

# Polyoxide Catalysts for Oxidation of Methane

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**Abstract**—The effect of modifying additives of copper, neodymium and molybdenum on acidity and dispersity of nickel catalyst was studied by temperature-programmed desorption of ammonia and scanning electron microscopy methods. Their activity in the reaction of partial oxidation of methane (POM) and dry reforming of methane (DRM) were measured. The NiCuNdMo/Al<sub>2</sub>O<sub>3</sub>HZSM-5 was found to be the best catalyst. The introduction of molybdenum into the composition of NiCuNd/Al<sub>2</sub>O<sub>3</sub>HZSM-5 catalyst was determined to increase general acidity of the catalyst from  $26.71 \cdot 10^{-4}$  to  $29.46 \cdot 10^{-4}$  mol/gKt, and also it increases the dispersion of the active phases of the catalysts surface. This data of change positively affects the activity of the catalyst in POM reaction, concentration of hydrogen in the reaction product compared with NiCuNd/Al<sub>2</sub>O<sub>3</sub>HZSM-5 increases from 60 to 70 vol. %. The investigation of the catalytic activity of NiCuNdMo/Al<sub>2</sub>O<sub>3</sub>HZSM-5 catalyst in the reaction of DRM has shown that equilibrium yield of H<sub>2</sub> and CO is observed in the temperature range of 650-900 °C. The main product in the process of oxidative conversion of methane by oxygen is hydrogen, whereas in the process of oxidative conversion of methane by carbon dioxide synthesis gas is formed

**Index Terms**—Nickel-containing catalyst, methane, oxygen, carbon dioxide, hydrogen.

## I. INTRODUCTION

Natural gas is the most abundant source for obtaining energy and new chemical compounds: synthesis-gas, hydrogen, alkenes etc.

Synthesis-gas is the source for preparing of oxygenates (methanol, dimethyl ether etc.), and also for preparing liquid and solid hydrocarbons using the Fischer-Tropsch method [1]-[5]. Hydrogen, which is included in the composition of synthesis-gas, finds an application in a number of large-scale chemical processes (ammonia production, hydrosulfination of fuels, hydrocracking of oil sources, isomerization of n-alkanes etc.). At the same time hydrogen may find the wide application as an alternative motor fuel in the future [6]-[11].

There are several methods of catalytic processing of methane to synthesis-gas and hydrogen – steam reforming, partial oxidation and dry reforming of methane.

Steam reforming is the main industrial process of preparing synthesis-gas and hydrogen from methane on nickel-containing catalysts. The disadvantage of this method

is the high ratio of H<sub>2</sub>: CO in the prepared mixture, which is not suitable Fischer-Tropsch synthesis to be obtain dimethyl ether, methanol. The other disadvantage of using this method is that a large amount of CO<sub>2</sub> is formed in the mixture and coke formation on the catalysts [12]-[16].

Partial oxidation of methane (POM) into synthesis-gas is widely studied both concerning the development of catalysts, and the technology of process. At present there are developed efficient catalysts based on noble metals, and also Ni, Co – perovskites, containing REE (rare earth elements), promoted by Pt, Fe, Cu [17]-[23]. Although desirable ratio H<sub>2</sub>/CO (1:1) can be obtained using the method of POM, this process requires special measures of precaution because of the danger of explosion, and also it is being tested at the laboratory at this moment.

Dry reforming of methane solves the problem of utilization of simultaneously two greenhouse gases methane and carbon dioxide in synthesis-gas [24]-[27]. DRM leads to the preparation of synthesis gas (H<sub>2</sub>/CO) of composition 1:1, which is convenient, in particular, for the preparation of polycarbonates or formaldehyde. Also application of DRM has been proved in cases, where there is a necessity in processing of the natural gas containing carbon dioxide. Such of a low grade natural gas requires the separation to make it a commercial product, at the same time carbon dioxide which is a pollutant in this case can be used as a reagent for the conversion of natural gas. The process of DRM has not found yet a wide distribution in industry, as the main problem is the coke formation of catalyst. The main efforts in this field are directed towards the development of the stable catalysts maintaining coke formation [28].

In present work the nickel-containing catalysts are studied in the processes of the oxidation of methane by oxygen and carbon dioxide.

