



Investigation of factors affecting the BET specific surface area of hopcalite prepared via the co-precipitation method

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ABSTRACT

Hopcalite (CuMnO_x) is a catalytic material capable of oxidizing CO at low temperatures, in which the specific surface area is one of the important parameters affecting catalytic activity. This study investigates the effects of the Cu:Mn molar ratio, pH value, precipitating agent combined with PEG and ultrasonication, as well as calcination temperature on the BET specific surface area of hopcalite prepared by the co-precipitation method. The materials were characterized by BET, SEM, and XRD. The results show that the specific surface area increased with increasing Mn content and reached a maximum value of 108 m²/g at a Cu:Mn molar ratio of 1:8. A pH of 8.5, the use of Na₂CO₃ combined with PEG and ultrasonication, drying at 110 °C for 24 h, and calcination at 350 °C for 3 h were the optimal conditions for obtaining the material with the highest specific surface area. SEM results showed that the optimized sample possessed a well-developed porous nanostructure, while XRD analysis confirmed that the material consisted of two main crystalline phases, CuO and MnO₂.

Introduction

The catalytic performance of hopcalite depends on various factors such as particle size, morphology, specific surface area, pore volume, pore size, and phase [1, 2]. Optimization of catalyst preparation conditions, such as drying temperature, drying time, calcination temperature, calcination time, and copper/manganese (Cu:Mn) molar ratio, has improved the performance of (CuMnO)_x catalysts for low-temperature CO oxidation [3-5]. In this paper, we investigated the effects of different parameters to determine a standard preparation procedure for the optimized catalyst. Various methods have been used to prepare hopcalite, including co-precipitation, sol-gel, reactive milling, and impregnation methods [6, 7]. Among these methods, co-precipitation simultaneously produces highly active sites on the catalyst [8, 9].

The main objective of this paper is to investigate in detail the factors affecting the preparation of hopcalite with a high specific surface area. The study shows that initial parameters such as the precipitating precursor, pH, Cu:Mn molar ratio, drying temperature, and calcination temperature have significant effects on the performance of hopcalite catalysts. In addition, the particle size of the (CuMnO)_x catalyst also affects catalytic activity. As particle size decreases, the catalyst surface area increases, resulting in a greater amount of CO being oxidized to CO₂ [10, 11].

Experimental

Materials:

CuSO₄·5H₂O, purity 99.5%, Sigma-Aldrich; MnSO₄·H₂O, purity 99.5%, Sigma-Aldrich; NaOH, purity 99.5%, Sigma-

Aldrich; Na_2CO_3 , purity 99.8%, Avantor; $\text{HO}-(\text{CH}_2\text{CH}_2)_n-\text{H}$ (polyethylene glycol, PEG), purity 98%, China.

Equipments

Hotplate magnetic stirrer, Arec, Velp, Italy; Ultrasonic processor, VCX 130, Sonics, USA; pH meter, HI 8314, Hanna, Romania.

Specialized research methods

BET surface area analyzer, Gemini VII, Micromeritics, USA; SEM-EDX instrument, JSM-IT800, JEOL, Japan; XRD instrument, D8 Advance, Bruker AXS, USA.

Methods

The co-precipitation method was used to prepare hopcalite. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were weighed at different metal molar ratios in the salts ($n_{\text{Cu}}:n_{\text{Mn}} = 1:1, 1:2, 1:4, 1:6, 1:8$), corresponding to samples CuMn1, CuMn2, CuMn4, CuMn6, and CuMn8. The precipitates were then formed using NaOH or Na_2CO_3 with PEG as a surfactant additive. The pH of the solution was varied from 7.5 to 10.5. The suspension was stirred with a hotplate magnetic stirrer and combined with ultrasonication while maintaining the solution temperature at 60 °C. The precipitate was then filtered and washed several times with distilled water until neutral to remove residual impurities, and dried at 110 °C for 24 h. The samples were calcined at 350 °C for 3 h [12].

Results and discussion

Effects of preparation parameters on the specific surface area of the Hopcalite catalyst

To optimize the preparation of the hopcalite catalyst, the main influencing factors, including the Cu/Mn molar ratio, pH of the precipitation medium, type of precipitating agent and surfactant additive, and calcination temperature, were investigated. The BET specific surface area was used as the evaluation criterion because it is one of the parameters determining the number of active sites and the efficiency of CO oxidation at low temperatures.

