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Nickel catalysts for nitrogen–hydrogen mixture purification from carbon oxides

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Objectives. *This study is devoted to developing new-generation nickel (Ni) catalysts for the purification of a nitrogen–hydrogen mixture from carbon oxides, which should encompass the best qualities of the NIAP-07-series solid catalysts.*
Methods. *This study used derivatographic and radiographic methods; temperature-programmed recovery, decomposition, and joint temperature-programmed decomposition and recovery; and low-temperature nitrogen adsorption (specific surface determination). The mechanical strength of catalysts was determined using an MP-2C device by crushing granules with an applied load on the end face. The chemical composition and catalytic activity were determined by the methods of TU 2178-003-00209510 Technical Conditions.*
Results. *Many studies regarding Ni–aluminum (Al)–calcium (Ca) methanation catalyst at all stages of its preparation have been conducted. It is demonstrated that Ni hydrocarboxyaluminate, a precursor of the active component of the catalyst, is formed when Ni hydroxocarbonate is mixed with active alumina in the presence of an aqueous solution of ammonia, and its chemical formula is established. Moreover, it was found that the mechanical strength of the catalyst is determined by the amount of industrial Ca aluminate added to the Ni–Al composition. The compositions of catalysts with different contents of the active component have been optimized.*
Conclusions. *The developed catalyst has a low activation temperature and high catalytic activity, thermal stability, and mechanical strength and is resistant to organic and alkaline carbon dioxide absorbers. The catalyst can be produced in the form of a ring, cylindrical tablets, and extrudates of various geometric sizes. The methanation unit at Stavrolen (Budennovsk, Stavropol krai, Russia) has begun commercially operating the catalyst.*

Keywords: *hydrogenation, carbon oxides, nickel catalyst, phase composition, mechanical strength, activation, catalytic activity, industrial use.*

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Никелевые катализаторы для процесса очистки азотоводородной смеси от оксидов углерода

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Цели. *Настоящее исследование посвящено разработке никелевого катализатора нового поколения для очистки азотоводородной смеси от оксидов углерода, который должен аккумулировать лучшие качества контактов серии НИАП-07.*
Методы. *Использованы дериватографический и рентгенографический методы анализа; методы температурно-программированного восстановления, разложения и совместного температурно-программированного разложения и восстановления; низкотемпературная адсорбция азота (определение удельной поверхности). Механическая прочность определялась на приборе МП-2С раздавливанием гранул с приложением нагрузки на торец. Химический состав и каталитическую активность определяли по методикам ТУ 2178-003-00209510.*
Результаты. *Выполнены исследования никельалюмокальциевого катализатора метанирования на всех стадиях его приготовления. Показано, что при смешении гидроксокарбоната никеля с активным оксидом алюминия в присутствии водного раствора аммиака происходит образование гидросокарбоалюмината никеля, являющегося предшественником активного компонента катализатора, и установлена его химическая формула. Обнаружено, что величина механической прочности катализатора определяется количеством технического алюмината кальция, добавляемого в Ni–Al композицию. Оптимизированы составы катализатора, имеющего различное содержание активного компонента.*
Выводы. *Разработанный катализатор имеет пониженную температуру активации, высокую каталитическую активность и термостабильность, большую механическую прочность, устойчивость к воздействию органических и щелочных абсорбентов-поглотителей углекислого газа. Катализатор может изготавливаться в форме кольца, цилиндрических таблеток и экструдатов с различными геометрическими размерами.*
Начата промышленная эксплуатация катализатора в установке метанирования ООО «Ставролен», г. Буденновск, Ставропольский край, Россия.

Ключевые слова: *гидрирование, оксиды углерода, никелевый катализатор, фазовый состав, механическая прочность, активация, каталитическая активность, промышленное внедрение.*

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INTRODUCTION

The fine purification of a nitrogen–hydrogen mixture (synthesis gas) from carbon oxides is used in the large-scale production of synthetic ammonia. The quality of methanation catalysts determines the performance as well as stability of the operation and technical and economic indicators of such industries. Methanation catalysts are produced by a number of foreign companies. In the Russian Federation, methanation catalysts are produced in Novomoskovsk by the catalyst production of *NIAP-CATALIZATOR*.

Methanation catalysts in the form of metal oxides contain nickel (Ni) as the active component, have a high reduction temperature, are manufactured using various carriers, and differ in geometric shape. The NKM-series catalysts manufactured in the Russian Federation (NIAP-07 and TO-2M)[1] are widely used in the chemical and petrochemical industries, among others.

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[1] *Tekhnicheskie usloviya TU 2178-003-00209510-2006. Katalizatory metanirovaniya* (Technical Conditions TU 2178-003-00209510-2006. Methanation catalysts) (in Russ.).