## II. EXPERIMENTAL

Experiments to test the efficiency of the catalysts in the process of POM and DRM were carried out using an automated flow catalytic setup (FCS - 1). The setup was composed of three main parts – preparation of initial gaseous mixture, catalytic quartz reactor of a flow type and chromatographer for the analysis of gases (Fig. 1). The reactor was a quartz tube of 25 cm in length, and its internal diameter was 9-9.5 mm. During the experiments, the reactor was vertically placed in an electric furnace, and the reactant mixture was supplied to the reactor from the top. After the reactant was passed through the catalyst bed, the converted gas left the reactor through a hole in the lower part of the reactor. Control of the composition and the expense of initial reacting mixtures, regulation of temperatures in the reactor, evaporator, and start of analysis were carried out using the

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software. The amounts of the reaction products were determined by an absolute calibration method using a gas chromatograph equipped with a thermal conductivity detector (HROMOS GH-1000). The separation of each component in a product was carried out by three columns with a (length of 2 m, internal diameter of 3 mm) filled with zeolite NaX (2 columns) and porapak-T, using argon as the carrier gas.



Fig. 1. Flow catalytic setup.

Conditions of the processes were 0.1 MPa, the temperature range used by us was 650-900 °C, ratio of methane: oxygen 2:1, ratio of methane : carbon dioxide was varied within the limits of 0.25-4.

The study of the morphology of the surface of polyoxide catalysts was carried out by scanning electron microscopy method using a scanning electronic microscope (Quanta 200i 3D). The formation of acidic centers on the surface of the catalysts was determined by thermoprogrammed desorption of ammonia method using a universal sorption gas analyzer (USGA -101).

The catalysts were prepared by the impregnation of  $\text{Al}_2\text{O}_3\text{HZSM-5}$  ( $S_{\text{BET}} = 308.6 \text{ m}^2/\text{g}$ ) with a solutions of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , drying at 350 °C (for 2 hours), and then calcination at 500 °C for three hours.

### III. RESULTS AND DISCUSSION

In the process of the oxidation of methane by oxygen the activities of the series of nickel-containing catalysts supported on various carriers ( $\text{Al}_2\text{O}_3\text{ZSM-5}$ , Siral-40, CaX,  $\text{Al}_2\text{O}_3$ , Siral-20, Siral-10 and AlSi) were studied in temperatures range of 600-900°C. Obtained results are shown, that according to the yield of products the catalyst supported on  $\text{Al}_2\text{O}_3\text{HZSM-5}$  synthetic zeolite is the optimal.

TABLE I: EFFECT OF CATALYST COMPOSITION ON THE CONCENTRATION OF PRODUCTS

CATALYSTS	THE COMPOSITION OF GASEOUS PRODUCTS, VOL. %						
	CH <sub>4</sub>	H <sub>2</sub>	CO	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	CO <sub>2</sub>	O <sub>2</sub>
1 WT% Ni/ $\text{Al}_2\text{O}_3\text{ZSM-5}$	25	20	5	3.5	-	16	2
2 WT% NiCo/ $\text{Al}_2\text{O}_3\text{ZSM-5}$	22.6	28	11	6.3	3	14.6	0.6
2 WT% NiMn/ $\text{Al}_2\text{O}_3\text{ZSM-5}$	11	35	20	7	5	20	0.2
2 WT% NiCr/ $\text{Al}_2\text{O}_3\text{ZSM-5}$	16	37	13	5	4	25	-
2 WT% NiCu/ $\text{Al}_2\text{O}_3\text{ZSM-5}$	4.9	60	15	13	7	9.1	-

The effect of the oxides of variable valence (Mn, Co, Cu and Cr) on activity of Ni/ $\text{Al}_2\text{O}_3\text{ZSM-5}$  catalyst is studied. The results are shown in Table I.

Prepared catalysts were tested in oxidative transformation of methane at  $\text{CH}_4 : \text{O}_2 = 2.0 : 1.$ ,  $V = 3900 \text{ h}^{-1}$ . Table I shows, that the most optimal composition for two-component catalyst is the NiCu, the concentration of hydrogen in the reaction products is 60 vol.%. According to the literature data addition of rare-earth elements increases selectivity and activity of oxide catalysts in the process of POM [29].

The most optimal composition of NiCu/ $\text{Al}_2\text{O}_3\text{ZSM-5}$  catalyst was modified by adding the salts of rare-earth elements - Ce, La, Nd and Sm. Obtained results were shown in Table II. Promoting effect is produced by the addition of neodymium, where the concentration in reaction products of hydrogen increases to 68 vol.%.

