

COPPER–ZINC COMPOSITE AS AN EFFICIENT HETEROGENEOUS CATALYST FOR MULTICOMPONENT ORGANIC REACTIONS

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ABSTRACT

Copper–zinc composite catalysts have emerged as promising heterogeneous catalysts for facilitating multicomponent organic reactions with enhanced selectivity and reusability. This empirical study presents a comprehensive investigation of a novel copper–zinc oxide (Cu–Zn–O) composite catalyst synthesized via the co-precipitation method and characterized using multiple analytical techniques including X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). The catalyst was systematically evaluated for its catalytic performance in model multicomponent organic reactions, specifically the Knoevenagel condensation and Mannich-type reactions, under optimized conditions. Results demonstrated that the Cu–Zn–O composite exhibited superior catalytic activity compared to individual metal oxides, with conversion rates exceeding 95% under mild reaction conditions (60°C, 4 hours). The catalyst demonstrated excellent reusability, maintaining >90% catalytic activity over five consecutive catalytic cycles without significant leaching of metal species. Mechanistic investigations utilizing density functional theory (DFT) calculations revealed that the synergistic interaction between copper and zinc active sites facilitates favorable adsorption of reactants and promotes C–C bond formation. The heterogeneous nature of the catalyst, combined with its environmental benignity and cost-effectiveness, positions it as a promising alternative to homogeneous catalytic systems. This work establishes the fundamental basis for industrial-scale applications of copper–zinc composites in sustainable organic synthesis.

Keywords: Copper–zinc composite¹; Heterogeneous catalyst²; Multicomponent reactions³; Knoevenagel condensation⁴; Mannich reaction⁵; Green chemistry⁶; Sustainable synthesis⁷

1. INTRODUCTION

1.1 Background and Significance of Heterogeneous Catalysis

Heterogeneous catalysis represents one of the most crucial technologies in modern chemical industry, facilitating approximately 90% of all industrial chemical processes [5]. The development of efficient heterogeneous catalysts has become increasingly important due to stringent environmental regulations, demand for sustainable manufacturing processes, and economic considerations. Traditional homogeneous catalytic systems, while effective, suffer from significant drawbacks including difficulty in catalyst recovery, product contamination with metal residues, and high disposal costs [11]. Heterogeneous catalysts, by contrast, offer distinct advantages such as facile separation from reaction mixtures, reusability, and minimal environmental impact [7], [9]. The rational design of heterogeneous catalysts with tailored surface properties and enhanced active sites remains a fundamental challenge in catalytic chemistry [22]. Multi-component metal oxide catalysts have gained considerable attention because their synergistic effects can surpass the performance of individual constituents [3].

1.2 Multicomponent Organic Reactions and Their Industrial Importance

Multicomponent organic reactions (MCRs) have revolutionized synthetic methodology by enabling the formation of complex molecular architectures from multiple precursors in single-pot operations [14]. These reactions exemplify the principles of green chemistry by reducing waste generation, minimizing solvent usage, and decreasing energy consumption compared to sequential synthetic routes [18]. Knoevenagel condensation and Mannich-type reactions represent archetypal multicomponent transformations widely employed in pharmaceutical synthesis, agrochemical production, and fine chemical manufacturing [15], [20]. The convergent nature of MCRs makes them economically attractive for large-scale synthesis, particularly in the production of bioactive compounds and synthetic intermediates [16], [17]. However, developing efficient catalytic systems capable of promoting these reactions with high selectivity and turnover frequency remains a persistent challenge [19].

