

## SURFACE SPECIES INVESTIGATION OF Ni-Fe CATALYSTS OF CO<sub>2</sub> HYDROGENATION BY TD MS ANALYSIS

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*The condition of Ni-Fe catalysts' surface was investigated by the method of thermally programmed desorption with mass spectral analysis of desorbed particles (TD MS). TD spectra indicated the desorption of CO<sub>2</sub> ( $m/z = 44$ ), CO ( $m/z = 28$ ) and H<sub>2</sub>O ( $m/z = 18$ ) particles from the surface of samples with high and low catalytic activity in the reaction of CO<sub>2</sub> hydrogenation. Intermediate compounds CHO\*, CH<sub>2</sub>O\* were not observed in the TD profiles for all investigated catalysts. On the basis of catalytic performance results and thermal desorption data it can be suggested that process of CO<sub>2</sub> hydrogenation over Ni-Fe catalysts proceeds via direct hydrogenation of CO<sub>2</sub> to CH<sub>4</sub>.*

**Keywords:** Ni-Fe catalysts; CO<sub>2</sub> hydrogenation; catalytic activity; TD-MS analysis.

### Introduction

Carbon dioxide is a component widely existing in nature, but is regarded as an air pollutant, so it's needed to reduce the concentration of it in the nature. One of the obvious ways is to reduce pollution by CO<sub>2</sub> by means of the catalytic conversion of waste CO<sub>2</sub> emitted from, i.e., enterprise. Among of various methods, hydrogenation of carbon dioxide not only reduces carbon dioxide but also produces methane. Methane is the cleanest fossil fuel for electricity production [1 – 3]. Therefore, developing a catalyst that can improve activity, selectivity, economic and environmental requirements to industrialize the process for carbon dioxide hydrogenation is very important. Carbon dioxide molecule is kinetically and thermodynamically stable so the reaction of carbon dioxide hydrogenation is endothermic and calls for use of efficient catalysts to obtain high methane yield. This reaction has been studied over metal catalysts Ni, Fe, Co, Cu, Ru, and Rh that were supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, and CeO<sub>2</sub> metal oxides [3 – 7]. According to the literature, among these catalysts, the iron unlike the nickel has low activity in catalysis of the hydrogenation of CO<sub>2</sub> [8, 9], although a computational screening study based on density functional theory calculations has indicated that Ni-Fe catalysts could be more active than the pure Ni catalyst [10]. So, the catalytic properties of bimetallic Ni-Fe catalyst seem to be promising for using in environmentally safe process.

It is important to study the surface properties of Ni-Fe system for understanding of mechanism for CO<sub>2</sub> hydrogenation. In the previous work we investigated catalytic structure and showed the efficiency of using Ni-Fe catalysts in the CO<sub>2</sub> hydrogenation [11, 12]. In this work, surface species adsorption properties of Ni-Fe catalysts of CO<sub>2</sub> hydrogenation with different Ni:Fe ratio were investigated by TD MS analysis.

### Experimental

Synthesis of Ni-Fe catalysts in the range of 0 – 100 mass % of nickel, with respective addition of iron was carried out by dissolving the proper amount of metals in nitric acid with subsequent

precipitation by ammonia and drying in air for 4 hours at 300 °C. Prior to the catalytic reaction, each catalyst was reduced with a mixed stream of hydrogen and helium at a ratio of 50:50 vol. % at 300 °C for 4 hours. The optimal temperature for catalysts reduction was determined with thermogravimetric method [11].

Methane production test for bimetallic Ni-Fe catalysts was carried out in a continuous flow fixed-bed reactor with 8 mm in diameter. Carbon dioxide and hydrogen were continuously fed into the reactor balanced with helium. Feed composition was fixed at 2 vol. % of CO<sub>2</sub>, 55 vol. % of H<sub>2</sub> and 43 vol. % of He. The reaction was carried out at the pressure of 0,1 MPa in the temperature range of 30–500 °C. Reaction products were analyzed by an online gas chromatograph (Shimadzu GC-2014) equipped with a thermal conductivity detector (TCD) using a molecular sieves packed column for the separation of CO<sub>2</sub>, CO, CH<sub>4</sub>. To compare the catalytic activities for the series, we chose the temperature of 350 °C at which the most active samples reached a steady maximum of activity.

