

Abstract

This thesis work aims to investigate different metal-oxide based materials as catalysts for the abatement of volatile organic compounds (VOCs) and carbonaceous particulate matter, i.e., nowadays typical atmospheric pollutants.

From the various synthesis procedures reported in the literature, the solution combustion synthesis (SCS) represents an easy, relatively economic and fast pathway for the preparation of catalytic powder materials. As well, the sol-gel procedure is a facile procedure that allows to prepare mesoporous materials with promising structural and catalytic performances. Consequently, these two procedures were carried out in order to synthesize active powder catalysts. Moreover, an in-situ synthesis procedure was used in order to prepare catalyzed monoliths (structured catalysts).

The catalysts investigated contain metals that are between the most abundant elements in the earth crust. Accordingly, the elements present in the catalysts were engineered with an eye towards the preparation of sustainable, low-temperature active and relatively economic catalysts. Oxide materials have been object of study due to their promising catalytic performances. In this sense, various single-metal and, particularly, mixed oxide catalysts were synthesized in order to better investigate their physico-chemical and catalytic properties in the catalytic abatement of VOCs and carbon soot.

Cerium oxide is a catalyst known by the redox behavior that occurs between Ce^{4+} and Ce^{3+} species, that allows the structure to storage oxygen. As well, manganese oxides have evidenced interesting catalytic performances mainly correlated to the occurrence of different oxidation state species ($\text{Mn}^{4+}|\text{Mn}^{3+}|\text{Mn}^{2+}$). Accordingly, efforts have been carried out in order to improve the catalytic activity of these materials, as of an example, by means of doping them with other elements, preparing mixed oxides, or by promoting cooperative interactions (or synergy) between different oxide phases.

The catalytic materials studied in this work were characterized by means of complementary characterization techniques, e.g., X-ray diffraction (XRD), N_2 physisorption at $-196\text{ }^\circ\text{C}$, field-emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), hydrogen and soot temperature-programmed reduction (H_2 -TPR, soot-TPR), oxygen temperature-programmed desorption (O_2 -TPD). The catalytic screenings were performed in a PID-controlled TPO setup. The powder catalysts were tested in a U-tube fixed-bed reactor, whereas the monoliths

were tested in a bench-scale stainless steel tubular reactor system. Propylene and ethylene were used as VOC probe molecules, whereas Printex-U was used as carbon soot surrogate.

Mixed cerium oxide-based families (Ce-Mn, Ce-Cu and Ce-Mn-Cu) were synthesized by means of the SCS. The best performance in propylene oxidation were attributed to beneficial interactions occurring between clusters of MnO_x that and CeO_2 . Instead, the co-presence of MnO_x , CuO and CeO_2 species was responsible of the excellent catalytic results in ethylene oxidation at low temperature. The catalysts that were deposited over SiC monoliths showed as well good catalytic performances, and converted the VOCs at temperatures below those required for the thermal non-catalytic oxidation. The powders and the monolith catalysts evidenced good catalytic stability and reproducibility.

Mesoporous manganese oxides (doped with Cu and/or Fe) were synthesized by means of the sol-gel technique. The optimum catalytic activities observed in VOC oxidation were correlated to the following aspects: high superficial population chemisorbed oxygen species and the improved low-temperature reducibility. As well, beneficial interactions between Mn, Cu and Fe most likely improve the activity of the parent Mn_2O_3 catalyst. Reproducible catalytic performances in VOC oxidation were observed for the most promising catalyst. Additional studies were carried out over the catalysts prepared by means of the sol-gel technique, in order to investigate their catalytic performance in soot oxidation under a stream containing 5 vol.% H_2O . Furthermore, the simultaneous soot and propylene oxidation was assessed. For the catalytic soot oxidation, the ratio between the $\text{Mn}^{3+}/\text{Mn}^{2+}$ species was the key parameter, whereas for the propylene oxidation reaction the key parameter was the improved low-temperature reducibility (caused by the incorporation of Cu in the Mn_2O_3 structure). Little deactivation for the soot oxidation reaction was observed under a gaseous stream containing H_2O and, as well over the severely aged catalysts. Remarkably, the contemporary soot-propylene oxidation test evidenced a probable cooperative effect from the propylene oxidation reaction, towards the oxidation of soot particles in “tight” contact with the catalyst.

Finally, a comparative study was performed between catalysts synthesized by means of the SCS and sol-gel technique. Different synthesis conditions evidenced marked changes in the physico-chemical properties of the catalyst. The best catalytic performances in VOC oxidation were attributed to the improved reducibility at low temperatures and to the increased amount of chemisorbed oxygen species, active for oxidation reactions. Similarly, the mentioned characteristics demonstrated to play a key role in the oxidation of soot particles in “tight” contact with the catalyst. On the other hand, the oxidation of soot particles under “loose” contact conditions highlighted the beneficial role of the catalyst’s “filter-like” morphology that seems to trap soot particles. Under the latter condition, the probable high amount of acid-sites characteristic of catalysts containing Mn_3O_4 seems co-responsible for the good catalytic performance observed in soot oxidation.