qiao, S.-Z. Regulating Electrocatalysts via Surface and Interface Engineering for Acidic Water Electrooxidation. *ACS Energy Lett.* **2019**, *4*, 2719–2730. [\[CrossRef\]](#)
13. Liao, M.; Duan, Q.; Xiang, R.; Tan, X.; Dai, Z.; Qin, H.; Xiao, H. Compounds: Rare earth-doped CuAl₂O₄ catalysts with superior catalytic performance for methanol steam reforming. *J. Alloys Compd.* **2025**, *1024*, 180229. [\[CrossRef\]](#)
14. Frank, B. Steam Reforming of Methanol over Cu/ZnO/Al₂O₃ Modified with Hydrotalcites. *Catal. Commun.* **2007**, *8*, 1684–1690. [\[CrossRef\]](#)
15. Tan, Z.; Fan, G.; Zheng, L.; Li, F. Promoted Surface-Interface Catalysis over Mn–Cr Incorporated Cu-Based Catalysts for Efficient Hydrogen Production from Methanol Decomposition. *ACS Catal.* **2024**, *14*, 11218–11230. [\[CrossRef\]](#)
16. Ye, R.; Xiao, S.; Lai, Q.; Wang, D.; Huang, Y.; Feng, G.; Zhang, R.; Wang, T. Advances in enhancing the stability of Cu-based catalysts for methanol reforming. *Catalysts* **2022**, *12*, 747. [\[CrossRef\]](#)
17. Zhang, M.; Liu, D.; Wang, Y.; Zhao, L.; Xu, G.; Yu, Y.; He, H. Recent advances in methanol steam reforming catalysts for hydrogen production. *Catalysts* **2025**, *15*, 36. [\[CrossRef\]](#)
18. Mao, Q.; Gao, Z.; Liu, X.; Guo, Y.; Wang, Y.; Ma, D. The Cu–Al₂O₃ interface: An unignorable active site for methanol steam reforming hydrogen production. *Catal. Sci. Technol.* **2024**, *14*, 3448–3458. [\[CrossRef\]](#)
19. Dasireddy, V.D.; Likozar, B. Cu–Mn–O nano-particle/nano-sheet spinel-type materials as catalysts in methanol steam reforming (MSR) and preferential oxidation (PROX) reaction for purified hydrogen production. *Renew. Energy* **2022**, *182*, 713–724. [\[CrossRef\]](#)
20. Kang, N.; Zhao, Z.; Yu, X.; Lin, J.; Lu, S. Tuning surface properties of CuCeOx catalysts with manganese and cobalt co-doping for CO oxidation. *J. Rare Earths* **2025**, *43*, 1643–1651. [\[CrossRef\]](#)
21. Rani, B.J.; Sivanantham, A.; Cho, I.S. Nanostructured spinel manganates and their composites for electrochemical energy conversion and storage. *Adv. Funct. Mater.* **2023**, *33*, 2303002. [\[CrossRef\]](#)
22. Liao, M.; Xiang, R.; Zhou, X.; Dai, Z.; Wang, L.; Qin, H.; Xiao, H. Enhancing effect of Mn²⁺ substitution in CuAl₂O₄ spinel for methanol steam reforming in a microreactor. *Renew. Energy* **2024**, *230*, 120815. [\[CrossRef\]](#)
23. Meng, H.; Yang, Y.; Shen, T.; Yin, Z.; Wang, L.; Liu, W.; Yin, P.; Ren, Z.; Zheng, L.; Zhang, J.; et al. Designing Cu⁰–Cu⁺ dual sites for improved C–H bond fracture towards methanol steam reforming. *Nat. Commun.* **2023**, *14*, 7980. [\[CrossRef\]](#)
24. Yan, Q.; Chen, S.; Qiu, L.; Gao, Y.; O'Hare, D.; Wang, Q. The synthesis of Cu_yMn_zAl_{1–z}O_x mixed oxide as a low-temperature NH₃-SCR catalyst with enhanced catalytic performance. *Dalton Trans.* **2018**, *47*, 2992–3004. [\[CrossRef\]](#)
