



**RESEARCH OF THE SYNTHESIS PROCESS OF ALIPHATIC
HYDROCARBONS WITH THE PARTICIPATION OF A CO-CATALYST
FROM SYNTHESIS GAS**

Nematov Khusan Ibodullayevich

PhD, Karshi engineering-economics institute

xusan85nematov@gmail.com

**ИССЛЕДОВАНИЕ ПРОЦЕССА СИНТЕЗА АЛИФАТИЧЕСКИХ
УГЛЕВОДОРОДОВ С УЧАСТИЕМ СОКАТАЛИЗАТОРА ИЗ СИНТЕЗ-
ГАЗА**

Нематов Хусан Ибодуллаевич

к.т.н. Каршинский инженерно-экономический институт

xusan85nematov@gmail.com

ABSTRACT: In this article, the characteristics of the synthesis of hydrocarbons from CO and H₂ in the presence of catalysts containing Co coated with alkali metals were studied, the results of the study of the catalytic effect of aluminum oxides and aluminosilicates of different porosity were presented, the liquid synthesis products for the sample based on aluminum oxide selectivity increased from 41 to 92% when potassium catalyst was added, selectivity of methane formation decreased from 29 to 4%, the effect of the nature of the support (Al₂O₃ and SiO₂) and 20Co/ The addition of potassium to the SiO₂ sample did not change the CO conversion by 86-87%, but increased the yield of C₅₊ hydrocarbons and their selectivity:

KEY WORDS: Aluminum oxide, catalyst, Co-K catalyst, Fischer-Tropsch, aliphatic hydrocarbons, Liquid hydrocarbons, CO conversion, Co-catalyst.

АННОТАЦИЯ: В статье изучены особенности синтеза углеводородов из CO и H₂ в присутствии катализаторов, содержащих Co, покрытых щелочными металлами, представлены результаты изучения каталитического действия оксидов алюминия и алюмосиликатов различной пористости. селективность образования метана с 29 до 4%, влияние природы носителя (Al₂O₃ и SiO₂) и 20Co/ Добавление калия в образец SiO₂ не изменило конверсию CO на 86-87%, но увеличило выход углеводородов C₅₊ и их селективность:

КЛЮЧЕВЫЕ СЛОВА: оксид алюминия, катализатор, Co-K катализатор, Фишера-Тропша, алифатические углеводороды, жидкие углеводороды, конверсия CO, сокатализатор.

In recent years, the demand for catalysts has been increasing, nowadays almost all catalysts and sorbents are imported. Catalysts containing especially Co are one of





the main catalysts of the process for obtaining aliphatic hydrocarbons from synthesis gas [1].

In recent years, the demand for petroleum products has increased due to the dwindling reserves of oil, which is why synthetic fuels are obtained from gas and coal as a result of research. By obtaining aliphatic hydrocarbons through the Fischer-Tropsch synthesis, fuels, polymer products and organic solvents are mainly obtained, and taking into account the need for these products, the study of new catalytic properties of Co-containing catalysts and the localization of these catalysts is one of the current problems [2].

Currently, hydrocarbon Fe- and Co-catalysts are used in industry to obtain aliphatic mixture from CO and H₂. Co-containing catalysts of the Fischer-Tropsch synthesis increase the yield of alkanes as a result of the reaction.

Co catalyst to increase the amount of high molecular hydrocarbons and reduce the concentration of gaseous products is one of the important tasks in the development of Fischer-Tropsch synthesis.

The introduction of alkali metals into the Co catalyst increases the average molecular weight of hydrocarbons and reduces methane production [3].

Cobalt catalysts are active in the synthesis of hydrocarbons from CO and H₂ at temperatures of 150 - 240 °C. As the temperature increases, their activity and selectivity change. An increase in temperature leads to an increase in CO conversion and an increase in the yield of synthesis products. If the total yield of C1-C4 and CO₂ hydrocarbons increases with increasing temperature, the yield of liquid hydrocarbons will exceed the maximum corresponding to the optimum temperature for obtaining these products. The selectivity of the catalyst for liquid hydrocarbons decreases with increasing temperature.

Temperature equally affects the main indicators of the process of synthesis of hydrocarbons from CO and H₂. The optimal synthesis temperature is their individual characteristic and is determined by the composition of the catalyst, as well as the conditions of its preliminary purification. The results of studying the influence of the nature of a wide variety of supports (alumina oxides and aluminosilicates of different porosity) on the properties of cobalt systems in the synthesis of hydrocarbons from CO and H₂ are presented [4].

