

Nickel-base cement-containing catalyst for the synthesis of methane from carbon oxides

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Abstract

We have considered in this paper the basic physical and chemical properties of nickel-base cement-containing methanation catalyst NIAP-07-07 (NKM-7). The catalyst was investigated by various methods including determination of catalytic activity, temperature-programmed reduction, decomposition, and joint temperature-programmed decomposition and reduction. We found that the interaction of nickel hydroxo-carbonate with aluminum oxide in the aqueous ammonia medium produces nickel hydroxo-carboaluminate, which is the precursor of the active component of the catalyst. It was found that the value of the mechanical strength of the catalyst significantly depends on the amount of technical calcium aluminate, which is added to the Ni-Al composition. Take into account optimized compositions catalyst are considered, including when the content of the active component is different. The manufacturing technology of the catalyst is worked out in relation to the conditions of its industrial production. The developed catalyst (NIAP-07-07) has a high catalytic activity, thermal stability and mechanical strength and is characterized by a reduced activation temperature. The catalyst can be made from the same mix material in the form of a ring, a cylindrical tablet and extrudates with different geometric dimensions.

Keywords: nickel-base cement-containing catalyst, carbon monoxide methanation, phase composition, mechanical strength, activation, catalytic activity

I. INTRODUCTION

For example, catalytic methanation of carbon oxides obtained from coal or biomass to the production of synthetic natural gas is gaining significant interest due to energy problems and the possibility of reducing greenhouse gas emissions [1, 2]. This catalytic methanation process is an integral part of the hybrid energy-metallurgical and catalytic technology of synthetic methane production.

In addition, catalytic methanation of carbon oxides implement allows for fine purification of hydrogen and hydrogen-containing gases from carbon oxides, that are catalytic poisons in many processes of inorganic and organic synthesis, provides protection of the environment from carbon oxides emitted in large quantities into the atmosphere. In many processes where it is necessary to clean the gas mixture from carbon monoxide, methanation it turns out is preferable to oxidation to CO₂ [3 – 6, 8 – 18].

Monoxide and carbon dioxide in the reaction mixture can enter into different reactions. First of all these are the main reactions of CO and CO₂ methanation:



Reactions (1), (2) are reversible and highly exothermic. The adiabatic increase of temperature for each percent of reacted CO and CO₂ is 74 C and 60 C, respectively [11]. The equilibrium constants of these reactions in the temperature range 200 -600 C are of the order 10¹-10¹² [9, 12]. Reactions (1) and (2), occurring in a large excess of hydrogen, can be considered as almost irreversible at temperatures from 150 C and more. As a result, by catalytic hydrogenation can be achieved via high degree of transformation of carbon oxides to methane.

Catalytic methanation allows to carry out of selective synthesis of methane using it as a chemical agent, fuel gas, as well as the use of exothermic reactions of methane synthesis in the transmission of chemical energy over long distances. Hydrogenation of carbon oxides has become widespread in industry due to the intensive development of hydrogen production processes [13].

Methanation catalysts used in high-temperature methane synthesis must meet the following requirements [7- 12]:

- a) high activity in the methanation process at a pressure of 1.5-3.0 MPa;
- b) reduced activation temperature;
- c) increased thermal stability without reducing activity during operation at temperatures up to 650 C;
- d) high mechanical strength;
- e) reduced hydraulic resistance (for which it is desirable to produce a catalyst in an annular form).

The largest number of studies aimed at the development of methanation catalysts were devoted to nickel catalysts. For the synthesis of these catalysts, a wide range of carriers was used, which includes oxides of aluminum, magnesium, calcium, silicon, chromium, aluminosilicates, kieselguhr, ceramics, kaolin, calcium aluminates, etc. [3-21].

The greatest thermal stability (650 C), of all the catalysts used in the industry of methanation, has a nickel-base cement-containing catalyst NIAP-07-02, however, it has an increased activation temperature. This necessitates the development of a methanation catalyst (NIAP-07-07) that meets these requirements.

II. RESEARCH AND DISCUSSION

X-ray studies to determine the phase composition and dispersivity of crystallites were carried out using the diffractometer DRON-3 (CuK α – radiation with graphite monochromator on the reflected beam). The International powder diffraction standards Committee (JCPDS) database was used for phase identification. Complex thermal studies were carried out using the optical derivatograph OD-103 (linear temperature rise rate 5 C /min). The total specific surface area was determined by low-temperature adsorption of nitrogen. The total porosity was calculated according to the true and apparent density. Apparent density (kg/dm³) was calculated by the formula:

$$\rho = \frac{m_1 - m_2}{v}, \quad (3)$$

where m_1 – the mass of the weighing bottle with the sample (kg); m_2 – the mass of the empty weighing bottle (kg); v – the capacity of the weighing bottle (dm³).

