In-situ XAS analysis of nanoshaped CuO/CeO$_2$ catalysts used for N$_2$O decomposition

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The goal of this research is to establish the working state and correlations between atomic structure and catalytic activity of nanoshaped CuO/CeO$_2$ catalysts used in N$_2$O decomposition reaction. The catalysts contain CuO nanoclusters dispersed over different CeO$_2$ morphologies: nano-rods and nano-cubes. N$_2$O is a side product of nitric and adipic acid production and a very potent greenhouse gas that is formed in amounts estimated at about 400 Mt/a of CO$_2$ equivalent. Consequently, the development of robust, active and selective catalysts for N$_2$O decomposition is of a great environmental and economical interest. CeO$_2$-based materials promoted by CuO represent a new class of catalysts that exhibit considerable activity in N$_2$O decomposition reaction between 300 and 500 °C [1-3], and are significantly cheaper and more efficient than Pt, Pd or Rh based catalysts.

In order to maximize the efficiency of the catalyst, the active site in this reaction needs to be identified and the mechanism clarified. In-situ Cu K-edge and Ce L3-edge XANES and EXAFS analysis was done on a set of CuO/CeO$_2$ catalysts with different ceria morphology (nano-cubes, nano-rods) and Cu loadings between 2 to 8 wt. %, during N$_2$O decomposition reaction, under controlled reaction conditions at 400 °C. The XAS spectra were measured in-situ, in a tubular reactor, filled with protective He atmosphere at 1 bar, first at RT, then during heating, and at final temperature of 400 °C, during catalytic reaction, when the catalyst was exposed to a small amount (0.2 vol%) of N$_2$O mixed with He.

The Cu K-edge and Ce L3-edge XANES and EXAFS analysis reveals changes in valence and local structure of Cu and Ce in the CuO/CeO$_2$ catalysts. In the initial state (in He at RT), copper is present in the form of CuO nanoparticles attached to the CeO$_2$ surface. After heating in He to 400 °C, partial (10%) reduction of Ce [Ce(IV)$\rightarrow$Ce(III)] is detected, significant part of Cu(II) is reduced to Cu(I) and Cu(0) species, and direct Cu-Cu bonds are formed. During catalytic N$_2$O decomposition at 400°C, all Ce(III) is oxidized back to Ce(VI), and a major part of Cu is oxidized back to Cu(II), with about 5% of Cu(I) remaining in equilibrium state. Observed structural and valence changes of copper strongly depend on its loading and CeO$_2$ morphology.

With systematic In-situ XAS analysis of different nanoshaped CuO/CeO$_2$ catalysts, we identified the structural characteristics and changes of Cu and Ce phases during catalytic N$_2$O decomposition reaction, which could lead to identification of the active catalytic site during the reaction and further improve the performance of these promising catalytic materials.

This research was supported by the Slovenian Research Agency (P1-0112 and P2-0150), and by the project CALIPSOplus under the Grant Agreement 730872 from the EU Framework Programme for Research and Innovation HORIZON 2020. We acknowledge access to the SR facilities of ELETTRA (beamline XAFS, pr. 20165258) and PETRAIII (beamline P65, pr. I-
20160044 EC) at DESY, a member of the Helmholtz Association (HGFW). We would like to thank Edmund Welter of PETRA III and Giuliana Aquilanti of ELETTRA for assistance during the experiment.