TABLE II: INFLUENCE OF THE ADDITIVES OF RARE EARTH ELEMENTS ON CONCENTRATION OF PRODUCTS

CATALYSTS	THE COMPOSITION OF GASEOUS PRODUCTS, VOL. %						
	CH <sub>4</sub>	H <sub>2</sub>	CO	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	CO <sub>2</sub>	O <sub>2</sub>
3 WT% NiCuLa/ $\text{Al}_2\text{O}_3\text{ZSM-5}$	9	53	15	6	7	12	-
3 WT% NiCuSm/ $\text{Al}_2\text{O}_3\text{ZSM-5}$	25	27	14	9	4	20	0.3
3 WT% NiCuCe/ $\text{Al}_2\text{O}_3\text{ZSM-5}$	16	48	12	11	5	8	-
3 WT% NiCuNd/ $\text{Al}_2\text{O}_3\text{ZSM-5}$	2	68	18	-	10	2	-

According to the literature data [30], [31], the activity of catalyst increases with the increase of the number of acidic centers of the catalyst. We have found out that the increase of the complexity of the composition of three-component catalyst by the addition of the W and Mo oxides of the acidic characters, leads to the increase of hydrogen to 69 vol. % in case of tungsten. When adding molybdenum to the composition of NiCuNd/ $\text{Al}_2\text{O}_3\text{HZSM-5}$  the catalyst the concentration of hydrogen in the reaction products increases to 70 vol. %.

Thus, among the studied nickel-containing catalysts the highest activity exhibits in the process of oxidative conversion of methane in the presence of oxygen by NiCuNd/ $\text{Al}_2\text{O}_3\text{HZSM-5}$  catalyst.

Dry reforming of methane is studied on NiCuNdMo/ $\text{Al}_2\text{O}_3\text{HZSM-5}$  catalyst. The effect of the temperature of reaction on the activity of the catalyst is studied in the temperature range of 600-900°C at volume rate of  $3600 \text{ h}^{-1}$  and ratio of  $\text{CH}_4/\text{CO}_2 = 2$  (Fig. 2). As shows figure, with the increase of the temperature of the process of DRM from 600 to 900 °C the conversion of methane increases from 4 % to 78 % and the conversion of carbon dioxide increases from 5 to 98 %. At 600 °C in the reaction products concentration of H<sub>2</sub> (1.6 vol. %) and CO (6.9 vol.%) is observed. With increasing the process temperature from 600 to 900 °C the concentration of hydrogen increase to 49.8 vol.% and carbon monoxide to 45.0 vol.% in the reaction products. The obtained experimental data show, that there is observed the equilibrium yield of H<sub>2</sub> and CO on this catalyst

in the whole temperature range, similar data were obtained in work [32] on the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. The Fig. 2 shows that at T = 850 °C the concentrations of hydrogen and carbon monoxide become stable and reach a plateau, related to this study, so effect of ratio CH<sub>4</sub>/CO<sub>2</sub> within the range from 0.5 to 4 on the activity of catalyst was studied at the given temperature. The results of the effects of the ratio of CH<sub>4</sub>/CO<sub>2</sub> on the activity of NiCuNdMo/Al<sub>2</sub>O<sub>3</sub> HZSM-5 are shown in Fig. 3.

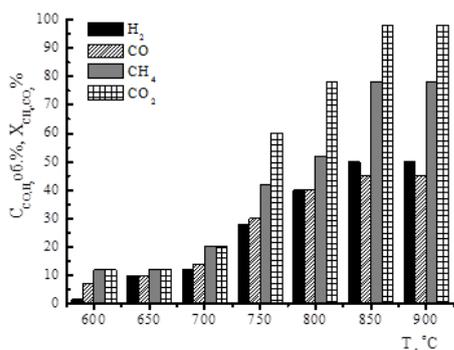


Fig. 2. Effect of the reaction temperature on the conversion of CH<sub>4</sub> and CO<sub>2</sub> and concentration of main products.

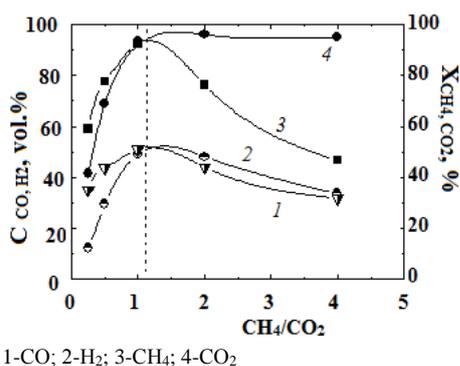


Fig. 3. Effect of ratio of CH<sub>4</sub>/CO<sub>2</sub> on the activity of catalyst at 850°C.

