

Investigations of the SHS Cobalt Based Catalysts in Reaction of Synthesis Gas Production from Natural Gas

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Abstract

By means of selfpropagating high-temperature synthesis method metaloceramics based on cobalt oxide was obtained and its catalytic activity in reaction of methane conversion into various content synthesis gas in two sectional separately heated reactor at atmospheric pressure was studied. Temperature and volume flow rate influence on the yield of catalytic reaction products was also investigated. It was shown that the fuel conversion in oxidation process reached 90-98%. The optima working conditions of methane catalytic oxidation processes were found.

Introduction

At present the methane processing with its conversion in the predetermined chemical products is one of the most important problems. While a too large number of research works concerning the methane oxidation this problem didn't getting till now its sufficient solution. The use of different catalysts results mainly in low yield of such products as methanol, formaldehyde and C₂ hydrocarbons.

The natural gas or associated petroleum gas mainly constituted of methane now are used as power generating source materials or present harmful emissions and petroleum gas flares resulting in environmental pollution. So, about 10% of natural gas only are used to produce chemical products. [1]. In this connection the works aimed at synthesis of efficient catalysts and improvement of methane oxidation technology are very urgent and pressing problems. [2].

The applications of efficient catalyst systems provide the simplest methods of their production. For this aspect there is very interesting to investigate activity of catalysts obtained by SHS method and that through their structure defects show very high catalytic activity in the high temperature oxidation processes. [3].

Experimental

Experiment methods

The catalytic activity of cobalt catalysts was studied in a flow running system equipped with two sectional separately heated quartz reactor. The diameters of both first and second sections were equal to $\varnothing = 1$ cm. The length of first section was $L=13$ cm, and that of second section was $L=10$ cm, each of these both sections was equipped with individual electrical furnace those temperature being controlled by thermoregulator with accuracy up to $\pm 1^\circ\text{C}$. The first bottom section served to preheating of the reaction mixture. On the quartz glass substrate of 3-5 mm fraction of the second section the predetermined catalyst amount (4 cm^3) was spread. In the catalyst mass at the center one thermocouple encapsulated into the quartz tube to control temperature during the experiment running out and in process of catalyst activation was provided. Before every subsequent experiment the catalyst was activated with oxygen ($Q=100\text{ cm}^3/\text{min.}$) at 600°C reactor temperature during 1 hour exposure. Then this reactor was blown down during 5-7 minutes with inert gas (N_2) fed at the same flow rate to remove oxygen residues.

The analysis system consisted of three chromatographs: «CHROME-5», «Gaschrome 3101» and 3700 model. The highly pure helium served as a gas-carrier. As sorbent there was used the Porapak Q and molecular sieves CaX. The calculations of the chromatograms were carried out by internal

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normalization method.

The initial composition of cobalt catalyst charge was as follows: 94% Co_3O_4 , 6% Al. The charge was thoroughly stirred, press-processed in a cylinder mould at 25 MPa pressure and then burned up in the muffle furnace. The initial heating temperature during 3 minutes was 790 °C. Then the charge was fired with magnesium metal powder and after SH-synthesis completed, it was removed out from the furnace. As showed by RFA analysis results the obtained catalyst sample contained: 1% Co, 1% Al, 35% CoO, 55% CoAl_2O_4 , 7% Co_3O_4 . The sample porosity was up to 51.9%, density - 2.48 g/cm^3 , specific surface - 1.18 m^2/g .

The methane catalytic conversion using the Gause - Zeidel one-factor experiment planning method was

investigated [4]. The temperature of the first section was constantly equal to 700 °C, at ratio $\text{CH}_4:\text{O}_2 = 2:1$, the flow rate of supplied reactant mixture being 9000 h^{-1} , and the temperature of the second section was varied by 100 °C temperature variation step within 400-800 °C range.

Results and discussion

The chromatography data proceeding enabled to find that the main products of methane oxidation conversion based on the SHS cobalt catalyst are the following substances: H_2 , CO, CO_2 and H_2O . Such products as C_2H_6 , CH_2O and of higher condensation weren't found. The results of chromatographic analysis of the compounds formed depending on the temperature of second reactor section are given on the Fig. 1 (a, b).

