Silica based heterometallic Ni, Co and Fe-containing nanocomposites in the reaction of CO_2 methanation

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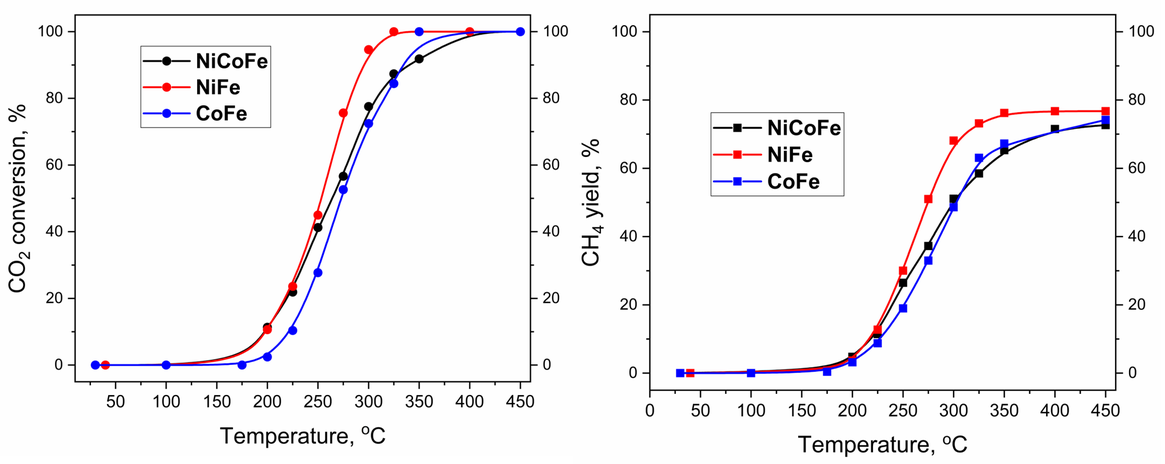
Object and Methods

For effective CO_2 methanation, heterometallic Ni, Co and Fe-containing nanocomposite catalysts have been prepared with solvate-stimulated modification, thermal decomposition, and chemical reduction stages using nanosilica A-300 as a carrier. The catalysts were characterized with nitrogen adsorption, X-ray powder diffraction and TPD MS surface analysis.

Catalityc activity



The conversion of CO_2 starts at about 200 C over all tested nanocomposites and reaches 100% at 325 °C for the sample Ni(80)Fe(200/SiO_2, 350 °C for Co(80)Fe(20)/SiO_2 and 450 °C for Ni(19)Co(77)Fe(4)/SiO_2. The amount of methane formed at the maximum CO_2 conversion temperature is 76% (325 °C) for NiFe/SiO_2, 68% (350 °C) CoFe/SiO_2 and 67% (450 °C) for NiCoFe/SiO_2. Chromatographic data do not indicate the formation of carbon monoxide.

Textural characteristic

The textural characteristics of nanocomposites (NCs) in the oxide and reduction forms are presented in the Table 1. The values of the specific surface area (SBET) and the specific pore volume (Vp) of all NCs in oxides form are decreased in comparison with the initial SiO2. The texture characteristics of NCs in metallic form are barely changed in comparison with their oxide's precursors. In addition, there is a significant increase in the contribution of mesopores to the total porosity while reducing the contribution of macropores. It can be assumed that the compaction of the carrier during the synthesis and preparing of NC is occurred. Texture analysis indicates the predominant macroporosity of the carrier, while for the synthesized NCs containing Co, Ni, and Fe in oxide and reduced form, mesoporosity predominates.

Table 1. Textural characteristics of nanocomposites in oxide and reduced forms.

