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ABOUT THE CAUSES OF DEACTIVATION OF THE NICKEL CATALYST METHANE CONVERSION IN THE COURSE OF ITS OPERATION

The results of studies of the chemical, phase composition, and structure of the samples of lining materials, and conversion catalysts of natural gas used in the mine unit are outlined. Possible mechanism of nickel ablation from catalyst that caused the reduction of the specific active surface of the catalyst and consequently its activity is described.

Introduction. The conversion of natural gas to produce hydrogen is a catalytic process. Nickel catalyst manifests the highest catalytic activity in these reactions, nickel content ranges from 3 to 40 wt. %. The main producers of these catalysts are the firms “Tonce”, “Sud-Chemie”, “Alvigo”, etc.

Nickel catalysts are obtained by double triple and quadruple dipping of the carrier with solutions of nickel salts and promoters. $\alpha\text{-Al}_2\text{O}_3$ (corundum) or other thermally stable materials were used as carriers. The finished catalyst is calcinated at 400°C to transfer nickel salts into oxides. The catalyst of this type is used at JSC “Grodno Azot” in the production of ammonia and methanol. In accordance with the planned modernization of JSC “Grodno Azot” in the workshops “Methanol” in summer in 2013 the production was stopped in order to install the new mining converter (Fig. 1). It required additional work to line the converter and load a new batch of catalyst. The NIAP 03-01 and NIAP 03-01B of the company “Alvigo”, with different geometrical dimensions were selected as catalysts. The catalyst NIAP 03-01B has larger granules of cylindrical shape, which were loaded only on the topmost layer of a catalyst basket.

When the workshops was put into operation, it was marked by a relatively low degree of natural gas conversion (95%), resulting in methane output 3.0 to 3.5%. This was the reason for stopping production and determining the causes of the nickel catalyst deactivation.

The loss of catalysts activity can be caused by three main reasons: thermal instability, the recrystallization of the active component and poisoning the nickel catalyst by the compounds of silicon, sulfur and others.

The objectives of this work were:

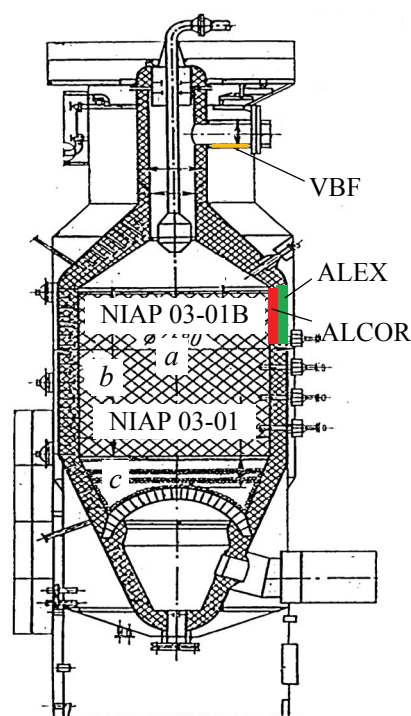
study of the chemical and phase compositions of the initial catalyst and the catalyst discharged from the converter after its stopping;

determination of the active substances contents of metallic nickel on the surface of the carrier;

composition of the lining materials “Alcor” and “Alex”.

Due to the fact that the catalyst activity is a function of many variables, in particular its chemi-

cal and phase compositions, and the composition of the gas phase, the purpose of this study was to determine the reasons for the low activity of nickel catalyst, which was observed in the early hours of the work.



The catalyst location in the apparatus:

a – centre; *b* – periphery; *c* – pit.

Fig. 1. The design of mining converter

Main part. When the catalyst discharged from the charge of the converter was examined, the following was noted:

1) colour change of the granule surface of the catalyst NIAP 03-01B in the upper near-wall layer and the catalyst NIAP 03-01 in the lower near-wall layers;

2) strong adhesion and formation of granules conglomerates of the catalyst NIAP 03-01 in the lower near-wall layers;

3) colour irregularity of granules on the layer of catalyst.

The study of the chemical and phase composition and structure of the samples was carried out

with modern facilities: X-ray diffractometer "D8 Advance" by "Bruker" (USA) and scanning electron microscope JEOL JSM - 5610LV (Japan) using an electronic probe energy dispersive X-ray fluorescent analysis of the brand JED 22-01.

