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PhD dissertation abstract

„$M_xCe_{1-x}O_{2-y}$ nanoparticles (M – noble metal) deposited on functionalized γ-Al_2O_3 surface as active and stable oxidation catalysts”

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Catalytic oxidation reactions of the toxic by-products of working engines are very important from the ecological point of view. That is the reason, that the catalysts appropriate for such reactions are still intensively developed and investigated. Systems dedicated to such processes must be active and selective, durable at high temperatures, and should be cheap.

The main aim of this work was to obtain highly dispersed, thermally stable and highly active $M_xCe_{1-x}O_{2-y}$ catalysts (M – active noble metal) deposited on the γ-Al_2O_3 support surface.

The active $M_xCe_{1-x}O_{2-y}$ nanoparticles (M = Ru, Rh; $x \leq 0.15$), chemically and morphologically uniform, were synthesized by the reverse microemulsion method. To enhance the strength of the interaction between hydrophobic nanoparticles and hydrophilic γ-Al_2O_3 support (what is crucial to obtain a stable system), the support surface was functionalized with a monolayer of carboxylic acid (ca).

The obtained $M_xCe_{1-x}O_{2-y}$/γ-Al_2O_3(ca) systems were characterized using the following methods: ICP-OES, SEM-EDS – chemical composition, electron microscopy (HRTEM, STEM-HAADF/EDS) – morphology and microstructure, BET – texture (surface area and porosity), powder diffractometry and Raman spectroscopy – structure and phase composition, XPS spectroscopy – chemical state of the atoms present on the surface. Next, the thermal stability of the samples in the oxidizing and reducing (H_2) environment was investigated in the temperature range up to 1000°C. Samples' reducibility (oxygen donation capability) was analyzed by thermal-programmed reduction method and by the XPS spectroscopy with *in situ* thermal treatments. The catalytic activity was checked in two processes: soot oxidation (using thermogravimetry) and propane oxidation (using gas chromatography). After the catalytic reactions, the samples were investigated with microscopic and XRD methods to check their stability under the reaction conditions.

The results obtained confirmed, that the main aim of this work was attained. It has been proved, that deposition of the nanoparticles on γ-Al_2O_3 support functionalized with carboxylic acids significantly improved their dispersion and thermal stability, with the monolayer of decanoic acid (da) providing the best performance. In the $M_xCe_{1-x}O_{2-y}/\gamma$-$Al_2O_3$(da) (M = Ru, Rh, $x \leq 0.15$) samples, the ceria particles (2-3 nm in size) were uniformly dispersed on the support surface. Doping with rhodium and ruthenium ions, as well as deposition on the support, improved the thermal stability and reducibility of ceria particles in the range ≤ 500°C. The $M_xCe_{1-x}O_{2-y}/\gamma$-$Al_2O_3$(da) catalysts were catalytically active in soot and propane combustion processes, and were deactivation-resistant in the successive catalytic cycles. In particular, the $Ru_{0.05}Ce_{0.95}O_{2-y}/\gamma$-$Al_2O_3$(da) system was the most interesting, because of the lowest reaction temperatures (soot oxidation: $T_{50\%}$ = 480°C, propane oxidation: $T_{50\%}$ = 225°C) and very high specific reaction velocity for propane oxidation (0.62 $\mu mol \cdot g^{-1} \cdot s^{-1}$). These values are very good for the oxide catalysts with such low noble metal content (0.8 wt.% of Ru in the sample).