

Nanostructured ceria-based catalysts for automotive application

Formulation of nanostructured systems for diesel and gasoline-type engines

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Summary

The aim of this work is the study of nanostructured CeO₂ catalysts for automotive application. In particular, the CeO₂ was investigated because it is considered an interesting catalytic material for diesel and gasoline-type engines. The reason of such attention to this oxide catalyst is due to its unique physico-chemical properties: it is able to take part to the oxidation reactions with a redox mechanism (namely Mars-van Krevelen-type mechanism) and it is able to store oxygen because it has a high oxygen storage capacity (namely OSC). Thanks to these interesting features, CeO₂ can work with different gas-phase oxygen compositions in the exhaust gas. Specifically, if the exhaust gas has low gas-phase oxygen concentration, the CeO₂ can release oxygen and it passes from Ce⁴⁺ to Ce³⁺ oxidation state. On the other hand, if the exhaust gas has high gas-phase oxygen composition, the Ce₂O₃ takes the oxygen from the atmosphere and passes to CeO₂ form (Ce³⁺ to Ce⁴⁺). Thanks to this ability, the CeO₂ is a suitable material to be used as catalytic system for the after-treatment technology in diesel and gasoline-type engines.

There are several routes to synthesize CeO₂. In this thesis, the hydrothermal procedure was one of the techniques studied. This synthesis was chosen since it is able to obtain CeO₂ nanostructures with more reactive crystalline planes, namely (1 0 0) and (1 1 0)-type planes, comparing with CeO₂ nanoparticles which have high abundance of (1 1 1)-type planes. In particular, the effect of two synthesis parameters (namely, ageing temperature and NaOH concentration) were investigated. The results have evidenced that, changing these two parameters, it is possible to obtain different CeO₂ nanostructures, like nanocubes, nanorods and nanoparticles. Different synthesis conditions may lead to several nanostructures effective toward the CO oxidation, soot combustion and NO_x oxidation, in different ways.

Moreover, it was evaluated the insertion of foreign metals inside CeO₂ structure, like copper and manganese. The textural properties of the Ce-Mn-Cu oxides catalysts highlighted the beneficial role of the insertion of such metals inside CeO₂ framework. Furthermore, it was investigated the behavior of Ce-Mn-Cu oxides catalysts towards CO

and soot oxidation reactions at different gas-phase oxygen concentrations (0.02, 0.5, 1.0 and 10 vol.%) in the reactant mixtures.

It was observed the most interesting catalyst for the CO oxidation reaction were the samples with Cu inside CeO₂ framework. The Cu promotes the surface redox mechanism for the oxidation process due to the presence of structural defects and the surface reducibility. For the CO oxidation reaction, the high vol.% O₂ values lead to competitive CO and O₂ adsorption on the catalyst surface thus reducing the catalytic performances for Ce-Mn-Cu oxides.

For the soot oxidation reaction, it was observed the lower the surface area the higher the reactivity. Moreover, the CeO₂ is a promising catalyst even at low vol.% O₂, possibly due to the low specific surface area. For all the samples, the presence of 10 vol.% O₂ in the mixture is the best condition to oxidize the soot particles.

Furthermore, another synthesis procedure, by means of the Multi-Inlet Vortex Reactor (MIVR), was used in order to obtain smaller particles of Ce-Cu oxides. The results towards the CO oxidation reaction have demonstrated interesting catalytic performances that are comparable or better to Pt/CeO₂ (Pt = 2 wt.%), a catalyst synthesized as commercial reference.