An increase in the established capacity of the ammonia synthesis unit from 1360 to 1700 t/day led to a decrease in the temperature of the synthesis gas at the inlet of the methanator to 270–290°C, indicating that methanation catalysts must be improved. Such improvement should be implemented through 1) the development of technology that would make it possible to obtain the active component, Ni, in a highly dispersed state; 2) the creation of technology that would enable the preparation of catalysts with a low activation temperature (220–230°C) that can be operated at high space velocities; and 3) the manufacturing of a catalyst that has various geometric shapes (cylindrical tablets, rings, and extrudates with or without an aperture).

This study is devoted to developing new-generation catalyst that encompasses the best qualities of the NIAP-07-series solid catalysts.

The object of the study is a Ni–Al (aluminum)–calcium (Ca) catalyst. Ni hydroxocarbonate (NHC), active alumina, industrial Ca aluminate (talyum), and aqueous ammonia were used as raw materials for its preparation.

MATERIALS AND METHODS

To determine the phase composition and dispersion of crystallites, X-ray diffraction studies were performed using a DRON-3 diffractometer (CuK$_\alpha$–radiation with a graphite monochromator on a reflected beam). To identify the phases, we used the database of the Joint Committee on Powder Diffraction Standards. Complex thermal studies were carried out using an OD-103 optical derivatograph (linear temperature rise rate of 5°C/min.). The total specific surface area was determined by low-temperature nitrogen adsorption. Total porosity was calculated from true and bulk density data. Bulk density was calculated by the formula

$$\rho = (m_1 - m_2)/V,$$

where m_1 is the mass of the measuring cylinder with an absorber, kg; m_2 is the mass of the graduated cylinder without an absorber, kg; and V is the volume of the cylinder, dm^3.

The mechanical strength was determined using an MP-2C device by crushing granules with an applied load on the end face. The chemical composition and catalytic activity during the process of methanation in a pilot plant at a pressure of 3.0 MPa and a space velocity of W = 4000 h^{-1} were determined by the methods described in TU 2178-003-00209510. The decomposition and activation processes were studied using temperature-programmed decomposition (TPD) and reduction (TPR) on a thermochromatographic installation.

RESULTS AND DISCUSSION

Catalyst development was based on many years of experience operating methanation catalysts [1–9] (in particular, those in the NIAP-07 [NKM] series) as well as on the results of studies regarding mixed-type catalysts [10–18].

The basis of the new-generation methanation catalyst NIAP-07-07 (NKM-7) is a Ni–Al composition, which is a precursor responsible for catalytic properties. It was found that the most profound interaction between nickel hydroxocarbonate (NHC) and active alumina (γ-Al_2O_3) occurs when the Al_2O_3/NiO ratio is no more than 1.2.

To identify the differences in the synthesis of the Ni–Al composition, X-ray studies of samples 1–4 were carried out, in which the concentration of aqueous ammonia used in the preparation (Table 1) and the non-processed mechanical mixture of NHC+γ-Al_2O_3 differed. To determine the interplanar spacing for all the studied samples, a line of 100% intensity corresponding to the reflection from a plane with a Miller index of 003 for Ni hydroxocarboaluminate (NHCA) was recorded at a speed of 0.25°/min in the angle range 2θ = 8–14°.

Table 1. The effect of the concentration of an aqueous solution of ammonia on the interplanar spacing of the Ni-containing phase

Sample №	C_{NH4OH}, %	*d*, Å
Mechanical mixture NHC+γ-Al_2O_3	Unprocessed	5.2
Talcovite ($Ni_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$)	–	7.54
1	0	7.6
2	5.0	7.8
3	15.0	7.8
4	25.0	7.8

According to the data given in card 15-0087 (PCPDF-WIN 1999 database), the Ni-containing phase $Ni_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ (*talcovite*) has an interplanar spacing of $d = 7.54$ Å and a hexagonal lattice.

Using data from the X-ray diffraction method of analysis, the interplanar spacing of the formed Ni-containing phase was determined (Table 1).

An X-ray analysis revealed that NHC was absent from the phase composition, and a new Ni-containing compound was recorded. It is worth noting that the use of ammonia during the preparation of an aqueous solution causes the interplanar spacing of the new Ni-containing phase to increase to 7.8 Å, which attests to the fact that, during the preparation at the mixing stage, a chemical interaction occurs between NHC and alumina with the addition of the $[Al(OH)_4]^{-1}$ anion into the NHC structure due to its anion exchange to CO_3^{-2} [19].

