

Summary of Doctoral Thesis

"Design and optimization of manganese oxide-based catalysts for low-temperature catalytic oxidation of indoor gaseous pollutants"

Candidate: Nadia Grifasi (s306329)

Supervisor: prof. Marco Piumetti

Co-supervisors: prof. Samir Bensaid

prof. Nunzio Russo

Indoor air pollution is recognized as a major concern due to its direct impact on human health. In fact, people spend most of their time indoors, where the accumulation of pollutants can lead to prolonged exposure and, consequently, significant health risks. Among the various indoor contaminants, gaseous molecules such as carbon monoxide (CO) and volatile organic compounds (VOCs), including ethylene, propylene, and toluene, are particularly problematic, even at relatively low concentrations. In this context, catalytic oxidation at low temperature has emerged as a promising solution for indoor air purification. This approach combines relatively low energy consumption with the possibility of operating under real indoor conditions. However, an important challenge remains the development of catalysts that are not only highly efficient but also cost-effective and capable of operating close to room temperature over extended periods of time. Manganese oxides have been extensively investigated for VOC oxidation, mainly due to their redox properties and structural flexibility. Nevertheless, their practical application in indoor environments is still limited by the relatively high temperatures required to achieve complete pollutant conversion. Starting from this limitation, the main aim of this Thesis was to design and optimize MnO_x-based catalysts capable of efficiently oxidizing CO and VOCs at low temperature, while maintaining high activity and long-term stability under continuous operation.

Following an initial overview of the target pollutants, their health implications, and the main synthesis and characterization techniques used in this work (Chapters 1 and 2), the research first focused on understanding how structural features influence catalytic performance. Precisely, in Chapter 3, particular attention was given to the role of crystalline phases and structural defects. The results clearly showed that catalytic activity is not governed by a single parameter, but rather by a combination of factors. The most effective catalyst was characterized by enhanced oxygen mobility, a high degree of surface acidity, and a synergistic interaction between different crystalline phases. This interaction promoted the formation of structural defects and the exposure of highly reactive crystal facets, both of which are known to facilitate oxidation reactions. Despite these improvements, however, the temperature required to reach complete conversion remained higher than desirable for indoor applications.

To address this limitation, gold nanoparticles were deposited onto the surface of the previous manganese oxide supports (Chapter 4). The presence of gold significantly enhanced catalytic performance, leading to a noticeable decrease in the temperatures required for oxidation. In particular, smaller nanoparticles proved to be more effective compared to larger ones. Interestingly, while some molecules showed a clear benefit, others (such as toluene and ethylene) were less sensitive to the presence of gold. However, although catalytic activity improved, the overall

performance did not appear sufficient to fully justify the use of such expensive material. For this reason, the research moved to an alternative strategy, involving the incorporation of a heteroatom into the manganese oxide structure, with the goal of increasing defect density and improving catalytic properties. Among the possible candidates, copper emerged as a particularly suitable choice due to its low cost and well-known redox behavior. In Chapter 5, a series of Cu-Mn mixed oxides was developed and thoroughly investigated. These materials exhibited remarkable catalytic performance, representing a significant step forward compared to the systems previously studied. One of the most outstanding results was the achievement of complete CO oxidation at room temperature, a key requirement for indoor applications. Even more importantly, this performance was maintained over long periods of time, demonstrating excellent stability under continuous operation. Notably, these results were obtained using very small amounts of catalyst, highlighting its high activity. The materials also showed strong resistance under challenging conditions, including high pollutant concentrations, oxygen-deficient atmospheres, the presence of moisture, and the simultaneous presence of different compounds. The superior performance of Cu-Mn oxides can be attributed to a combination of structural and chemical features. These include a high concentration of reactive oxygen species, which play a crucial role in oxidation reactions, as well as enhanced oxygen mobility within the material. In addition, strong interactions between copper and manganese promote the formation of oxygen vacancies, which are often considered active sites for catalytic processes. Another important aspect was the structural disorder, which contributed to an increased density of defects, further enhancing catalytic activity. Interestingly, the factors controlling performance were found to depend on the specific molecule investigated. For example, different behaviors were observed for CO and ethylene, suggesting that distinct reaction mechanisms are involved and highlighting the overall complexity of the system.

In the final part of the Thesis (Chapter 6), attention was shifted to the broader implications of catalytic oxidation, particularly the formation of CO₂ as a by-product. Although CO₂ is generally not a critical issue in indoor environments at the concentrations produced by these reactions, its generation still raises questions in terms of overall sustainability. To address this aspect, the work explored the possibility of reusing CO₂ within a circular economy framework, proposing it as a precursor for catalyst synthesis. In this context, a novel solvothermal synthesis route based on the use of pressurized CO₂ was developed. This method allowed the preparation of materials with high surface area and a large number of structural defects, both of which are desirable properties for catalytic applications. The synthesis parameters were found to play a crucial role in determining the final characteristics of the materials. In particular, shorter synthesis times were more effective in preserving structural defects and reactive oxygen species, which are essential for achieving high catalytic performance. Although this approach is still at a preliminary stage, it provides an interesting perspective for future developments. By integrating pollutant removal with CO₂ valorization, it may be possible to move toward more sustainable and circular processes, where waste products are reintroduced into the system as valuable resources.

Overall, this Thesis would highlight how a rational design of manganese-based catalysts, combined with targeted modifications such as heteroatom incorporation, can lead to significant improvements in low-temperature catalytic oxidation. At the same time, it emphasizes the importance of balancing performance, cost, and sustainability when developing materials for real-world indoor air purification applications.