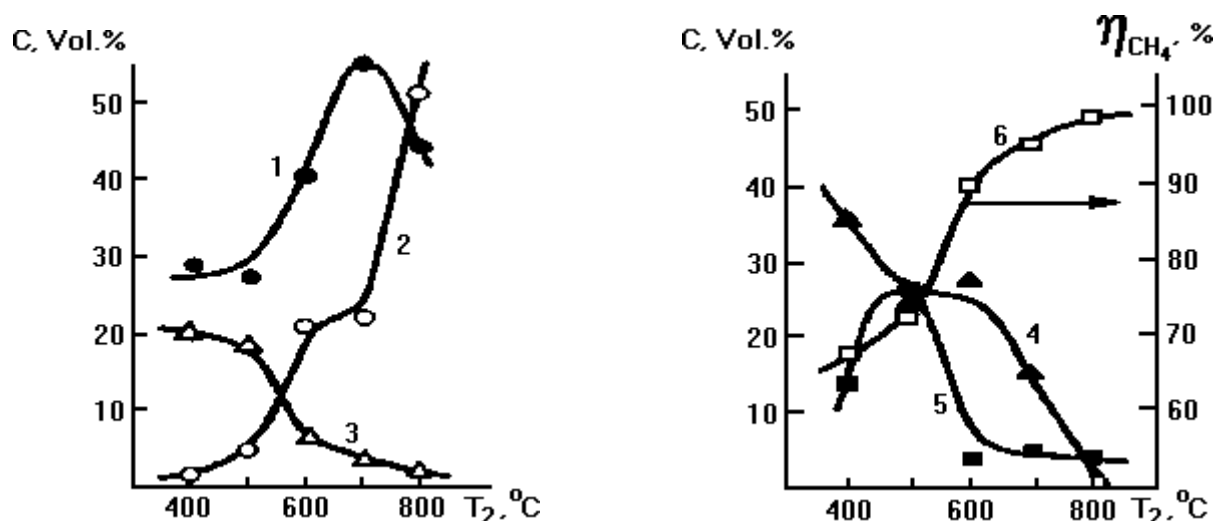


Fig.1. Dependence of reaction product yield on the temperature of second reactor section:
1 - H_2 , 2 - CO, 3 - CH_4 , 4 - CO_2 , 5 - H_2O , 6 - methane conversion

As is evident from these figures, the methane catalytic oxidation reaction is running all over the studied temperature range. Practically the methane concentration is regularly decreases with temperature increasing, the methane conversion (Fig.1a) being increased from 70% at 400 °C to 98% at 800 °C temperature. With the reactor temperature increase the hydrogen concentration increases and passes through its maximum equal to 55% at respective temperature up to 700 °C, then it starts decreasing and at 800 °C achieves the value of 47% volume. The carbon oxide concentration increases with temperature increase. Apparently, a small more gently slopping section located at 600-700 °C temperature interval evidences

changes of oxidation running conditions on the catalyst surface.

This assumption is evidently confirmed by the fact that referred on the hydrogen concentration change curve at 600 °C temperature there is located a point of inflection while at 600-700 °C temperatures the rate of concentration changes achieves its maximum.

The chromatographic analysis data on the carbon dioxide concentration changes showed that till to 600 °C temperature the curve of its concentration changes is more gently slopping and after 600 °C temperature achieved, it begin sharply decreasing and at $T=800$ °C the CO_2 traces were only found on the chromatogram.

The behavior of water vapor concentration changes in the reaction products on the fig 1b shows that this curve passes through its maximum falling on the 500 °C temperature and at 500-600 °C temperatures there is observed a sharp decrease of curve values practically down to constant 4-4.5 vol. %. The increase in water amounts at 400-500 °C temperatures is evidence that within this temperature range the processes of more complete catalytic oxidation with formation of large amounts of such compounds as CO₂ and H₂O are running out.

Apparently, 500-600 °C temperatures present a transition temperature range for this process because while the amounts in carbon dioxide are still quite substantial the water vapor concentration changes in reaction products achieve maximum rates. Note should be taken that for the above mentioned temperature range the specific S-inflection plotted graph is shown by both the curve of changes in water amounts and by the curve of changes in carbon oxide concentrations. Within this temperature interval the rates of hydrogen accumulation are increasing. Within 700-800 °C temperatures range the curve of carbon oxide concentration is sharply risen up while that of carbon dioxide concentrations in reaction products is sharply dropped.

So, referred on the obtained gas chromatography data there is evident that the formation of such predetermined products as carbon oxide and hydrogen occurs all over studied temperature range, the H₂ and CO ratios varying with the temperature changes.

It is well known that H₂ and CO are source materials for synthesis of the most organic compounds: production of aliphatic hydrocarbons; oxo-synthesis or olefins hydroformylation with formation of aldehydes; synthesis of carboxylic acids and their derivatives. In the above mentioned the hydrogen and carbon oxide ratios have very substantial importance [5]. For example, the methanol synthesis is based on the use of the synthesis-gas at H₂:CO= 2:1 ratio. In this connection by calculation methods there were plotted diagrams of [H₂]/[CO] and [H₂]+[CO]/([H₂O]+[CO₂]) dependence on the temperature of second reactor section basing on which there may be chosen the mostly suitable conditions of the experiment carrying-out.

