Synergistic effect between manganese and copper oxides in boosting low-temperature catalytic oxidation of indoor pollutants

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Significance and Relevance

This study presents insights into the field of environmental catalysis by demonstrating the successful oxidation of pollutants at low temperatures, a challenging task in catalytic processes. The significant impact of this work concerns the achievement of promising results without using precious metals, which typically drive high-performance catalysts. The synergy between copper and manganese positively influenced the catalytic performance, enhancing the overall activity, and allowing it to completely oxidize pollutants at low temperatures. Moreover, the use of a simple and reproducible synthesis redox technique further amplifies the potential for scaling this approach, offering a cost-effective solution for addressing environmental pollution.

Preferred and 2nd choice for the topic: Air cleaning and combustion/Automotive and stationary emission control
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

In recent years, there has been growing interest in air purification, particularly with regard to indoor air pollution, which can pose greater risks to health than outdoor pollution. Among the various pollutants present in the atmosphere, Volatile Organic Compounds (VOCs), commonly found in products like paints and cleaning agents, are among the most prevalent[1]. One promising method for eliminating these contaminants is catalytic oxidation at low temperatures. Manganese oxide catalysts show great potential in this area, but the temperatures required to effectively remove common indoor pollutants like CO and ethylene remain relatively high[2]. However, mixed oxides such as copper-manganese oxides have demonstrated significant catalytic activity for the oxidation of CO and VOCs, offering advantages in terms of effectiveness, longevity, and cost-efficiency[3]. The synergistic effect between copper and manganese oxides could further enhance their catalytic performance, enabling pollutant removal at lower temperatures. This approach shows considerable promise for improving indoor air quality and promoting the health and well-being of individuals in enclosed spaces.

Materials and Methods

Manganese oxides with different copper loading (1-10 wt.% of Cu) were synthesized through Solution Combustion Synthesis (SCS) introducing 1 wt.% and 3wt.% of copper in the structure. To avoid phase segregation as the amount of copper in the structure increases, a different synthesis (redox) technique has been proposed in the case of 10wt.%, introducing some modifications to the procedures found in the literature. The synthesized materials were subsequently characterized through different physicochemical techniques and then the catalytic activity was investigated by simulating a real polluted atmosphere containing CO or ethylene as target molecules in a concentration of 100 ppm over 50 mg of catalyst. Finally, time-on-stream (TOS) analyses were carried out on the best-performing catalyst to investigate the performance and stability of this sample better.

Results and Discussion

The presence of copper within the structure demonstrated an extremely positive impact on catalytic performance, as revealed in Figure 1. A preliminary screening was carried out by testing CO as a target molecule. In this context, when comparing the samples obtained via the SCS method, a small increase in copper content (from 1wt.% in $Cu_{0.01}Mn_{0.99}$_SCS to 3wt.% in $Cu_{0.03}Mn_{0.97}$_SCS) significantly improved the catalytic activity, enabling complete oxidation of CO at a relatively low temperature of 100 °C in the case of $Cu_{0.03}Mn_{0.97}$_SCS sample. These preliminary results were then compared to those obtained with $Cu_{0.1}Mn_{0.9}$_redox, which showed surprising results. Specifically, the CO was fully oxidized at an incredibly low temperature of just 23 °C, maintaining a 100 % conversion for a continuous 6-hour period in the presence of the reagent mixture. This outstanding catalytic performance could be attributed to the increased surface area (329 m^2g^{-1} against 15 m^2g^{-1} and 7 m^2g^{-1} for $Cu_{0.01}Mn_{0.99}$_SCS and $Cu_{0.03}Mn_{0.97}$_SCS) and the enhanced Mn-Cu interfaces, which create defects that further boost catalytic activity. Subsequently, since both $Cu_{0.03}Mn_{0.97}$_SCS and $Cu_{0.1}Mn_{0.9}$_redox demonstrated the best performances, they were also tested for the oxidation of ethylene, which is much more complex to oxidize at low temperatures. Once again, the redox sample exhibited superior results, achieving over 95 % conversion at 150 °C. These results demonstrate the effectiveness of this catalyst in oxidizing complex molecules without the use of noble metals, utilizing a simple and scalable synthesis procedure.

