

Proceedings of the International Conference on Oxide Materials for Electronic Engineering, May 29–June 2, 2017, Lviv

Catalytic Properties of Ni–Fe Systems in the Reaction of CO₂ Methanation at Atmospheric Pressure

R. MESHKINI–FAR^a, A. DYACHENKO^a, S. GAIDAI^a, O. BIEDA^{a,*}, M. FILONENKO^b
AND O. ISCHENKO^a

^aTaras Shevchenko National University of Kyiv, 64/13 Volodymyrs'ka Str., Kyiv, 01601, Ukraine

^bNational Pedagogical Dragomanov University, 9 Pirogova Str., Kyiv, 01601, Ukraine

Catalytic activity, phase composition, and morphology of binary Ni–Fe metallic systems in CO₂ hydrogenation were investigated. High methane yield was detected in the region of high Ni content, except the sample with 75% of Ni which has shown a sharp drop in activity. By means of scanning electron microscopy-energy dispersive X-ray and X-ray diffraction methods the differences in surface structuring of active (Ni₈₀Fe₂₀) and inactive (Ni₇₅Fe₂₅) catalysts were revealed. High methane yield for the former might be explained by defective porous superficial layer of catalyst grains, whereby for the latter the specific surface is diminished due to sintering.

DOI: [10.12693/APhysPolA.133.1088](https://doi.org/10.12693/APhysPolA.133.1088)

PACS/topics: 82.30.Hk, 82.30.–b, 82.20.–w

1. Introduction

Methanation of CO₂, on the one hand, is an ecologically important reaction, and on the other hand it allows to obtain the important fuel — methane. The problem of development of highly active catalyst which is industrially usable is not solved still [1–3]. This reaction was studied over the supported catalysts, with active phases based on Ni, Fe, Co, Cu, Ru, Rh, and oxide supports like SiO₂, Al₂O₃, ZrO₂, TiO₂, and CeO₂ [4, 5]. The literature data show that one of the most promising catalytic activities was shown by Ni-based systems [6, 7].

One of the disadvantages for pure Ni-based catalysts is their low thermal stability, which can be solved by addition of iron to the catalyst. Fe is known to be a structure-modifying agent that increases the thermal stability of catalysts. From the other side, Fe can promote the adsorption and the dissociation of CO₂, thus promoting the catalytic activity [8].

Structure and catalytic properties of bulk Ni–Fe systems with different Ni:Fe ratio were investigated in this work.

2. Experimental

Synthesis of catalysts was performed as follows. The solution of calculated quantities of metal nitrates was obtained by dissolution of metals in concentrated nitric acid. Hydroxides were precipitated from it by excess of ammonia. The precipitate was dried in air for 4 h at 110 °C and subsequently for 5 h at 300 °C. The pre-reduction of the samples was performed in flow of 50% H₂ in helium at 4 h at 300 °C.

Specific surface (S_{sp}) was measured by the method of argon low temperature adsorption.

X-ray diffraction (XRD) analysis was performed using MiniFlex 600 diffractometer (Rigaku, Japan) with Cu K_{α} radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ region of 10–100°. Crystallite sizes were estimated from reflex broadening using the Scherrer formula [9].

The morphology of samples and the chemical analysis were studied on the Tescan Mira 3 LMU scanning electron microscope (SEM) equipped with energy-dispersive X-ray (EDX) detector (Oxford INCA).

Catalytic activity of the samples was studied in 2% CO₂ + 55% H₂ mixture (balanced with He), at total flow of 100 cm³/min and sample mass of 1 g. The reactor with inner diameter of 8 mm contained a 1 mm glass tube with a thermocouple inside, put in the catalyst bed. The pre-treatment of sample in the reaction mixture was made by gradual increase of the catalyst temperature to 450 °C over 3 h. The exiting gaseous mixture was analyzed by gas chromatograph with a thermal conductivity detector (Shimadzu GC-2014, 1 m length packed column, molecular sieves 5A).

To compare the catalytic activities for the series, the temperature of 325 °C at which the most active samples reached a steady maximum of activity was chosen.