Summarizing and analyzing the experimental data, obtained during the complex investigation of the lining samples of the brands "Alex" and "Alcor", and the catalysts from various parts of the apparatus, it was determined:

- 1) the lining materials "Alcor" and "Alex" have no silicon compounds;
- 2) absence of Ni on the catalyst surface in the upper layer of the apparatus;
- 3) presence of calcium aluminate compounds on the granules surface of the catalyst NIAP 03-01B, located in the upper near-wall layer of the catalyst (Fig. 2);

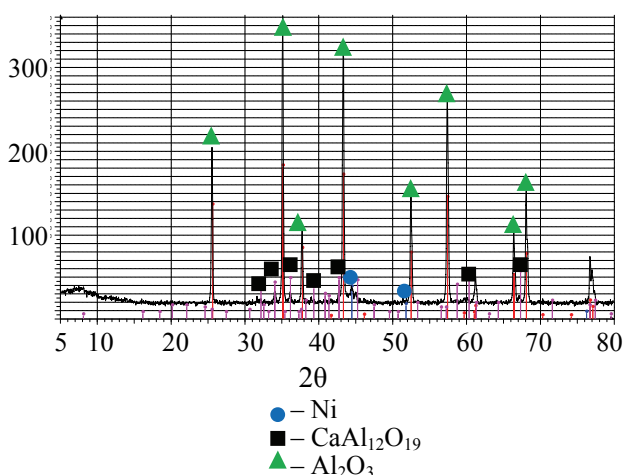


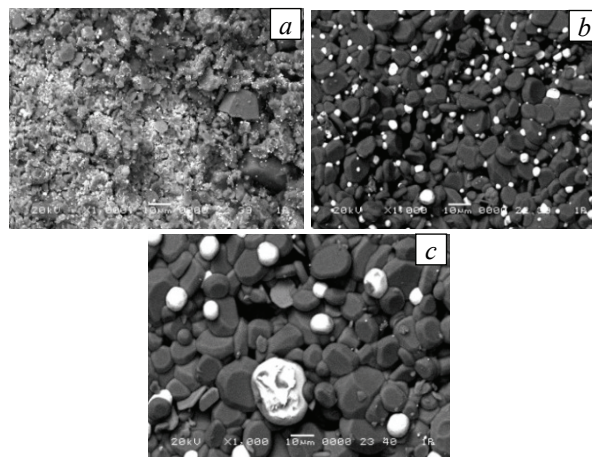
Fig. 2. X-ray diagram of scrape layer from the catalyst NIAP 03-01B surface after the discharge (periphery)

- 4) agglomeration of nickel crystallites of on the granules surface located in the lower layer of the catalyst (Fig. 3);

5) the presence of silicon on the granules surface of the catalyst. In addition, silicon compounds in large quantities are present in other areas of the system: deposits on the outside of the reaction tubes of the tube furnace, and on the surface of the average temperature of the catalyst the CO conversion lay the assumptions about nickel ablation from the surface of the catalyst.

To ground the elemental metallic nickel ablation from the catalyst surface even at high temperatures (1,000–1,300°C) is not possible, because the phenomenon of nickel ablation from a face-centered cubic lattice is not described in scientific literature. Because the ablation is established, it can be explained by the fact that the temperature in the catalyst bed was higher than 1,450°C and metallic nickel could pass into the molten state, and then as a result of evaporation, and it would pass

into the gas phase. It could also be explained by presence of some substance, which reacts with nickel in an extremely active state, forming a volatile compound, passing from the surface of the catalyst to the gas phase.



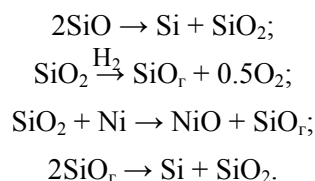
The location of the catalyst in the converter:
a – center; b – periphery; c – pit

Fig. 3. Microphotographs of the investigated catalyst surface NIAP 03-01

It is known [1] that the nickel and metals of group VIII manifest a pronounced tendency to form alloys. The elements of group VIII, in particular nickel, react with a number of non-metals (primarily B, C, Si, P) and usually form stable compounds. So, nickel reacts with silicon with the formation of a broad class of compounds called silicides [1–4]. With the increase in the number of Si atoms in the silicide phase, the transition from one-dimensional to two-dimensional and three-dimensional structures of silicon atoms is observed. Lower silicides have a metallic structure; the silicon atoms being isolated.

The presence of silicon in the system is of particular interest, as it is unacceptable. Primarily, it is due to the fact that at temperatures above 1,000°C oxygen compounds of silicon form gaseous silicon monoxide [5]. It is known that gaseous oxygen compounds, in particular silicon, are often unsaturated, very reactive particles that can vigorously react with other solid or liquid substances.

Taking into account this fact, we can assume that the silicon monoxide formed at 1,000–1,200°C is adsorbed on the nickel crystallites; the disproportionation reaction taking place, for example:



The resulting Si reacts with high reactive elemental nickel and forms depending on the temperature and the equivalent ratio of the elements, incongruent melting compounds presented in the table. The presence of melt on the surface of the catalyst may cause nickel ablation from the surface of the granules.