To study the desorbed particles from the surface of the catalyst a quadrupole mass spectrometer (MS) MX 7304 (“Selmi”, Ukraine) was used. The reduced catalyst was exposed under hydrogenation experiment conditions. The catalyst then was cooled to ambient temperature, and then heated linearly in vacuum at 14°/min up to 800 °C while the effluent stream was analyzed for m/z range of 10 – 100 by on-line MS MX7304A.

## Results and discussion

In the first part of our research, the catalytic behavior of bimetallic Ni-Fe catalysts in the range of concentrations from 0 to 100 % of nickel was studied [11]. The chemical composition and the results of the catalytic performance tests of the Ni-Fe catalysts under investigation are summarized in Table 1. Based on the results, the higher yield of CH<sub>4</sub> is observed at the temperature of 300–400 °C and it drops sharply at the temperature of 500 °C. The maximum CH<sub>4</sub> yields reaching 66.5 % were obtained at 350 °C for Ni<sub>80</sub>Fe<sub>20</sub> catalyst.

**Table 1.** The chemical composition and the results of catalytic performance test of Ni-Fe catalysts in the reaction of CO<sub>2</sub> hydrogenation

Sample		Reaction product	Yield, %				Sample		Reaction product	Yield, %			
mass % Ni	Fe		Temperature, °C				mass % Ni	Fe		Temperature, °C			
			300	350	400	500			300	350	400	500	
100	0	CH <sub>4</sub>	32	53.8	60.1	5.2	70	30	CH <sub>4</sub>	50.8	62	59.1	2
		CO	3.8	7	8.5	5			CO	6.2	4.1	4.9	5
90	10	CH <sub>4</sub>	65.8	65	60.4	7.9	50	50	CH <sub>4</sub>	27.8	40	41.4	7.4
		CO	1.3	1.4	1.4	1.3			CO	2.3	2.6	3.9	2.4
80	20	<b>CH<sub>4</sub></b>	<b>65.8</b>	<b>66.5</b>	<b>61.9</b>	<b>9.9</b>	20	80	CH <sub>4</sub>	15	35	15	4.5
		<b>CO</b>	<b>2</b>	<b>1.5</b>	<b>1.5</b>	<b>1.5</b>			CO	2.2	2.5	4.5	2.3
75	25	<b>CH<sub>4</sub></b>	<b>6.4</b>	<b>15</b>	<b>1.1</b>	<b>2.1</b>	0	100	CH <sub>4</sub>	0	0	1.5	6.6
		<b>CO</b>	<b>10.9</b>	<b>18</b>	<b>9.1</b>	<b>1.3</b>			CO	10.8	36.4	34.8	4.2

Apart from methane, carbon monoxide is observed as a reaction product in all cases. However, a CO production increase is associated with a methane production decrease. The highest yield of CH<sub>4</sub> was observed for the sample with 80 mass. % of Ni (Ni<sub>80</sub>Fe<sub>20</sub>), whereas for the sample with 75 mass. % of Ni (Ni<sub>75</sub>Fe<sub>25</sub>) catalytic performance drops sharply and reaches a relative minimum in CO<sub>2</sub> hydrogenation. While all other catalysts always show higher selectivity

to CH<sub>4</sub> than to CO, Ni<sub>75</sub>Fe<sub>25</sub> catalyst gives rise to higher selectivity for CO than for CH<sub>4</sub>. According to the studies of Fe-Ni alloys [13], when nickel content is in a concentration range of less than 72 % or more than 77 %, two-phase regions with  $\gamma$ -phase and intermetallic FeNi<sub>3</sub> are observed. But in the composition range 72–77 % of nickel, there is only FeNi<sub>3</sub> compound in the form of a homogeneous solid solution [13].

The observed effect of the catalytic activity increase (increase of methane yield at the same conditions) in the Ni<sub>80</sub>Fe<sub>20</sub> sample is related to the presence of phase interfaces in the catalytic systems. It is known that the catalytic activity of mixtures depends on the phase composition. The heterogeneous mixtures have higher catalytic activity than homogeneous phase due to interface properties. Moreover, the catalytic properties of the mixtures depend on the presence of the organized structures and chemical compounds in them. The formation of intermetallic compounds reduces the catalytic activity of the system [14].

