

The Impact of the Phase Composition of Ni - Fe Catalytic Systems on their Activity in the Reaction of CO₂ Methanation

R. Meshkini Far^{1,*}, A. Dyachenko¹, O. Bieda¹, M. Filonenko², O. Ischenko¹

¹Taras Shevchenko Kyiv National University, 64 Volodymyrs'ka Str, 01601 Kyiv, Ukraine

²National Pedagogical Dragomanov University, 9 Pirogova Str, 01601 Kyiv, Ukraine

* r.meshkinifar@gmail.com

The catalytic properties of Ni-Fe system were investigated in concentrations interval of 100 - 65 wt. % Ni. 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 % H₂ - 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. % CO₂ - 55 vol. % H₂ - 43 vol. % He). - up to 350°C.

As a result, the most active samples are in the concentration range of 60-70 wt. % Ni and 80-100 wt. % Ni. It is consistent with the literature data [1], because in 72-77 wt. % Ni we observe the formation of FeNi₃ intermetallide at 493 °C.

For the active Ni₈₀Fe₂₀ sample, a CO₂ conversion starts after 150 °C, while the maximum amount of CH₄ (60%) is formed at 300 °C. The amount of CO formed after 200 °C remains low and does not exceed 7%. For the inactive Ni₇₅Fe₂₅ sample, the transformations start at a higher temperature (250 °C), while the reaction products (basic CH₄ and secondary CO) are produced approximately in equal amounts (up to 8%) in the temperature range 350 - 370 °C.

Studying the structure of the samples by X-ray analysis before and after catalytic action showed that the samples before the recovery exist as NiO and Fe₃O₄ phases. After using samples in methanation reaction, the diffraction pattern shows a cubic face-centered crystalline phase with cell parameters a bit smaller than in γ -solution iron in nickel. It corresponds to the Fe-Ni intermetallides of variable composition with the same crystal structure as in Ni (see Table). For comparison: unit cell parameter of pure Ni is approximately 3.520, for pure Fe – approximately 3.568.

Table. XRD data of the Ni-Fe catalysts

Sample	T, °C	Phase	Cell parameter, Å	Crystallite size (Scherrer), nm
Ni ₈₀ Fe ₂₀ before reaction	300	NiO	4,182	5-7
	300	Fe ₃ O ₄	8.367	12-19
Ni ₈₀ Fe ₂₀ after reaction	300	Ni/Fe	3.537	9-13
	500	Ni/Fe	3.542	10-13
Ni ₇₅ Fe ₂₅ before reaction	300	NiO	4.186	5-8
	300	Fe ₂ O ₃	8.338	5-8
Ni ₇₅ Fe ₂₅ after reaction	300	Ni/Fe	3.561	18-23
	500	Ni/Fe	3.556	18-20

[1] N.V. Grum-Grjmailo, *Chemistry bounds in the metals alloys*, Moscow: NA of USSR, 1960 (in Russian).