Effect of the Cu/Mn molar ratio

The samples were prepared under the same conditions: pH = 8.5; Na_2CO_3 as the precipitating agent combined with PEG and ultrasonication; drying at 110 °C for 24 h; and calcination at 350 °C for 3 h. Different Cu/Mn molar ratios were investigated.

The results in Table 1 show that the specific surface area increased progressively as the Mn content increased over the Cu/Mn molar ratio range from 1:1 to 1:8. Sample CuMn8 exhibited the highest surface area,

107.6 m^2/g , which was more than twice that of CuMn1 [13]. The increase in surface area may be explained by the increased Mn content, which promotes the formation of more amorphous manganese oxide phases and limits crystal growth during calcination. At the same time, MnOx acts as a porous framework-forming component, increasing pore volume and the number of active surface sites. In addition, on the hopcalite catalyst surface, CO oxidation occurs mainly at active oxygen sites formed at the CuOx–MnOx interfacial contact. As the surface area increases, the number of active sites also increases, favoring CO adsorption and oxygen activation, thereby enhancing catalytic activity.

Table 1: Effect of the Cu/Mn molar ratio on the specific surface area

Cu/Mn ratio	Sample	S_{BET} (m^2/g)
1:1	CuMn1	52
1:2	CuMn2	69
1:4	CuMn4	77
1:6	CuMn6	90
1:8	CuMn8	108

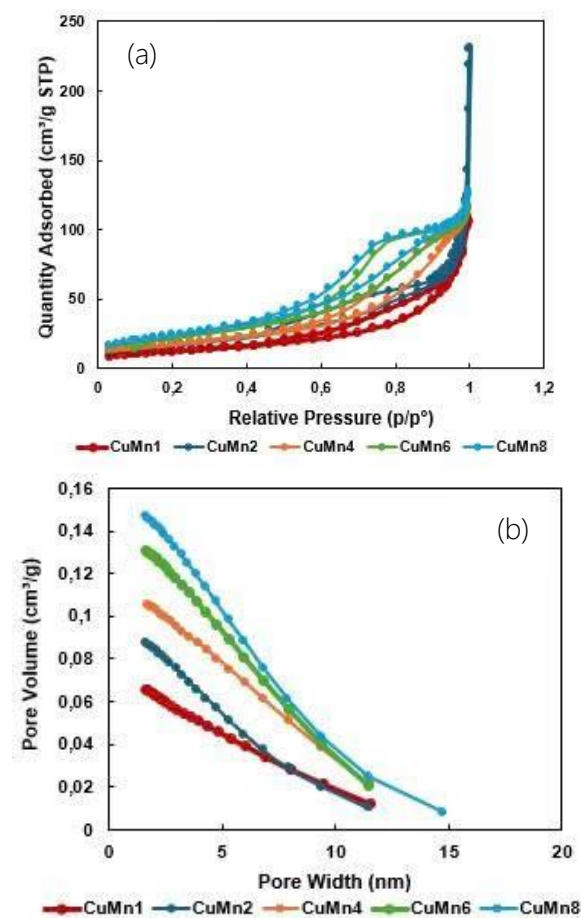


Fig 1: (a) N_2 adsorption-desorption isotherms of the samples; (b) Pore-size distribution plots of the samples

The results in Figure 1a show that all material samples exhibited Type IV adsorption-desorption isotherms according to the IUPAC classification. This is characteristic of mesoporous materials ($2\text{ nm} < d < 50\text{ nm}$). The desorption branch lies above the adsorption branch and exhibits a form equivalent to the H2/H3 type according to the IUPAC classification, characteristic of a complex and heterogeneous pore structure [14, 15].

The hysteresis loops of all samples appeared over a relatively high relative-pressure range ($p/p_0 \approx 0.4\text{--}0.95$), confirming capillary condensation within the porous structure. The total adsorption capacity increased progressively from CuMn1 to CuMn8. In particular, CuMn8 exhibited the widest hysteresis loop in the range $p/p_0 \approx 0.6\text{--}0.9$, indicating that its mesopore density and volume were higher than those of the other samples.