Table 1

Synthesis of hydrocarbons from CO and H₂ in Co/carrier catalysts T=190 °C,
R=1 atm

catalyst	X _{CO} %	Output g/m ³	Selectivity %
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Co/Al ₂ O ₃ (1)	47	6	4	87	3	5	4	90	1
Co/Al ₂ O ₃ (2)	58	15	10	96	4	11	8	80	1
Co/Al ₂ O ₃ (3)	67	19	17	104	4	12	12	75	1
Co/Al ₂ O ₃ (4)	51	17	14	76	3	14	13	72	1
Co/ Ac(1)	16	2	2	29	2	5	5	88	2
Co/ Ac(2)	23	2	1	43	3	4	3	91	2
Co/ Ac(3)	22	3	2	40	1	6	5	88	1
Co/ Ac(4)	30	5	5	52	2	7	8	84	1
Co/ Ac(5)	34	6	7	58	0	8	9	83	0

In the studied series of catalysts for 10 Co/AC(1-5) samples, high selectivity for target synthesis products (83-91%), their low yield (29-58 g/m³) and low CO conversion of 16-34% were observed.

10Co/Al₂O₃(1-4) systems showed high activity: XCO 51-67%, the yield of liquid hydrocarbons was 76-104 g/m³, therefore, the study of the properties of Co-catalysts in the synthesis of hydrocarbons 1 from CO and H₂ -4 was carried out in the presence of samples prepared on the basis of Al₂O₃ with structural properties similar to supports. (Table 1) Properties of Co-system catalysts prepared on the basis of SiO₂ for Fischer-Tropsch. Fischer-Tropsch synthesis catalysts were also studied. To increase the activity of the catalyst, the amount of cobalt in Co/Al₂O₃ and Co/SiO₂ samples was increased to 20%.

We studied the influence of the nature of the support (Al₂O₃ and SiO₂) on the properties of 20Co-1K / Al₂O₃ and 20Co-1SiO₂ catalysts. Comparison of this series of samples at a synthesis temperature of 200°C showed that the addition of 1% potassium resulted in a significant decrease in CO conversion for the alumina-based Co-system: from 94 to 67% (Figure 1).



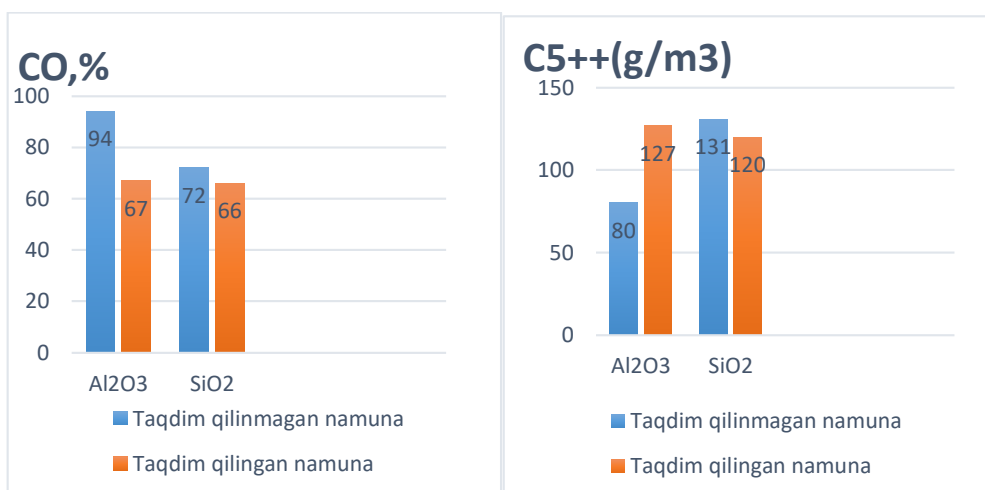


Figure 1. Effect of catalyst nature on CO conversion of $20\text{Co}(0-1)\text{K}/\text{Al}_2\text{O}_3$ (SiO_2) and yield of C_{5+} product in hydrocarbon synthesis from CO and H_2 at $T=200^\circ\text{C}$.

