

Nanodispersed Ni-Catalysts with Additives in Partial Oxidation of Methane

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Abstract

Catalytic activity of Ni-Zn-surface-skeletal catalysts modified by Rh, Au, Ti, Mo and W in the reaction of methane partial oxidation has been studied. Influence of catalysts of conditions preparation on its catalytic activity was researched. It was shown that introduction of additives in Ni-Zn catalysts promote to increasing of activity in the process of methane partial oxidation to synthesis-gas and thermostability of skeletal Ni-catalysts thanks to the change of its faseous composition and the predominance of reduced form of Ni in catalysts structure.

Introduction

There is considerable interest in the production of synthesis gas by partial oxidaiton of methane [1]. The number of studies relating to this route exceeds that of methane coupling or condensation route [2]. Nickel catalysts are predominantly employed for the partial oxidation to synthesis gas [3]. However, considerable carbon deposition on the nickel metallic surfaces has been considered to be a limitation of this process. In order to minimize carbon deposition on the active metallic surfaces, it is preferable to deposit metals which can form the carbides like Mo and W [4,5] The purpose of this communication is therefore to study the effect of addition of Mo or W to Ni-skeletal system and to evaluate the activity of the resulting systems for the conversion of methane to synthesis gas.

Skeletal catalysts have high specific surface and high-dispersed Ni-particles due to original method of Ni-foil surface loosening [6]. This method includes the following operations: -pretreatment of Ni-foil, -electroplating of Ni foil surface by Zn, -thermal treatment at 350-700°C in inert atmosphere to obtain thermo diffuse Ni-Zn alloy, -leaching of Zn from the alloy (by KOH), -drying and removal of

pyrophority, -introduction of modifying additives. By this method we can obtain catalytic active porous Ni with high specific surface area that is $(0.8-1.6) \cdot 10^4$ times higher than that for Ni-foil. Catalyst contained only two crystal phases after leaching: Ni⁰ and intermetallid NiZn.

The advantage of the method for preparation of porous metal surfaces on a smooth foil is the possibility to change chemical composition of the porous surface layer.

The aim of the present research is to prepare nanosized Ni-Me (Me – Rh, Ti, Au, Mo, W) – catalysts by electroplating on the Ni-skeletal basis and to determine the effect of the additives on the textural properties, the interaction of metallic components in Ni-Me catalysts and catalytic activity in the partial oxidation of methane to syngas.

Experimental

Catalysts were characterized by different physico-chemical methods. Specific surface areas (BET) of the catalyst samples were measured using a Micromeritics 2100E Accusorb Instrument. Nitrogen was used as absorbate at liquid nitrogen temperatures. X-Ray diffraction (XRD) of powder patterns was measured by Dron-4 diffractometer using a Co K_α radiation. Chemical analysis of catalysts was performed by emission spectral analysis (DFS-13).

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Steady-state reaction study was performed in a fixed-bed flow reactor at 600-800°C under atmospheric pressure. Prior to reaction the catalyst was calcined *in situ* under helium flow (20 cm³/min) at the reaction temperature during 1 h. CH₄ and air mixed gas (CH₄:O₂ = 2; *w* = 18-20 cm³/min) were introduced to the catalyst which was heated in nitrogen up to the reaction temperature. Products of the reaction were analyzed by a gas chromatograph directly connected to the outlet of the reactor with a thermal conductivity detector (Crystallux 4000M, Gazochrom-3101) using columns packed with Porapak-Q and molecular sieve CaA.

Results and Discussion

For synthesis of bimetallic Ni-Me catalysts the method of electrodeposition on a Ni-Zn basis has been used. In the Table 1 the data for quantity of the additives of metals entered into a base are presented.

The results indicate that the amount of metal additives was changed from 2.5 wt.% for Mo/Ni-Zn up to 7.0 wt.% for Rh/Ni-Zn. The surface of Ni-Zn base is 33 m²/g and the introduction of all listed metals with an exception of Mo leads to essential increase of the specific surface. The total volume of pores is 0.123 cm³/g for Ni-Zn and increases in 2-4 times in dependence from the nature of introduced metal. The greatest increase of the surface and volume of pores observed after W introduction. The radiuses pores distribution of the investigated catalysts is presented on a Fig. 1. Figure 1 shows that the initial Ni-Zn-catalyst is characterized by pores with the size equaled 15 and 58 Å. Electrodeposition of Mo, W, Au, Rh on Ni-Zn-base leads to the micropores disappearance and the radius of the basic pores decreases from 58 to 50 Å.

