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In situ XRD study of Mn-containing oxide catalysts

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Mn-containing oxides exhibit high catalytic activity in the reactions of total oxidation of hydrocarbons and CO. It was found that increase in the calcination temperature to 950–1000C lead to the growth of catalytic activity for MnOx-Al2O3 catalysts. In situ XRD studies of MnOx-Al2O3 catalysts shown that active component of the catalysts was formed via decomposition of the high-temperature precursor (cubic spinel Mn3-xAlxO4) followed by the appearance of aggregates consisting of imperfect Mn3O4+δ oxide and amorphous Mn-Al-O phase. The decomposition was accompanied by the formation of weakly bound oxygen which appears to be active in oxidation reactions. The structure of the active component was directly related to the composition of the high-temperature precursor - the higher the concentration of manganese cations are in the Mn3-xAlxO4 cubic spinel, the more Mn3O4 and weakly bound oxygen appear in the decomposition product [1]. When Al is replaced by Ga, a significant decrease in catalytic activity is observed.
To understand the origin of active component of Mn-containing catalysts, detailed mechanism of high-temperature precursor decomposition was investigated on the model systems – singlephase spinels Mn3-xAlxO4 and Mn3-xGaxO4. In situ XRD analysis indicates that during heating and cooling in the air both spinels decompose at the temperatures range of 400-800oC. This process is accompanied by partially oxidation of Mn2+ to Mn3+ and cation vacancies formation in the spinel structure that leads to decompomposition of initial spinet into two spinel-type phases. Under heating Mn3-xAlxO4 oxide decomposes according to nucleation ang grow mechanism due to the diffusion of Mn cations toward the surface and its segregation into nanoparticles of β-Mn3O4. Spinodal decomposition of initial spinel occurs during cooling caused by Mn3+ clustering. For Mn3-xGaxO4 spinel, products of decomposition are different during cooling and heating. Decomposition of Mn3-xGaxO4 leads to formation of two spinel structures with the samilar Mn/Ga ratio but different oxygen content. In situ XRD study shown that difference in catalytic activity in CO oxidation in MnOx-Al2O3 and MnOx-Ga2O3 catalysts is due to different mechanism of precursor decomposition.

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