



Research article

Sol-gel synthesis, characterization and catalytic activity of manganese-doped calcium cobalt oxide

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ABSTRACT

This study investigates manganese-doped calcium cobalt oxide (MCCO - $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$, $x = 0-0.3$) as a catalyst for the environmentally significant reduction of 4-nitrophenol (4-NP). While cobalt oxides are known catalysts, this work provides the first systematic evaluation of Mn-doping effects in $\text{Ca}_3\text{Co}_2\text{O}_6$ for this application. MCCO materials were synthesized via sol-gel, with FTIR confirming phase formation after 10 h of calcination 1000°C and XRD revealing lattice parameter shifts consistent with Mn incorporation. SEM and BET analyses showed that Mn doping significantly altered particle morphology and textural properties, including non-monotonic changes in specific surface area. Catalytic evaluation using NaBH_4 showed optimal performance for the MCCO sample with $x = 0.1$, achieving the highest apparent rate constant ($k_{\text{app}} = 0.412 \text{ min}^{-1}$) and 98.77 % 4-NP reduction efficiency within 10 min at pH 8. This composition also demonstrated good reusability, retaining 94.76 % efficiency after eight cycles. These findings highlight the critical role of Mn doping level in tuning the structural properties and catalytic performance of $\text{Ca}_3\text{Co}_2\text{O}_6$, identifying MCCO-0.1 as a highly efficient and reusable catalyst for 4-NP reduction.

1. Introduction

The demand for sustainable and efficient catalysts in environmental remediation continues to drive intensive research into novel materials that facilitate chemical reactions under moderate conditions [1]. A major focus within this field is the development of transition metal oxides, renowned for their catalytic potential in diverse chemical processes, including pollutant degradation, hydrogen production, and

organic synthesis. Among these materials, cobalt-based oxides have garnered particular interest due to their versatility, structural stability, and catalytic efficacy in both oxidation and reduction reactions [2].

$\text{Ca}_3\text{Co}_2\text{O}_6$, a cobalt-based oxide with a unique layered architecture, presents as a promising candidate for catalytic applications. To enhance its catalytic performance, modifications to its structure have been investigated through the introduction of dopants, notably manganese (Mn) [3,4]. As a transition metal with multiple oxidation states, Mn can

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significantly improve the catalytic characteristics of materials by modifying their electronic properties, surface area, and redox activity. Incorporating Mn into the $\text{Ca}_3\text{Co}_2\text{O}_6$ lattice yields the compound $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$ (MCCO), a mixed metal oxide that potentially combines the advantageous properties of both cobalt and manganese oxides [5]. The influence of Mn-doping levels on the redox activities of MCCO in the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) remains unstudied and is the focus of this investigation. This conversion holds considerable industrial relevance, as 4-AP is an important precursor in the pharmaceutical and chemical sectors [6,7]. Traditional methods to achieve this transformation typically require elevated temperatures or pressures; however, effective catalysts such as metal oxides enable this reaction to occur under ambient conditions, utilizing sodium borohydride (NaBH_4) as a reducing agent [7].

This study aims to synthesize $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$ (MCCO) with various Mn doping levels ($x = 0$ to 0.3) to explore the impact of Mn substitution on crystal structure, particle size, and catalytic activity. Characterization of the materials employed techniques such as Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) to elucidate their structural and morphological attributes. Catalytic efficiency was examined through the reduction of 4-NP to 4-AP using NaBH_4 across different pH environments, focusing on identifying the optimal pH for peak performance. Additionally, catalyst reusability was assessed over multiple reaction cycles to evaluate its viability for practical applications.

2. Experimental methods

2.1. Synthesis of materials

The $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$ compounds were synthesized according to an established method, specifically targeting compositions with Mn concentrations where x varies from 0 to 0.3, resulting in $\text{Ca}_3\text{Co}_2\text{O}_6$ (CCO), $\text{Ca}_3\text{Co}_{1.9}\text{Mn}_{0.1}\text{O}_6$ (MCCO-0.1), $\text{Ca}_3\text{Co}_{1.8}\text{Mn}_{0.2}\text{O}_6$ (MCCO-0.2), and $\text{Ca}_3\text{Co}_{1.7}\text{Mn}_{0.3}\text{O}_6$ (MCCO-0.3) [8]. The synthesis began by dissolving precise stoichiometric quantities of calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), manganese nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), and citric acid in 10 mL of distilled water. The solution was stirred vigorously for 30 min until full dissolution, producing a characteristic red-pink solution.

Subsequently, the solution was heated in a water bath at 80°C for 20 h to initiate gel formation. The resulting gel was then dried at 200°C for 7 h to obtain a solid, which was ground into a fine powder using an agate mortar to ensure homogeneity. The powder was transferred into crucibles and heated at $200^\circ\text{C}/\text{h}$ to 1000°C and then kept for 12-hour incineration at the final temperature. After cooling, the resultant materials were finely ground to achieve a uniform powder suitable for further analyses.

2.2. Material characterization

Structural phases were analyzed by X-ray diffraction (XRD) on a Bruker AXS diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5404 \text{ \AA}$). Data were collected from $2\theta = 5^\circ$ to 80° with 0.02° step sizes. Particle morphology and size were examined via scanning electron microscopy (SEM) using a Hitachi S-4800. Fourier-transform infrared (FTIR) spectra were recorded on a Jasco FT/IR 4700 using ATR mode ($400\text{--}4000 \text{ cm}^{-1}$, 2 cm^{-1} resolution). Surface area and porosity were determined from N_2 adsorption-desorption isotherms measured at 77 K with a Micromeritics MicroActive TriStar II Plus analyzer.