It was shown by XRD method that the initial Ni-Zn-catalyst contained 2 phases: Ni-metal and Ni-Zn-intermetallid (Fig. 2a). By of W electrodepo-

Table 1
Properties of Me/Ni-Zn catalysts (Me – Rh, Au, Mo, W, Ti)

Sample	[Me], %						S _{BET} , m ² /g	V _{ads} , cm ³ /g	
	[Rh]	[Au]	[Mo]	[W]	[Ti]	[Ni]			[Zn]
Rh/Ni-Zn	7.0					72	13	45	0.487
Au/Ni-Zn		5.5				62	25	61	0.348
Mo/Ni-Zn			2.5			60	30	23	0.238
W/Ni-Zn				5.0		65	21	95	0.438
Ti/Ni-Zn					3	67	24	not detected	not detected
Ni-Zn						71	24	33	0.123

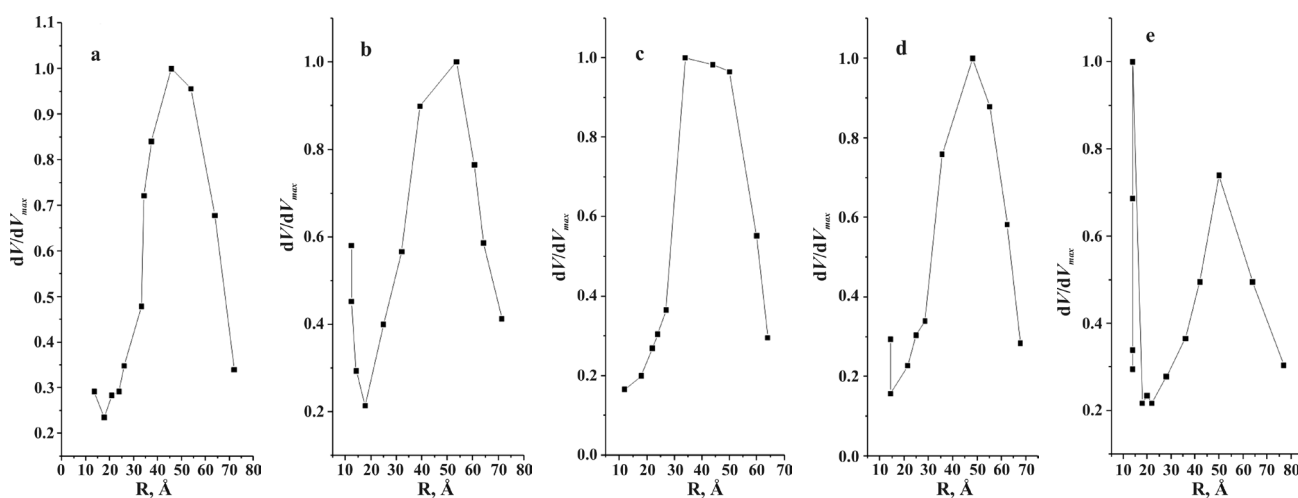


Fig. 1. Pores distribution for different Me/Ni-Zn-catalysts: a – Mo/Ni-Zn; b – Au/Ni-Zn; c – W/Ni-Zn; d – Rh/Ni-Zn; e – Ni-Zn.

sition on the Ni-Zn-base full destruction of Ni-Zn-intermetallid takes place, Ni^0 remains and reflexes characterized W-metal appears (Fig. 2b).