From Figure 1b, the maximum volume per gram of catalyst (cm^3/g) for the samples can be arranged in decreasing order as follows: CuMn8 (0.146); CuMn6 (0.131); CuMn4 (0.105); CuMn2 (0.087); CuMn1 (0.068).

Effect of pH

The effect of pH during co-precipitation was investigated at a Cu/Mn molar ratio of 1:8, using $\text{Na}_2\text{CO}_3 + \text{PEG} + \text{ultrasonication}$. The specific surface area (S_{BET}) increased sharply from $34\text{ m}^2/\text{g}$ at pH 7.5 to a maximum of $108\text{ m}^2/\text{g}$ at pH 8.5, but decreased to $77\text{ m}^2/\text{g}$ and $66\text{ m}^2/\text{g}$ when the pH was further increased to 9.5 and 10.5, respectively. At a lower pH (7.5), precipitation of the metal hydroxides was incomplete, resulting in an imbalance in the Cu and Mn composition of the precipitate and reducing the ability to form the hopcalite structure. In contrast, at excessively high pH (> 9.0), the precipitation rate was too rapid, causing strong particle agglomeration and reducing porosity and surface area after calcination. At pH = 8.5, Cu^{2+} and Mn^{2+} co-precipitated uniformly, forming a precursor with small and homogeneously distributed particles. After calcination, the resulting material exhibited a well-developed porous structure and the highest surface area. Therefore, a pH of 8.5 was selected as the optimum condition [12].

Effect of precipitating agent and additive

To investigate the roles of the precipitating agent and surfactant, the samples were prepared under the same conditions: pH = 8.5, Cu/Mn molar ratio = 1:1, drying at $110\text{ }^\circ\text{C}$ for 24 h, and calcination at $350\text{ }^\circ\text{C}$ for 3 h, with only the precipitating agent and additive varied.

Table 2: Effect of the precipitating agent and additive on the specific surface area

Sample	Preparation condition	S_{BET} (m^2/g)
M1	NaOH	27
M2	Na_2CO_3	41
M3	$\text{Na}_2\text{CO}_3 + \text{PEG}$	47
M4	$\text{Na}_2\text{CO}_3 + \text{PEG} + \text{ultrasonication}$	52

The table 2 shows that replacing NaOH with Na_2CO_3 significantly increased the surface area. This may be explained by carbonate decomposition during calcination, which generates CO_2 , creates additional pores, and suppresses particle sintering. With the addition of PEG, the surface area increased further because of the role of the surfactant in controlling nucleation and particle growth. In particular, PEG can self-assemble into micelles and act as a soft template, helping to form a more uniform porous structure. Combining ultrasonication increased the dispersion of precipitated particles and reduced local agglomeration, thereby producing smaller particles and a larger surface area. Therefore, the preparation condition using $\text{Na}_2\text{CO}_3 + \text{PEG} + \text{ultrasonication}$ simultaneously produced the highest specific surface area [16].

Effect of calcination temperature

The samples were prepared under the same conditions: pH = 8.5, Cu/Mn molar ratio = 1:1, and drying at $110\text{ }^\circ\text{C}$ for 24 h. After drying, the samples were ground into powder and then calcined. Calcination was performed in a furnace at a heating rate of $2\text{--}5\text{ }^\circ\text{C}/\text{min}$. Calcination temperatures from $300\text{ }^\circ\text{C}$ to $400\text{ }^\circ\text{C}$ were investigated for 3 h. Investigation of the calcination temperature for samples M1 to M4 in Table 4 showed that all samples exhibited the highest BET surface area at $350\text{ }^\circ\text{C}$.

Table 3: Effect of calcination temperature on the specific surface area of the CuMnOx catalyst

No.	Sample	Calcination temperature ($^\circ\text{C}$)	S_{BET} (m^2/g)
1	M ₁	300	22
		350	27
		400	23
2	M ₂	300	31
		350	41
		400	32
3	M ₃	300	37
		350	47
		400	29
4	M ₄	300	41
		350	52
		400	36

Structural and compositional characterization of the optimized hopcalite catalyst

SEM results

The surface morphology of the hopcalite catalysts, prepared under optimal conditions (pH 8.5 and a Cu:Mn molar ratio of 1:8), was investigated using scanning electron microscopy (SEM). Measurements were performed at an accelerating voltage of 3.0 kV and a working distance of approximately 10.4 mm, utilizing a secondary electron detector (SED) to obtain high-resolution images at a magnification of 5,000 $\times$.