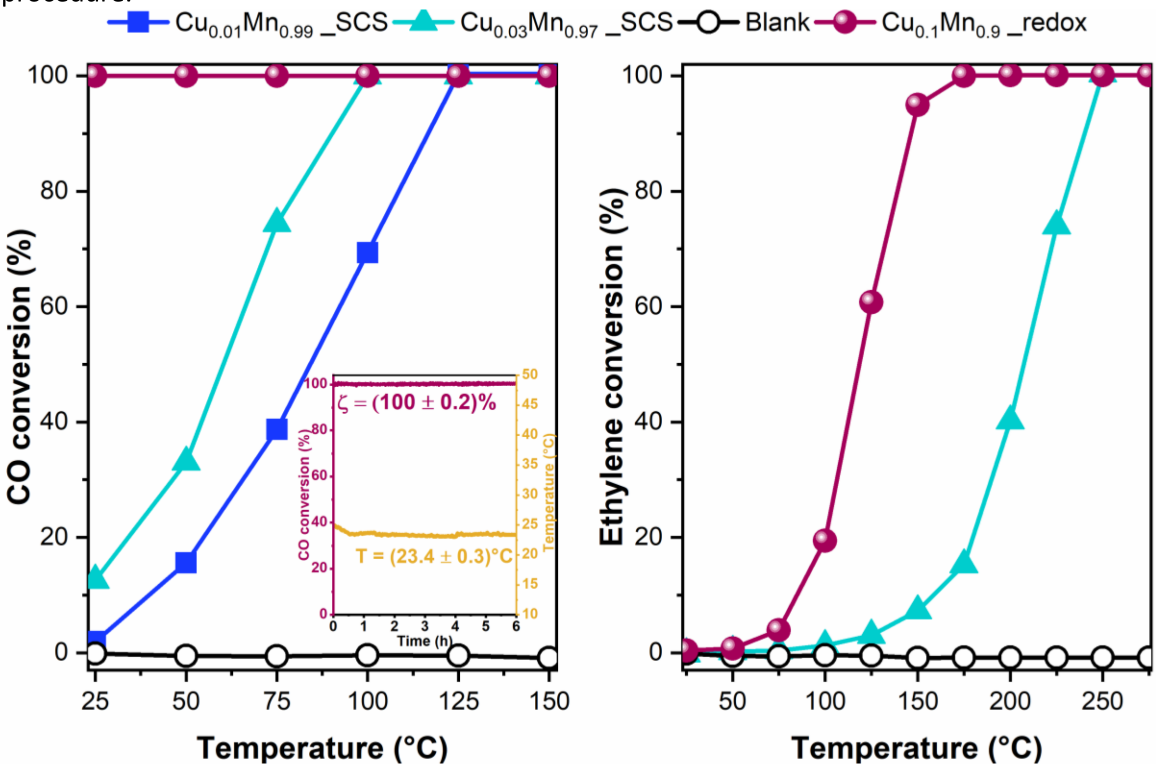

Figure 1 Catalytic oxidation of CO (left) and ethylene (right) over the investigated samples.

In conclusion, the topic proposed in this work is particularly challenging due to some limitations (i.e., low concentrations of pollutants, low temperatures adopted, and the complexity of the target molecules). However, the promising results achieved without the use of noble metals are a positive indication for the development of more cost-effective technologies. Further investigations into the reaction mechanism and deeper characterizations are currently ongoing to better understand the synergistic interactions between the Mn and Cu phases, along with the amounts of reactive oxygen species and structural defects. New pollutants will also be tested and optimizations will be pursued to reduce the temperature required for VOC oxidation, thus enhancing catalytic performance.

References

1. Guo, Y., Wen, M., Li, G., An, T. Appl Catal B, **2021**, 281.
2. Grifasi, N., Sartoretti, E., Montesi, D., Bensaid, S., Russo, N., Deorsola, F. A., Fino, D., Novara, C., Giorgis, F., Piumetti, M. Appl Catal B, **2025**, 362.
3. Cocuzza, C., Sartoretti, E., Novara, C., Giorgis, F., Bensaid, S., Russo, N., Fino, D., Piumetti, M. Catalysis Today, **2023**, 423.

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