2.3. Catalytic activity toward 4-NP reduction

To evaluate the catalytic activity of CCO and MCCO in reducing 4-nitrophenol (4-NP), a solution of 4-NP/ NaBH_4 was prepared by mixing 100 mL of 0.1 mM 4-NP solution with 12.5 mL of 0.5 M sodium

borohydride (NaBH_4), adjusting the pH to values between 8 and 12 using 5 M sodium hydroxide (NaOH). For each catalytic test, 40 mg of CCO or MCCO powder was added to 112.5 mL of the prepared 4-NP/ NaBH_4 solution in a beaker, and the mixture was stirred continuously to maintain uniform distribution of the catalyst. Samples were collected at regular intervals, filtered, and transferred into a quartz cuvette for absorbance measurements between 360 and 500 nm, utilizing a UH5300 spectrophotometer (Hitachi, Japan).

The concentration of 4-NP was quantitatively determined using a calibration curve based on absorbance at 402 nm, and the apparent reaction rate constant (k_{app}) was derived from the slope of the linear plot of $\ln(C_0/C_t)$ versus reaction time.

For assessing the reusability of the MCCO-0.1 catalyst, the reaction solution post-reduction was centrifuged at 8000 rpm for 15 min. The solid catalyst was then recovered and reintroduced into a fresh 4-NP/ NaBH_4 solution (adjusted to pH 8) under identical experimental conditions. Absorbance measurements were conducted as previously described, and this reuse process was repeated across a total of nine cycles to evaluate the catalyst's stability and longevity in practical applications.

All syntheses of the MCCO materials and catalytic activity measurements were conducted in triplicate, and the presented results represent the means with standard deviations.

3. Results and discussion

3.1. FTIR spectra

The synthesis of MCCO involves key stages, including gel formation at 80°C , nitrate decomposition at 200°C , organic compound degradation between $500\text{--}1000^\circ\text{C}$, and final oxide formation at 1000°C . Carbonate decomposition, notably of CaCO_3 , occurs between $627\text{--}1227^\circ\text{C}$, whereas CoCO_3 and MnCO_3 decompose at lower temperatures ($177\text{--}627^\circ\text{C}$) [9, 10].

Fourier-transform infrared (FTIR) spectra of MCCO reveal the influence of calcination temperature on the structural properties of the materials. In Fig. 1a-d, characteristic absorption bands appear at 1426 cm^{-1} , 875 cm^{-1} , and 670 cm^{-1} , indicative of carbonate groups [11]. The peak at 1426 cm^{-1} typically corresponds to the asymmetric stretching (ν_3) of the C-O bond, the peak at 875 cm^{-1} is usually assigned to the out-of-plane bending (ν_2) of the CO_3^{2-} ion, and the peak at 670 cm^{-1} is often associated with the in-plane bending (ν_4) of the O-C-O bonds. These bands decrease progressively with increased calcination temperature and disappear entirely at 1000°C , signaling complete decomposition of CaCO_3 . Notably, strong absorption bands around 590 cm^{-1} and 520 cm^{-1} correspond to Co-O stretching vibrations, while the band near 424 cm^{-1} represents Ca-O vibrations, indicating successful phase formation between 900°C and 1000°C [12–14].

Further analysis (Fig. 2) compares FTIR spectra of CCO and MCCO following calcination at 1000°C for different time periods. After 8 h of calcination, weak carbonate bands are still detectable but disappear after 10 and 12 h. Co-O and Ca-O vibrations persist, indicating that the materials are fully formed. The absence of significant differences between samples calcined for 10 and 12 h suggests that a 10-hour duration at 1000°C is optimal for complete carbonate removal and efficient synthesis of the target material.

3.2. SEM micrographs

Scanning electron microscopy (SEM) images of the MCCO samples (Fig. 3) reveal distinct variations in particle size across different compositions. The CCO sample displays a range of particle sizes without apparent agglomeration. However, with increasing Mn content (x), particle agglomeration becomes more prominent, likely due to the incorporation of Mn oxides, which reduce the melting point of MCCO relative to CCO. This structural adjustment impacts particle morphology