25. Herdem, M.S.; Sinaki, M.Y.; Farhad, S.; Hamdullahpur, F. An overview of the methanol reforming process: Comparison of fuels, catalysts, reformers, and systems. *Int. J. Energy Res.* **2019**, *43*, 5076–5105. [\[CrossRef\]](#)
26. Li, Y.; Zhang, Y.; Qian, K.; Huang, W. Metal–Support Interactions in Metal/Oxide Catalysts and Oxide–Metal Interactions in Oxide/Metal Inverse Catalysts. *ACS Catal.* **2022**, *12*, 1268–1287. [\[CrossRef\]](#)
27. Pang, J.; Li, Q.; Su, G.; Sun, B.; Song, M.; Hua, Y.; Zhang, W.; Meng, J.; Shi, B. Tailoring Dual High-Valence Cu–O–Mn Active Sites to Enhance VOC Catalytic Oxidation. *Environ. Sci. Technol.* **2025**, *59*, 9812–9826. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Ding, J.; Zhao, L.; Yang, Y.; Liu, J. Unraveling the role of a Cu dopant in formaldehyde catalytic oxidation over a La_{0.8}Sr_{0.2}Mn_{1–x}Cu_xO₃ perovskite: An experimental and theoretical study. *J. Mater. Chem. A* **2025**, *13*, 7371–7380. [\[CrossRef\]](#)
29. Lu, T.; Su, F.; Zhao, Q.; Li, J.; Zhang, C.; Zhang, R.; Liu, P. Catalytic oxidation of volatile organic compounds over manganese-based oxide catalysts: Performance, deactivation and future opportunities. *Sep. Purif. Technol.* **2022**, *296*, 121436. [\[CrossRef\]](#)
30. Saw, S.; Datta, S.; Chavan, P.; Gupta, P.; Kumari, S.; Sahu, G.; Chauhan, V. Significance and influence of various promoters on Cu-based catalyst for synthesizing methanol from syngas: A critical review. *J. Chem. Technol. Biotechnol.* **2023**, *98*, 1083–1102. [\[CrossRef\]](#)
31. Fajin, J.L.; Cordeiro, M.N.D. Insights into the mechanism of methanol steam reforming for hydrogen production over Ni–Cu-based catalysts. *ACS Catal.* **2021**, *12*, 512–526. [\[CrossRef\]](#)
32. Lin, J.; Guo, Y.; Chen, X.; Li, C.; Lu, S.; Liew, K.M. CO Oxidation over Nanostructured Ceria Supported Bimetallic Cu–Mn Oxides Catalysts: Effect of Cu/Mn Ratio and Calcination Temperature. *Catal. Lett.* **2018**, *148*, 181–193. [\[CrossRef\]](#)
33. Kang, R.; Wei, X.; Bin, F.; Wang, Z.; Hao, Q.; Dou, B. Reaction mechanism and kinetics of CO oxidation over a CuO/Ce_{0.75}Zr_{0.25}O_{2–δ} catalyst. *Appl. Catal. A Gen.* **2018**, *565*, 46–58. [\[CrossRef\]](#)
34. Zedan, A.F.; Polychronopoulou, K.; Asif, A.; AlQaradawi, S.Y.; AlJaber, A.S. Cu–Ce–O catalyst revisited for exceptional activity at low temperature CO oxidation reaction. *Surf. Coat. Technol.* **2018**, *354*, 313–323. [\[CrossRef\]](#)
35. Abed, S.H.; Reshak, A.H. Optimization of CuAl₂O₄ Nanoparticles for Enhanced Photocatalytic Degradation of Organic Dyes Under UV and Visible Light. *J. Fluoresc.* **2025**, *35*, 6797–6812. [\[CrossRef\]](#)
36. Torres-Ochoa, J.A.; Cabrera-German, D.; Cortazar-Martinez, O.; Bravo-Sanchez, M.; Gomez-Sosa, G.; Herrera-Gomez, A. Peak-fitting of Cu 2p photoemission spectra in Cu⁰, Cu¹⁺, and Cu²⁺ oxides: A method for discriminating Cu⁰ from Cu¹⁺. *Appl. Surf. Sci.* **2023**, *622*, 156960. [\[CrossRef\]](#)