Mechanical strength was determined on the device MP-2C by crushing the catalyst granules with the application of a load on the disk face. The catalytic activity in the methanation process was determined on a pilot plant at a pressure of 3.0 MPa. Activation studies were carried out using the method of temperature-programmed reduction on a thermochromatographic installation.

Undoubtedly, the NKM series methanation catalysts (NIAP-07) are the leaders among the known catalysts in the world. However, there is a need for further improvement of catalysts for the methanation process. First of all, this is due to the need to reduce the reduction temperature of the catalysts, reduce

the dynamic resistance, reduce the content of expensive active component (nickel) and, accordingly, the cost of catalysts.

Nickel-base cement-containing catalyst was chosen as the object of research. As raw materials used in its preparation, nickel hydroxo-carbonate NiCO₃·Ni(OH)₂·4H₂O, active aluminum oxide and technical calcium aluminate (high-alumina cement) were used.

The basis of the new generation methanation catalyst NIAP-07-07 (NKM-7) is a nickel-aluminum composition, which is a precursor of the catalyst, which is responsible for its catalytic properties. It is prepared by chemical mixing of nickel hydroxo-carbonate and active aluminum oxide γ -Al₂O₃ in the presence of a liquid reagent in the form of an aqueous ammonia solution. The studies allowed to establish the necessary ratio of Al₂O₃/NiO in the preparation of Ni-Al composition, in which the deepest interaction between nickel hydroxo-carbonate and γ -Al₂O₃ occurs in an aqueous ammonia medium.

The prepared samples of Ni-Al composition are characterized by the absence of nickel hydroxo-carbonate in the phase composition. Only a new nickel-containing compound and γ -Al₂O₃, were recorded in the phase composition. In addition, it was found that such treatment leads to an increase in the value of the interplane space of the nickel-containing phase from 5.08 Å, which is typical for nickel hydroxo-carbonate to 7.6–7.8 Å in the presence of a liquid reagent in the form of an aqueous solution of ammonia. The increase in the interplanar space of the nickel component in the nickel-aluminum composition after treatment with a liquid reagent, testifies to the fact that during the preparation at the mixing stage a chemical interaction between nickel hydroxo-carbonate and active aluminum oxide occurs and the adding of an aluminate anion [Al(OH)₄]⁻¹ into the structure of nickel hydroxo-carbonate is done.

The analysis of experimental data obtained with the use of derivatographic and radiographic methods of analysis, temperature-programmed reduction, decomposition and joint temperature-programmed decomposition and reduction, allowed us to establish that the structure of the nickel component of Ni–Al composition (after its treatment with an aqueous solution of ammonia) includes along with Ni and Al also ions of CO₃²⁻ and OH⁻. Thus, the compound containing the active component, presumably identified as nickel hydroxo-aluminate NiAl(OH)₄, is nickel hydroxo-carboaluminate Ni₆Al₂CO₃(OH)_{3.5}·4H₂O.

In order to prepare a nickel-base cement-containing catalyst containing 25 wt.%, 28 wt.%, 31 wt.% and 36 wt.% NiO in a nickel-aluminum composition in which NiO=45.9 wt.%, high-alumina cement was added in various amounts. In table 1 the calculated data of the chemical composition of the mix material for catalyst are given. It can be noted that the minimum amount of high-alumina cement (28%) will have a mix material containing 36% NiO, and the maximum amount of high-alumina cement (45.5%) has a mix material for catalyst containing 25% NiO.

Table 1. The content of components in the catalyst charge, wt. %

Constituent	Batch number			
	1	2	3	4
NiO	25.0	28	31.0	36
Al ₂ O ₃	29.5	33	36.6	36
High-alumina cement	45.5	39	32.4	28

A mechanical mixture consisting of a non-calcined nickel-aluminum mass, high-alumina cement and graphite was moistened with condensate. The received mix material for catalyst was tableted on a rotary tablet machine in the form of cylindrical rings with an outer diameter of 10 mm and tablets with a diameter of 6 mm.