3. Results and discussion

For the different Ni:Fe ratios, all the investigated samples in the Ni-rich region (Ni:Fe = 100:0–65:35) have shown the significant catalytic activity in the temperature region of 220–450 °C except the sample Ni:Fe=75:25 which has shown poor activity. The highest values of CO₂ conversion were demonstrated by all the active samples above 300 °C, with low dependence of it upon further temperature increase up to 500 °C. The absence of activity for 75:25 component ratio can be explained by formation of FeNi₃ phase which is presumably inactive in CO₂ methanation. According to Ni–Fe phase diagram [10], this compound is formed as a single phase in the region of 72–77% Ni and is stable below 493 °C.

*corresponding author; e-mail: a_byeda@chem.knu.ua

For the samples with Ni content other than 75% the catalytic activity is high (see Fig. 1), which according to mentioned phase diagram corresponds to the existence of two metallic phases, namely FeNi₃ intermetallide and excess solid solutions which are either rich with Ni or with Fe. Thus, it can be assumed that the catalytic activity is connected to the existence of phase boundaries between different phases. It is a known fact that heterogeneous mixtures generally have higher catalytic activity than homogeneous ones.

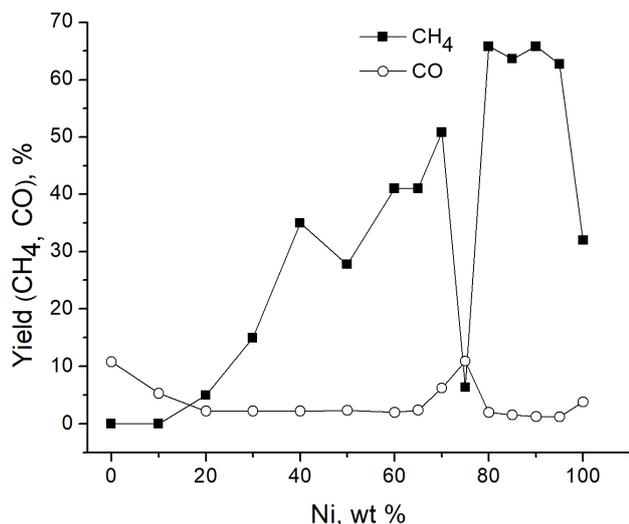


Fig. 1. CH₄ and CO yield versus Ni content at 325 °C.

Studying the structure of the samples by X-ray analysis before and after catalytic reaction (for the reduced samples see patterns in Fig. 2) showed that the samples before the reduction exist as NiO and Fe₃O₄ phases.

After using samples in methanation reaction, the diffraction pattern for them shows a face-centered cubic (fcc) crystalline phase with cell parameters of 3.54–3.56 Å, which are intermediate between that for pure fcc Ni (3.520 Å) and for pure fcc Fe (3.568 Å), see Table I. This indicates the existence of different fcc phases (including FeNi₃) and/or solid Fe–Ni solutions. Presence of small quantities of NiO on the diffractograms can be explained by surface oxidation upon the exposition of sample to air before the XRD analysis, as samples are presumably fully reduced at the time of catalytic run. Small size of crystallites indicates the small size of grains of metal in the samples.

SEM studies of the Ni₈₀Fe₂₀ and Ni₇₅Fe₂₅ (active and inactive ones) revealed the significant difference in the structure (Fig. 3).

The active Ni₈₀Fe₂₀ with $S_{sp} = 16 \text{ m}^2/\text{g}$ exists as big agglomerates (up to tenths of micrometers) sintered from particles of defective rounded shape, with diameter about 80–100 nm, with 100–1000 nm (Fig. 3a,b) pores in the structure.

Ni₇₅Fe₂₅ sample shows (Fig. 3c) big agglomerates with more or less flat surface, without big pores. This is easily explained because the size of metallic nanoparticles