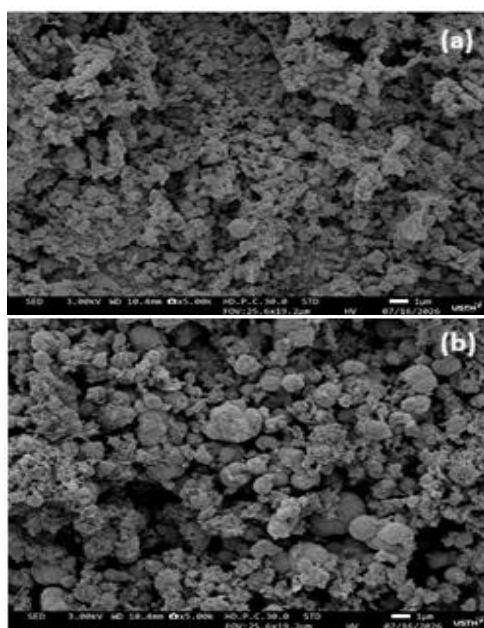


Fig 2: SEM morphological characteristics of the prepared hopcalite samples: (a) Na_2CO_3 +PEG; (b) Na_2CO_3 +PEG+ultrasonication

Figure 2 compares the morphological characteristics of the samples synthesized via two different dispersion methods. The sample prepared using conventional mechanical stirring with Na_2CO_3 and PEG (Figure 2a) displays non-uniform aggregates ranging from several to tens of micrometers, forming a heterogeneous porous network. In contrast, the incorporation of ultrasonication (Figure 2b) produces irregular polyhedral and spherical self-assembled agglomerates that are significantly more uniformly dispersed. These observations confirm that the structure-directing agent (PEG) plays a crucial role in controlling sintering and particle growth in both processes. Furthermore, the application of ultrasonic energy provides superior performance compared to conventional mechanical stirring by effectively promoting the homogeneous dispersion of Cu^{2+} and Mn^{2+} precursors and stimulating uniform nucleation, which ultimately forms a well-developed, highly porous self-assembled nanostructure.

XRD results

The XRD pattern of sample CuMn8, prepared using Na_2CO_3 + PEG + ultrasonication; pH = 8.5; Cu:Mn molar ratio = 1:8; drying at 110 $^\circ\text{C}$ for 24 h; and calcination at 350 $^\circ\text{C}$ for 3 h, is shown in Figure 3a.

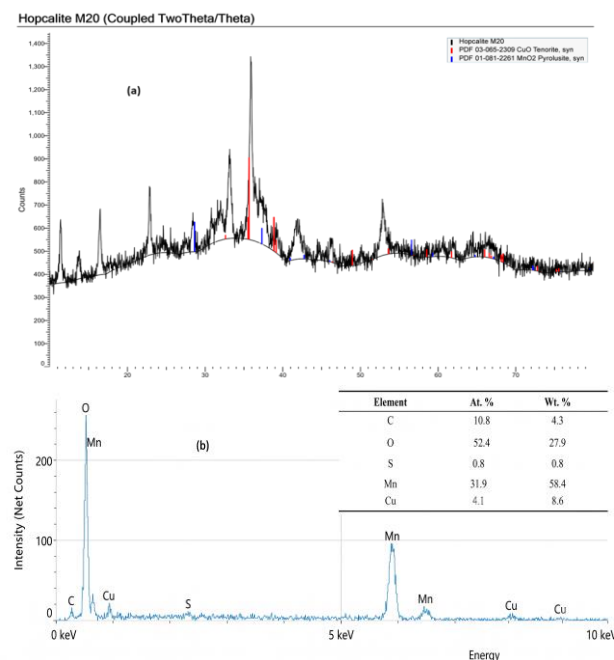


Fig 3: (a) XRD pattern and (b) EDX spectrum of the CuMn8 sample.