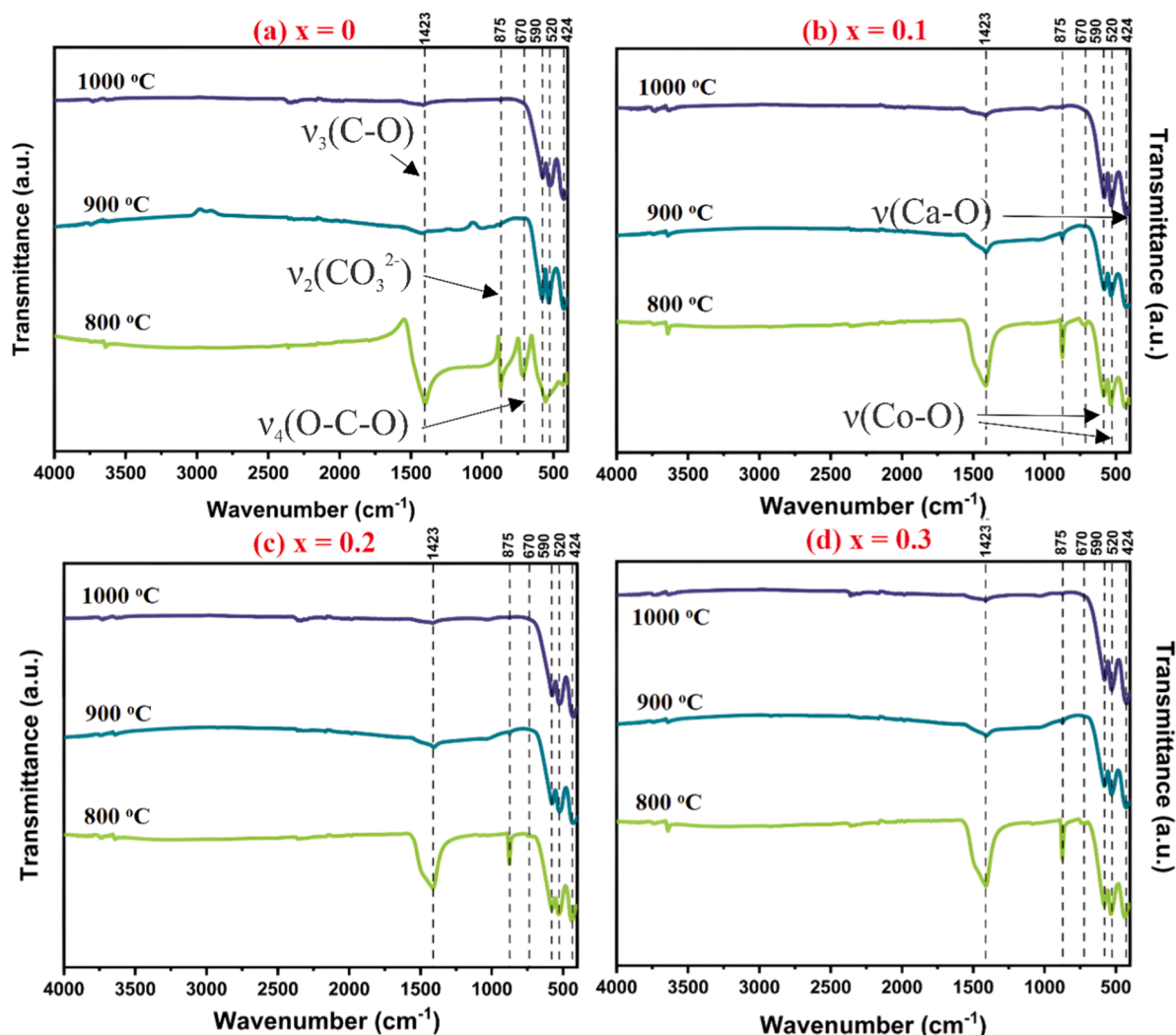


Fig. 1. FTIR spectra of CCO and MCCO synthesized after calcination for 10 h at 800–1000 °C with (a) $x = 0$; (b) $x = 0.1$; (c) $x = 0.2$ and (d) $x = 0.3$.

and distribution, with potential implications for catalytic properties.

3.3. XRD patterns

X-ray diffraction (XRD) analysis was employed to confirm the structural identity of the synthesized $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$ (MCCO) materials, with compositions ranging from $x = 0$ to $x = 0.3$ (Fig. 4). The XRD diffraction peaks of MCCO correspond closely to the standard reference pattern (JCPDS #89-0629), verifying that the primary phase present is $\text{Ca}_3\text{Co}_2\text{O}_6$ (CCO). The retention of diffraction peaks despite the substitution of Co by Mn confirms that the main CCO crystal structure remains intact.

In Mn-doped samples, additional minor peaks appear near $2\theta \approx 36.5^\circ$ and $2\theta \approx 37.2^\circ$, corresponding to Mn_2O_3 and MnO_2 phases, respectively, indicating the presence of minor manganese oxide impurities within the MCCO structure [15] [16]. It is well-established that certain manganese oxides, particularly MnO_2 , can exhibit significant catalytic activity, especially under specific synthesis conditions designed to enhance surface properties and defect concentration [17].

Furthermore, subtle shifts in peak positions and intensities suggest lattice alterations due to Mn substitution. When focusing on the diffraction angle around 34.24° which aligns with the (030) plane, the peak shifts to higher angles with an increase in Mn content from $x = 0$ –0.3 (Table 1), likely due to lattice distortions introduced by Mn doping. Crystallite sizes were calculated from the Scherrer equation for

this specific peak (Table 1), showing a trend of varying crystallite sizes with Mn content, which suggests that Mn substitution significantly influences both crystallite size and crystallinity of the primary MCCO phase.

3.4. BET results

To investigate the textural properties such as specific surface area and porosity, which are crucial for heterogeneous catalysis, N_2 adsorption-desorption isotherms were measured at 77 K. The key parameters are summarized in Table 2. It is important to note that the BET method determines the total surface area accessible to N_2 molecules, encompassing not only the external surface of primary particles but also surface roughness and any interparticle porosity. This effective surface area is directly relevant for surface-dependent catalytic processes, irrespective of the primary particle size [18].

BET analysis (Table 2) shows that the surface area of pure CCO ($x = 0$) is $4.03 \text{ m}^2/\text{g}$, which decreases significantly with Mn doping, dropping to $1.44 \text{ m}^2/\text{g}$ for $x = 0.1$ and $0.93 \text{ m}^2/\text{g}$ for $x = 0.2$, but partially recovering to $3.37 \text{ m}^2/\text{g}$ for $x = 0.3$. The reduction in surface area with lower Mn content indicates that Mn substitution may cause structural densification, while the increase at $x = 0.3$ suggests defect formation or microstructural changes that expose more surface.

The t-plot analysis further highlights these changes, with micropore areas increasing from $0.70 \text{ m}^2/\text{g}$ in CCO to $1.30 \text{ m}^2/\text{g}$ for MCCO-0.1,

