Catalytic and Structural Properties of Co-Fe Systems in the Reaction of CO_2 Methanation

A. Dyachenko[1], M. Zhludenko[1], O. Bieda[1], S. Gaidai[1], M. Filonenko[2], O. Ischenko[1]

[1]*Taras Shevchenko Kyiv National University, 64 Volodymyrs'ka Str, 01601 Kyiv, Ukraine*
[2]*Dragomanov National Pedagogical University, 9 Pirogova Str, 01601 Kyiv, Ukraine*

Many research studies has been devoted to explore the process of carbon dioxide recycling into high energy content fuels or industrially important compounds. Among these, methanation processes have been proposed to be an effective method for the utilization of CO_2.

The catalytic properties of Co-Fe system were investigated in concentrations range of Co 0-100 wt. % in the reaction of CO_2 methanation. Synthesis of the catalysts was carried out by dissolving the proper amount of metal in nitric acid with subsequent precipitation by ammonia and subsequent drying, and reducing the obtained oxides to metals by the gas mixture (50 vol % H_2 - 50 vol % He) at atmospheric pressure, at the temperature of 300°C for 1 hour. The final step of the synthesis is a run of a catalyst in the reaction mixture (about 2 vol. % CO_2 - 55 vol. % H_2 – 43 vol. % He) - up to 350°C.

The catalytic activity of Co-Fe systems grows with the increasing of Co concentration: for the range of 0-10 Co wt. % - CH_4 yield is about 3 %; 14-50 wt% - CH_4 yield is increased up to 40%; 70-80 wt. % - CH_4 yield is about 60 % and 85-93 wt. % - CH_4 yield is reached its maximum amount (100 %). The sample of pure cobalt demonstrates 57 % of CH_4 yield.

Formation of carbon monoxide, as a co-product of CO_2 methanation, was observed for the samples with a low–middle Co wt.%. and also for the pure Co. The catalysts with 85-93 wt. % of Co demonstrated high activity with 100% CH_4 selectivity at the 150-300 ^{0}C. It could be explained by the heterogenous state of these samples.

XRD analysis of the samples with high Co wt.% ($Co_{75}Fe_{25}$, for example) before catalytic reaction has shown the presence of substituted spinel phase $Co_{3-x}Fe_xO_4$. After catalytic process α-Fe solid solution (cell parameter 2,842 Å) and α-Co solid solution (cell parameter 3,558 Å) were observed. Calculated crystallite size for these samples was 20 nm.

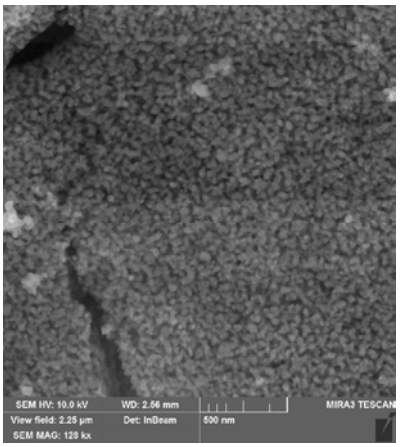

Fig. Scanning electron micrograph of $Co_{75}Fe_{25}$

Analysis with SEM-EDX method showed the next averaged elemental composition (at. %) of the $Co_{75}Fe_{25}$ sample after the catalytic run: Fe:Co = 27:73, (Fe+Co):O = 85:15 (which corresponds to $Me:Me_3O_4$ ratio of 95:5, indicating that sample is in the metallic state). These samples consist of spherical particles with a size of 15-20 nm (see figure).

It could be concluded that the high catalytic activity of Co-Fe materials enriched with Co is determined by specifics of their structure.