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Research Article

INVESTIGATION OF THE EFFECT OF Co ON Ni/Al2O3 CATALYST FOR METHANE CARBONATE CONVERSION

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J.J. Javharov
Doctoral Student, Samarkand State University, Samarkand, Uzbekistan

ABSTRACT

In the work, the activated Ni-Co catalyst for the conversion of methane to carbonates was prepared by placing γ-Al2O3 in solutions of nickel and cobalt nitrates. The time dependence of methane conversion was studied for different catalysts. In these processes, CO2/CH4=1:1,41 1 ratio was obtained.

As a result of the research conducted, the methane effect of Co on Ni/Al2O3 catalyst for conversion. The following possible mechanism was proposed.

The purpose of the work is to study the effect of Co on the conversion of methane to carbonate, and the dependence of these processes on catalysts of different compositions, time and temperatures.

KEYWORDS

Methane, aluminium oxide, catalyst, conversion, nickel, cobalt.

INTRODUCTION

Synthesis gas is a mixture of carbon monoxide and hydrogen. The ratio of CO:H2 varies from 1:1 to 1:3 depending on the synthesis gas production method. Synthesis gas production was considered

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one of the most important tasks of modern gas chemistry. Different H2/CO ratios of synthesis gas can produce different valuable products.

There are four ways to get synthesis gas from methane:

• Steam conversion

$CH_4 + H_2O \leftrightarrow CO + 3H_2$

$\Delta H = +206$ Kj/mol (1)

•Partial oxidation with oxygen

$CH_4 + 1/2O_2 \leftrightarrow CO + 2H_2$

$\Delta H = +35.6$ Kj/mol (2)

• Autothermal conversion

$CH_4 + 2O_2 \leftrightarrow 2CO_2 + 2H_2$

$\Delta H = +802$ Kj/mol (4)

(excess methane)

$CH_4 + H_2O \leftrightarrow CO + 3H_2$

$\Delta H = +247$ Kj/mol

$CH_4 + H_2O \leftrightarrow CO + 3H_2$

$\Delta H = +206$ Kj/mol

• Carbonate conversion

$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$

$\Delta H = +247$ Kj/mol (3)

Carbonate conversion is one of the simplest one-step processes, and the importance of a catalyst is crucial for this process.

To study the effect of ZrO_2 on the activity of the Ni-catalyst, $10Zr/Al_2O_3$ (without nickel) $5Ni5Zr/Al_2O_3$ $10Ni10Zr/Al_2O_3$ catalysts were prepared by adding γ-Al_2O_3 additives to the aqueous solution. Studying the conversion of CH_4 + CO_2 mixture on Pt/ZrO catalyst with the addition of molecular oxygen to the reactive system gave good results [1-8].

The incorporation of Fe into the Ni catalyst affects its activity and selectivity. The effect of Fe addition on the Ni/Al_2O_3 sample was studied. When the nickel content of the Ni-Fe catalyst is 5%, the coke formation decreases, and then the coke formation increases with the increase of the iron catalyst content. But iron reduces the activity of the catalyst, which leads to a decrease in conversion. Thus, to further reduce coke formation, it is preferable to use a catalyst with a low content of nickel and iron. In order to stop the reduction of catalyst activity, the amount of iron in it should also be small [9-14].

Co-catalysts are similar to nickel systems in terms of activity and stability. Like CoOMgO solid solutions and perovskites, cobalt oxide catalysts lose their activity when the composition of $Ca_{0,8}Sr_{0,2}Ti_{0,8}Co_{0,2}O_3$ changes. Among the $Co/MgO/SiO_2$ catalysts, the most active is the system containing 50% MgO, the ability of cobalt to reduce coke formation is known from the literature. [15-18].

Experimental Part

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Co(NO3)3 ·6H2O 97% nickel-free salt was used as a source of Co in the work. In order to evaluate the activity of the Co catalyst, 5Co/Al2O3 and 10Co/Al2O3 (without nickel) samples were first prepared, and the experimental results of the conversion of methane to carbon dioxide were studied. A 30% solution of catalysts was swallowed for 14 hours. Then, the catalyst was separated from the solution and dried at 350-400 °C for 3 hours under nitrogen flow and reduced to the state of 5-7 mm granules.

LXM-80 (detector with thermal conductivity) and Crystal 2000 (flame ionization detector) chromatographs were used for the methane conversion reaction.

RESULTS AND DISCUSSION

To evaluate the activity of the Co catalyst, 5Co/Al2O3 and 10Co/Al2O3 (nickel-free) samples were first prepared, which were used to convert methane to carbon dioxide. The experimental results are presented in Table 1.

Table 1. Results of experiments on the conversion of methane into carbon dioxide on the Co/Al2O3 catalyst (CO2/CH4-1.41;)

Catalyst	Temperature	Product yield				Conversion yield	
		H_2	CO	CH_4	CO_2	CH_4	CO_2
5So/Al2Few	800	0,8	6,1	39,6	53,4	4,7	13,9
	850	2,0	11,2	37,1	49,6	9,7	19,1
	900	6,1	21,2	32,4	40,3	17,3	31,1
10So/Al2O3	800	2,3	13,2	36,1	48,4	10,3	19,9
	850	5,4	20,8	30,9	42,7	15,2	27,8
	900	7,3	25,0	29,4	38,3	19,2	33,4

Tests showed that the Co/Al2O3 catalyst slightly increased the reaction rate of methane to carbon dioxide conversion in the UKM process. The cost of converting methane to carbon dioxide and the yield of synthesis gas is low. As can be seen from the data in Table 1, the activity of the Co/Al2O3 catalyst is much lower than that of Ni/Al2O3. Methane and carbon dioxide conversions for 10Co/Al2O3 catalyst at 900°C are 19% and 33%, respectively. As the cobalt content in the Co/Al2O3 catalyst increased from 5% to 10%, its activity increased slightly.

