$M_xCe_{1-x}O_{2-y}$ nanoparticles (M = noble metal) deposited on functionalized alumina as highly active and stable combustion catalysts

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Abstract: New, effective method for the synthesis of highly dispersed ceria-based nanocatalysts (2-4 nm) was developed. In this method, the hydrophobic $M_xCe_{1-x}O_{2-y}$ nanoparticles were stabilized on the functionalized γ-Al_2O_3 surface. The morphology, texture, structure, thermal stability (oxidizing and reducing environment), as well as the chemical properties of these systems, were carefully studied. The catalytic activity of obtained systems in the successive soot and propane oxidation was also determined. Synthesized, uniform catalysts are very stable and show promising catalytic properties in the studied combustion processes.

Keywords: doped ceria, alumina functionalization, combustion catalysts

1. Introduction

Nanosized cerium oxide is a very important catalytic material, because of its unique properties [1]. However, ceria nanoparticles become unstable at high temperatures, during the catalytic processes. Two methods are known as efficient to prevent this phenomenon. The first one is doping of the cerium oxide with other metal ions, often active in the catalytic processes (e.g. noble metals), and the second is deposition of the oxide on a high surface area supports. In this work, these two methods were used simultaneously to maximize the dispersion, stability and catalytic activity of the ceria-based catalysts.

The reverse microemulsion synthesis is a simple way to obtain very small and uniform (<5 nm) pure or doped ceria nanoparticles [2,3]. Unfortunately, the particles synthesized using this method always have some amount of organic compounds adsorbed on the surface. It may prevent their effective deposition on popular hydrophilic supports (e.g., alumina), due to a strong tendency to agglomeration and further sintering at high temperatures. The interaction between the support and nanoparticles may be strengthened by proper functionalization of the support's surface [2,4] (Fig.1).

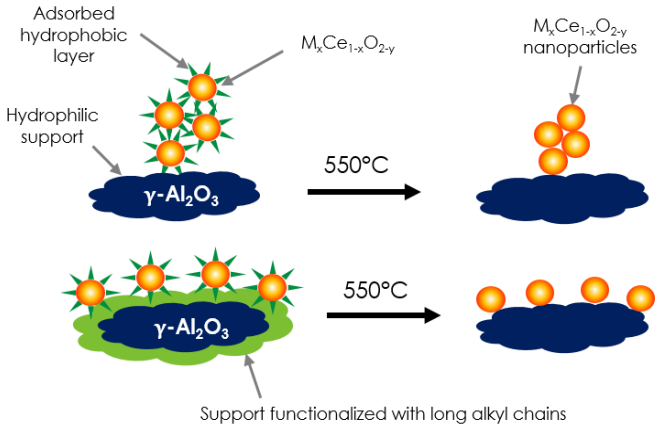

Figure 1. Scheme illustrating applied approach [2].

2. Experimental

Functionalization of the support (γ-Al_2O_3, S_{BET} = 102 m^2/g) was achieved by the chemical reactions of the coupling agents (decanoic acid or decyltriethoxysilane) [2,4] with the hydroxyl groups present on the surface of γ-Al_2O_3. $M_xCe_{1-x}O_{2-y}$ nanoparticles (M = Ru, Rh or Pd, $x \leq 0.15$) were synthesized by the reverse microemulsion method [2,3], and then were deposited by impregnation on the functionalized support, to obtain (M+Ce)/Al ratio equal to 1/10 [2]. After synthesis, the samples were dried and purified by heating in the air at 550˚C.

TGA and FTIR methods were used to study the interaction between the adsorbed organic layer and the support, and to estimate the concentration of the adsorbed organic compound on the support surface. The samples after $M_xCe_{1-x}O_{2-y}$ deposition and purification were studied using the FTIR, SEM-EDS, XRD and Raman spectroscopy methods to determine the purity, metals content and the structure of synthesized systems. Morphology and textural properties were studied by the HRTEM, STEM-HAADF and BET methods. *In situ* XPS was also used to study the changes of surface properties after thermal treatment in the oxidizing or reducing environment. The reducibility (H_2-TPR) and catalytic properties of the systems in the three successive cycles of the soot and propane oxidation were also determined.

3. Results and discussion

$M_xCe_{1-x}O_{2-y}$ nanoparticles obtained by the microemulsion method are very small (2-4 nm), uniform, and have narrow particle size distribution. After deposition on the functionalized alumina, the nanoparticles are homogeneously dispersed, mostly as single units, what improves the availability of the catalyst active surface (Fig. 2). Additionally, the obtained systems demonstrate high resistance to sintering up to 800˚C in oxidizing (air), as well as in the reducing (H_2) atmosphere.

The reducibility of the $M_xCe_{1-x}O_{2-y}$ nanoparticles deposited on the functionalized support is about 10% higher than for the particles deposited on bare alumina. The catalytic activity of such systems is also higher. For example, $Ru_{0.05}Ce_{0.95}O_{2-y}$ deposited on the alumina functionalized with a monolayer of decanoic acid shows the temperature of 50 % propane conversion (T_{50}) in total oxidation at 225˚C, while for the oxide deposited on bare alumina T_{50} = 236˚C.

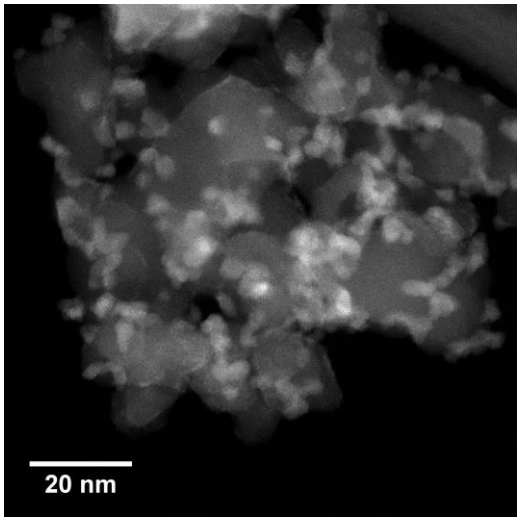

Figure 2. STEM-HAADF image of $Ru_xCe_{1-x}O_{2-y}$ nanoparticles deposited on alumina functionalized with the decanoic acid monolayer.

4. Conclusions

It has been shown, that the proposed, new approach to the synthesis of nanostructured ceria/alumina catalysts brings very promising results. Significant improvement in the dispersion and thermal stability of the active ceria particles correlate well with the catalytic properties. The systems show high activity in soot and propane oxidation, as well as enhanced stability in the successive catalytic cycles.

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References

1. T. Montini, M. Melchionna, M. Monai, P. Fornasiero, Chem. Rev. 116 (2016) 5987
2. K.A. Ledwa, L. Kępiński, Appl. Surf. Sci. 400 (2017) 212
3. M. Kurnatowska, W. Miśta, P. Mazur, L. Kępiński, Appl. Catal. B: Environm.148–149 (2014) 123
4. M. Cargnello, J.J. Delgado Jaén, J.C. Hernández Garrido, K. Bakhmutsky, T. Montini, J.J. Calvino-Gámez, R.J. Gorte, P. Fornasiero, Science 337 (2012) 713