Processing of Methane over the Oxide Catalysts

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Abstract—Catalysis of the supported oxide catalysts in the direction of the methane oxidation reaction is investigated. Modified nickel-containing catalysts studied at the reaction of partial oxidation of methane to synthesis gas. The effect of modifying additives (cerium and lanthanum oxides) on the activity and resistance to coking NiO / γ -Al₂O₃ catalyst was defined. The introduction of cerium and lanthanum oxides increases resistance to catalyst coking. Rising of lanthanum modified catalyst activity associated with a decrease in its recovery temperature and increased dispersion of particles of metallic nickel. It is found that the developed 3% NiO + 2% La_2O_3 / y-Al₂O₃ catalyst for 250 hours under laboratory conditions (CH₄: $O_2 = 2$: 1, $T_r = 750^{\circ}C$ and $W = 1000 \text{ h}^{-1}$) does not lose its activity. It was determined that the use of a tungsten heteropoly acid as the active phase supported on Al₂O₃ can direct the process towards the formation of ethylene.

Index Terms—Methane, oxidation, catalyst, ethylene, synthesis gas.

I. INTRODUCTION

The catalytic conversion of natural gas into motor fuel components, the raw material for the petrochemical industry and organic synthesis for over 20 years is the subject of intensive research are driven by the problem of reducing the resources of hydrocarbons of petroleum origin [1]. Of particular interest in this respect are the partial oxidation of methane to synthesis gas and an oxidizing dimerization of methane to C_2 hydrocarbons [2]-[5].

Syngas is a feedstock for the oxygenates (methanol, dimethyl ether, etc.), as well as for the preparation of liquid and solid hydrocarbons by Fischer-Tropsch synthesis. Hydrogen, which is part of the synthesis gas, is used in a number of large chemical processes (production of ammonia, fuel hydrotreating, hydrocracking of petroleum feedstock, the isomerization of n-alkanes and others).

At the same time, hydrogen can be widely used in the future as an alternative engine fuel [6]-[8].

 C_2 - C_4 olefins are of considerable interest as a raw material for industrial organic synthesis, which are widely used for the preparation of polymer materials, plastics, alcohols, esters, carboxylic acids, components of motor fuels, and others.

Ethylene production ranks first in terms of production among basic petrochemicals. On its basis produced the majority of organic synthesis products and polymer materials such as polyethylene, polyvinyl chloride, polystyrene, ethylene oxide, ethylene glycol, synthetic ethyl alcohol and al.

For countries with large reserves of cheap natural gas, the practical implementation of these processes today seems economically justified [9]-[12]. Therefore, the creation of highly efficient, selective and stable catalysts for processing light hydrocarbons to produce valuable products of petrochemical synthesis is an important practical and strategic objective.

We report here on the activity of silicon and aluminum oxides, and a new series of catalysts on the base of $H_8[Si (W_2O_7)_6] nH_2O$ and NiO-La₂O₃, supported on SiO₂ and Al₂O₃ to be tested in partial oxidation processes and oxidative dimerization of methane.

II. MATERIALS AND METHODS

Experiments to test the catalytic activity of the catalysts developed conducted on an automated flow set to the temperature range 600-850°C at atmospheric pressure. This set consists of three main parts - the preparation of the initial gas mixture, the catalyst quartz flow reactor and gas chromatograph for analysis. The reactor is a quartz tube 25 cm in length and an internal diameter of 9-9.5 mm.

During the experiments, the reactor is placed vertically incoming stream fed into an open top portion and exits through the hole in the bottom of the vial. Control composition and flow rate of the reacting starting compounds, the reactor temperature regulation, the evaporator assays run through software. The reaction products were identified by chromatography on device "Chromos GC-1000" using an absolute calibration method and a thermal conductivity detector. Separation of components was carried out on two columns (length 2 m, internal diameter 3 mm) filled with NaX zeolite and porapak -T, carrier gases - helium and argon.

Determination textural properties of developed catalysts and carriers (specific surface (S_{sp}), pore volume and pore size distribution) were carried out by low-temperature nitrogen adsorption at 77 K on the automatic equipment BEL Japan Inc and heat argon desorption on device BELSORP-mini II. Before beginning the sample test is produced its degassing consists in heating of the sample in the stationary gas flow at a predetermined temperature to remove from the surface of the test material absorbed gases and vapors. The instrument can examined simultaneously to three samples independently. Pressure sensor - 0.666 Pa / min. Weight of catalyst 2.92 g. Experience time 3 hours. Pressure of saturated vapour 102.19 kPa. Vm = 30.563 cm³ (STP) g⁻¹. The surface area calculated by a BET equation.