After the tablet machine, the mechanical strength of all test batches studied experimental batches is almost the same (18-19 MPa), but in the finished catalyst, the mechanical strength differs significantly (see Table 2). First of all, this difference is due to the content of high-alumina cement, which is being hydrated during hydrothermally treatment, and hydration products form a mechanically strong catalyst frame. For example, in batch No. 4, the catalysts have a minimum amount of high-alumina cement (28 wt. %) and their mechanical strength reaches 64 MPa. At the same time, increasing the amount of injected high-alumina cement from 28 wt.% to 45.5 wt.% promotes the growth of mechanical strength from 64 MPa to 78 MPa. It can also be noted that the catalyst in the form of tablets has a apparent density $\gamma = 1.32 - 1.36 \text{ kg/dm}^3$, it has $\gamma = 1.05 - 1.08 \text{ kg/dm}^3$ in the form of ring (table 2). This difference in apparent density can be explained by the geometric shape that affects the packing of granules in the cylinder.

The creation of a mechanically strong structure of NIAP-07-07 (NKM-7) catalysts is carried out not by increasing the pressing forces, as in the manufacture of tableted catalysts, a very high level of internal micro-stresses is formed, which has a negative impact on the catalyst during operation (the mechanical strength of the catalysts is reduced, and, as a consequence, the lifetime of the contacts between the active substance and the base is reduced). This problem is solved through the use of especially pure special high-alumina cements (have good hydraulic binding properties), in particular, technical calcium aluminate introduced into the catalyst [14].

Samples of catalysts were prepared in laboratory and pilot conditions and their complex physico-chemical and physico-mechanical studies were carried out. Taking into account the obtained data, further development of the technology was carried out on the industrial equipment of the catalyst production of LLC "NIAP-KATALIZATOR".

The dependences of temperature-programmed decomposition and reduction of NIAP-07-07 catalyst in hydrogen are shown in Fig. 1.

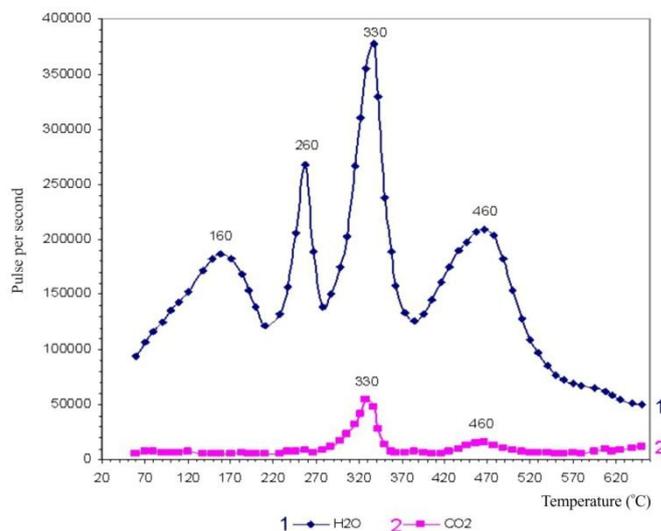


Fig. 1. Schedules temperature-programmed decomposition and reduction of the catalyst NIAP-07-07 in H₂

Activation of the finished catalyst (see Fig. 1) is combined with decomposition processes and is characterized by four effects in release into the gas phase of H₂O, which have maximums of temperatures 160°C, 260°C, 330°C and 460°C. Starting at a temperature of 210-220 °C, gibbsite is decomposed to γ -Al₂O₃ and H₂O, as well as the removal of interlayer water from hydroxo-carboaluminate nickel. In this case, a certain amount of highly dispersed NiO is formed and reduced to Ni at the same time. Activation of the main part of NiO occurs in the temperature range 380-650°C. In addition, a small amount of CO₂ is released into the gas phase, which is formed as a result of the low-temperature decomposition of CaCO₃ in the reducing medium.

For the developed catalysts (they have a low content of the active component, a low activation temperature and are capable of being manufactured in various geometric shapes) the evaluation of catalytic properties was carried out taking into account the soak period (10, 20 and 30 h) at 650°C. The results of the studies are given in table 3.

The data presented in table 3, allow to reveal the general regularity of increase of catalytic activity with growth of the content of the active component. As well as for the standard catalyst NIAP07-01 (Neo = 39.5%), the developed contacts (with NiO = 25 - 33%) at 650 °C retain their catalytic activity, which is approximately 169 - 175 °C, regardless of the duration (10 - 30 h) exposure at this temperature.

In table. 4 comparative characteristics of industrial catalyst NIAP07-01 (KM-1) and promising catalyst NIAP-07-07 (NKM-7) are given. The advantages of NIAP-07-07 catalyst (NKM-7) are, first of all, that it is more active in the low-temperature (230-300 °C) reduction region despite the significantly lower content (8.5 wt.%) of the active component. The new catalyst has higher thermal stability and lower apparent density. Its fractional void volume is approximately 1.5 times greater due to changes in geometric shape.

