Low-temperature CO oxidation over MnO_x catalysts synthesized via a CO_2-assisted solvothermal route

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Highlights

- MnO_x catalysts showed near-room temperature CO oxidation without noble metals
- Synthesis time strongly affected activity, surface area, and crystallite size
- Short synthesis preserved defective MnO_x rich in reactive oxygen species
- Cu doping enabled complete CO conversion at room temperature with high stability

1. Introduction

Indoor air pollution poses a significant health risk, with carbon monoxide representing one of the most hazardous indoor contaminants due to its colorless, odorless, and toxic nature[1]. Low-temperature catalytic oxidation of CO to CO_2 is a promising solution and manganese oxides are widely investigated for this application because of their redox versatility, multiple oxidation states, and ability to generate reactive oxygen species[1,2]. In this study, MnO_x catalysts were synthesized through an innovative CO_2-assisted solvothermal route involving the formation of a high surface area manganese carbonate precursor followed by thermal conversion to the oxide. By tuning CO_2 pressure and synthesis time, catalytically active MnO_x for low-temperature CO oxidation were obtained, while copper addition further enhanced catalytic performance. The use of CO_2 as a reactive agent fits within a circular economy framework, highlighting the sustainability and environmental relevance of the proposed approach.

2. Methods

For the synthesis of MnO_x samples, the procedure reported by Lee et al.[3] was suitably modified to tailor the desired material properties. The manganese precursor was dissolved in methanol at room temperature and transferred to a stainless-steel autoclave, where pure CO_2 was introduced. By tuning pressure (6-16 bar) and reaction time (2-4 days), MnO_x oxides with different physico-chemical properties were obtained. The sample nomenclature adopts the format MnO_x_XbYd, where X indicates the CO_2 pressure in bar and Y the carbonate synthesis time in days. To further improve catalytic performance, a copper-doped sample was prepared following the same procedure, adding copper precursor to the initial solution, achieving a Cu/(Cu+Mn) ratio of 15 wt.%. MnO_x obtained from the calcination of commercial $MnCO_3$ was used as reference. The catalysts were characterized using TGA, N_2 physisorption at -196 °C, XRD, XPS, O_2-TPD, and STEM-EDX analyses. Catalytic performance was evaluated under simulated polluted conditions using 100 ppm of CO and 50 mg of catalyst, while GHSV variation and stability tests were performed on the most active sample.

3. Results and discussion

The catalytic activity was summarized in Figure 1. All manganese oxides exhibited promising performance, with activity strongly dependent on the synthesis conditions. Notably, MnO_x_6b2d and MnO_x_16b2d showed the highest activity, achieving measurable CO conversion close to room temperature, an outstanding result for noble-metal-free catalysts. In particular, MnO_x_6b2d reached T_{10} below room temperature with a conversion rate of 107.7 µmol h^{-1} g^{-1}, while MnO_x_16b2d exhibited a T_{10} of 27 °C and a conversion rate of 89.4 µmol h^{-1} g^{-1}. They displayed superior low-temperature activity compared to the commercial MnO_x reference. These results were attributed to the presence of highly

reactive surface oxygen species and efficient Mn^{3+}/Mn^{4+} redox cycling, as confirmed by XPS and O_2-TPD analyses. In contrast, MnO_x_16b4d showed significantly lower activity, with higher $T_{10}/T_{50}/T_{90}$ values and a reduced conversion rate, consistent with its lower specific surface area, reduced oxygen mobility, and fewer defective oxygen species. The introduction of copper had a marked positive effect: the $CuMnO_x$ catalyst achieved complete CO conversion already at room temperature and maintained stable activity for at least 8 h under operative conditions. Moreover, high conversion was preserved even at elevated GHSV. From a synthetic standpoint, increasing CO_2 pressure during precursor formation (6-16 bar) at constant reaction time induced only minor changes in catalytic performance, mainly affecting room-temperature conversion. In contrast, extending the synthesis time from 2 to 4 days at constant pressure significantly deteriorated activity. Longer exposure promoted crystallite growth (from 7.4 to 12.6 nm) and reduced surface area (from 159 to 91 $m^2\ g^{-1}$), decreasing the number of accessible active sites. Shorter synthesis times instead preserved a more defective structure.

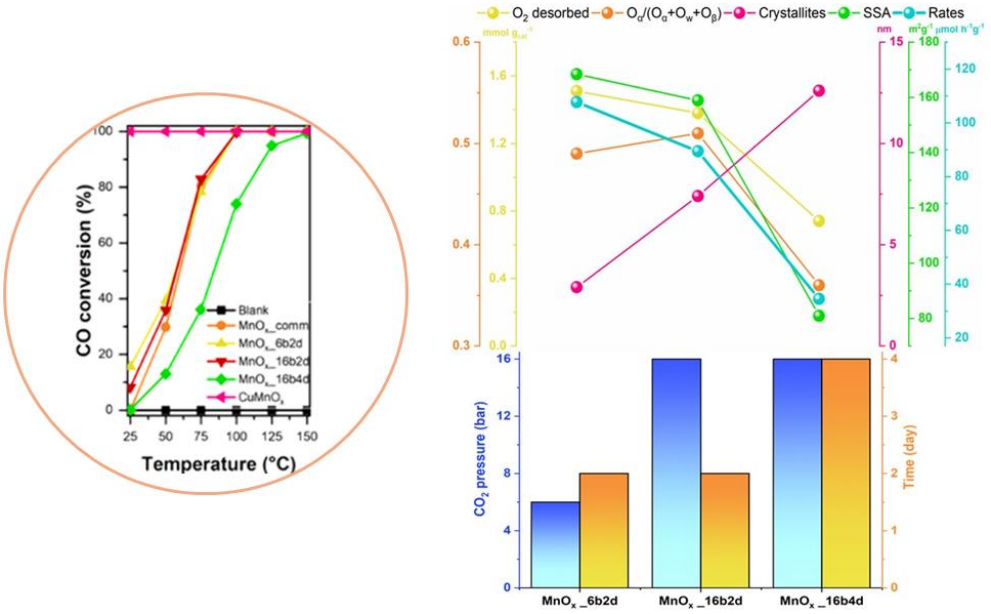

Figure 1. Catalytic results and correlation between synthesis conditions and properties of MnO_x samples

4. Conclusions

These results demonstrated that synthesis time played a more critical role than CO_2 pressure in determining the catalytic and physicochemical properties of MnO_x catalysts. In summary, all synthesized manganese oxides were catalytically active toward CO oxidation, with their performance strongly dependent on the preparation conditions. The incorporation of copper led to a significant improvement, enabling full CO conversion and long-term stability at ambient temperature.

References

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Keywords

Indoor pollution; low-temperature CO oxidation; manganese-based oxides

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