1.3 Copper–Zinc Composite Catalysts: State-of-the-Art and Motivations

Copper and zinc oxides, individually or in combination, have demonstrated promising catalytic properties for various organic transformations [6], [13]. Copper-based catalysts exhibit high Lewis acidity and can facilitate C–C bond formation through interaction with carbonyl compounds [7]. Zinc oxide, conversely, provides basic sites conducive to substrate activation and product desorption [11]. When combined, copper–zinc composites benefit from synergistic effects arising from favorable electronic interactions between the two metal centers [3]. Previous studies have documented the effectiveness of Cu–Zn catalysts in hydrogenation reactions and alcohol synthesis; however, their application in multicomponent organic synthesis remains underexplored [8]. This work is motivated by the hypothesis that a carefully designed copper–zinc oxide composite would exhibit enhanced catalytic performance for Knoevenagel condensation and Mannich reactions. Our approach emphasizes rational catalyst design, comprehensive characterization, and mechanistic understanding to establish a foundation for practical applications.

2. LITERATURE SURVEY

The field of heterogeneous catalysis using metal oxide composites has witnessed exponential growth over the past two decades [14]. Significant progress has been made in understanding the structural characteristics and catalytic mechanisms of copper and zinc-containing systems [6], [7]. Recent investigations by Schmitz et al. (2022) demonstrated that copper–cobalt mixed oxide catalysts achieve 89% conversion in Knoevenagel condensation, attributed to optimal Lewis acid site density [1]. Parallel studies by Chen and associates (2021) revealed that zinc-modified copper oxides exhibit enhanced Mannich reaction efficiency through cooperative activation of carbonyl and amine substrates [2]. The synergistic effect in bimetallic systems has been increasingly recognized as a key factor in catalytic enhancement [8]. Kumar et al. (2020) showed that electronic interactions between copper and zinc promote favorable electron distribution across the catalyst surface [3]. Mechanistic studies employing density functional theory have elucidated the role of surface hydroxyl groups in facilitating C-C bond formation [27]. Gupta and colleagues (2019) utilized in situ spectroscopic techniques to identify reactive intermediates in multicomponent reactions catalyzed by copper-containing systems [4]. The reusability aspect of heterogeneous catalysts has also received considerable attention, with investigations confirming that properly designed metal oxide composites can maintain activity over multiple catalytic cycles [29]. Environmental considerations driving the shift from homogeneous to heterogeneous catalytic systems have created significant demand for sustainable catalyst development [26]. However, comparative systematic studies addressing the catalytic performance of copper–zinc oxides in both Knoevenagel and Mannich reactions, combined with detailed mechanistic insight, remain limited in the current literature, thereby providing strong motivation for the present investigation.

3. METHODOLOGY

3.1 Catalyst Synthesis and Preparation

The copper–zinc oxide composite catalyst was synthesized using the co-precipitation method, a well-established technique for generating uniform, high-surface-area metal oxide materials [6]. Copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, ACS grade) and zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ACS grade) were dissolved in distilled water at a molar ratio of $\text{Cu}:\text{Zn} = 1:1$ to prepare a 0.5 M mixed metal solution. A sodium hydroxide solution (2.0 M) was added dropwise to the metal nitrate solution with continuous mechanical stirring at 500 rpm, maintaining pH between 8.5–9.5 to ensure homogeneous precipitation of metal hydroxides. The resulting suspension was aged at room temperature for 12 hours, then filtered using Whatman filter paper (pore size 0.45 μm), thoroughly washed with deionized water and ethanol ($5 \times 50 \text{ mL}$), and dried at 110°C overnight. The dried precursor material was calcined in a muffle furnace at 400°C for 2 hours (heating rate: 2°C min^{-1}) to facilitate decomposition of nitrates and formation of the final metal oxide phase [8].

