

Abstract

The purpose of this dissertation work was to thoroughly investigate CuO-CeO₂ materials as catalysts for N₂O decomposition reaction. Solids were synthesized by advanced preparation techniques (glycothermal method, hydrothermal method, wet impregnation and precipitation) that resulted in high BET specific surface area, enhanced material reducibility, and nanocrystalline size of CuO and CeO₂ phases. CuO-CeO₂ materials were further thoroughly characterized by a variety of techniques: HRTEM, STEM-HAADF, STEM-EDX, STEM-EELS, SEM, N₂ physisorption, XRD, H₂-TPR, XPS, DR UV-Vis, DRIFTS, CO-TPD and dissociative N₂O adsorption. Catalytic N₂O decomposition was tested at ambient pressure in a fixed-bed quartz reactor in temperature range from 300 to 550 °C.

Results of N₂O decomposition emphasized a crucial role of BET specific surface area of CeO₂ support in the studied process. Different loadings of copper (4, 6, 10 and 15 wt. %) were supported by wet impregnation method. By increasing copper loading from 4 to 15 wt. %, the growth of CuO particles from highly dispersed Cu species, through small CuO clusters and finally to bulk CuO phase takes place. The highest activity was observed for the 10i-Cu/CeO₂-GT-160 material containing 10 wt. % of Cu, which has the highest amount of small CuO clusters. Further increase of Cu loading to 15 wt. % results in the formation of segregated and less active bulk CuO phase.

The role of CeO₂ morphology and exposed crystalline planes of ceria on catalytic properties of CuO-CeO₂ system in N₂O decomposition reaction was also investigated. Cu clusters populating easily reducible {100} and {110} planes of CeO₂, as preferentially exposed on CeO₂-R and CeO₂-C supports, exhibit normalized activity about 20 % higher, compared to copper on {111} planes of CeO₂-P. The most likely reasons for observed superior catalytic performance of a solid containing 4 wt. % of Cu on CeO₂-R support occur mainly from combination of more reactive {110} and {100} planes exposed on CeO₂ nanorods surface (which facilitates oxygen mobility and active sites regeneration) with high BET specific surface area of this support, the latter enabling higher active metal dispersion and formation of highly reducible copper defect sites.

Based on the data obtained from *ex situ*, *in situ* and *operando* examinations, the mechanism of catalytic N₂O decomposition over CuO-CeO₂ catalyst was proposed. N₂O adsorption and further decomposition through weakening of N-O bond, abstraction of oxygen and N₂ desorption takes place on binuclear Cu⁺ sites. Formed mono(oxo)dicopper [Cu-O-Cu]²⁺ species require an additional labile oxygen atom to complete the catalytic cycle and regenerate binuclear Cu⁺ sites through molecular oxygen desorption. The predominant source of labile oxygen is located on CeO₂, therefore, the Ce³⁺/Ce⁴⁺ redox pair actively participates in active binuclear Cu⁺ site regeneration through enhanced oxygen mobility. NO and H₂O have completely different inhibiting actions on the N₂O decomposition reaction. Water molecules strongly and dissociatively bind to oxygen vacancy sites of CeO₂ and block further oxygen transfer as well as regeneration of catalyst active sites. On the other hand, the effect of NO is expressed through competitive oxidation to NO₂, which consumes labile oxygen from CeO₂ and decelerates [Cu⁺ Cu⁺] active site regeneration.

Keywords: N₂O decomposition; CuO-CeO₂ catalyst; small CuO clusters; nanoshaped CeO₂; synergetic effect; *in situ* and *operando* mechanism examinations