

Catalytic properties features of perovskite-type ferrites in dry (carbon dioxide) methane reforming

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The perovskite-type ferrites GdSrFeO_4 , $\text{Gd}_2\text{SrFe}_2\text{O}_7$, GdFeO_3 and solid solutions $\text{Gd}_{2-x}\text{Sr}_{1+x}\text{Fe}_2\text{O}_7$ ($x = 0.1-0.6$) were synthesized by the high temperature solid-state reactions and by sol-gel technology.

The complex physico-chemical investigations showed that synthesized catalysts are well-crystalline homogenous perovskite-type ferrites with different number of perovskite layers GdSrFeO_4 ($n = 1$), $\text{Gd}_2\text{SrFe}_2\text{O}_7$ ($n = 2$), GdFeO_3 ($n = \infty$) and solid solutions $\text{Gd}_{2-x}\text{Sr}_{1+x}\text{Fe}_2\text{O}_7$. Samples obtained by ceramic technology are in microcrystalline state and the iron atoms are found in Fe^{3+} state, which is magnetically ordered; oxides prepared by sol-gel technology are in nanocrystalline state and iron atoms are in a heterovalent state (Fe^{3+} coexists with Fe^{4+}) in three different symmetry fields.

The maximum conversion ($\alpha_{\text{CH}_4} = 37\%$, $\alpha_{\text{CO}_2} = 57\%$) and products formation rate ($W_{\text{H}_2} = 0.07 \text{ mol}/(\text{h}\cdot\text{g})$, $W_{\text{CO}} = 0.16 \text{ mol}/(\text{h}\cdot\text{g})$) were achieved by performing the reaction at an equimolar ratio of CH_4 and CO_2 . In spite of high temperatures the catalytic activity did not decrease during 40 hours. The catalyst demonstrated the high resistance to coke formation.

Among the reaction products the water was detected in almost all investigated ferrites, the quantity of generated carbon monoxide was 2–4 times greater than the quantity of hydrogen and carbon dioxide conversion was almost two times higher than methane conversion. Activation energies of CO formation and the corresponding values of $\ln k_0$ were less than the similar values of E_a and $\ln k_0$ for hydrogen. On the base of these data it was suggested that the DRM reaction was complicated by the reverse steam reforming of CO.

It was shown that an increase in the number of perovskite layers (n) in the complex oxides structure led to an increase in the catalytic activity. A partial substitution or complete replacement of Gd^{3+} ions by Sr^{2+} ions led to some reduction of activity. Among the systems of variable composition $\text{Gd}_{2-x}\text{Sr}_{1+x}\text{Fe}_2\text{O}_7$ obtained by the sol-gel technology samples had the highest activity at $x = 0.3$. The increase in strontium content led to lowering the symmetry of the surroundings of Fe^{3+} atoms and to occurrence of heterovalent state of iron atoms (Fe^{3+} , Fe^{4+}) with oxygen vacancies. It influenced an increase in the total surface acidity and catalytic activity in terms of CO_2 conversion. The catalytic activity increased in the row SrFeO_{3-x} ($n = \infty$) \approx GdSrFeO_4 ($n = 1$) \approx $\text{Gd}_{2-x}\text{Sr}_{1+x}\text{Fe}_2\text{O}_7$ ($n = 2$) $<$ GdFeO_3 (ceramic) ($n = \infty$) $<$ GdFeO_3 (sol-gel) ($n = \infty$). Higher catalytic properties of perovskite-type ferrites synthesized by sol-gel technology can be associated with their nanocrystalline state, a porous structure, as well as with heterovalent iron state and oxygen vacancies, which probably are favorable for the surface oxidation-reduction reactions and the process of CO_2 activation.

Acknowledgment. The reported study was supported by the Russian Foundation for Basic Research grant 14-03-00940.