The figure shows, that the dependence of the conversion of methane on the ratio of CH<sub>4</sub>/CO<sub>2</sub> has an extremal character with the maximum located in the region close to 1 and corresponds to 92.6 %. The curves of the target products of the reaction of hydrogen and carbon monoxide also possess maximal values (H<sub>2</sub> - 49 vol. % and CO - 50 vol. %) at the ratio of CH<sub>4</sub>/CO<sub>2</sub> close to 1. Increase of the value of the ratio leads to sufficiently rapid decreasing of methane conversion. In contrast to methane, conversion of carbon dioxide at the ratio close to 1 reaches 92.3% with a further reaching of the plateau values of the order of 96%. According to [33] carbon dioxide interact with hydrogen which is spent on formation of water and carbon.

One may state, that the most optimal ratio for the process of DRM is the stoichiometric ratio, under which the maximal concentration of synthesis gas and the highest conversion of initial reagents are achieved.

The effect of volume rate on the process of DRM is studied in the range of from 1800 to 14400 h<sup>-1</sup>. Obtained results (Fig. 4) show, that, with increasing volume rate from 1800 to 3600 h<sup>-1</sup> both the conversion and the yields of reaction products are at the similar level.

Thus, the most optimal technological parameters of the

preparation of synthesis gas in the process of DRM on NiCuNdMo/Al<sub>2</sub>O<sub>3</sub>HZSM-5 catalyst are: temperature - 850 °C, volume rate - 3600 h<sup>-1</sup> and ratio CH<sub>4</sub>: CO<sub>2</sub>- 1:1.

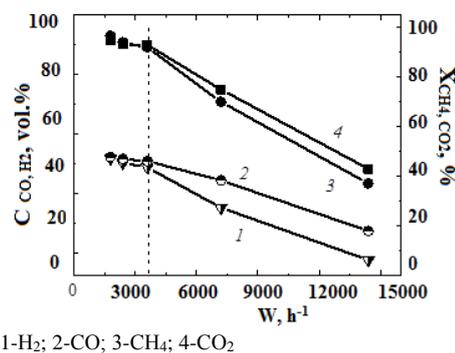


Fig. 4. Effect of volume rate on the activity of catalyst.

It should be noted, that in the process of oxidative conversion of methane by oxygen the main product is the hydrogen, while in the process of dry reforming of methane the synthesis gas is formed.

For the disclosure of the reason of activity of modified catalysts they were studied with the application of the methods of scanning electronic microscopy (SEM) and thermoprogrammed desorption of ammonia (TPD).

The morphology of the surface of the catalysts depending on the introduction of modified additives was studied using the method of scanning electronic microscopy, obtained results are shown in Fig. 5.

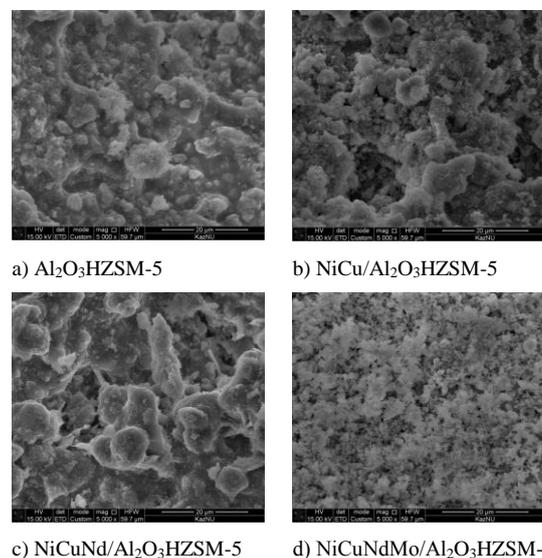


Fig. 5. Microphotographs of catalysts.

Fig. 5 shows that the increase of the complexity of the composition of polyoxide catalyst leads to the increase of the dispersion of active phases of the surface, which positively affects the catalytic activity of catalysts.