Among the studied samples we have selected pure nickel, pure iron, the best (Ni<sub>80</sub>Fe<sub>20</sub>) and the worst (Ni<sub>75</sub>Fe<sub>25</sub>) catalysts. Desorption of particles from the surface active site of these samples was investigated by TD MS analysis. For Ni<sub>80</sub>Fe<sub>20</sub>, Ni<sub>75</sub>Fe<sub>25</sub> and Ni samples methane and carbon monoxide are the products of hydrogenation process, while in the case of pure Fe sample methane is not formed at all, and the only carbon monoxide is product of CO<sub>2</sub> and H<sub>2</sub> interaction.

The experimental data shows that the desorption peaks of CO, CO<sub>2</sub> and H<sub>2</sub>O are symmetrical (Fig.). It suggests that CO, CO<sub>2</sub>, and H<sub>2</sub>O molecules are formed near the surface by recombination of the corresponding atoms. It means that the carbon, oxygen and hydrogen atoms exist separately on the catalyst surface [15]. Generally, if a process undergoes a formal kinetics

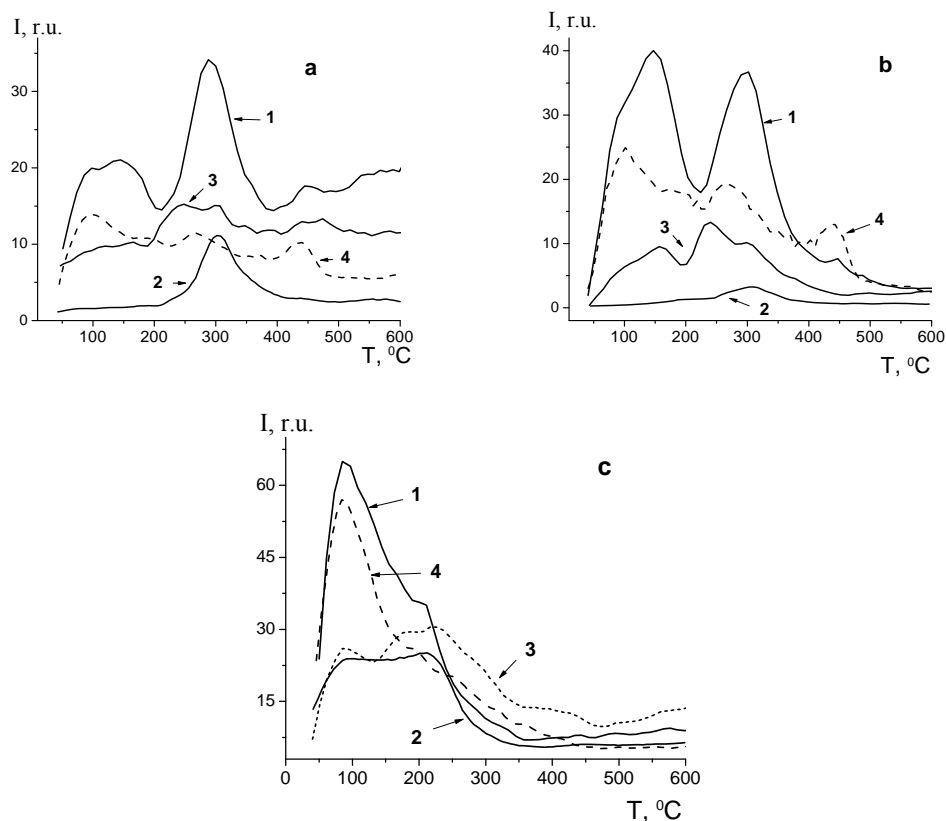
$$-\frac{d\theta}{dt} = k\theta^n,$$

where  $\theta$  is surface coverage and  $n$  is the kinetic order of the process, in the case of linear heating the peak (rate versus temperature) must be asymmetrical for  $n = 1$  and nearly symmetrical for  $n = 2$  [15]. The symmetrical form of all desorption peaks, even for CO, suggests the second order of desorption, thus, the recombination of separate atoms into the CO molecule.

TD data of the maximum peak temperature ( $T_m$ ) can be divided into three ranges (see Table 2): 80–180°C – particles weakly bound to the surface; 200 – 350°C – particles with desorption temperature close to reaction of hydrogenation temperature; 400–500°C – particles firmly bound to catalyst surface.

