DEVELOPMENT OF PRODUCTION OF NATURAL GAS PRIMARY REFORMING CATALYST

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ABSTRACT
The activity of the prepared catalyst samples was determined according to TU 113-03-352-87 according to the method TU 113-03-313-85 "Nickel GIAP-3-6N catalyst for the conversion of gaseous hydrocarbons". The organization of production is planned at OJSS "Maksam-Chirchik" and is included in the list of innovative works of SJSC "Uzkimyosanoat".

Key words: Hydrocarbon gas, Chemical composition, nickel, Mixed catalysts.

1. INTRODUCTION

Hydrocarbon gas conversion catalysts are divided into two main groups: for primary reforming - endothermic, flowing in tube furnaces and auothermal reforming in shaft converters.

Mixed catalysts contain 23-26% NiO, which is 2-3 times more than in supported catalysts. Mixed catalysts lose strength when heated in air above 800 °C.

Due to the high content of nickel and the method of its introduction, mixed catalysts lose strength to a greater extent upon reduction. The binding of nickel to a low-activity form can occur both during preparation and during operation.

2. MAIN PART

In view of these disadvantages, the average duration of operation of mixed catalysts rarely exceeds 3 years [1]. Therefore, to date, all major foreign companies use supported catalysts for the conversion of hydrocarbon gases.

Characteristics of catalysts for the primary reforming of hydrocarbon gases.

| Catalyst brand | Catalyst type | Shape, dimensions | Chemical composition, % mass. | Bulk density, kg / dm³ | Mech. End strength / MPa | Activity: residual CH₄ content, % vol. | Carrier |
|----------------|---------------|-------------------|-------------------------------|------------------------|------------------------|--------------------------------|--------|
| GIAP-19        | Inflicted     | 14,5x6,5x12 rings | NiO-11                        | 0,9+1,2                | 35+60                 | 1,3+2,5                      | 37 5   |
| GIAP-19        | Mixed         | 15x7x12 rings     | NiO-26                        | 0,9-1,0                | 36+6                  | 1,3+2                        | A1₂O₃  |
| AKN-M (c / c)  | Angarsk       | Inflicted         | NiO-6,0/6,0                   | 1,4/1,2                | 18/5                  | -                            | A1₂O₃, CaO |
| DKR-1 (K)      | Inflicted     | 15,0/17,0 ±2,0    | NiO-12,0±2                    | 1,2±0,2                | 30/2                  | 9,5÷10,7                     | A1₂O₃  |
| NIAP-03-01     | Inflicted     | 7-hole 16,5x14x3  | NiO-11,0                      | 1,0±0,1                | 40/3                  | 3,3                          | A1₂O₃, CaO |
Katalco 25-4Q, Katalco 57-4QJonhsonmatthey
Katalco 25-4Q, Katalco 57-4Q
Inflicted
4-hole cylinders 16x9,5 19x19
NiO-18,0 0,95 7/6
NiO-16,0 0,90 7/6
- 9,3-10,5 CaO/A1_2O_3
- 9,3-10,5 CaO/A1_2O_3

RK- 211
RK -201
RK-67-7H
HaldorTopsoe
Inflicted
7-hole cylinders 16+17/9+11/3
+ 4
NiO>9,0 NiO>14,0 NiO>15,0
0,9+1,0 Not measured. > 2,5
- 10,26+ 10,45 MgAl2O3+ calcium aluminate
K-0,3 -0,6

G-90 LDP
SudChemil AG
Inflicted
5-hole cylinders 16x16
NiO-11,0±1 0,9=1 40 >3
- 8,0+ 9,4 calcium aluminate

At OJSS "Maksam-Chirchik", a technology for the production of a supported nickel catalyst for the primary reforming of hydrocarbons under the brand name ChKR-3-06 was developed. The catalyst was prepared by impregnating a support consisting of aluminum oxide with the addition of 4-5% calcium oxide with nickel nitrate.

The cooking technology was as follows. The carrier is prepared from alumina, wood flour, nitric acid by adding a binder solution - Ca(N0₃)₂, based on the content of 3-5% by weight CaO in the finished carrier.

The carrier is wilted, dried at 100-130 °C and calcined at a temperature of 1300-1360°C with a gradual rise in temperature. The carrier is impregnated with a mixed solution of NiNO₃ and A1 (NO₃)₃ at a ratio of 3: 1.

The concentration of NiNO₃ in the impregnating solution is 480 g/dm³. A binder solution is added to the impregnating solution at the rate of 0.3% CaO in the impregnating solution.

Determination of the activity of the prepared catalyst samples was carried out according to TU 113-03-352-87 by the method TU 113-03-313-85 "Nickel GIAP-3-6N catalyst for the conversion of gaseous hydrocarbons".