Formation of acidic centers on the surface of catalysts was studied using the thermoprogrammed desorption of ammonia (TPD), obtained data are shown in Table III. According to the obtained data in Table III shows that ammonia desorption from the catalysts surface proceeds at three temperature ranges on all catalysts. Within the temperature range of 50-200°C ammonia is desorbed from the centers of an average

strength, from strong acidic centers - higher than 300°C, which corresponds to the data of works [34], [35]. With increasing composition of the catalyst (NiCuNdMo/Al<sub>2</sub>O<sub>3</sub>ZSM-5) the amount of the catalyst desorbed from average strength acidic centers increases from 6.32·10<sup>-4</sup> to 9.78·10<sup>-4</sup> compared to Ni/Al<sub>2</sub>O<sub>3</sub>ZSM-5, and the amount of ammonia desorbed from weak acidic centers from 7.22·10<sup>-4</sup> to 14.87·10<sup>-4</sup> mol/g Cat increases too.

TABLE III: RESULTS OF THERMO-PROGRAMMED DESORPTION OF AMMONIA FROM CATALYSTS

Sample	T <sub>max</sub> , °C	Amount of adsorbed ammonia	
		mol/g Cat	total amount mol/g Cat
1 wt% Ni/ Al <sub>2</sub> O <sub>3</sub> ZSM-5	130	7.22·10 <sup>-4</sup>	18.09·10 <sup>-4</sup>
	230	6.32·10 <sup>-4</sup>	
	620	4.55·10 <sup>-4</sup>	
2 wt% NiCu/ Al <sub>2</sub> O <sub>3</sub> ZSM-5	160	9.02·10 <sup>-4</sup>	22.36·10 <sup>-4</sup>
	280	8.13·10 <sup>-4</sup>	
	660	5.21·10 <sup>-4</sup>	
3 wt% NiCuNd/ Al <sub>2</sub> O <sub>3</sub> ZSM-5	135	12.35·10 <sup>-4</sup>	26.71·10 <sup>-4</sup>
	275	8.55·10 <sup>-4</sup>	
	650	5.81·10 <sup>-4</sup>	
4 wt% NiCuNdMo/ Al <sub>2</sub> O <sub>3</sub> ZSM-5	120	14.87·10 <sup>-4</sup>	29.46·10 <sup>-4</sup>
	250	9.78·10 <sup>-4</sup>	
	640	4.81·10 <sup>-4</sup>	

#### IV. CONCLUSION

Thus, in the reaction of the oxidation of methane by oxygen the nickel containing catalysts supported on various carriers such as Al<sub>2</sub>O<sub>3</sub>ZSM-5, Siral-40, CaX, Al<sub>2</sub>O<sub>3</sub>, Siral-20, Siral-10 and AlSi were studied. The highest activity was exhibited by the catalyst Ni/Al<sub>2</sub>O<sub>3</sub>ZSM-5, while the concentration of hydrogen in the reaction products is 20 vol. %. The increase of activity of Ni/Al<sub>2</sub>O<sub>3</sub>ZSM-5 catalyst was found out to be adding observed when of metal oxides of varied valency (Mn, Co, Cu and Cr). The most optimal composition is NiCu, the concentration of hydrogen in the reaction of product is 60 vol. %. Addition of rare-earth elements to the composition of NiCu/Al<sub>2</sub>O<sub>3</sub>ZSM-5 changes the activity of the catalyst. The highest promoting effect is shown by neodymium, the concentration of hydrogen in the reaction products increases to 68 vol.%. The increase of complexity of composition NiCuNd/Al<sub>2</sub>O<sub>3</sub>HZSM-5 catalyst by the addition of W and Mo oxides of acidic character, leads to the increase of yield of hydrogen to 69 and 70 vol.%, correspondingly.

With introducing the molybdenum into composition of NiCuNd/Al<sub>2</sub>O<sub>3</sub>HZSM-5 catalyst of hydrogen concentration in the reaction products increases from 60 to 70 vol.% which is explained by increase in acidity of the catalyst 26.71·10<sup>-4</sup> to 29.46·10<sup>-4</sup> mol / g Cat and also by increases of dispersion of the active phase of the catalyst surface.

The study of the process DRM on the NiCuNdMo/Al<sub>2</sub>O<sub>3</sub>HZSM-5 catalyst has shown, that the optimal conditions of the process are the ratio CH<sub>4</sub>:CO<sub>2</sub> – 1:1, T - 850 °C, W - 3600 h<sup>-1</sup> while the concentration of formed hydrogen is 48.9 vol.%, the concentration of carbon monoxide is 50.9 vol.%, conversion of methane – 92.6 % and conversion of carbon dioxide – 93.2 %. It was found that the equilibrium yield of H<sub>2</sub> and CO is observed in the process of DRM in the range of temperatures from 650 to 900 °C.

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