**Table 2.** The peaks temperature ( $T_m$ ) of desorbed particles from the samples' surface

Sample	Particle		
	CO (m/z = 28)	CO <sub>2</sub> (m/z = 44)	H <sub>2</sub> O (m/z = 18)
Ni <sub>80</sub> Fe <sub>20</sub>	100, 140, 290, 440	90, 145, 300, 440	90, 210
Ni <sub>75</sub> Fe <sub>25</sub>	300	300	90, 210
Ni	245, 300, 440	100, 150, 240, 300	90, 175, 230
Fe	100, 260, 440	100, 270, 440	90



**Fig.** TD profile of CO (a), CO<sub>2</sub> (b) and H<sub>2</sub>O particles for the samples: 1 – Ni<sub>80</sub>Fe<sub>20</sub>, 2 – Ni<sub>75</sub>Fe<sub>25</sub>, 3 – Ni and 4 – Fe.

TD spectra of CO and CO<sub>2</sub> from surface of Ni<sub>75</sub>Fe<sub>25</sub> catalyst has the only maximum at 300 °C, but for surface of Ni<sub>80</sub>Fe<sub>20</sub> there are peaks in the range of 90–440 °C. TD maximum at 130°C can be attributed to the weak physical adsorption.

TD spectra of CO from surface of inactive Ni<sub>75</sub>Fe<sub>25</sub> catalyst has the greater intensity than for CO<sub>2</sub>, in good agreement with the results of the catalytic performance (Table 1) which show that between all of the tested catalysts the lowest yield of CH<sub>4</sub> (6 %) and the highest yield of CO (11 %) at 300 °C (see Table 1) are observed for Ni<sub>75</sub>Fe<sub>25</sub> catalyst. Thus, it can be assumed that CO<sub>2</sub>, which is adsorbed on the active site, breaks up into CO and O. CO is firmly chemisorbed on the active site and inhibits the progress of CO<sub>2</sub> hydrogenation process. In contrast, the intensity of the TD spectra of CO<sub>2</sub> and CO from surface of active Ni<sub>80</sub>Fe<sub>20</sub> catalyst is almost the same at 300°C. Based on these results, we can conclude that process of CO<sub>2</sub> hydrogenation over Ni-Fe catalysts proceeds via direct hydrogenation of CO<sub>2</sub> to CH<sub>4</sub>. The chemisorbed CO<sub>2</sub> on the catalyst active centers, which are located at the interface boundary, is dissociated completely to C\*<sub>ads</sub> and O\*<sub>ads</sub>. Then adsorbed carbon quickly reacts with available hydrogen (adsorbed on the catalysts surface or from the gas phase) and CH<sub>4</sub> is desorbed in result. Water is formed by the similar mechanism from the adsorbed oxygen and available hydrogen. The limiting step in this process is the formation of H<sub>2</sub>O from the adsorbed OH\*<sub>ads</sub> group with adsorbed H\*<sub>ads</sub>. The formation of CH<sub>4</sub> is fast, so in the TD spectra CH\*<sub>ads</sub>, CH<sub>2</sub>\*<sub>ads</sub>, CH<sub>3</sub>\*<sub>ads</sub> intermediates are not recorded. TD MS analysis of surface species in active and inactive samples showed that CO<sub>2</sub> hydrogenation process onto Ni-Fe catalysts has the mechanism that does not involve oxygen-containing intermediates. If the

process proceeds via an intermediate CO, the TD spectra of intermediates, namely CHO\*, CH<sub>2</sub>O\* would have been recorded. The data shown in Fig. 1c indicate that there is no peak of water on the TD spectrum from surfaces of Ni<sub>80</sub>Fe<sub>20</sub> and Ni<sub>75</sub>Fe<sub>25</sub> at 300 °C, and this fact confirms that the oxygen is generated by dissociation of CO<sub>2</sub> rather than by dissociation of water at this temperature. These results are in good agreement with the mechanism that was reported in the previous literature [16].