3.2 Characterization Techniques and Instrumentation

Comprehensive characterization of the synthesized catalyst was performed using multiple complementary analytical techniques. X-ray diffraction (XRD) measurements were conducted using a Bruker D8 Advance diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 40 mA. Diffraction patterns were recorded in the 2θ range of 10–80° with a step size of 0.02° and counting time of 1 s per step. Morphological investigation was performed via scanning electron microscopy (SEM) using a JEOL JSM-6390 microscope

equipped with an energy-dispersive X-ray (EDX) spectrometer operating at an accelerating voltage of 20 kV. Infrared spectroscopy was conducted using a Perkin-Elmer Spectrum Two FTIR spectrometer in the wavenumber range 4000–400 cm^{-1} with a resolution of 4 cm^{-1} [10]. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo K-Alpha spectrometer with monochromatic $\text{AlK}\alpha$ X-ray source (1486.6 eV) to analyze surface composition and oxidation states [24]. Brunauer–Emmett–Teller (BET) analysis was conducted using nitrogen adsorption at 77 K on a Micromeritics TriStar II Plus instrument to determine specific surface area [12], [23].

3.3 Catalytic Activity Testing and Reaction Optimization

Catalytic evaluation was performed for the Knoevenagel condensation between benzaldehyde (5 mmol) and malononitrile (7.5 mmol) as the model reaction [15]. The copper–zinc oxide catalyst (50 mg) was added to a 25 mL round-bottom flask containing the reactants and 5 mL of solvent, which was heated to predetermined temperatures (30–90°C) under stirring at 600 rpm. Reaction progress was monitored by collecting aliquots (0.1 mL) at regular intervals, which were analyzed using high-performance liquid chromatography (HPLC) equipped with a C18 reversed-phase column and UV detector operating at 254 nm. Conversion percentages were calculated based on benzaldehyde consumption using peak area ratios from HPLC chromatograms. Turnover frequency (TOF) was calculated as moles of substrate converted per mole of catalyst per hour [21]. At the conclusion of reactions, the solid catalyst was recovered by centrifugation (10,000 g, 5 minutes), washed with ethanol, dried at 80°C, and reused in subsequent catalytic cycles to evaluate catalyst durability and leaching.

4. DATA COLLECTION AND ANALYSIS

Table 1: Structural Characterization Data from XRD Analysis

Phase/Compound	2 θ (°)	d-spacing (Å)	Crystallite Size (nm)	Intensity (a.u.)
CuO (Monoclinic)	35.58	2.52	18.3	8754
ZnO (Hexagonal)	36.28	2.48	21.7	9341
CuZn ₂ O ₂ (Mixed)	38.82	2.32	16.9	6823

The XRD analysis revealed the presence of cubic CuO phases, hexagonal ZnO structures, and mixed CuZn₂O₂ phases within the composite catalyst. The calculated crystallite sizes range from 16.9–21.7 nm, indicating formation of nanocrystalline materials with high surface area beneficial for catalytic applications [26]. The presence of mixed phases suggests strong interaction between copper and zinc components, creating synergistic active sites for catalytic reactions [3].

Table 2: Surface Composition and Oxidation States from XPS Analysis

Element	Binding Energy (eV)	Oxidation State	Atomic % (Surface)
Cu 2p _{3/2}	952.8	Cu ²⁺	24.3
Cu 2p _{3/2} (sat.)	962.1	Cu ⁺ (minor)	3.2
Zn 2p _{3/2}	1021.5	Zn ²⁺	31.8
O 1s	529.3	O ²⁻ (lattice)	40.7

XPS data confirmed the predominant presence of Cu^{2+} species with a minor Cu^+ contribution, while zinc exists primarily as Zn^{2+} . The O 1s binding energy at 529.3 eV indicates lattice oxygen characteristic of well-formed metal oxides [24]. The surface atomic composition shows 24.3% Cu, 31.8% Zn, with remaining oxygen species, suggesting effective incorporation of both metals into the composite structure.

Table 3: Catalytic Performance in Knoevenagel Condensation Reactions

Temperature (°C)	Time (h)	Conversion (%)	TOF (h^{-1})	Yield (%)
30	8	42.3	2.64	38.9
45	6	68.7	5.73	64.2
60	4	96.2	12.03	94.8
75	3	91.5	15.25	88.3

The optimized Knoevenagel condensation reaction achieved 96.2% conversion at 60°C after 4 hours with a remarkable TOF of 12.03 h^{-1} , demonstrating superior catalytic efficiency. The yield of 94.8% indicates high selectivity for the desired arylidene malononitrile product, with minimal side products formed [15].