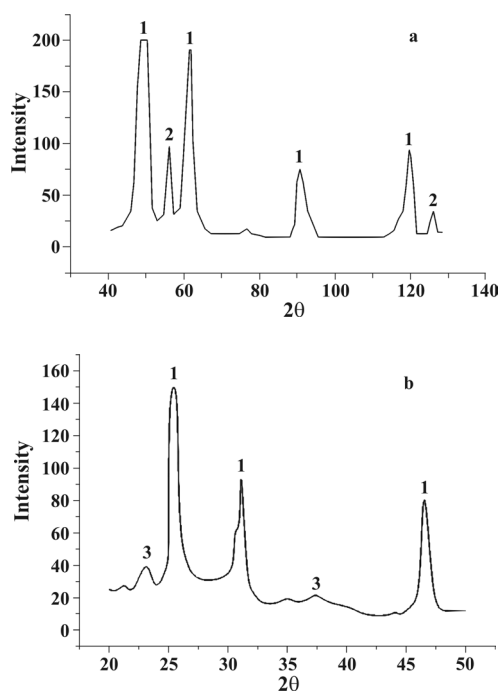


Fig. 2. XRD patterns of: a – Ni-Zn-catalyst; b – W/Ni-Zn-catalyst: 1 – Ni; 2 – NiZn; 3 – W.

The similar picture is also observed in case of electrodeposition of Au on a Ni-Zn base (Fig. 3a). Gold is precipitated as a metal phase Au^0 , Ni-Zn intermetallid is destroyed, Ni^0 metal phase is remained and a small amount of ZnO appears (Fig. 3a). XRD study of Rh/Ni-Zn-catalysts patterns are presented in Fig. 3b. The results of Ni-Rh-catalysts obtained by electrodeposition method it was discovered that the destroy of Ni-Zn intermetallid is not occurred, the metallic Ni-centers also are remained. At the same time on X-ray patterns the peaks testifying the existence of metallic Rh in the composition of Ni-Rh catalysts are found.

At Ti and Mo electrodeposition, interaction of precipitated metals with the base metal with formation of intermetallids takes place. So in a case of Ti electrodeposition there is no full destruction of Ni-Zn intermetallid, metal Ni is remained and Ni-Ti intermetallid and ZnO are formed (Fig. 4b).

At Mo electrodeposition, there is deeper interaction of Mo with the Ni^0 base with formation of Ni_3Mo and Ni_4Mo intermetallids. In this case Ni-Zn-intermetallid is remained (Fig. 4a).

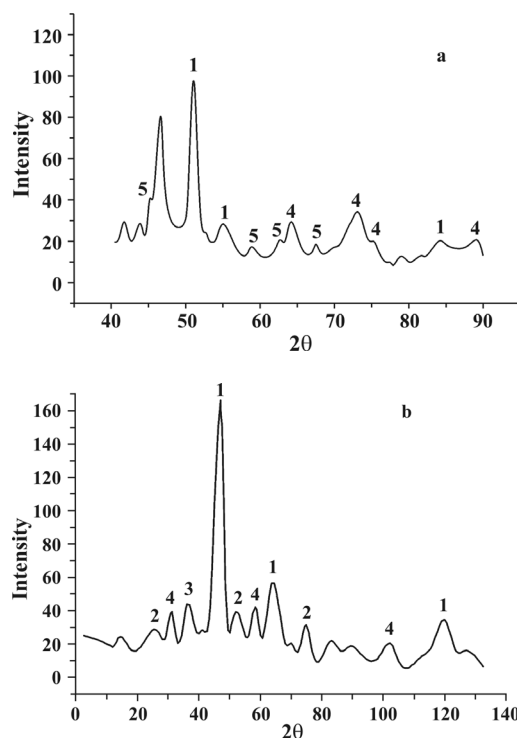


Fig. 3. XRD patterns of: a – Au/Ni-Zn-catalyst: 1 – Ni; 2 – NiZn; 3 – ZnO; 4 – Au; 5 – ZnO; b – Rh/Ni-Zn-catalyst: 1 – Ni; 2 – NiZn; 3 – ZnO; 4 – Rh.