37. Napruszewska, B.; Walczyk, A.; Duraczyńska, D.; Kryściak-Czerwenka, J.; Michalik, A.; Karcz, R.; Śliwa, M.; Serwicka, E. The Synthesis of Cu–Mn–Al Mixed-Oxide Combustion Catalysts by Co-Precipitation in the Presence of Starch: A Comparison of NaOH with Organic Precipitants. *Catalysts* **2022**, *12*, 1159. [\[CrossRef\]](#)
38. Liu, P.; Wei, G.; Liang, X.; Chen, D.; He, H.; Chen, T.; Xi, Y.; Chen, H.; Han, D. Synergetic effect of Cu and Mn oxides supported on palygorskite for the catalytic oxidation of formaldehyde: Dispersion, microstructure, and catalytic performance. *Appl. Clay Sci.* **2018**, *161*, 265–273. [\[CrossRef\]](#)
39. Liu, T.; Yao, Y.; Wei, L.; Shi, Z.; Han, L.; Yuan, H.; Li, B.; Dong, L.; Wang, F.; Sun, C.-Z. Preparation and Evaluation of Cu-Mn-Oxide as High Efficiency Catalyst for CO Oxidation and NO Reduction by CO. *J. Phys. Chem. C* **2017**, *121*, 12757–12770. [\[CrossRef\]](#)
40. Xu, X.; Liu, X.; Ma, L.; Liang, N.; Yang, S.; Liu, H.; Sun, J.; Huang, F.; Sun, C.; Dong, L. Construction of Surface Synergetic Oxygen Vacancies on CuMn₂O₄ Spinel for Enhancing NO Reduction with CO. *ACS Catal.* **2024**, *14*, 3028–3040. [\[CrossRef\]](#)
41. Venkataswamy, P.; Rao, K.N.; Jampaiah, D.; Reddy, B.M. Nanostructured manganese doped ceria solid solutions for CO oxidation at lower temperatures. *Appl. Catal. B Environ.* **2015**, *162*, 122–132. [\[CrossRef\]](#)
42. Yang, S.; Zhou, F.; Liu, Y.; Zhang, L.; Chen, Y.; Wang, H.; Tian, Y.; Zhang, C.; Liu, D. Morphology effect of ceria on the performance of CuO/CeO₂ catalysts for hydrogen production by methanol steam reforming. *Int. J. Hydrogen Energy* **2019**, *44*, 7252–7261. [\[CrossRef\]](#)
43. Gawande, M.B.; Goswami, A.; Felpin, F.-X.; Asefa, T.; Huang, X.; Silva, R.; Zou, X.; Zboril, R.; Varma, R.S. Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis. *Chem. Rev.* **2016**, *116*, 3722–3811. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Lin, X.; Li, S.; He, H.; Wu, Z.; Wu, J.; Chen, L.; Ye, D.; Fu, M. Evolution of oxygen vacancies in MnOx-CeO₂ mixed oxides for soot oxidation. *Appl. Catal. B Environ.* **2018**, *223*, 91–102. [\[CrossRef\]](#)
45. Castaño, M.H.; Molina, R.; Moreno, S. Cooperative effect of the Co–Mn mixed oxides for the catalytic oxidation of VOCs: Influence of the synthesis method. *Appl. Catal. A Gen.* **2015**, *492*, 48–59. [\[CrossRef\]](#)
46. Daza, Y.A.; Kuhn, J.N. CO₂ conversion by reverse water gas shift catalysis: Comparison of catalysts, mechanisms and their consequences for CO₂ conversion to liquid fuels. *RSC Adv.* **2016**, *6*, 49675–49691. [\[CrossRef\]](#)
47. Nishimoto, M.; Tokura, R.; Nguyen, M.T.; Yonezawa, T. Copper materials for low temperature sintering. *Mater. Trans.* **2022**, *63*, 663–675. [\[CrossRef\]](#)
48. Sanches, S.; Flores, J.H.; De Avellez, R.; Da Silva, M.P. Influence of preparation methods and Zr and Y promoters on Cu/ZnO catalysts used for methanol steam reforming. *Int. J. Hydrogen Energy* **2012**, *37*, 6572–6579. [\[CrossRef\]](#)

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