After studying the time dependence of methane conversion, using 4Ni/Al2O3, 4Ni2Co/Al2O3, 4Ni4Co/Al2O3, 4Ni8Co/Al2O3 catalysts

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CO2:CH4=1,41, temperature 800 °C, experimental time 14 hours (Fig. 1), Ni- with the addition of Co to the catalyst, CH4 conversion was found to be very low (30-60%) in the initial time period, but after 4-6 hours the methane conversion increased to its maximum value.

As can be seen from the curves shown in Figure 1, the time to reach the maximum value of methane conversion increases with the increase of cobalt content in the Co-Ni catalyst. This phenomenon can be explained by the fact that nickel and cobalt first form a common transition phase with low activity, and then turn into a stable phase with high activity. The greater the amount of cobalt in the catalyst, the longer the process of its transformation into the active phase lasts. After transition time, 4Ni2Co/Al2O3 and 4Ni4Co/Al2O3 catalysts show high activity in methane conversion, similar to 4Ni/Al2O3 catalyst (>92%), and methane conversion in 4Ni8Co/Al2O3 catalyst decreases sharply (<84%) ... Thus, to Ni catalyst the addition of cobalt (>4% Co) causes its activity to decrease.

Figure 1. Time dependence of methane conversion for different catalysts, t = 800 ⍰.

In order to study the time change of methane and carbon dioxide conversion, a graph of the time dependence of methane conversion in the presence of 4Ni4Co/ Al2O3 catalyst was made: CO2:CH4 ratio = 1.41. At a temperature of 800 °C, the experimental time was 14 hours (Figure 2). As can be seen from the graph, the growth rate of CH4 conversion is significantly higher than the growth rate of CO2 conversion. During the first 2 hours, CO2 conversion is higher than CH4 conversion but then decreases. After 5-6 hours of

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catalyst operation, CO2 conversion reaches the highest rate - 81%, CH4> 92%.

Figure 2. Time dependence of methane and carbon dioxide conversion on 4Ni4Co/Al2O3 catalyst, t = 800 ⍰

According to the results of the study of the influence of the CO2/CH4 volume ratio on the main parameters of the methane carbon dioxide conversion process for the Co catalyst, it was found that the CO2/CH4 volume ratio decreased. The increase in the formation of coke leads to a decrease in the activity of the catalyst. Therefore, the volume of CO2/CH4 =1:1 was low in 4Ni4Co/Al2O3 catalyst. several experiments were conducted in order to study the stability of the nickel catalyst with cobalt added to the catalyst. The experimental results are presented in Figure 3.

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Fig. 3 Dependence of CH4 and CO2 conversion on time and 4Ni4Co/Al2O3, 4Ni/Al2O3 catalysts.

Under these conditions, CO2 conversion is always higher than CH4 conversion. For the 4No/Al2O3 catalyst, the conversion of CH4 as well as CO2 was maximal at the initial time point, then decreased during the reaction. The reaction was stopped after 8 hours due to heavy coke formation in the reactor. For the 4Ni4Co/Al2O3 catalyst, the conversions of CH4 and CO2 at the beginning of the reaction are not high (47% and 56%), but after 4 hours of reaction, their conversions reach the highest values 76% and 84.2%). After that, CH4 and CO2 conversions gradually decrease due to coke formation. As shown in the graph (Figure 3), the reaction of UKM with the addition of cobalt to 4Ni4Co/Al2O3 catalyst can take 2 times longer (up to 16 hours), which can be expressed in the form of 4Ni4Co/Al2O3 cobalt. It is more stable than 4Ni4Co/Al2O3 nickel.

During the experiment, the amount of working coke was determined every 2 hours. Figure 4 shows the results of the study of the change in the mass of catalysts in the UKM process at a temperature of 800°C. For all samples, an increase in catalyst mass was observed during the initial time period. Then, having a constant value, the increase in mass stopped.

The largest increase in mass is 16Ni/Al2O3 - 7,8%, 4Ni/Al2O3 - 6,4%, 4Ni2Co/Al2O3 - 5,6%, 4Ni4Co/Al2O3 - 4,6%, and the least is 4Ni8Co/Al2O3 - 3,8%.

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Figure 4. The time dependence of the weight gain of the catalyst (CO2: CH4 =1.41. τ = 850)

It can be seen that the increase in the mass of the catalyst increases with the increase in the amount of Ni in it. Cobalt addition to Ni/Al2O3 reduces coke formation. The greater the amount of cobalt in the catalyst, the greater its mass.

Based on the obtained data (Figures 2, 3 and 4), a conclusion was made about the high activity of the 4Ni4Co/Al2O3 catalyst and its ability to reduce coke formation. Thus, the incorporation of cobalt into the Ni/Al2O3 catalyst contributes to a significant decrease in coke formation. But the catalyst also causes a decrease in activity. An increase in the amount of Ni in the Ni/Al2O3 catalyst leads to an increase in coke formation.

CONCLUSION

1. The time dependence of methane conversion was studied for different catalysts.
2. Co(NO3)3 ·6H2O 97% nickel-free salt was used as a source of Co in the work.In order to evaluate the activity of the Co catalyst, 5Co/Al2O3 and 10Co/Al2O3 (without nickel) samples were first prepared, and the experimental results of the conversion of methane to carbon dioxide were studied.
3. As a result of the research conducted, methaneconversionThe following possible mechanism of the reaction was proposed.

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