An analysis of the obtained data shows that, regardless of the concentration of an aqueous solution of ammonia, the interplanar spacing of this compound remains constant and equal to 7.8 Å (Table 1), allowing us to assume that the dispersion of this Ni-containing phase in the prepared samples will also remain constant. X-ray diffraction studies of activated samples 1–4 showed that the dispersion of Ni in said samples does not change and remains at 60–70 Å. Since the resulting Ni-containing compound is a precursor of the NIAP-07-07 (NKM-7)-brand Ni methanation catalyst prepared through the chemical mixing of the initial raw material components in an aqueous ammonia medium, it is of particular interest to study the composition of this compound. An analysis of the experimental data obtained using derivatographic and radiographic methods of analysis, temperature-programmed recovery, decomposition, and combined recovery allowed us to establish that the structure of the Ni component of the Ni–Al composition after being treated with an aqueous solution of ammonia along with Ni contains the anions $[Al(OH)_4]^{-1}$, CO_3^{-2}, and OH^{-1}. Thus, this compound is NHCA. It was established experimentally that the NHCA composition formed during the preparation of Ni–Al has a structure similar to that of NHC.

To prepare a Ni–Al–Ca catalyst containing 25 (p. 1), 28 (p. 2), 31 (p. 3), and 36 (p. 4) mass % NiO, varying amounts Ca aluminate were added to the Ni–Al composition. Table 2 shows the calculated data of the catalyst mixture's chemical composition. It is worth noting that the minimum amount of Ca aluminate (28%) will have a catalyst mixture containing 36% NiO, and the maximum amount of Ca aluminate (45.5%) will have a catalyst mixture containing 25% NiO.

A mechanical mixture consisting of non-calcined Ni–Al mass, Ca aluminate, and graphite was molded in the form of rings with external diameters of 10 mm and tablets with diameters of 6 mm.

Table 3 presents data related to the phase composition, mechanical strength, and bulk density of the finished catalyst that has passed the hydrothermal treatment (HTT) stage.

With equal values of the mechanical strength of all the studied experimental batches at the input of the tablet machine, after the tablet machine and in the finished catalyst values of the mechanical strength differ (Table 3).

The increase in the mechanical strength of the catalyst after the HTT stage from 15–17 to 64–78 MPa is explained by the fact that the Ca aluminate added

Table 2. Calculated content of the components in the catalyst mixture

Batch №	1	2	3	4
$NiO–Al_2O_3$, mass %	54.5	61	67.6	72
Calcium Aluminate, mass %	45.5	39	32.4	28

Table 3. Phase composition, mechanical strength, and bulk density of the finished catalyst with different contents of $NiO–Al_2O_3$ and Ca aluminate

Batch №	Phase composition	Mechanical strength, MPa	γ, kg/dm³
1	Ni hydroxocarboaluminate, γ-Al_2O_3, C_3AH_6, $Al(OH)_3$, $CaCO_3$, graphite	78	1.05
2		75	1.07
3		67	1.07
4		64	1.08

to the Ni–Al composition acts as a hydraulic binder, which hydrates during hydrothermal treatment, and the hydration products in the form of highly basic Ca aluminate (C_3AH_6–$3CaO\cdot Al_2O_3\cdot 6H_2O$) and Al hydroxide modifications gibbsite form a mechanically strong catalyst frame. Small pressing forces and the use of the HTT stage contribute to the fact that in the finished catalyst, there is practically no internal microstress that has a negative effect on the mechanical strength during either its activation or future operations.

To determine the minimum activation temperature, studies were carried out using the TPR method. Studies have shown that the activation process of the NIAP-07-07 catalyst is combined with the decomposition of the Ni component (NHCA) and is multistage.

Starting from a temperature of 210–220°C, gibbsite is decomposed to γ-Al_2O_3 and water, and interlayer water is removed from the NHCA. Simultaneously, a certain amount of highly dispersed NiO is formed and reduced to Ni. The process of removing interlayer water is accompanied by the formation of a finely dispersed phase of Ni hydroxoaluminate, which decomposes upon further heating in the hydrogen duct with the release of CO_2 into the gas phase. In the same temperature range (270–370°C), NiO begins to be actively activated. The maximum rate of NiO activation at this stage is achieved at 330°C. The bulk of NiO is reduced when the temperature is 380–650°C.

Table 4 shows results of catalytic activity in the methanation reaction of the studied catalysts with different contents of the active component and also, for comparison, the catalytic activity of the NIAP-07-01 catalyst containing 39% NiO, which is used as a standard sample to evaluate the correct operation of the installation. The CO content in the nitrogen–hydrogen mixture at the inlet to the methanation reactor was 0.65–0.72 vol %, which is 2–3 times more than its content before being added to an industrial methanator.