Diffraction data (XRD) were obtained on apparatus Bruker AXSD2 Phaser (LYNXEYE high speed detector)

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powder x-ray BrukerD2 using CuK α radiation, voltage 30 kV and current 15 mA. Radiographs were collected in 2⁰ angle between 10° and 90° with a scan speed of 5°/ min. The average size of the crystallite of the catalyst was evaluated by X-ray diffraction peak of the expansion using Scherrer equation D = 0.9 λ / β cos θ , where λ -wave length of the radiation (h = 0.154 nm) Cu K α , β -half-width of the peak, and θ -Bragg diffraction peak angle.

Morphology of surface oxide catalysts was performed by scanning electron microscopy Quanta 200i 3D.

Temperature-programmed reduction (TPR) was performed in a laboratory setting, including the gas preparation system with a tubular reactor furnace and a thermal conductivity detector. Hydrogen reduction was carried out by passing the gas mixture (5% H₂ and 95% Ar) through a reactor at a rate of 30 ml / min. Linear heating rate was 10^{0} C / min. The changing the concentration of hydrogen in the stream was monitored using a thermal conductivity detector.

Quantitative determination of the absorbed hydrogen was performed by calibration, built on the basis of reducing of accurate batches of NiO.

Catalysts were prepared by co capillary wetness impregnation of the support with solutions of nitrates and subsequent drying at 300° C (2 h) and calcination at 500° C for three hours.

III. RESULTS AND DISCUSSION

Known from the literature [13]-[15] that the active phase for the production of synthesis gas by partial oxidation of methane is the nickel oxide.

Therefore, were synthesized nickel catalysts, supported on alumina for the production of synthesis gas from methane.

It was studied the effects of nickel oxide contents in the concentration range of 0.05 to 10 wt. % supported on alumina, on the direction of the process. Fig. 1 shows the effect of concentration of the active phase on a support for methane conversion and hydrogen and carbon monoxide yields at a reaction temperature of 750° C.



Fig. 1. Effect of nickel oxide concentration on yield of reaction products.

The figure shows that an increase in the nickel content of 0.05 wt. % to 10 wt. % increases the methane conversion and synthesis gas outputs. Moreover, since the concentration of nickel oxide on the support of 3 wt. % begins a sharp increase of methane conversion and synthesis gas output.

A further increase in the nickel oxide content up to 10% does not affect the yield of synthesis gas. Over the 3% Ni / γ -Al₂O₃ catalyst hydrogen yield reaches 34%, mono oxide - increases to 24% and the carbon dioxide yield is reduced to 0.5%, the methane conversion was 96%.

It should be noted that with increasing nickel oxide content of 3 wt. % to 10 wt. % conversion parameters and the output of desired products are not changed. Perhaps this is due to the same active phase composition of the catalyst.

In order to further improve the efficiency of 3 wt. % Ni / γ -Al₂O₃ in the reaction of partial oxidation of methane, the catalyst was modified with rare earth elements.

Phase intensity reflexes with increasing nickel content of from 3% to 10% on the support is not changed substantially.

It is clear from X- rays, that after the oxidation of methane over these catalysts in the spectrum appears reflex referring to the metal nickel. This change is due to the fact that during the partial oxidation of methane under the influence of the reaction medium (CH₄, H₂, CO), some of the nickel oxide is reduced to metallic nickel.



Legend: a- 1% Ni-; b- 3% Ni-; c - 5% Ni-; d- 7% Ni-; e - 10% Ni / γ -Al₂O₃ Fig. 2. XRD spectra of 1-10% Ni / γ -Al₂O₃ before and after the reaction.

Based on the review of the literature [16], [17] the oxides of cerium and lanthanum are selected as modifying additives (Fig. 3).



 $1-Ni\ /\ Al_2O_3;\ 2-\ Co\ /\ Al_2O_3;\ 3-\ NiSe\ /\ Al_2O_3;\ 4-\ NiLa\ /\ Al_2O_3$ Fig. 3. Effect of modifiers on the catalytic activity of Ni / Al_2O_3 catalyst.

TABLE I: TEXTURAL CHARACTERISTICS OF THE CATALYSTS

| Catalyst | S _{sp} ., м ² /g | The spec. pore vol., sм ³ /g | Average pore size, нм |
|--------------------------------------|--------------------------------------|---|--------------------------|
| Ni/Al ₂ O ₃ | 161 | 0.069 | 1.7 |
| Ni-Ce/Al ₂ O ₃ | 158 | 0.068 | 1.7 |
| Ni-La/Al ₂ O ₃ | 163 | 0.070 | 1.7 |

Fig. 3 shows that the best results are obtained at NiLa / Al_2O_3 catalyst, where the degree of methane conversion reaches 95%, yields of hydrogen and carbon monoxide -

46.4 and 40.0%, respectively.