From the above mentioned dependences (Fig.2) it is apparent that the maximum of [H₂]+[CO]/([H₂O]+[CO₂]) ratios is falling on 800 °C temperature range while at this temperature the [H₂]+[CO] ratio is close to the unity. Therefore as regards the choice of optimum conditions enabling to obtain such valuable product as methanol the temperature up to 700 °C where

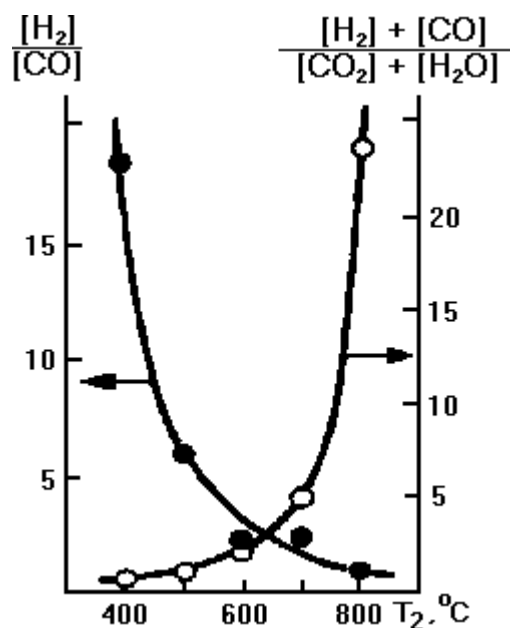


Fig.2. Dependence of the [H₂]/[CO] and ([H₂]+[CO])/([H₂O]+[CO₂]) ratios on the second reactor section temperature

[H₂]+[CO] ratio being close to two, is preferred.

As far as concerns power aspects, the lower temperature down to 600 °C is more suitable but in this temperature range the ratios between incomplete oxidation products [H₂]+[CO] and complete oxidation products ([H₂O]+[CO₂]) are too small. So that, apparently, it is suitable to consider the most advantaged alternative outstanding its economical efficiency.

In our opinion the temperature up to 700 °C is more preferable, therefore the further investigations of catalytic activity in processes of synthesis gas production were carried out at T₁=700 °C, T₂=700 °C and ratio CH₄:O₂=2:1, the gas mixture flow rate being varied within 4500-13,500 h⁻¹. The chromatography analysis data proceeding of methane catalytic oxidation products on the cobalt catalyst resulted in the obtaining of dependence presented on the Fig.3. It shows that with increase in flow rate from 4500 up to 13,500 h⁻¹ the hydrogen concentrations increase and then further increase in flow rate the latter pass their gently slopping maximum falling on the flow rate range within 9000-11,250 h⁻¹. The carbon oxide concentrations pass too through a feebly marked maximum at Q=9000 h⁻¹, when the concentrations of water vapor and CO₂ pass their minimum, the CO₂ minimum corresponding to the maximum of carbon oxide concentrations. While the H₂O minimum falls on the same flow rate range that the maximum of hydrogen concentrations. The changes in methane concentrations

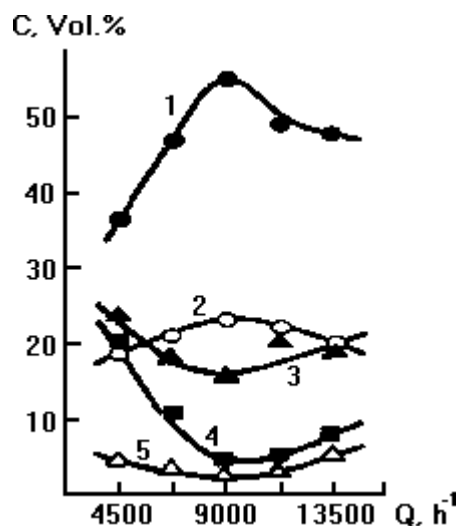


Fig.3. Dependence of products yield on the flow rate

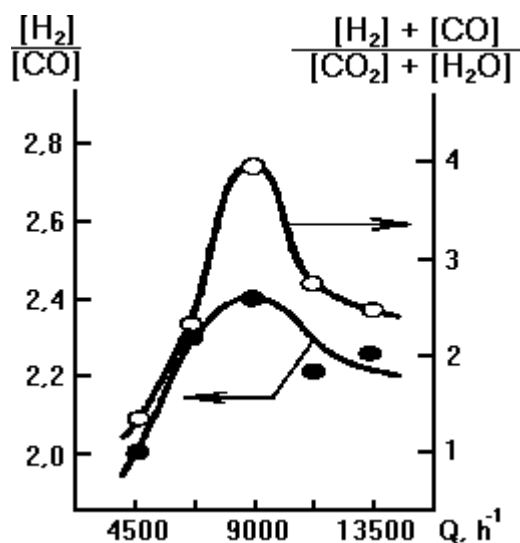


Fig.4. Dependence of $[H_2]/[CO]$ and $([H_2]+[CO])/([H_2O]+[CO_2])$ ratios on the flow rates

are marked still less than that of concentrations of reaction products, passing through their minimum falling on the 9000 h⁻¹ flow rate.

