

CATALYSIS, PHOTOCATALYSIS

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

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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 GdFeO_3 , SrFeO_{3+x} , and two-dimensional perovskite-type layered structures GdSrFeO_4 , $\text{Gd}_2\text{SrFe}_2\text{O}_7$, $\text{Gd}_{2-x}\text{Sr}_{1+x}\text{Fe}_2\text{O}_7$ ($x = 0.1-0.6$), belonging to Ruddlesden–Popper phases $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ ($n = 1, 2$) 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 (Fe^{+3}) and oxides obtained by sol-gel technology (Fe^{+3} in the three different surrounding and Fe^{+4}).

Reaction products of carbon monoxide hydrogenation are hydrocarbons $\text{C}_1 - \text{C}_5$, the main of them are methane, ethylene, propylene. The greatest amount of olefins formed in the reaction was observed at the stoichiometric $\text{CO} : \text{H}_2$ ratio. It was found that perovskite catalytic activity (rate of product formation) in the catalytic hydrogenation of carbon monoxide increases in the series: $\text{SrFeO}_{3-x} < \text{GdSrFeO}_4 < \text{Gd}_{1.6}\text{Sr}_{1.4}\text{Fe}_2\text{O}_7 < \text{Gd}_{1.8}\text{Sr}_{1.2}\text{Fe}_2\text{O}_7 < \text{Gd}_2\text{SrFe}_2\text{O}_7 < \text{GdFeO}_3$, 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).

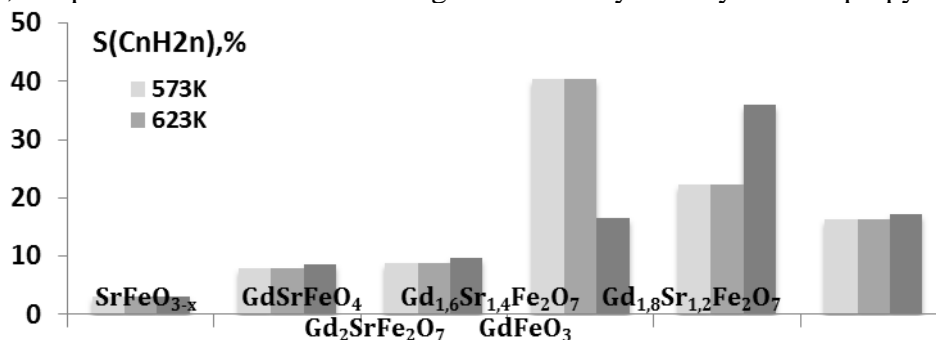


Fig. Total olefin selectivity during the reaction in a ratio of $\text{CO} : \text{H}_2 = 1 : 2$

The increase in strontium content in the layered $\text{Gd}_{2-x}\text{Sr}_{1+x}\text{Fe}_2\text{O}_7$ oxides to $x = 0.6$ decreases the symmetry of Fe^{+3} 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 (Fe^{3+} , Fe^{4+}) favors the CO activation, which leads to C^{\cdot} and CH_x^{\cdot} 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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