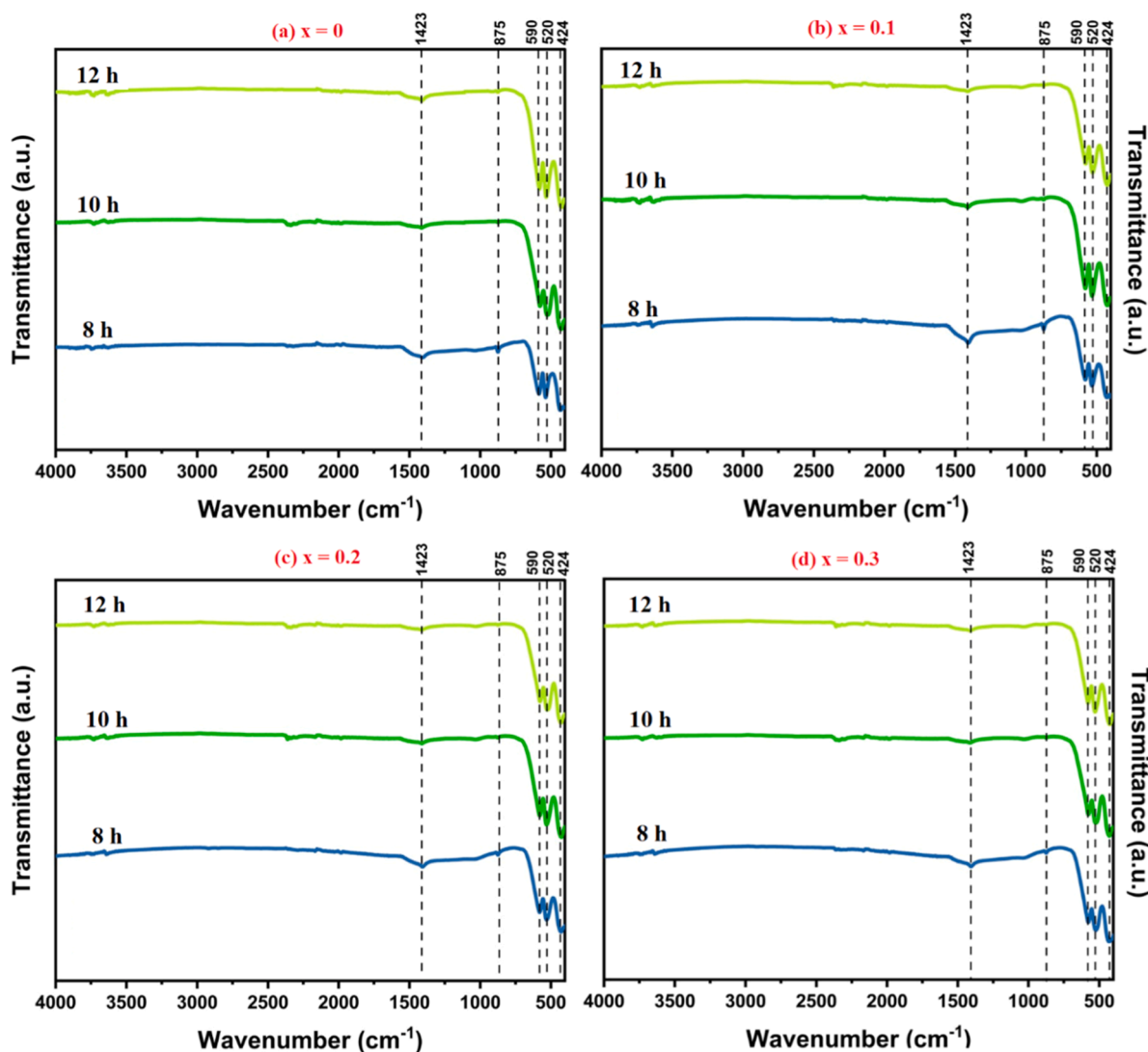


Fig. 2. FTIR spectra of CCO and MCCO synthesized after calcination at 1000 °C for various time intervals with (a) $x = 0$; (b) $x = 0.1$; (c) $x = 0.2$ and (d) $x = 0.3$.

then decreasing for MCCO-0.2 and rising sharply to 2.76 m²/g in MCCO-0.3. This pattern implies that higher Mn levels promote microporosity, likely through induced structural defects, enhancing potential applications in gas storage or selective adsorption.

Barrett-Joyner-Halenda (BJH) adsorption results indicate a substantial mesopore area in CCO (5.43 m²/g), which declines with Mn doping to 4.44 m²/g for MCCO-0.1 and 1.61 m²/g for MCCO-0.2, before dramatically increasing to 10.25 m²/g for MCCO-0.3. The large discrepancy between BJH adsorption and desorption values, especially in MCCO-0.3, suggests a complex pore network characterized by restricted or ink-bottle pores, which could affect adsorption-desorption dynamics [19].

Overall, the results demonstrate that Mn content can be strategically adjusted to tailor the material's surface and pore properties, making Mn-doped CCO promising for catalytic and adsorption applications.

3.5. Catalytic activity of MCCO

The reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP), catalyzed by NaBH₄ in the presence of MCCO, was investigated using UV–visible spectroscopy (Fig. 5) to assess the catalytic efficiency of the undoped CCO and Mn-doped MCCO. Given the substantial excess of NaBH₄ (0.5 M) relative to 4-NP (0.1 mM), the reaction followed pseudo-first-order kinetics, with the rate dependent primarily on the

concentration of 4-NP [20].

3.5.1. Effect of mn content on catalytic activity

The $\ln(C_0/C)$ vs. time plots (Fig. 6a) illustrate an initial induction phase, during which minimal change occurs in the concentration of 4-NP. This phase likely results from dissolved oxygen reacting preferentially with NaBH₄ before the initiation of 4-NP reduction. Upon depletion of dissolved oxygen, the reaction proceeds with measurable kinetics. The apparent catalytic rate constants (k_{app}) were derived from the linear portion of the $\ln(C_0/C)$ plot post-induction phase. Among the catalysts tested, MCCO-0.1 exhibited the shortest induction period (Fig. 6a) and the highest k_{app} (Fig. 6b), indicating superior catalytic activity for 4-NP reduction by NaBH₄. Therefore, MCCO-0.1 was selected for further analysis to examine pH effects on catalytic efficiency.

The BET analysis and catalytic activity results together provide a comprehensive understanding of the effects of Mn doping on calcium cobalt oxide (CCO) and its implications for catalytic applications. The BET data reveal that Mn doping reduces the overall surface area of CCO at lower doping levels but introduces notable structural changes, particularly in microporosity and mesoporosity. Despite this decrease in surface area, the catalytic performance of Mn-doped CCO (MCCO) shows a clear enhancement, especially for MCCO-0.1, which exhibited the highest apparent rate constant (k_{app}) for the reduction of 4-nitrophenol (4-NP).