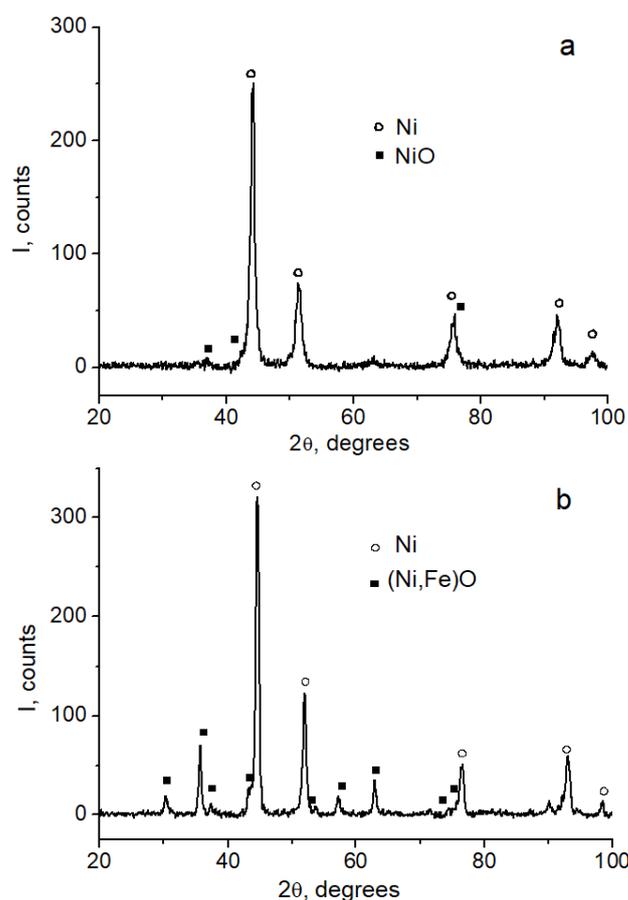


Fig. 2. XRD of Ni₇₅Fe₂₅ (a) and Ni₈₀Fe₂₀ (b) after catalysis at 300 °C.

XRD data of the Ni–Fe catalysts.

TABLE I

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

(Fig. 3d) is much lower in this sample, *ca.* 20–40 nm. The particles are sintered into dense structure with low microporosity. It is noteworthy that the specific surface of Ni₇₅Fe₂₅ is much lower ($S_{sp} = 2 \text{ m}^2/\text{g}$) than for Ni₈₀Fe₂₀, and this obviously has the influence on its low catalytic activity.

SEM-EDX analysis of the elemental composition was performed in several points for each sample. For Ni₈₀Fe₂₀ sample the content of oxygen was found to be as low as 1%, supporting the suggestion that the oxygen was only

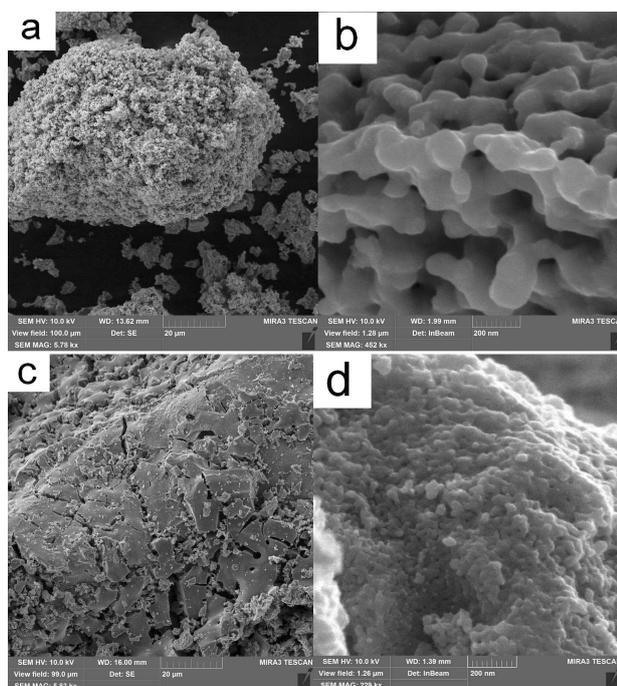


Fig. 3. Micrographs of $\text{Ni}_{80}\text{Fe}_{20}$ ((a) 20 μm , (b) 200 nm) and $\text{Ni}_{75}\text{Fe}_{25}$ ((c) 20 μm , (d) 200 nm).

superficial. The Ni:Fe ratio for all regions of analysis (see Table II) was similar to that given by synthesis, signifying the even distribution of metals in the volume of the sample.

EDX analysis of $\text{Ni}_{80}\text{Fe}_{20}$ sample.

TABLE II

Region #	Content [at.%]			Ni : Fe ratio	
	Fe	Ni	O	By analysis	By synthesis
1	23.43	75.79	0.78	76.38:23.62	80:20
2	21.01	78.18	0.81	78.83:26.87	
3	26.58	72.82	0.60	73.26:26.74	
4	19.54	79.19	1.27	80.21:19.79	

EDX analysis of $\text{Ni}_{75}\text{Fe}_{25}$ sample.