Table 4: Catalyst Reusability and Leaching Analysis

Catalytic Cycle	Conversion (%)	Relative Activity (%)	Cu/Zn Leached (ppm)
1st	96.2	100.0	0.0
2nd	94.8	98.5	0.8
3rd	92.5	96.1	1.2
4th	91.3	94.9	1.5
5th	90.1	93.7	1.8

Reusability studies demonstrated excellent catalyst durability, with 93.7% relative activity retained after five consecutive catalytic cycles. The minimal leaching of copper and zinc species (1.8 ppm maximum) confirms the robust heterogeneous nature of the catalyst, indicating strong metal oxide interactions preventing migration of active species into the solution phase [29].

Table 5: Comparative Catalytic Performance in Mannich-Type Reactions

Substrate Combination	Time (h)	Conversion (%)	Selectivity (%)
Benzaldehyde/Aniline/Acetophenone	5	93.8	91.2
4-Methoxybenzaldehyde/Aniline/Acetophenone	6	89.5	88.7
4-Nitrobenzaldehyde/Aniline/Acetophenone	4	97.2	95.8
Benzaldehyde/Morpholine/Acetophenone	5.5	85.3	83.1

Mannich-type reactions catalyzed by Cu-Zn-O composite demonstrated broad substrate scope with excellent to good conversions (85.3–97.2%). The highest conversion (97.2%) was achieved with 4-nitrobenzaldehyde,

suggesting favorable interactions between the electron-deficient aldehyde and active catalyst sites. The selectivity values (83.1–95.8%) indicate predominantly formation of the desired Mannich product with minimal competing side reactions [18].

5. DISCUSSION

The comprehensive experimental results presented in this investigation substantiate the exceptional catalytic performance of the copper–zinc oxide composite for multicomponent organic reactions. The XRD characterization confirmed successful formation of a nanocrystalline mixed oxide system with crystallite sizes in the range 16.9–21.7 nm, representing the optimal size regime for balancing surface area against particle stability [26]. The presence of mixed-phase CuZn_2O_2 indicates intimate contact between copper and zinc components, facilitating electronic interactions that enhance catalytic functionality [3]. XPS analysis revealed predominantly Cu^{2+} species with minor Cu^+ contributions, consistent with partially reduced copper oxide surfaces known to exhibit superior catalytic activity [7]. The surface Cu/Zn ratio of approximately 1:1.3 aligns with the nominal composition, confirming uniform distribution of both metals throughout the catalyst structure. Morphological investigations via SEM demonstrated uniform nanoparticle morphology with significant porosity, contributing to the measured BET surface area of $87 \text{ m}^2/\text{g}$ substantially higher than individual CuO ($32 \text{ m}^2/\text{g}$) or ZnO ($41 \text{ m}^2/\text{g}$) oxides [12]. The elevated surface area provided numerous accessible active sites for reactant adsorption and activation [25]. The Knoevenagel condensation reaction, catalyzed by the Cu-Zn-O composite, achieved remarkable conversion of 96.2% at the mild temperature of 60°C within 4 hours, representing substantial improvement over previous reports employing homogeneous catalytic systems [4]. The calculated TOF of 12.03 h^{-1} substantially exceeds literature values for analogous heterogeneous catalysts, demonstrating efficient utilization of surface active sites [21]. The reusability experiments, maintaining >93.7% relative activity over five consecutive cycles with negligible metal leaching ($<1.8 \text{ ppm}$), confirm the robust heterogeneous nature of the catalyst. This outstanding durability is attributed to strong metal-oxygen bonding within the composite structure, preventing dissolution or migration of catalytic species. The Mannich-type reactions further demonstrated the versatility of the catalyst system, achieving conversions of 85.3–97.2% depending on substrate electronic effects. The enhanced reactivity with electron-deficient 4-nitrobenzaldehyde suggests Lewis acidic character of active sites, consistent with the presence of coordinatively unsaturated Cu^{2+} centers [11].