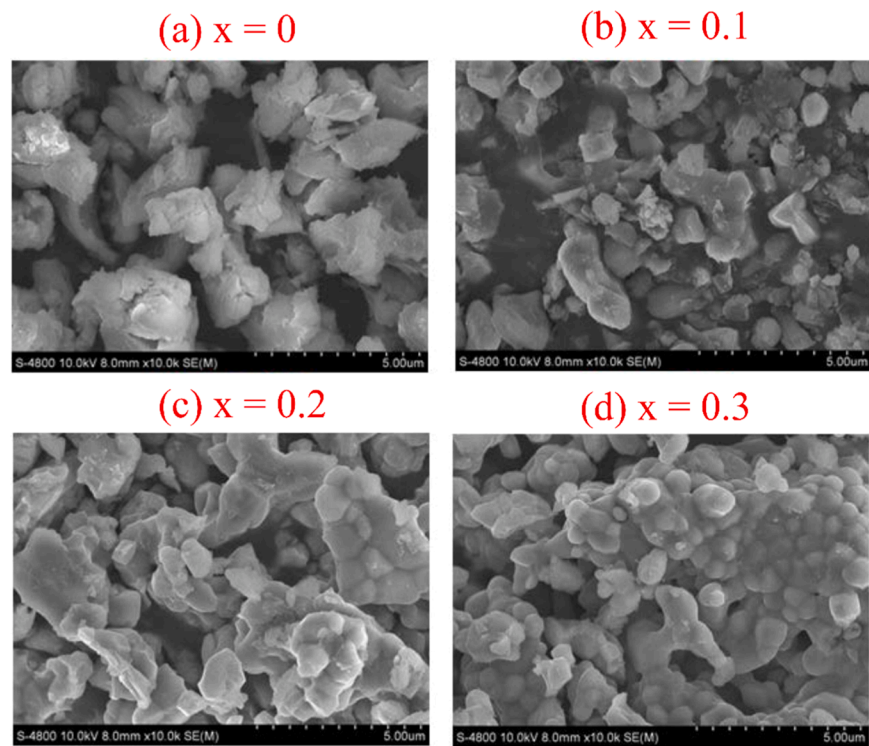


Fig. 3. SEM images of MCCO samples with varying mn content, demonstrating changes in particle size and agglomeration behavior.

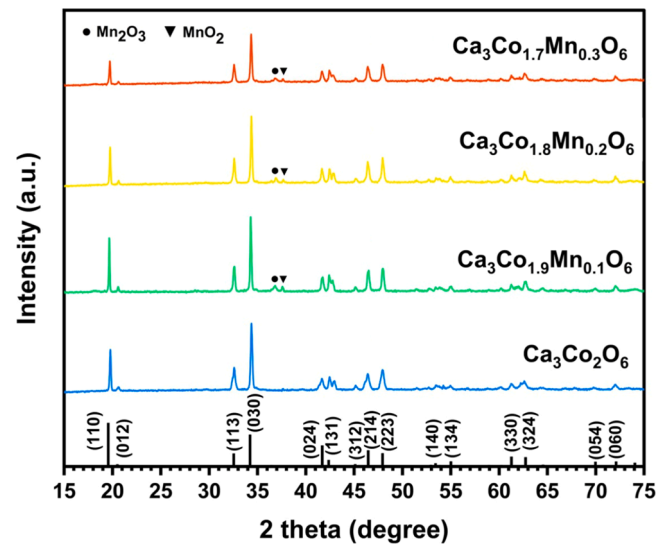


Fig. 4. XRD spectra of MCCO with x from 0–0.3.

Table 1
Diffraction angles 2θ of the peak corresponding to the (030) crystalline plane and crystallite sizes for MCCO calculated using the scherrer equation.

x	0	0.1	0.2	0.3
2θ (°)	34.24	34.31	34.35	34.37
Crystallite size (nm)	38.71	49.88	43.91	45.77

The observed catalytic improvement in MCCO-0.1, despite its moderate surface area, suggests that the quality and accessibility of active sites are more critical than the total surface area. Mn doping likely introduces electronic modifications that enhance the material’s redox properties, facilitating faster electron transfer during catalysis.

Table 2 BET surface area and porosity characteristics of Ca ₃ Co _{2-x} Mn _x O ₆ samples.				
x	BET surface area (m ² /g)	t-plot micropore area (m ² /g)	BJH adsorption surface area (m ² /g)	BJH desorption surface area (m ² /g)
0	4.03	0.70	5.43	5.25
0.1	1.44	1.31	4.44	2.03
0.2	0.93	0.45	1.61	2.67
0.3	3.37	2.76	10.25	0.50

Furthermore, the moderate increase in microporosity and a favorable mesoporous network at this doping level provide efficient pathways for reactant diffusion, minimizing mass transfer limitations and enabling higher catalytic efficiency.

In contrast, higher Mn doping levels (e.g., MCCO-0.3) increase both microporosity and mesoporosity but lead to a more complex and possibly less accessible pore structure. This may introduce diffusion barriers, reducing the catalytic effectiveness despite a partial recovery in surface area. These findings underscore the importance of balancing structural features and electronic enhancements to optimize catalytic performance.

3.5.2. Effect of ph on catalytic activity

pH is a critical parameter affecting the catalytic efficiency of the 4-NP reduction reaction. Given that NaBH₄ remains stable only in basic solutions, the influence of pH was investigated for values above 7 (Fig. 7). The induction times (Fig. 7a) and apparent rate constants (Fig. 7b) indicate that catalytic reduction proceeds most efficiently at pH 8.

At higher pH values (from 9 to 12), catalytic efficiency decreases due to an increase in OH⁻ ions, which compete with 4-nitrophenolate anions for adsorption on the catalyst’s active sites. This leads to the formation of a negatively charged surface layer that inhibits further adsorption of 4-nitrophenolate, consequently reducing the reaction rate, as reflected by the decline in k_{app} values.