TABLE III

Region #	Content [at.%]			Ni : Fe ratio	
	Fe	Ni	O	By analysis	By synthesis
1	31.82	36.74	31.45	53.60:46.40	75:25
2	22.03	72.71	5.26	76.75:23.25	
3	51.59	24.49	23.92	32.19:67.81	
4	28.30	65.60	6.09	69.86:30.14	
5	25.21	53.15	21.64	67.83:32.17	

For $\text{Ni}_{75}\text{Fe}_{25}$ the elemental composition in different points (see Table III), however, differs dramatically, with Ni:Fe ratio being from 1:2 to 2:1 in spite of the expected stable 3:1, signifying the enrichment of the surface layer of agglomerates with Fe. Moreover, the oxygen content is high, and correlated with found Fe content — the richer is the area with Fe, the greater content of O is found. This is controversial to the suggestion that only the FeNi_3 phase is present in this sample. However, according to the XRD data (Fig. 2a), only an fcc metallic

phase is found. Thus, it can be concluded that surface of grains of $\text{Ni}_{75}\text{Fe}_{25}$ catalyst is enriched with iron, which readily oxidizes at ambient conditions after the catalytic test and forms the superficial FeO_x layer. This dramatic difference in the volume distribution of metals between $\text{Ni}_{80}\text{Fe}_{20}$ and $\text{Ni}_{75}\text{Fe}_{25}$ is surprising, and the factors that influenced it are unclear at the moment. Moreover, since $\text{Ni}_{70}\text{Fe}_{30}$ demonstrated high catalytic activity again just like $\text{Ni}_{80}\text{Fe}_{20}$, it can possibly signify that $\text{Ni}_{75}\text{Fe}_{25}$ is a synthetic outlier. However, all the samples were obtained by exactly the same method in exactly the same conditions, and $\text{Ni}_{75}\text{Fe}_{25}$ synthesis was repeated again. The second sample has shown the same low activity as the original one. Hence, further investigations of the causes of uniqueness of catalyst with this exact metal ratio will be continued. The working hypothesis can be formulated as follows: FeNi_3 phase which is formed at the pre-reduction of the stoichiometric mixture of oxides possesses low activity as a catalyst itself, and tends to sinter after formation and give a catalyst with low specific surface.

4. Conclusions

A series of binary Ni-Fe metallic catalysts for CO_2 hydrogenation were obtained and tested at atmospheric pressure. All the samples rich with Ni show the significant catalytic activity which is much higher than that for pure Ni, except the sample with Ni:Fe=75:25 which has shown low activity and surface enriched with iron, in contrary to the previous suggestions about the formation of single FeNi_3 compound. It can be suggested that stoichiometric mixture tends to form a single phase at the pre-reduction, which is readily sintered further.

References

- [1] S. Hwang, J. Lee, U.G. Hong, J. Lee, J.G. Seo, J.H. Baik, D.J. Koh, H. Lim, I.K. Song, *J. Industr. Eng. Chem.* **19**, 2016 (2013).
- [2] G. Garbarino, P. Riani, L. Magistri, G. Buska, *Int. J. Hydr. Energy* **39**, 11557 (2014).
- [3] W. Wang, Sh. Wang, X. Ma, J. Gong, *Chem. Soc. Rev.* **40**, 3703 (2011).
- [4] D. Aaron, C. Tsouris, *Separat. Sci. Technol.* **40**, 321 (2005).
- [5] M.L. Cubeiro, H. Morales, M.R. Goldwasser, M.J. Perez-Zurita, F. Gonzalez-Jimenez, *Appl. Catal. A Gen.* **189**, 87 (1999).
- [6] Z. Kowalczyk, K. Stolecki, W. Raróg-Pilecka, E. Miśkiewicz, E. Wilczkowska, Z. Karpiński, *Appl. Catal. A Gen.* **342**, 35 (2008).
- [7] S. Abate, Ch. Mebrahtu, E. Giglio, F. Deorsola, S. Bensaid, S. Perathoner, R. Pirone, G. Senti, *Industr. Eng. Chem. Res.* **55**, 4451 (2016).
- [8] S. Hwang, U.G. Hong, J. Lee, J.H. Baik, D.J. Koh, H. Lim, I.K. Song, *Catal. Lett.* **142**, 860 (2012).
- [9] A. Monshi, M.R. Foroughi, R.M. Monshi, *World J. Nano Sci. Eng.* **2**, 154 (2012).
- [10] C.-W. Yang, D.B. Williams, J.I. Goldstein, *J. Phase Equilib.* **17**, 552 (1996).