The X-ray diffraction (XRD) analysis shown in Figure 3a indicates the presence of diffraction peaks corresponding to two main crystalline phases: CuO (tenorite), represented in red, and MnO_2 (pyrolusite), represented in blue. Specifically, the characteristic CuO diffraction peaks occur at $2\theta = 35.5^\circ$, 38.9° , 48.9° , and 53.6° , corresponding to the (-111) , (111) , (-202) , and (020) crystal planes, respectively. Meanwhile, the MnO_2 peaks were observed at $2\theta = 28.6^\circ$, 37.3° , 42.8° , and 56.6° , corresponding to the (110) , (101) , (111) , and (211) planes, respectively [17]. Within the detection limit of the instrument, no diffraction peaks of impurity phases such as Cu_2O , Mn_2O_3 , Mn_3O_4 , or residual sulfate salts were observed. Therefore, it can be stated that the co-precipitation method using Na_2CO_3 together with PEG and ultrasonic assistance, drying at 110 $^\circ\text{C}$ for 24 h, and calcination at 350 $^\circ\text{C}$ for 3 h successfully synthesized a CuO– MnO_2 mixed oxide with high crystallinity. However, XRD data alone are not sufficient to confirm the formation of a solid solution, the presence of amorphous phases, or phase interactions at the atomic scale.

EDX results

The EDX measurement of the sample prepared using Na_2CO_3 + PEG + ultrasonication; pH = 8.5; Cu:Mn molar

ratio = 1:8; drying at 110 °C for 24 h; and calcination at 350 °C for 3 h is shown in Figure 3b.

The EDX analysis shows the presence of five elements: C, O, S, Mn, and Cu, with corresponding atomic percentages (At.%) of 10.8%, 52.4%, 0.8%, 31.9%, and 4.1%, respectively. Oxygen accounted for the highest proportion (52.4 at.%), reflecting the oxide nature of the CuMnOx mixed-oxide material. Oxygen in the EDX spectrum includes lattice oxygen, oxygen adsorbed on the surface, and possibly a portion of oxygen in adsorbed hydroxyl groups.

Among the metallic elements, Mn accounted for 31.9 at.%, whereas Cu accounted for only 4.1 at.%, indicating that the material was Mn-rich. Considering only the metallic fraction, the Cu:Mn molar ratio was approximately 1:7.8. This value is very close to the initial design ratio (Cu:Mn = 1:8), indicating that the co-precipitation process was highly effective and that the loss of Cu or Mn during synthesis was insignificant.

In addition, a small amount of sulfur (0.8 at.%) was detected in the sample. This is mainly attributable to the precursors used in the synthesis, CuSO₄ and MnSO₄; therefore, a very small amount of sulfate ions may have remained adsorbed on the catalyst surface or may not have been completely removed during washing. The low sulfur content (<1 at.%) indicates that the sample washing process was relatively effective and that the residual sulfate amount was insignificant. Thus, the prepared hopcalite material consisted predominantly of Cu, Mn, and O. The metallic components were distributed relatively uniformly over the sample surface, and the measured metal ratio was consistent with the metal ratio in the initial feed materials.

Conclusions

This study investigated the effects of preparation parameters on the specific surface area of hopcalite synthesized by the co-precipitation method. The results show that as the Cu:Mn molar ratio increased progressively from 1:1 to 1:8, the specific surface area also increased, reaching a maximum of 107.6 m²/g for the sample with a 1:8 ratio. A pH of 8.5, the use of Na₂CO₃ combined with PEG and ultrasonication, drying at 110 °C for 24 h, and calcination at 350 °C for 3 h were the optimum preparation conditions for obtaining a material with a high specific surface area and a well-developed pore system. SEM images showed that combining PEG and ultrasonication promoted the formation of a porous nanostructure with more uniform dispersion. XRD results demonstrated that the calcined material consisted of two main crystalline phases, CuO (tenorite) and MnO₂ (pyrolusite), with no Cu₂O,

Mn₂O₃, Mn₃O₄, or residual sulfate phases detected within the detection limit of the measurement. The results provide a basis for selecting preparation conditions for Hopcalite with a high specific surface area for subsequent studies of CO oxidation catalytic activity.

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