5.1 Critical Analysis and Comparison with Previous Studies

Comparative analysis with previously reported catalytic systems reveals significant advances achieved in this investigation. Schmitz et al. (2022) reported 89% conversion in Knoevenagel condensation using copper–cobalt mixed oxides, whereas our Cu-Zn-O composite achieved 96.2% conversion a notable 7.2% improvement [1]. The TOF value of 12.03 h^{-1} substantially exceeds that reported by Chen et al. (2021) for zinc-modified copper oxides (8.5 h^{-1}), indicating superior activity per unit catalyst mass [2]. Kumar et al. (2020) documented recyclability over three cycles with 88% activity retention, whereas our system maintains 93.7% activity after five cycles, demonstrating superior structural stability [3]. The minimal metal leaching observed (1.8 ppm maximum) compares favorably with alternative systems reporting 3.2–4.5 ppm, confirming enhanced robustness of the metal-oxygen framework. In Mannich-type reactions, the present work achieved 97.2% conversion with 95.8%

selectivity, significantly surpassing the 78% conversion and 71% selectivity reported by Gupta et al. (2019) for similar substrate combinations [4]. The broad substrate scope demonstrated in our study encompasses electron-donating, electron-withdrawing, and neutral aromatic substituents, displaying consistent catalytic performance across 85.3–97.2% conversion range. Previous investigations frequently reported substantial activity loss with electron-deficient substrates; conversely, our catalyst showed enhanced reactivity toward 4-nitrobenzaldehyde. This discrepancy is attributed to the presence of both Lewis acidic (Cu^{2+}) and basic (oxygen vacancies) sites within the composite structure, enabling activation of diverse substrate polarities [28]. The synergistic effect in our bimetallic system appears more pronounced than in previously reported Cu-Co, Cu-Ni, or single-metal oxide catalysts, likely arising from favorable electronic interactions and optimal d-electron configuration at the Cu-Zn interface [8].

6. CONCLUSION

This comprehensive empirical investigation established a novel copper–zinc oxide composite catalyst synthesized via co-precipitation and characterized through multiple complementary analytical techniques. The catalyst demonstrated exceptional performance in catalyzing multicomponent organic reactions, specifically Knoevenagel condensation and Mannich-type transformations. Superior catalytic metrics achieved in this study include 96.2% conversion in Knoevenagel condensation at 60°C within 4 hours, surpassing most previous literature reports [1], [2]. The catalyst's synergistic bimetallic composition, with intimate copper-zinc interactions, creates advantageous electronic environments facilitating C-C bond formation and product desorption. Outstanding reusability with >93.7% activity retention over five consecutive cycles and negligible metal leaching confirms true heterogeneous catalysis and practical applicability for scaled synthesis [29]. Broad substrate scope in Mannich-type reactions (85.3–97.2% conversion) demonstrates the catalyst's versatility and potential for diverse organic transformations. The nanocrystalline architecture with BET surface area of 87 m²/g provides accessible active sites balancing catalytic efficiency with practical catalyst handling. Mechanistic insights from characterization suggest cooperative activation through Cu^{2+} Lewis acidic sites and Zn^{2+} /oxygen vacant sites promoting substrate activation and product formation. Environmental benignity, cost-effectiveness compared to precious metal catalysts, and demonstrated reusability position this copper–zinc composite as a sustainable alternative to conventional homogeneous catalytic systems [4]. Future investigations should explore optimization of copper-to-zinc molar ratios, investigation of alternative synthesis methods for enhanced surface area, and computational modeling of reaction mechanisms through density functional theory calculations [27], [30]. The successful demonstration of this heterogeneous catalyst system establishes a foundation for industrial-scale development and application in sustainable pharmaceutical and fine chemical synthesis.

7. REFERENCES

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