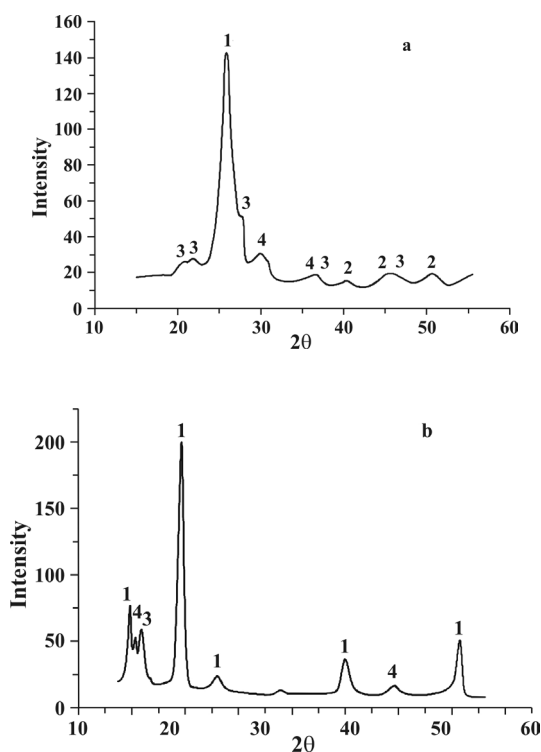


Fig. 4. XRD patterns of: a – Mo/Ni-Zn-catalyst: 1 – Ni; 2 – NiZn; 3 – Ni_3Mo ; 4 – Ni_4Mo ; b – Ti/Ni-Zn-catalyst: 1 – Ni; 2 – NiZn; 3 – NiTi; 4 – ZnO.

Results of Me/Ni-Zn catalysts tests are presented in Table 2. Conversion of methane over Rh/Ni-Zn-catalyst at 750°C is 63.2%. In products of reaction alongside with CO and H₂, CO₂ and H₂O are found. CO selectivity is 76.1%, on CO₂ – 23.9%. The activity of this catalyst is gradually reduced because of sintering of high dispersed metal particles at this temperature.

Au/Ni-Zn-catalyst has shown high activity and selectivity in the partial oxidation of methane to synthesis-gas. On this catalyst CO and H₂ are formed at 600°C. Conversion of methane is 60.3%, CO selectivity – 70.8%. However this catalyst is not stable and after 2-hours methane flow over catalyst at 600°C more CO₂ (83.4%) is formed and the quantity of CO decreases up to 16.6%. It was revealed that after tests this catalyst contains Au, Ni and small amounts of NiO, ZnO and carbon. Probably formation of NiO, ZnO and carbon is the reason of CO selectivity decreasing.

Mo/Ni-Zn catalyst does not change the properties within 8 hours at 600°C. By XRD method it has been found that during the tests Ni-Zn, Ni₃Mo, Ni₄Mo-intermetallids is destructed and after tests metal Ni⁰ and small amounts of NiO, Mo₂C and C

appears. Conversion of methane at 600°C over this catalyst is 79.7% with CO selectivity equaled to 78.9%. Also small amounts of CO₂ are found. With increase of temperature up to 800°C catalyst activity decreases to 10% because of the sintering and in these conditions methane is oxidized up to CO₂.

In the Ti/Ni-Zn-catalyst CH₄ conversion at 600°C is 49.5%. This catalyst exhibited good stability. But when the reaction temperature was changed from 600°C to 800°C, CH₄ conversion decreased markedly to give equal amounts of CO, H₂ and small amount of CO₂ (Table 2). Selectivity towards CO + H₂ formation is 83.9-87.1%. After tests the strong interaction between Ti and Ni-Zn-base and the formation NiZnTiO₄-compound were found.

W/Ni-Zn catalyst is less active in partial oxidation of methane. Conversion of methane is 20-25% at 600°C within 2 hours and basically CO and H₂ are formed. After six hours of catalyst work the quantity of formed CO decreases and CO₂ quantity increases. Conversion of methane is constant by remained equaled to 20-25%. After the tests metal Ni⁰ is remained however the oxidized nickel and carbon are absent. It is possible to explain decrease of CO selectivity after 4 hours by the formation of carbon and NiO.

Table 2

Rh/-, Au/-, Mo/-, W/Ni-Zn-catalysts in methane partial oxidation
[CH₄] = 35.5 vol.%; [O₂] = 18 vol.%; w = 0.3 cm³/s