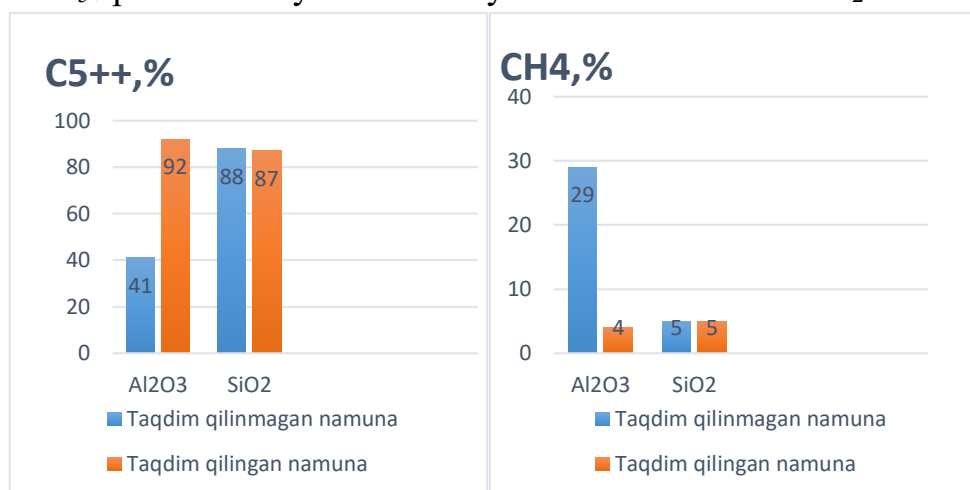


Figure 2. Effect of $20\text{Co}(0-1)\text{K}/\text{Al}_2\text{O}_3(\text{SiO}_2)$ catalyst on the selectivity of C_{5+} and CH_4 in the synthesis of hydrocarbons from CO and H_2 at $T=200^\circ\text{C}$.

Productivity of liquid products increased from 80 to 127 g/m^3 at the same time as hydrocarbon chain growth probability α increased sharply from 0.68 to 0.91 . The addition of potassium to the $20\text{Co}/\text{SiO}_2$ catalyst resulted in a reduction of X_{CO} from 72 to 66% , while the yield of liquid hydrocarbons decreased from 131 to 120 g/m^3 .

For the sample based on aluminum oxide, the selectivity of liquid synthesis products decreased from 41 to 92% with the addition of a potassium catalyst, and the selectivity of methane formation decreased from 29 to 4% (Fig. 2). The addition of potassium to the $20\text{Co}/\text{SiO}_2$ catalyst did not change these selectivity indicators, which were $87-88\%$ and 5% , respectively.

Comparison of these catalysts at the optimal synthesis temperature showed that the introduction of 1% K into the Co-systems led to a different increase in the activity





of the catalysts (Table 2). The addition of potassium to the alumina-based Co-catalyst helped to increase the conversion of CO from 72 to 82%, while increasing the liquid synthesis products from 112 to 138 g / m³ and the selectivity of their formation from 75 to 81 %.

Table 2

Synthesis of hydrocarbons from CO and H₂ in the presence of 20Co-(0-1)M sitell catalysts. CO / H₂ = 1: 2, P = 0.1 Mpa

Catalyst	°C	X _{CO} %	Output g/m ³				Selectivity %				a
			CH ₄	C ₂ - C ₄	C ₅₊	CO ₂	C ₅₊	CH ₄	C ₂ -C ₄	CO ₂	
Co/Al ₂ O ₃	190	72	20	15	112	17	75	12	9	4	0.86
Co- 1K/Al ₂ O ₃	210	82	16	10	138	24	81	8	6	5	0.87
Co/SiO ₂	210	86	18	17	140	21	79	9	9	4	0.83
Co-1K/ SiO ₂	220	87	13	14	147	24	82	6	7	4	0.82

The addition of potassium to the 20Co/SiO₂ sample did not change the CO conversion by 86-87%. The yield of C₅₊ hydrocarbons and their selectivity increased slightly: from 140 to 147 g/m³ and from 79 to 82%, respectively. C₁-C₄ hydrocarbon emissions decreased from 35 to 26-27 g/m³ for the catalysts on both supports. An increase of 10-20 °C in the optimal synthesis temperature was observed for all samples.

For the first time, activation of Co-catalyst with metals of group I (Li, Na, K, Rb, Cs) was found to increase the yield of liquid hydrocarbons and increase their average molecular weight in Fischer-Tropsch synthesis. A correlation was established between the catalytic activity and selectivity of the nature of the alkali metal 20So-M/Al₂O₃(SiO₂). The method of preparation of the catalyst is based on the sequence of impregnation of active metals and increases the efficiency of synthesis of hydrocarbons from CO and H₂ in the process, the conversion of CO and the formation of high C₅₊ products.

For Fischer-Tropsch synthesis, a Co-K catalyst was adopted, which allows the selection of liquid hydrocarbons with a synthesis gas output of up to 138 g/nm³. In this case, the resulting hydrocarbons are enriched with heavy fractions:

In summary, as a result of the research conducted, the synthesis of hydrocarbons from CO and H₂ on Co/carrier catalysts was studied for 10Co/AC(1-5) samples, and the selectivity of liquid synthesis products for the aluminum oxide-based





sample with the addition of a potassium catalyst 41 to 92%, the selectivity of methane formation was found to decrease from 29 to 4%.

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