Table 2. Phase composition and mechanical strength of ring-annular catalyst with different content of NiO, Al₂O₃ and high-alumina cement

Batch number	High-alumina cement in input materials (wt.%)	The phase composition of the finished catalyst	Mechanical strength (MPa)			Apparent density (kg / dm ³)
			After tableting	After hydrothermal treatment	Finished catalyst	
1	45.5	Ni ₆ Al ₂ CO ₃ (OH) _{3.5} ·4H ₂ O, graphite, C ₃ AH ₆ , γ-Al ₂ O ₃ , CaCO ₃ , Al(OH) ₃ ,	19	59	78	1.05
2	39	Ni ₆ Al ₂ CO ₃ (OH) _{3.5} ·4H ₂ O, graphite, C ₃ AH ₆ , γ-Al ₂ O ₃ , CaCO ₃ , Al(OH) ₃ ,	18	55	75	1.07
3	32.4	Ni ₆ Al ₂ CO ₃ (OH) _{3.5} ·4H ₂ O, graphite, C ₃ AH ₆ , γ-Al ₂ O ₃ , CaCO ₃ , Al(OH) ₃	18	52	67	1.07
4	28	Ni ₆ Al ₂ CO ₃ (OH) _{3.5} ·4H ₂ O, graphite, C ₃ AH ₆ , γ-Al ₂ O ₃ , CaCO ₃ , Al(OH) ₃	19	49	64	1.08

Table 3. The catalytic activity of the catalyst NIAP-07-07 with different NiO contents (by P = 3.0 MPa; W = 4000 h⁻¹, CO_{in} = 0.70 – 0.72 % vol.)

№ lot number	The content of NiO in the catalyst (wt.%)	Catalytic activity: breakthrough temperature of CO = 10 ppm (°C)			
		Reduction at 400 C	Overheating time at 650 C, 10 h	Overheating time at 650 C, 20 h	Overheating time at 650 C, 30 h
1	25	164	175	174	174
2	28	163	173	172	173
3	31	160	171	169	171
NIAP07-01	39.5	153	157	160	161

Table 4. Comparative characteristics of industrial (NIAP07-01) and new (NIAP-07-07) methanation catalysts

№ п/п	Indicator	NIAP-07-01	NIAP-07-07
1	Appearance	Tablet	Ring
2	External diameter (mm)	5.5 ± 1.0	10.0 ± 0,5
	Height (mm)	4.5 ± 0.5	6.0 ± 0.9
	Internal diameter (mm)	–	4.0 ± 0.5
3	Mass fraction of nickel normalized by NiO (wt.%)	36.0 ± 3.0	33.0 ± 3.0
4	Apparent density (kg/dm ³)	1.1 ± 1.3	1.06 ± 0.2
5	Mechanical strength (crushing strength) not less than (MPa):	2.0	–
	a) by generatrix		
6	b) on the face	–	60
	Catalyst activity: minimum temperature (°C), providing a volume fraction of CO at the outlet of not more than 0.001 and not more than 0.03 CO ₂ (at a pressure of up to 3 MPa, a volume velocity of 4000 h ⁻¹ , a volume fraction in the starting gas of 0.6–0.7 CO) at the following reduction temperatures:	When NiO=39.5 wt.%	When NiO=31.0 wt.%
	230 °C	225	190
	250 °C	205	170
	300 °C	175	160
	360 °C	160	160
550 °C	160	160	
7	Thermostability	10 h by 550 °C	30 h by 650 °C
8	Fractional void volume (m ³ /m ³)	0.315	0.46
9	Service life not less than (years)	10 – 15	10 – 15
10	The possibility of manufacturing different geometric shapes	Tablets	Tablets of different size, rings, molded granules

III. CONCLUSION

In this article, we have considered the features of the manufacturing technology of the new methanation catalyst NIAP-07-07 (KM-7), as well as have resulted its optimized compositions, including when the content of the active component is different. On the basis of a complex of physico-chemical and physico-mechanical studies of laboratory and pilot batches of NIAP-07-07 catalyst, it was found that the catalyst is different by increased mechanical strength, thermal stability and catalytic activity. The final working-off of the catalyst production technology was carried out on the industrial equipment of the catalyst production LLC "NIAP-KATALIZATOR". Catalyst NIAP-07-07 (NKM-7) of various geometric shapes (ring, tablet, extrudate), allows, among other things, to implement effective purification of synthesis gas from carbon oxides at increased volumetric flow rates and provide sustainable exploitation of the catalyst in the methanator at gas inlet temperatures of about 200 °C.

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