Sample	S_{BET}, m^2/g	S_{micro}, m^2/g	S_{mezo}, m^2/g	S_{macro}, m^2/g	V_{micro}, cm^3/g	V_{mezo}, cm^3/g	V_{macro}, cm^3/g	V_{p}, cm^3/g	$R_{p,V}$ nm
SiO_2	271	24.4	239.6	6.5	0.025	0.501	0.149	0.674	17.4
$Ni_{19}Co_{77}Fe_4/SiO_2$ (o)	222	14.2	202.1	5.8	0.007	0.737	0.114	0.858	18.7
$Ni_{19}Co_{77}Fe_4/SiO_2$ (r)	218	9.4	201.8	7.2	0.005	0.732	0.142	0.879	19.2
$Ni_{80}Fe_{20}/SiO_2$ (o)	206	40.2	163.0	2.7	0.019	0.670	0.056	0.745	12.9
$Ni_{80}Fe_{20}/SiO_2$ (r)	187	37.6	146.3	2.8	0.019	0.650	0.056	0.726	12.0
$Co_{80}Fe_{20}/SiO_2$ (o)	187	44.7	139.5	2.7	0.023	0.709	0.058	0.790	13.5
$Co_{80}Fe_{20}/SiO_2$ (r)	186	43.6	140.0	2.4	0.022	0.757	0.056	0.835	13.4

X-Ray analysis

XRD patterns were collected for the NCs in the oxide and reduction form. As a result of synthesis, crystallites of the corresponding oxides are formed on the surface of silica. According to the Scherrer equation in each sample it was possible to estimate the size of only the dominant oxide (Table 2). The fine-crystalline phase of the dominant metal was detected on XRD patterns of nanocomposite catalysts after their exposure in the reaction of CO_2 methanation.

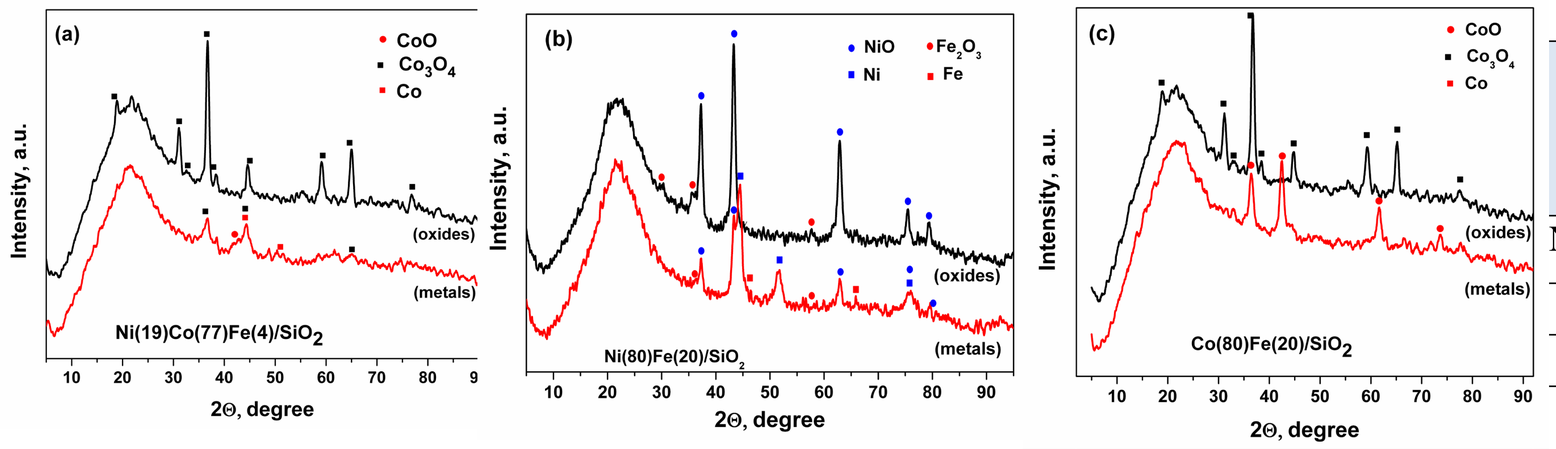


Table 2. Crystallite size of oxide nanocomposites

NC	Phase	(hkl)	2Θ, degree	Crystallite size (Scherrer), nm
$Ni(19)Co(77)Fe(4)/SiO_2$	Co_3O_4	311	36,7	22
$Ni(80)Fe(20)/SiO_2$	NiO	200	43,6	20
$Co(80)Fe(20)/SiO_2$	Co_3O_4	311	36,8	29

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