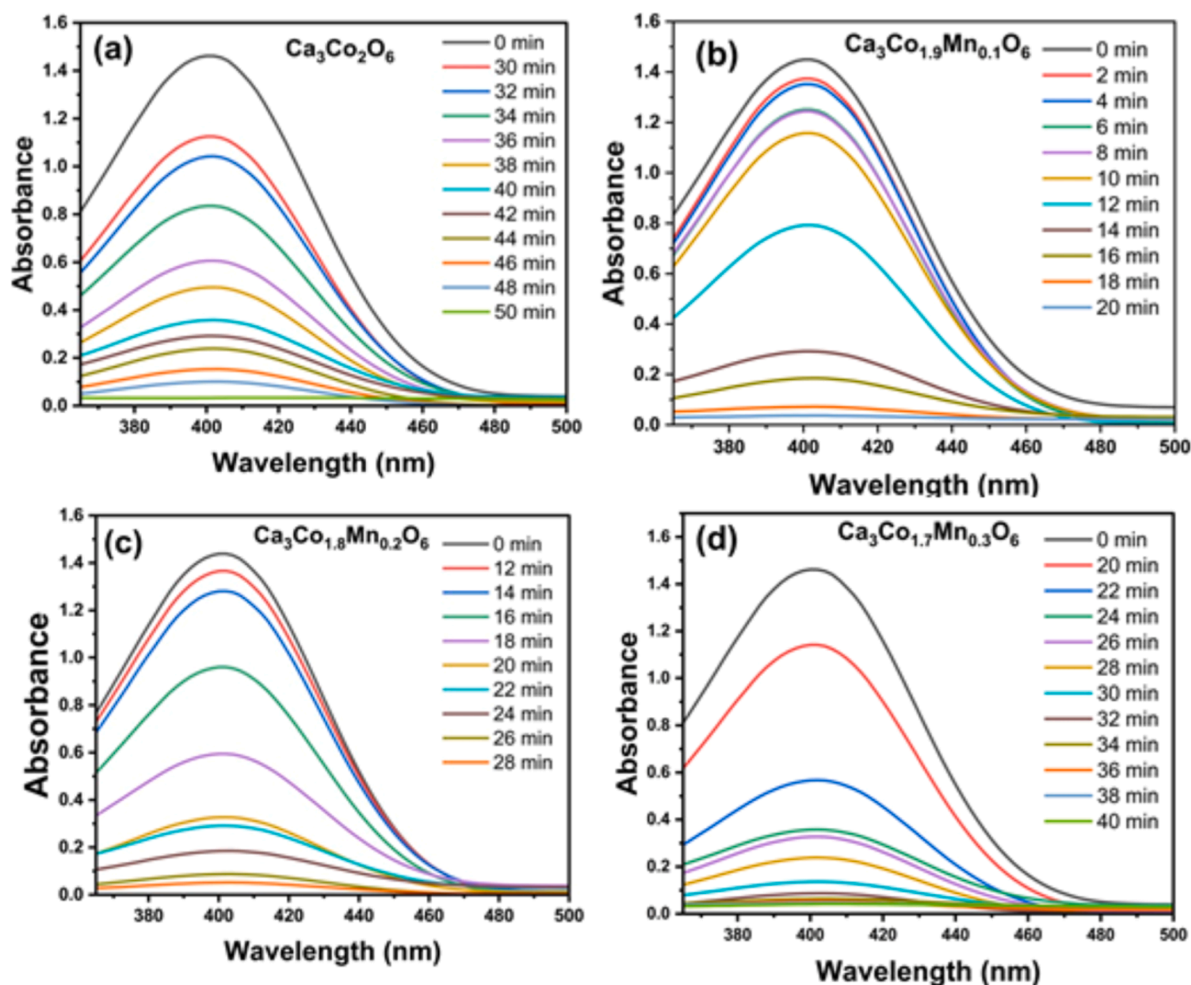


Fig. 5. uv-visible spectra of the reaction medium over time using CCO and MCCO catalysts.

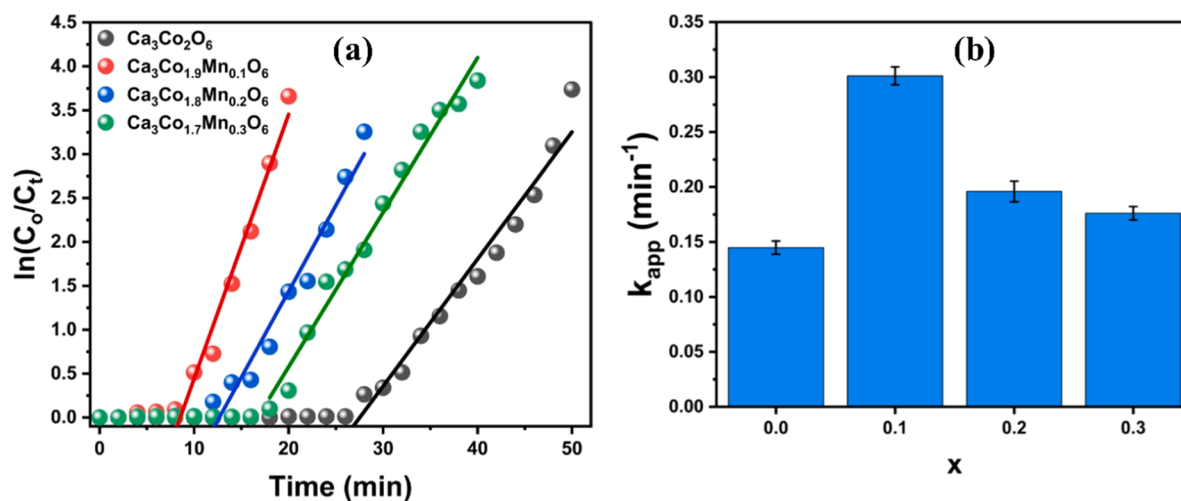


Fig. 6. Plot of $\ln(C_0/C_t)$ vs. Time (a) and apparent rate constants (b) for MCCO-catalyzed 4-NP reduction with varying mn content ($x = 0-0.3$).