The activity was determined at a temperature of 500 and 700°C for 7 hours, taking a sample of converted gas every hour for analysis.

Before determining the activity, the catalyst was reduced in a stream of hydrogen at a temperature of 500°C for 6 hours.

Gas analyzes were carried out chromatographically on an M-3700 and LKhM-8 MD chromatograph, according to the methodological manual of the TZL chromatography sector. The results of the test of activity are presented in table. 2.

### Table 2

| Brand catalyst | Mixing composition of the carrier | Moistur capacity, % | Fur Strength kg/cm² at the end | Activity at W=6000h | Gas at the entrance to the reactor, SG | Reactor outlet gas | Note |
|----------------|---------------------------------|---------------------|-------------------------------|---------------------|--------------------------------------|--------------------|------|
| CHKR-3-06 NiO-9.7% thrice soaked | Alumina, solution Cat(NO₃)₂ of calculation for 4% CaO, wood flour-6% HNO₃ | 18 | 188 | 2,2,0=2,2/1 | 35,3 | 2,0 | 12,8 | 500°C |
| | | | | | 35,3 | 2,2 | 13,9 |
| | | | | | 32,7 | 1,9 | 14,8 |
| | | | | | 30,7 | 1,8 | 15,4 |
| | | | | | 31,6 | 2,0 | 14,8 |
| | | | | | 32,1 | 1,8 | 14,7 |
| | | | | | 32,1 | 1,8 | 15,1 |
| | | | | | md.32,8 | | |
| | | | | | 3,4 | 17,0 | 9,3 |
| | | | | | 3,4 | 17,0 | 9,3 |
| | | | | | 4,1 | 18,1 | 7,8 |
| | | | | | 3,8 | 17,5 | 8,3 |
| | | | | | 3,3 | 17,6 | 6,3 |
| | | | | | 5,0 | 18,7 | 7,3 |
| | | | | | 2,5 | 16,4 | 9,8 |
| | | | | | md.3,7 | | |

As follows from the data obtained, the prepared catalyst provides a conversion rate of 63% on average at 500°C. 93% at 700°C and 99.4-99.5% at 800°C.
Comparison of the concentrations of CO and CO\(_2\) at the outlet of the reactor shows that at endothermic conversion of natural gas proceeds predominantly according to reaction (1).

Comparison of the activity of the catalysts obtained by us with the catalysts of foreign firms, table. 3 shows that the ChKR catalyst is not inferior in activity to catalysts for the primary reforming of natural gas.

**Table 3**

| Manufacturers     | Angarsk Russia | Dorogobuzh Russia | NIAP Russia | NIAP Tallinn Estonia | Jon. Matt. | HoldTops oe | SuedCh em | Chirchik Uzbekistan |
|-------------------|----------------|-------------------|-------------|----------------------|------------|-------------|------------|---------------------|
| Content           |                |                   |             |                      |            |             |            |                     |
| Residual methane, % vol. | 4 at 800°C | 10.4 - 10.7 at 700°C | 3.3 at 800°C | 3.3 at 800°C | 10.5 at 700°C | 10.45 at 700°C | 9.4 at 700°C | <9.56 at 700°C |

The results of testing the activity of the developed catalyst were compared with the data of the operating AM-76 unit of OJSS "Maksam-Chirchik".

In the tube furnace of shop AM-2 there is mainly a catalyst of the brand "HoldTopsoeAS" (Denmark) with a GIAP-8 addition. At a temperature in the tubes of 840°C, the residual methane content was 6-7% vol., CO - 10.8% vol. and CO\(_2\) - 8% vol.

**CONCLUSION**

This comparison once again confirms the conclusion that the developed catalyst meets the requirements for the catalysts of primary endothermic reforming in terms of activity.

It follows from the table that the CHK 3-07 catalyst in all respects is not inferior to the world's best samples.

The developed technology for preparing the CHK 3-07 catalyst is as follows:
- Mixing of oxides of aluminum and calcium with nitric acid with a concentration of 20%.
- Forming the resulting paste in the form of cylinders.
- Wetting and drying formed
- Calcination at a temperature of 1400 °C.
- Grinding of the pumped-over cylinders.
- Moistening of the resulting powder, forming on a tablet machine.
- Three times impregnation with a solution of Ni(NO\(_3\))\(_2\) = 3: 1.
- Drying after each impregnation at a temperature of 250 - 300°C.
- After the last impregnation, calcination at a temperature of 500°C.

Organization of production is planned at OJSS "Maksam-Chirchik" and is included in the list of innovative works of SJSC "UzKimyosanoat".

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