The catalysts were tested by the BET method. The results are shown in Table I. As seen from the table, the texture of the catalysts are not very different from each other.

The specific surface area of nickel catalyst modified with lanthanum oxide is $163 \text{ m}^2 / \text{g}$.

However, the addition of cerium and lanthanum oxides increases the resistance of a nickel catalyst to coke deposition (Fig. 4).



(a) NiLa/γ-Al₂O₃, (b) NiCe/γ-Al₂O₃,
(c) NiCo/γ-Al₂O₃, (d) Ni/γ-Al₂O₃
Fig. 4. SEM micrographs.

As seen in Fig. 4, after 30 hours of testing in the oxidation of methane on Ni / γ -Al₂O₃ catalyst surface is formed of carbon filaments. Modified by cobalt sample was also subjected to carbonization. While the introduction of cerium oxide and / or lanthanum oxide in the Ni / γ -Al₂O₃ catalyst lowers the carbonization of catalyst.

Oxides of aluminum and silicon have been studied in dimerization of methane to ethylene in the reaction condition: ratio of CH₄: $O_2 = 2$: 1, $W = 2000 \text{ h}^{-1}$ and $T_r = 700-850^{\circ}\text{C}$. The results are shown in Table II.

TABLE II: INFLUENCE OF REACTION TEMPERATURE ON THE ACTIVITY OF OXIDES

| Oxides | T,⁰C | Concentration, vol. % | | | | |
|------------------|------|-----------------------|----------|------|-----------------|--|
| | | H_2 | C_2H_4 | СО | CO ₂ | |
| SiO ₂ | 700 | - | 4.5 | 15.8 | 14.5 | |
| | 750 | 0.96 | 4.8 | 17.2 | 13.3 | |
| | 800 | 2.5 | 4.5 | 14.3 | 16.3 | |
| | 850 | 4.1 | 4.2 | 12.3 | 18.4 | |
| Al2O3 | 700 | 1.2 | 4.1 | 6.6 | 26.4 | |
| | 750 | 4.5 | 4.2 | 6.9 | 22.6 | |
| | 800 | 7.9 | 4.3 | 8.1 | 21.5 | |

As seen from the table, the reaction temperature and the nature of the oxides are not greatly affect the composition of the reaction products. Over the silicon and aluminum oxides formed hydrogen, ethylene, and carbon oxides. On SiO_2 with increasing reaction temperature is increasing hydrogen and carbon dioxide concentration. Ethylene and carbon dioxide outputs decrease with increasing temperature passing through a maximum at 750°C.

On alumina with an increase in reaction temperature is an increase in the yield of hydrogen, carbon monoxide and carbon dioxide concentration decrease from 26.4 to 21.3 vol. %. Maximum ethylene concentration 4.8 vol. % is observed at 750oC on silica.

Further oxides was supported by tungsten heteropoly acid

(HPA) with a concentration of 3 wt. %. Note that with the application of HPA selectivity to ethylene is increased, the highest yield of ethylene (5.9 vol. %) is observed over the catalyst HPA / Al_2O_3 .

IV. CONCLUSION

Thus, changing the catalyst composition and the conditions of the oxidation of methane can obtain valuable products as synthesis gas, and ethylene. Supporting of tungsten heteropoly acid on alumina leads to improved selectivity on ethylene.

For the process of partial oxidation of methane to synthesis - gas was developed an effective 3% NiO + 2% La_2O_3 / γ -Al₂O₃ catalyst. Based on the study of the complex physical and chemical methods (XRD, SEM and BET) found that modification of NiO / Al₂O₃ by lanthanum oxide provides a selective, resistant to carbonization catalyst.

It is shown that during the modifying the catalyst by la2o3 the new phases formed, raised the dispersity of the catalyst and decreased the temperature of reduction of nickel oxide.

It is found that the catalyst of 3% nio + 2% la2o3 / yal2o3 for 250 hours under laboratory conditions (ch4: o2 = 2: 1, tr = 750oc and w = 1000 h-1) does not lose its activity.

Further work will focus on the test of developed catalyst $(3\% \text{ NiO} + 2\% \text{ La}_2\text{O}_3 / \gamma \text{-} \text{Al}_2\text{O}_3)$ in a pilot plant under real conditions of the partial oxidation of methane to synthesis gas.

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