Given the lack of prior studies on the catalytic activity and reaction mechanism of CCO and MCCO for 4-NP reduction, we propose a mechanism based on analogous studies [21]. Mixed transition metal oxides, particularly those involving manganese and cobalt, often exhibit complex redox behaviors and synergistic catalytic properties arising from the interaction between the metal species. Partial substitution of

Co^{3+} with Mn induces a redox balance, as some Co^{3+} ions are reduced to Co^{2+} to counterbalance Mn oxidation from Mn^{3+} to Mn^{4+} : $\text{Mn}^{3+} + \text{Co}^{3+} \rightarrow \text{Mn}^{4+} + \text{Co}^{2+}$ [22]. Further characterization using XPS is suggested as future work to provide direct confirmation of the hypothesized variations in cobalt and manganese oxidation states, which we suppose to drive the catalytic activity.

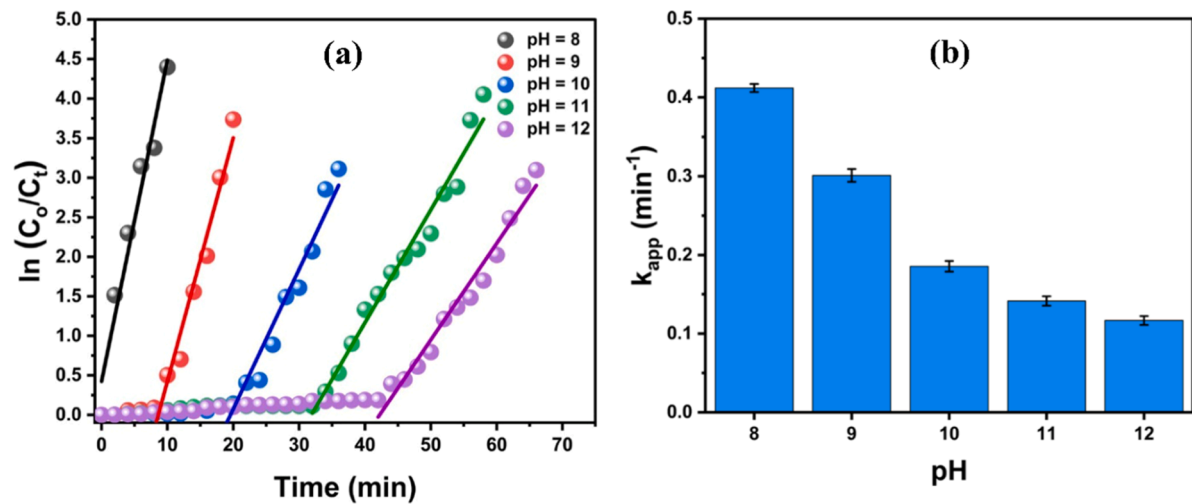


Fig. 7. Plot of $\ln(C_0/C_t)$ vs. Time (a) and apparent rate constants (b) for MCCO-catalyzed 4-NP reduction across different pH levels.

Within this framework, we hypothesize that Co^{2+} sites function as primary catalytic centers, adsorbing BH_4^- and 4-nitrophenolate (4-NPate^-), while Co^{3+} sites might adsorb water, facilitating the formation of H_2O^+ and OH^- . Crucially, in this $\text{Ca}_3\text{Co}_2\text{O}_6$ structure, the Ca^{2+} ions possess a stable $[\text{Ar}]$ electron configuration, making their direct participation in the electron transfer steps of the 4-NP reduction unlikely, in contrast to the variable oxidation states accessible to Co and Mn. Therefore, we posit that calcium's primary role is structural, stabilizing the intricate $\text{Ca}_3\text{Co}_2\text{O}_6$ lattice which hosts the catalytically active Mn/Co redox centers and influences their local electronic environment.

Following the activation steps, OH^- ions could initiate the attack on adsorbed BH_4^- , releasing hydride species (H_2O^-), which subsequently reduce the adsorbed 4-NPate^- to the intermediate 4-nitrosophenol (4-NSP). The continued supply of H_2O^- from BH_4^- decomposition would then facilitate the further reduction of 4-NSP to the final product, 4-aminophenol (4-AP), completing the transformation of the nitro group (NO_2) to an amine group (NH_2).

The catalytic efficiency of $\text{Ca}_3\text{Co}_{1.9}\text{Mn}_{0.1}\text{O}_6$ was benchmarked against cobalt-based catalysts from previous studies (Table 3). Our catalyst achieved a rate constant of $6.8 \times 10^{-3} \text{ s}^{-1}$ and a yield of 98.77 % within 10 min using 40 mg of catalyst with 0.1 mM 4-NP and 500 mM NaBH_4 . In contrast, Huang et al. (2017) reported a lower rate constant of $1.5 \times 10^{-3} \text{ s}^{-1}$ with 0.2 mg of Co_2P nanowires, 1 mM 4-NP, and 1000 mM NaBH_4 . Similarly, Zhang et al. (2021) observed a rate constant of $4.0 \times 10^{-3} \text{ s}^{-1}$ using 1 mg of Co_3O_4 on halloysite nanotubes, also lower than our catalyst's performance. While Hasan et al. (2016) reported a slightly higher rate constant of $7.0 \times 10^{-3} \text{ s}^{-1}$ using Co-carbon composites, the complex synthesis of metal-organic framework (MOF)-derived catalysts may limit scalability relative to our more straightforward method. Mogudi et al. (2016) utilized 2 mg of mesoporous Co_3O_4 for the reduction of 0.35 mM 4-NP with 100 mM NaBH_4 over 70 min, indicating

lower efficiency relative to our catalyst. The enhanced catalytic activity of $\text{Ca}_3\text{Co}_{1.9}\text{Mn}_{0.1}\text{O}_6$ likely results from Mn doping within the $\text{Ca}_3\text{Co}_2\text{O}_6$ lattice, which promotes electron transfer and increases the number of active sites, highlighting the catalyst's promise for environmental applications.