An analysis of the presented experimental data on the catalytic activity of the studied catalysts shows that after activation at 210°C, the regulatory value of CO (<10 ppm) in the purified gas is not reached. However, a mere 10°C increase in the activation temperature caused the catalysts to exhibit identical catalytic activity regardless of the content of the active component. The temperature of the CO slip in the purified gas is 214°C. A further increase in the activation temperature to 230°C leads to an increase in catalytic activity only in catalyst samples with a high content (36–39 mass %) of the active component. It must be noted that the activation of the studied catalysts at 220–230°C makes it possible to achieve high values of catalytic activity sufficient for their industrial operation.

Thus, the conducted studies have confirmed that the NIAP-07-07 catalyst begins to be activated at 220°C, which is more than 100°C cooler than the methanation catalysts used for industrial conditions.

Table 4. The catalytic activity of Ni catalysts during the methanation process

Activation temperature, °C	The residual CO content in the purified gas, ppm				CO content in the purified gas, vol %
	NIAP-07-01	NIAP-07-07			
	mass % NiO				
	39	25	31	36	
After 210	>10	>10	>10	>10	0.70
After 220	0.00	0.00	0.00	0.00	0.70
215	0.00	0.00	0.00	0.00	
214	>10	>10	>10	>10	
After 230	0.00	0.00	0.00	0.00	0.72
215	0.00	0.00	0.00	0.00	
214	0.00	0.00	0.00	0.00	
213	0.00	>10	0.00	0.00	
208	0.00	–	0.00	0.00	
207	>10	–	>10	0.00	
202	–	–	–	0.00	
201	–	–	–	>10	

Table 4. Continued

Activation temperature, °C	The residual CO content in the purified gas, ppm				CO content in the purified gas, vol %
	NIAP-07-01	NIAP-07-07			
	mass % NiO				
	39	25	31	36	
After 550	0.00	0.00	0.00	0.00	0.65
176	0.00	0.00	0.00	0.00	
175	0.00	>10	0.00	0.00	
171	0.00	–	0.00	0.00	
170	0.00	–	>10	0.00	
167	0.00	–	–	0.00	
166	0.00	–	–	>10	
154	0.00	–	–	–	
153	>10	–	–	–	

It can also be noted that, even with an active component content of 25–31 mass %, the developed catalysts will ensure stable long-term operation in compliance with the regulatory values of the methanation stage since the working temperature of the methanator is 300–320°C.

The activation process at 550°C led to a significant increase in catalytic activity for all samples studied. One can note that the catalytic activity tends to increase as the content of the active component increases. In addition, it was found that the developed catalysts practically retain their catalytic activity at 165–175°C even after overheating at 650°C for 30 h, which confirms their high thermal stability.

In ammonia synthesis units, the converted gas is purified from CO_2 in absorbers using absorbers such as Beinfield and Karsol alkaline solutions as well as organic absorbers in the form of aqueous solutions of monoethanolamine and activated methyldiethanolamine [20, 21]. Due to technological violations, the absorption of absorbents from the stage of purification of the converted gas from CO_2 to the methanation reactor can occur. In most cases, for Ni–Al catalysts, a decrease in catalyst activity and an increase in the gas-dynamic resistance of a methanation reactor occur [22]. As a result of these studies, it was established that the developed catalysts remain highly stable when exposed to these absorbents at 280–320°C [23, 24].

In 2017, an NIAP-07-07 catalyst with a lower activation temperature was loaded into the methanator of the CO methanation unit of the Pyrogas Separation and Benzene Production workshop at *Stavrolen* (Budennovsk, Stavropol krai, Russia). The catalyst was activated by process gas. After heating, the temperature in the methanator was increased to 220°C, and the CO content at the inlet of the reactor was increased to 0.7–0.8 vol % with a load of 4000–6000 m^3/h. After the methanator began operating (inlet temperature: 235°C; temperature in the catalysis zone: 255°C), the total residual content of CO and CO_2 in the purified methane–hydrogen fraction was less than 1 ppm. The catalyst provides the necessary degree of purification from oxygen-containing compounds at a load of feedstock of up to 16 000 m^3/h.

CONCLUSIONS

It was established that, under the selected conditions for preparing a mechanical mixture of HNC and active alumina with a liquid reagent, a chemical interaction occurs between the two and NHCA is formed as a result of this chemical reaction. The compositions of the catalyst with various amounts of the active component were optimized, and the temperature regions of the active phase precursor's activation process were determined. The catalyst has a low activation temperature and high catalytic activity, thermal stability, and mechanical strength. It can be created from the same catalyst mixture by tableting or extrusion in the form of granules of various geometric shapes and sizes. As a result, the catalyst has been used for industrial purposes.

The authors declare no conflicts of interest.

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