Influence of manganese oxide crystalline structure and gold nanoparticle size on low-temperature air pollutant abatement

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Highlights

- AuNPs on MnO_x catalysts were studied for low-temperature CO and VOC oxidation
- Gold addition boosted activity, achieving complete CO conversion at 60 °C
- A critical AuNP size was identified, strongly influencing catalytic performance
- MnO_2-based, high–surface area catalysts showed optimal NP dispersion and activity

1. Introduction

In recent years, indoor air purification has attracted increasing interest. Among the major atmospheric contaminants, CO and Volatile Organic Compounds (VOCs), widely present in paints and household products, are the most prevalent molecules[1]. One effective strategy for their elimination is low-temperature catalytic oxidation. In this framework, manganese oxides have demonstrated considerable potential as catalysts for CO and VOC oxidation due to their high activity, stability, and cost-effectiveness[2]. Various crystalline phases of manganese oxides (including MnO_2 and Mn_2O_3) display distinct catalytic behaviors, governed by their redox properties and structural defects, which make them suitable for the oxidation at moderate temperatures[3]. The presence of noble metals, such as gold nanoparticles (AuNPs), on the catalyst surface can further improve catalytic efficiency, enabling enhanced performance at even lower temperatures.

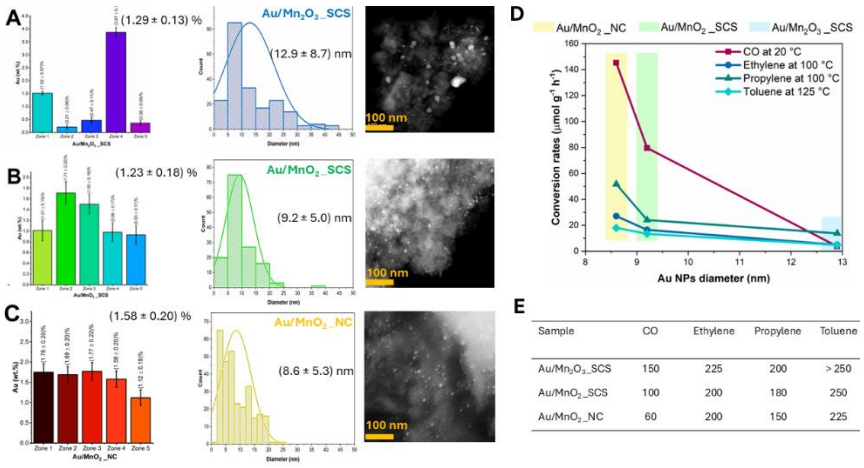
2. Methods

Manganese oxides with two distinct crystalline phases (MnO_2 and Mn_2O_3) were prepared using Solution Combustion Synthesis (SCS) and Nanocasting (NC) approaches, following protocols previously reported in our work[3]. Gold nanoparticles (1 wt.%) were introduced by means of a sol-immobilization technique to improve catalytic efficiency. The resulting catalysts were thoroughly characterized using different physico-chemical methods, including N_2 physisorption at -196 °C, XRD, XPS, H_2-TPR, O_2-TPD, and STEM-EDX analyses. Catalytic performance was evaluated under conditions simulating a realistic polluted atmosphere, containing CO, ethylene, propylene, or toluene as target compounds at a concentration of 100 ppm, using 50 mg of catalyst. These probe molecules were selected because they are representative indoor air contaminants (e.g., CO) and exhibit low reactivity toward oxidation at mild temperatures (e.g., VOCs). In addition, cyclic experiments and time-on-stream (TOS) tests were conducted on the most active catalyst to further assess its activity and long-term stability.

3. Results and discussion

The catalytic evaluations yielded interesting outcomes, with CO oxidation showing particularly outstanding performance. Notably, complete CO conversion was achieved at an exceptionally low temperature of 60 °C, with conversion exceeding 50% already at room temperature. The findings of this work underline the beneficial role of AuNPs in enhancing CO oxidation, especially when compared with the corresponding bare supports. Although CO exhibited the most pronounced improvement, evidencing a substantial reduction in the oxidation temperature of 90 °C for the NC sample compared to the Au-free catalyst counterpart (T_{100} = 60 °C for Au/MnO_2_NC versus 150 °C for MnO_2_NC) a

significant temperature decrease of approximately 50 °C was also recorded for the investigated VOCs, demonstrating the strong potential of AuNPs in promoting the oxidation of gaseous pollutants compared the pure oxide. The catalysts synthesized with the SCS method revealed lower activity, probably due to the lower specific surface area (52 m^2g^{-1} for Au/MnO_2_NC compared to 40 m^2g^{-1} for Au/MnO_2_SCS and 21 m^2g^{-1} for Au/Mn_2O_3_SCS), which may have negatively influenced the Au NPs deposition. Another key factor was the influence of the MnO_x crystalline structure on nanoparticle deposition and dispersion. In this regard, the MnO_2 phase proved to be the most effective, providing an optimal distribution of AuNPs. Both SCS and NC samples exhibited a more uniform nanoparticle dispersion and a narrower size distribution, with average particle sizes of 9.2 nm and 8.6 nm, respectively, suggesting a correlation between nanoparticle dimensions and catalytic activity (Figure 1). As previously mentioned, the highest catalytic efficiency was obtained with the high surface area catalyst, indicating that an increase of this parameter improved nanoparticle dispersion and stronger interaction with reactant molecules. Moreover, the results allowed the identification of a "critical radius," below which catalytic performance markedly improved, particularly for CO oxidation, pointing to a strong structure sensitivity for this reaction. Also, VOCs exhibited a sort of sensitivity toward size dimension, more pronounced for ethylene and propylene, instead for toluene.



Sample	CO	Ethylene	Propylene	Toluene
Au/Mn_2O_3_SCS	150	225	200	> 250
Au/MnO_2_SCS	100	200	180	250
Au/MnO_2_NC	60	200	150	225

Figure 1. AuNPs distribution, average diameter, and STEM images (A-C), the relationship between Au diameter and catalytic performance (D), the temperature at which the conversion is complete (E) for all the pollutants

4. Conclusions

The results demonstrated that the incorporation of gold nanoparticles significantly improved catalytic performance toward all the investigated compounds. In addition, a clear correlation between nanoparticle size and catalytic activity was identified. Achieving complete conversion at such low operating temperatures not only contributed to reduced energy demand but also broadened the potential for the development of cleaner and more sustainable air purification technologies. Overall, these outcomes emphasized the key role of both catalyst composition and morphology in the rational design of advanced materials for efficient air pollutant abatement.

References

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Keywords

Indoor pollution; low-temperature oxidation; manganese oxides; VOC abatement.

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