3.5.3. Reusability of the catalyst

The practical applicability of MCCO-0.1 as a catalyst was further evaluated through reusability tests over nine cycles under optimal conditions (pH 8). As shown in Fig. 8, catalytic efficiency remained high over the initial cycles, decreasing only slightly from 98.77 % (Cycle 1) to 94.76 % after eight cycles. However, a more substantial decline to 83.19 % was observed in the ninth cycle. This significant decrease suggests the onset of more pronounced catalyst deactivation pathways after prolonged operation. While pinpointing the exact cause would require detailed post-reaction characterization (e.g., XRD, XPS, TEM, ICP analysis) of the used catalyst, which was not performed in this study, several factors could contribute to this degradation. Plausible reasons include: (i) gradual leaching of active metal species (Co or Mn) into the reaction medium over repeated cycles; (ii) subtle structural degradation, amorphization, or phase changes in the catalyst induced by the repeated redox cycling under reaction conditions; or (iii) accumulation of strongly adsorbed species (reaction intermediates, products like borates, or impurities) on the active sites, leading to poisoning or blockage. The notable drop after the eighth cycle may indicate a cumulative threshold effect where these processes significantly impact the available active sites or structural integrity. Despite this eventual decline, the results demonstrate considerable operational stability and effectiveness for the MCCO-0.1 catalyst through the first eight cycles under the tested conditions.

To gain a more comprehensive understanding of the catalyst's long-term stability, future investigations will employ techniques such as XRD, SEM, TEM, and XPS to characterize the catalyst's morphological and chemical state following repeated reaction cycles. This will provide critical insights into any potential deactivation mechanisms.

4. Conclusion

This study successfully synthesized $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$ (MCCO) materials with Mn doping levels ranging from $x = 0\text{--}0.3$. Structural analyses via FTIR and XRD verified phase formation at 1000°C , with Mn doping influencing crystallite size and lattice structure. The catalytic efficiency of MCCO was evaluated through 4-NP reduction in NaBH_4 . MCCO-0.1 exhibited the highest catalytic performance, achieving a 98.77 % reduction of 4-NP within 10 min at pH 8. Furthermore, MCCO-0.1

Table 3
Catalytic activity of of CCMO-0.1 compared with other studies.

Catalyst	Catalyst amount (mg)	[4 - NP] (mM)	[NaBH ₄] (mM)	Reaction time (min)	k _{app} (s ⁻¹)	Ref.
$\text{Ca}_3\text{Co}_{1.9}\text{Mn}_{0.1}\text{O}_6$	40	0.1	500	10	$(6.8 \pm 0.5) \times 10^{-3}$	This study
BNWs	0.2	1	1000	-	1.5×10^{-3}	[23]
$\text{Co}_3\text{O}_4/\text{HTNs}$	1	0.12	48	11	4.0×10^{-3}	[24]
Co - CC	0.27	0.168	255	2.17	7.0×10^{-3}	[25]
Meso - Co_3O_4	2	0.35	100	70	-	[26]

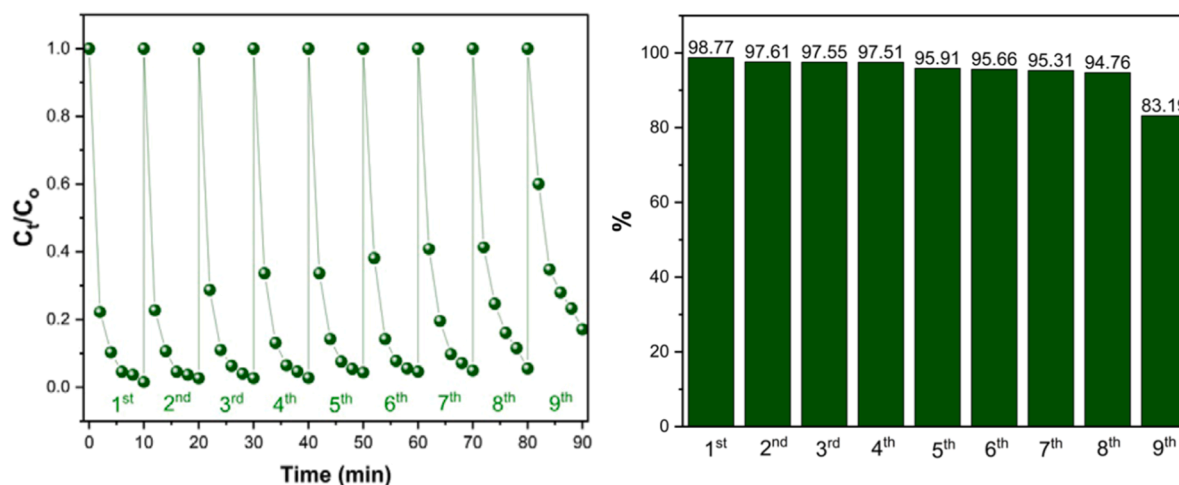


Fig. 8. Plot of C/C_0 versus time (a) and 4-NP removal efficiencies after 10 min of reaction for nine usage cycles of MCCO-0.1.

displayed strong reusability, maintaining over 94.76 % efficiency after eight cycles. These findings underscore the potential of Mn-doped MCCO as an effective catalyst for environmental remediation, warranting further optimization to enhance stability and functionality.

CRedit authorship contribution statement

T.A. Tran: Funding acquisition, Data Curation, Writing - Original draft. T.H. Nguyen: Investigation, Data Curation. D.P.T. Tien: Methodology, Formal analysis. L.V.T. Nguyen: Investigation, Data Curation. T. P. Hoang: Conceptualization, Writing - Review & Editing, Supervision, Project administration. Truong-Tho Nguyen: Formal analysis, Visualization. L.V.T. Son: Visualization. Gunel Imanova: Conceptualization, Writing - Review & Editing, Supervision. S.H. Jabarov: Formal analysis, Resources. V.T. Nguyen: Methodology, Writing - Review & Editing, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The datasets supporting the findings of this study are available from the corresponding authors or the first author upon reasonable request.

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