In-situ XAS analysis of nanoshaped CuO/CeO_2 catalysts used for N_2O 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_2O decomposition reaction. The catalysts contained CuO nanoclusters dispersed over different CeO_2 morphologies: nano-rods and nano-cubes. N_2O 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_2O 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_2O 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_2O 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_2O 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)→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_2O 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_2O 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.

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