Catalyst	T, °C	Duration of tests, h	X _{CH₄} , %	S _{CO₂} , %	S _{CO} , %	S _{H₂} , %	Phase composition of catalysts after testing
Rh/Ni-Zn	650	-	11.2	57.6	42.4	not detected	
	750	-	63.2	23.9	76.1		
Au/Ni-Zn	600	2	60.3	29.1	70.9		Ni ⁰ , Au ⁰ , C, NiO, ZnO
	800	2	64.9	83.4	16.6		
Mo/Ni-Zn	600	2	79.7	21.1	78.9	not detected	Ni ⁰ , NiO, Mo ₂ C; C
	600	6	78.0	23.2	76.8		
	800	2	10.0	100	-		
Ti/Ni-Zn	600	2	49.5	12.9	34.1	53.0	NiZnTiO ₄
	800	2	24.8	16.1	35.4	48.5	
W/Ni-Zn	600	2	20.0	1.8	98.2	not detected	Ni ⁰ , W ⁰
	600	2	23.0	3.6	96.4		
	600	2	20.0	16.1	83.9		
	800	2	38.7	43.3	35.9	20.8	
	900	2	42.3	15.2	35.7	49.2	
	950	2	70.4	-	45.2	54.8	

The highest activity in partial oxidation of methane has been found over the W/Ni-Zn catalyst at 950°C. Conversion of methane is 70.4%, CO + H₂ selectivity is 100% (Table 2). The analysis of the results presented in the Table 2 shows that the majority of investigated high dispersed powders of catalysts have low thermal stability and at 600-800°C tem-

peratures are easily oxidized. In this connection the method of preparation of Me/Ni-Zn metal powders on a ZrO₂ massive surface stabilized by Y₂O₃ (YSZ) has been developed. The prepared samples (Rh/Ni-Zn/YSZ, Mo/Ni-Zn/YSZ, Au/Ni-Zn/YSZ) have been tested in partial oxidation of methane at 900 and 950°C (Table 3).

Table 3
Rh/Ni-Zn/YSZ-, Au/Ni-Zn/YSZ-, Mo/Ni-Zn/YSZ-catalysts in methane partial oxidation
[CH₄] = 35.5 vol.%; [O₂] = 18 vol.%; w = 0.3 cm³/s

Catalyst	T, °C	Duration of tests, h	X _{CH₄} , %	S _{CO₂} , %	S _{CO} , %	S _{H₂} , %
Rh/Ni-Zn/YSZ	800	2	37.9	37.2	31.2	31.6
	900	2	44.4	12.1	38.1	49.8
	950	2	66.0	7.3	41.9	50.8
Au/Ni-Zn/YSZ	800	2	22.4	57.5	25.9	16.6
	900	2	32.0	18.4	44.1	37.5
	950	2	44.9	8.2	41.1	50.7
Mo/Ni-Zn/YSZ	800	2	17.8	58.1	35.7	6.2
	900	2	26.9	17.6	42.2	40.2
	950	2	32.8	1.1	45.9	53.0

The results show that the sequence of CH₄ conversions (%) at 950°C is as follows: Rh/Ni-Zn/YSZ (66.0) > Au/Ni-Zn/YSZ (44.9) > Mo/Ni-Zn/YSZ (32.8). While that of the CO + H₂ selectivity's (%) as follows: Mo/Ni-Zn/YSZ (98.9) > Rh/Ni-Zn/YSZ (92.7) > Au/Ni-Zn/YSZ (91.8). There was the selectivity oxidation of methane to CO and H₂ together with apart of total oxidation to CO₂ and H₂O.

All received results are explained by the change of phase structure of the investigated catalysts during the tests. The most active catalysts contain only reduced forms of metals (Ni⁰, W⁰, Ni⁰, Rh⁰). The most stable samples have the raised stability to carbonization.

Conclusions

Methods of Me (Rh, Au, Mo, W, Ti) electrodeposition on a Ni-skeletal base have been developed. It was shown that during Au and W electrodeposition Au⁰, W⁰, Ni⁰ metal phases are remained and a full destruction of the Ni-Zn phase takes place. At the Rh electrodeposition Ni⁰, Ni-Zn phases are remained and Rh⁰, ZnO are formed. Deep interaction of electrodeposited Mo and Ti with Ni⁰ and Ni-Zn base leads to Ni₃Mo, Ni₄Mo and NiTi intermetallids formation. Catalyst tests have shown that the highest

conversion of methane and CO + H₂ selectivity at partial oxidation was observed on powder of W/Ni-Zn and bulk Rh-Ni-Zn/YSZ catalysts at 950°C.

The most active catalysts contain only the reduced form of Ni⁰. The most stable samples had considerably improved resistance to carbon formation.

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