It is known [3] that even the most low melting substances evaporate and pass into the gaseous state. The chemical phenomena of dissociation and association, and the evaporation process are quite complex. There are some data on metal oxides evaporation; oxides or the products of their partial or total decomposition pass into the gaseous phase. It is shown [3] that there are gas molecules Me_xO_y , metal vapours, oxygen (molecular and atomic), polymer gaseous molecules and others in the vapour oxides. From the series of studies on the evaporation of oxides of alkaline earth elements (III–VI groups) of the periodic system, it follows that if vapour contains gas molecules, their volatility will be greater than that which should be according to the calculations, provided that during the evaporation there is decomposition into free atoms. The behavior of silicides melt can be fully described with experimental data and energy characteristics of gaseous silicides, i.e., the energy required to break molecules into separate atoms, in particular nickel and silicon, which would allow us to make different thermodynamic calculations of the most likely processes. Due to the absence at this stage of research such calculations we can only imply the processes that occur on the surface of the granules of the catalyst and in the shaft of the converter.

The melting temperature of Ni and Si compounds [3]

No.	Compounds composition	Melting temperature, °C
1	Ni_3Si	1,162
2	Ni_2Si_2	1,255
3	Ni_2Si	1,290
4	Ni_3Si_2	845
5	$NiSi$	995
6	$NiSi_2$	1,000

The fact that the maximum degree of ablation is typical for upper near-wall surface can be explained by the hydrodynamics of the process, i.e. the gas flow distribution within the volume of the shaft of the converter and various temperature conditions influencing the course of the disproportion reactions of oxygen-containing compounds of silicon and interaction of Ni and Si.

Thus, the above mentioned explanation of nickel ablation from the surface of the granules NIAP 03-01B is based on the experimental data,

according to which silicon compounds are detected in the catalyst composition of the base layer, in large quantities in the materials on the outer side of the reaction tube, the layer of dust on the catalyst.

Taking into account the possibility of occurrence of the above-described processes, it is possible to explain the “adhesion” of the granules of the catalyst due to the fact that the silicides melt formed during the evaporation of vaporous substance contained in the gas phase combined or separately, is adsorbed on the surface of the granules of the catalyst and the vapor – liquid – solid phase transitions depending on temperature, may contribute to the solid-phase interaction of contacting granules of the catalyst. The silicon monoxide can also adsorb onto the surface of the granules of the catalyst and can be in various forms depending on the temperature of the granules and composition of the gas phase.

The described mechanism of nickel ablation from the granules surface of the catalyst explains some of the observed phenomena taking place in the shaft of the converter. Thus, the presence of nickel on the lining walls of the shaft of the converter is confirmed by electron microscopy and X-ray analysis; nickel may be in the form of oxide. From this point of view, one can explain the agglomeration of nickel crystallites on the granules surface having a relatively lower temperature than the granules of the upper layers of the catalyst. When analyzing the data of electron microscopy crystallites in the lower layers on the catalyst surface are larger than nickel crystallites on the catalyst surface in the upper layers. Obviously, vaporous nickel, when adsorbed on the surface of the nickel crystallites, is capable of phase transition from vapour to melt and crystallite due to temperature in the catalyst layer.

The agglomeration of nickel crystallites on the corundum surface can occur in a parallel way to the described phenomenon, and independently as well. The nickel crystallites on the granules surface in the upper layers, where the temperature is higher, are formed mainly in the course of nickel oxide reduction. It is formed by the nickel nitrate decomposition, evenly distributed on the impregnated carrier. In the catalyst located in the lower part of the shaft of the converter, the temperature and hydrodynamic conditions differ from the temperature and hydrodynamics of the upper layers. The formation of spinels and their subsequent transformation into NiO and then in metallic nickel is typical mainly for the bottom layers. In addition, the formation of complex spinels is possible, for example $NiO \cdot Al_2O_3 \cdot NiAl_2O_4$. In this case the formation of spinels can be local. Therefore, the sources for the nickel crystallites growth in a reducing environment can be nickel oxide as well as

spinel; their location not being uniform. In this case quite large nickel crystallites can be formed.

There is a small amount of calcium compounds on the white granules of the catalyst surface, probably due to contact with the dust of the catalyst surface from the lining containing calcium aluminate. This phenomenon is characteristic only for the upper layer of the catalyst, in other examples of the catalyst compounds calcium is not found.

Conclusion. It is established that the cause of the catalyst NIAP 03-01 low activity is a reduction in the specific surface of the active component (nickel) due to its ablation. Nickel ablation from the surface of the catalyst upper layers could occur as a result of the presence of the silicon compounds, which formed the basis for the formation on the surface the catalyst granules incongruently melting in the temperature range 1,000–1,290°C compounds Ni_xSi_y , which served as a source of nickel vapour or its compounds with silicon ablated from the granules surface.

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