The diagrams of $[H_2]/[CO]$ and $([H_2]+[CO])/([H_2O]+[CO_2])$ dependence shows (Fig.4) that the most advantaged ratio between the products of incomplete and complete oxidation corresponds to the 9000 h⁻¹ flow rate. From the $[H_2]/[CO]$ ratio it is evident that the most suitable flow rate is equal to 4500 h⁻¹ but the amounts of water and CO₂ in the reaction products being sharply increasing.

So, there is shown that the methane catalytic oxidation conversion begins running out at quite low temperatures (400 °C) and within a large flow rate range. The mechanism of reaction changes with temperature changing on the catalyst surface, i.e.: when temperature increased, the decrease in incomplete oxidation products is occurred.

Our investigations provided that before every subsequent experiment the catalyst was activated with oxygen at the 600 °C reactor temperature during 1 hour exposure.

As the above mentioned experiments were carried out basing on the Gause - Zeidel one-factor experiment planning method there was used not a newly prepared SHS cobalt catalyst but the catalyst prepared for first experiment and all subsequent experiments were carried out using this latter.

When first experiment was carried out, it was found the catalyst in the reactor perfectly different by its appearance compared with the initially loaded one. Its surface became oily, black and its dispersion degree increased. The thermocouple encapsulated in a

quartz shell and immersed in catalyst layer was removed out with substantial difficulty, apparently, it was resulted of its sintering occurred during catalytic reaction and considerable resinification.

To remove carbon deposits the cobalt catalyst was re-loaded in the reactor with encapsulated thermocouple and after reactor heated up to 600 °C, the oxygen was blown down.

The above mentioned activation method resulted in the catalyst mass heating up to temperatures substantially exceeding the reference one that is evidence of exothermal processes running out in the catalyst mass through the carbon and black deposits burn-out.

The complete process of the above mentioned cobalt catalyst reduction takes up to 1/2 hour (Fig.5). As it is evident from this figure the catalyst temperature passes its strongly marked maximum and decreases down to the temperature determined with the thermoregulator.

To make sure that the activity of studied cobalt catalyst isn't subjected to changes with the time after first experiment carried out, the control experiment providing reconstruction of the conditions of one of early experiments was performed. There was found that the reiteration in reaction product yield both for their quality and quantity characteristics meets the experiment error.

Conclusion

The results given in this article show that the real possibility to carry out methane partial catalytic oxidation into synthesis gas exists. Unlike the gasphase

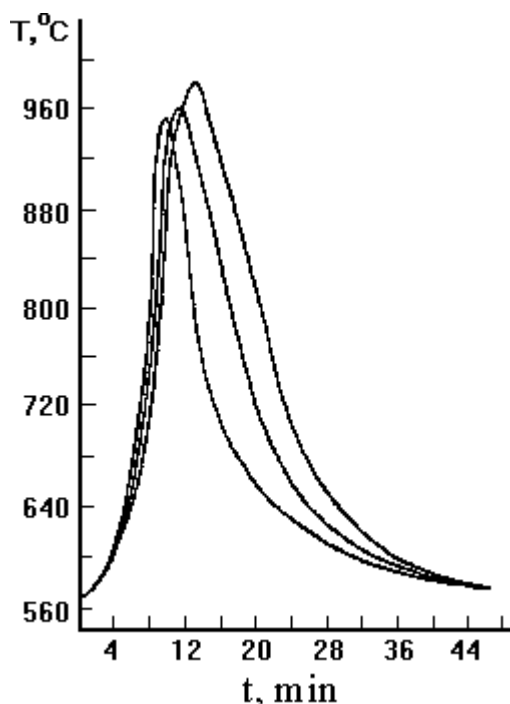


Fig.5. Temperature warming up of catalytic mass in during time of activation.

process [5,6], where temperature is 1350-1450°C, maximum temperature at catalytic oxidation is about 600-800°C. It is found out that the ratio H_2/CO may be operated in a wide range by variation of such factors as reactor temperature and flow rate.

Thus, there was shown that the use of cobalt catalyst makes available the efficient obtaining of the synthesis gas from methane, the hydrogen/carbon oxide ratios being predetermined. It was found that the methane conversion achieves up to 90-98% in conditions of synthesis gas obtaining.

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