The application of perovskite-type ferrites in the catalytic hydrogenation of carbon monooxide

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Studied in this paper layered oxides and solid solutions were synthesized by the high temperature solid-state reactions and by sol-gel technology. Among synthesized ferrites there are three-dimensional perovskites GdFeO₃, SrFeO₃₋ₓ, and two-dimensional perovskite-type layered structures GdSrFeO₄, Gd₂SrFe₂O₇, Gd₂₋ₓSrₓFe₂O₇ (x = 0.1–0.6), belonging to Ruddlesden-Popper phases Aₓ₋₁BₓO₃₋₁₋₁ (n = 1.2) that are built up from the blocks of perovskite layers with different thickness. X-ray powder diffraction confirmed the presence of single phase for samples obtained both by high temperature solid state reactions and by sol-gel technology as well. Scanning electron microscopy demonstrated a decrease in size of complex ferrite particles from 10 μm, obtained by ceramic technology, up to 200 nm, obtained by the sol-gel technology. Mössbauer spectroscopy showed the difference of electronic state of complex ferrite, prepared by ceramic technology (Fe³⁺) and oxides obtained by sol-gel technology (Fe³⁺ in the three different surrounding and Fe⁴⁺).

Reaction products of carbon monooxide hydrogenation are hydrocarbons C₁–C₅, the main of them are methane, ethylene, propylene. The greatest amount of olefins formed in the reaction was observed at the stoichiometric CO : H₂ ratio. It was found that perovskite catalytic activity (rate of product formation) in the catalytic hydrogenation of carbon monooxide increases in the series: SrFeO₃₋ₓ < GdSrFeO₄ < Gd₁.₆Sr₁.₄Fe₂O₇ < Gd₁ₓSr₁₋ₓFe₂O₇ < Gd₂SrFe₂O₇ < GdFeO₃, that is in correlation with the number of alternating perovskite layers in the ferrites structure varying from 1, 2 to ∞. However, samples with n = 2 showed the highest selectivity for ethylene and propylene (Fig).

The increase in strontium content in the layered Gd₂₋ₓSrₓFe₂O₇ oxides to x = 0.6 decreases the symmetry of Fe³⁺ ions and increases the number of oxygen vacancies, which affect the selectivity (its maximum value was observed at x = 0.3). It was suggested that heterovalent state of iron (Fe³⁺, Fe⁴⁺) favors the CO activation, which leads to C· and CHₓ· radicals formation. It was shown that under the influence of the reaction medium and the temperature a change in the active centers state occurs. Probably this change consists in partial iron reduction.

Higher catalytic performance of perovskite-like ferrites synthesized by sol-gel method can be related to their nanocrystalline state with a porous structure, as well as to iron heterovalent state.

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