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Summary of doctoral dissertation

The role of the architecture of $Ce_{1-x}REE_xO_{2-x/2}$ and $Au/Ce_{1-x}REE_xO_{2-x/2}$ (REE- rare-earth element) hierarchical materials in catalytic oxidation of C, CO and C_3H_8.

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This Dissertation describes the role of the architecture of the hierarchical ceria-based gold catalytic systems in the catalytic combustion processes, aiming to provide knowledge to ground the quest of searching new catalysts for environmental applications on an informed basis. In particular, it presents the results of the catalytic activity, selectivity, and stability of the materials in the reactions of carbon monoxide, propane, and soot oxidation, while the structural hierarchy is an examined property of the special interest.

Three goals were set in this work: (i) elaboration of the synthetic procedure for obtaining hierarchical ceria-based $Ce_{1-x}(REE)_xO_{2-x/2}$ (REE- rare-earth element) catalytic supports along with investigation of their properties and catalytic performance, (ii) elaboration of the knowledgeable strategy of decoration of hierarchical supports by gold nanoparticles having desired size, (iii) examining the catalytic properties of gold-decorated ceria-based hierarchical catalysts and determining the role of the materials architecture in catalytic performance.

The synoptic description of the structural hierarchy, surface properties and catalytic performance has been obtained by the following techniques: TEM, HRTEM, SAED, ET, STEM-XED, SEM, XEDS, PXRD, SI-EELS, ATR-FTIR, Raman, H_2-TPR, CO-TPR, TPD-MS, N_2 physisorption, TGA, NAP-XPS, along with CO, C_3H_8 and soot catalytic oxidation tests. Moreover, statistical analysis of the TEM-derived particles size data for assessment of stability of the metal active phase as well as new approach for TOF calculation has been presented.

The proposed hydrothermal and wet chemical methods allow to obtain mixed-cerium oxide hierarchical particles having star-shaped and tube-like morphology and differing in texture. Particles are characterized by three levels of hierarchical organization, and each level of the hierarchical structure has its own functionality and is vulnerable to further modifications.

As synthesized hierarchical catalyst supports show the improved catalytic performance in CO, propane and soot oxidation when compared to non-hierarchical powdered nanoparticles. This effect has been explained by the phenomenon of the facilitated mass transfer and the increased active sites availability due to the introduced hierarchical architecture. The analysis of the temperature-dependent and dopant-dependent PXRD profiles had allowed to assess structural stability of the supports. Rietveld refinement of PXRD had allowed to get insight into microstructure of the materials. Also, the microscopic analysis and developing the temperature-dependent profiles of specific surface area based on N_2 physisorption study had allowed

to characterize morphological stability of the systems. Two dopant-dependent architecture transformation patterns induced by temperature has been observed, and the fine architecture of the ceria-based hierarchical particles is preserved up to 600°C that is particularly important in the low-temperature catalytic oxidation processes.

The knowledgeable control of the gold deposition onto hierarchical materials is reached by adjustment of the value of the surface coverage parameter in the urea deposition-precipitation method. Its calculation is based on the knowledge of the total surface area of the hierarchical catalyst support. Among three studied variables, i.e., the surface NO_3^- contamination, the curvature of the surface, and the ratio of the total support surface area to the molar content of gold precursor, the last one is decisive factor in growth of desired-size gold nanoparticles on ceria systems. The proposed gold decoration approach allows to produce variety of gold-decorated hierarchical catalysts.

The gold-decorated ceria hierarchical catalysts outperform non-hierarchical gold-decorated ceria nanocubes in propane and CO oxidation. Also, the process of doping the materials by Gd^{3+} further increase propane oxidation activity showing two-fold TOF increase. Moreover, such Gd^{3+}-doped catalyst shows four-fold TOF increase over the undoped non-hierarchical one, proving the synergistic effect of doping and structural hierarchy in propane oxidation. The increased activity in CO oxidation has been ascribed to the maximization of Au/ceria interface contact in hierarchical systems and the confinement of Au nanoparticles within pores of hierarchical support.

The texture differences between studied systems plays important role in catalytic performance for non-decorated catalytic supports. This effect is not observed for decorated systems; however, the presence of gold nanoparticles significantly improves selectivity of the propane oxidation. The stability of Au nanoparticles is increased by their confinement in the porous hierarchical structure when compared to the gold-decorated ceria nanocubes in which Au nanoparticles are present only at the surface.

To sum up, the introduction of hierarchy into ceria systems enhances catalytic activity in the studied combustion processes. The fine architecture of catalyst support is retained in low temperature regimes and the metallic active phase is stabilized due to confinement. However, pore geometry and size may restrict the growth of optimally sized Au NPs leading to activity decline, as demonstrated in CO oxidation reaction. Also, doping modifies particles architecture that influences the process of growth of Au nanoparticles. Thus, the knowledge of the material architecture and its temperature-dependent stability is necessary for the precise design of active multifunctional hierarchical catalysts.