From the results of catalytic performance and thermal desorption one can suggest the following mechanism for the reaction of CO<sub>2</sub> hydrogenation over Ni-Fe catalysts:

1. CO<sub>2</sub> + [ ] → [O.....C.....O]
2. [O.....C.....O] → [C] + 2[O]
3. H<sub>2</sub> + 2 [ ] → 2[H]
4. [C] + [H] → [CH] + [ ]
5. [CH] + [H] → [CH<sub>2</sub>] + [ ]
6. [CH<sub>2</sub>] + [H] → [CH<sub>3</sub>] + [ ]
7. [CH<sub>3</sub>] + [H] → CH<sub>4</sub> + 2[ ]
8. [O] + [H] → [OH] + [ ]
9. [OH] + [H] → H<sub>2</sub>O + 2[ ],

where [ ] – free space on the surface of the catalyst; formation of methane (steps 4 – 7) is fast and formation of water (steps 8–9) is slow.

## Conclusion

A series of the Ni-Fe catalysts were prepared by the co-precipitation of the hydroxides. All samples were reduced in the same conditions, and they were applied to the methane production from CO<sub>2</sub> and H<sub>2</sub>. Among the tested catalysts, Ni<sub>80</sub>Fe<sub>20</sub> showed the best catalytic performance in terms of conversion of CO<sub>2</sub> and yield for CH<sub>4</sub>. It has been shown that the conversion of CO<sub>2</sub> to methane is significantly increased over the bimetallic nickel-iron catalysts compared to the pure nickel catalyst. The experiments illustrate that the best catalysts have a Ni/Fe ratio above 4. TD MS analysis of active and inactive samples' surface showed that CO<sub>2</sub> hydrogenation process over Ni-Fe catalysts has the mechanism that does not involve oxygen-containing intermediates. Based on results of catalytic performance and thermal desorption one can suggest that process of CO<sub>2</sub> hydrogenation over Ni-Fe catalysts proceeds via direct hydrogenation of C atom (formed in CO<sub>2</sub> dissociation) to CH<sub>4</sub>.

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## **ДОСЛІДЖЕННЯ ЧАСТИНОК НА ПОВЕРХНІ Ni-Fe КАТАЛІЗАТОРІВ ГІДРОГЕНУВАННЯ CO<sub>2</sub> МЕТОДОМ ТД МС АНАЛІЗУ**

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*Методом термопрограмованої десорбційної мас-спектрометрії (ТД МС) досліджено стан поверхні Ni-Fe каталізаторів реакції гідрогенування CO<sub>2</sub>. На ТД спектрах зареєстровано десорбцію частинок CO<sub>2</sub> (m/z = 44), CO (m/z = 28) та H<sub>2</sub>O (m/z = 18) з поверхні зразків, що проявили високу та низьку каталітичну активність у реакції гідрогенування CO<sub>2</sub>. Проміжні сполуки CNO\*, CH<sub>2</sub>O\* не спостерігалися на ТД профілях для всіх досліджуваних зразків. На основі результатів каталітичної активності та термічної десорбції зроблено припущення, що процес конверсії CO<sub>2</sub> в метан на Ni-Fe каталізаторах відбувається через пряме гідрогенування карбону без утворення проміжних кисневмісних сполук.*

# ИССЛЕДОВАНИЕ ЧАСТИЦ НА ПОВЕРХНОСТИ Ni-Fe КАТАЛИЗАТОРОВ ГИДРОГЕНИРОВАНИЯ CO<sub>2</sub> МЕТОДОМ ТД МС АНАЛИЗА

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Методом термoproграммированной десорбционной масс-спектрометрии (ТД МС) исследовано состояние поверхности Ni-Fe катализаторов реакции гидрогенирования CO<sub>2</sub>. По ТД спектрах зарегистрировано десорбцию частичек CO<sub>2</sub> ( $m/z = 44$ ), CO ( $m/z = 28$ ) та H<sub>2</sub>O ( $m/z = 18$ ) с поверхности образцов, которые показали высокую и низкую активность в реакции гидрогенирования CO<sub>2</sub>. Образование промежуточных соединений CNO\*, CH<sub>2</sub>O\* не наблюдалось ни для одного из исследованных образцов. Из полученных результатов по изучению каталитической активности и термической десорбции сделано предположение, что процесс конверсии CO<sub>2</sub> в метан на Ni-Fe катализаторах происходит путем прямого гидрогенирования атомарного углерода без образования промежуточных кислородсодержащих соединений.