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Ce- and Cu-modified OMS-2 catalysts for low-temperature CO oxidation

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The complete oxidation of VOCs and CO, that are hazardous to humans is effectively carried out using catalysts, main component of which are noble metals. However, due to their high cost, noble metal replacement with more accessible metals remains the issue of the day. For this reason, it becomes expedient to search for an alternative to platinum- and palladium-containing catalytic complexes for low-temperature CO oxidation process.

Manganese dioxide with the octahedral molecular sieves (OMS-2) structure is one of the promising catalysts for complete oxidation of VOCs and CO [1]. High mobility of lattice oxygen due to presence of defects of doubly and triply charged manganese ions in the framework leads to a sufficiently high activity of pure OMS-2 in these processes. Catalytic activity of OMS-2 can be increased by its modifying with cations of various metals (Ag^+ , Cu^{2+} , Fe^{3+} , Ce^{4+} , etc.) [2, 3]. Among metals of variable valence, cerium and copper are of the greatest interest due to peculiarities of the redox transitions $\text{Ce(III)} \rightleftharpoons \text{Ce(IV)}$ in CeO_x [4] and $\text{Cu(II)} \rightleftharpoons \text{Cu(I)}$ in Cu_xO [5].

Hydrothermal synthesis (HTS) is one of the methods to obtain cerium- and copper-containing OMS-2 (M-OMS-2, M = Ce, Cu) [6, 7]. The purpose of this work was to study effect of modifiers nature on the OMS-2 catalytic properties prepared by hydrothermal method in low-temperature CO oxidation, as well as to establish hydrothermal treatment conditions (pressure) effect on M-OMS-2 catalysts properties. Two series of catalysts #Ce and #Cu were prepared by HTS. For #Ce series, $\text{KMnO}_4 + \text{Mn(NO}_3)_2 + \text{Ce(NO}_3)_3 + \text{HNO}_3$ (120 °C, 24 h), for #Cu series – $\text{KMnO}_4 + \text{Cu(NO}_3)_2 + \text{NH}_4\text{Cl} + \text{HCl}$ (200 °C, 48 h). The synthesis pressure was controlled by filling autoclave with different amounts of mother liquid.

Results of elemental composition (XRF) and crystal structure (XRD and Raman spectroscopy) showed that there is a clear correlation between HTS pressure and amount of introduced modifier. Thus, pressure increase led to increase of metals content in the samples. In addition, higher pressure led to increased defectiveness of OMS-2 crystal lattice in copper series and almost complete rearrangement of OMS-2 structure in a cerium series. According to XRD and low-temperature nitrogen adsorption-desorption data (BET), samples obtained under more severe HTS conditions have higher phase dispersity and larger specific surface area of particles. Catalytic experiments on CO oxidation were carried out in a quartz reactor in temperature programming mode at molar ratio $\text{O}_2/\text{CO} = 8/1$ with GHSV of $90\,000\text{ h}^{-1}$. It was determined that in #Cu series, the catalyst synthesized at a higher pressure exhibits highest catalytic activity among the samples of both series. For both #Ce samples, catalytic properties are noticeably weaker, probably, due to lower content of OMS-2 phase. Further research will be focused on studying properties of Ce-OMS-2 catalysts prepared by modified procedure and properties of supported catalysts based on Cu-OMS-2.

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