

RESEARCH ON THE PROCESS OF SYNTHESIS OF ALIPHATIC HYDROCARBONS FROM SYNTHESIS GAS WITH THE INTRODUCTION OF A CO-CATALYZER

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ANNOTATION: This article examines the characteristics of hydrocarbon synthesis from CO and H₂ in the presence of Co-containing catalysts coated with alkali metals, presents the results of studying the catalytic effect of aluminum oxides and aluminosilicates of various porosities; the selectivity of liquid synthesis products for the aluminum oxide-based sample decreased from 41 to 92%, the selectivity of methane formation from 29 to 4%, the effect of the base nature (Al₂O₃ and SiO₂) on the properties of 20Co-1K / Al₂O₃ and 20Co-1SiO₂ catalysts, and the introduction of potassium into the.

KEYWORDS: Aluminium oxide, catalyst, Co-K catalyst, Fischer-Tropsch, aliphatic hydrocarbons, liquid hydrocarbons, CO conversion, Co-catalyst.

АННОТАЦИЯ: В данной статье исследуются характеристики синтеза углеводородов из CO и H₂ в присутствии кобальтсодержащих катализаторов, покрытых щелочными металлами, представлены результаты изучения каталитического эффекта оксидов алюминия и алюмосиликатов различной пористости; селективность жидких продуктов синтеза для образца на основе оксида алюминия снизилась с 41 до 92%, селективность образования метана — с 29 до 4%, исследовано влияние природы основания (Al₂O₃ и SiO₂) на свойства катализаторов 20Co-1K/Al₂O₃ и 20Co-1SiO₂, а также введение калия в состав катализатора.

КЛЮЧЕВЫЕ СЛОВА: Оксид алюминия, катализатор, Co-K катализатор, Фишер-Тропш, алифатические углеводороды, жидкие углеводороды, конверсия CO, Co-катализатор.

INTRODUCTION: In recent years, the demand for catalysts has been steadily increasing; currently, almost all catalysts and sorbents are imported based

on HCl. In particular, Co-containing catalysts are one of the primary process catalysts for obtaining aliphatic hydrocarbons from synthesis gas [1].

In recent years, due to the constant depletion of oil reserves, the demand for petroleum products has been increasing; therefore, as a result of research, synthetic fuels are being obtained from gas and coal. Fuels, polymer products, and organic solvents are primarily obtained by obtaining aliphatic hydrocarbons through the Fischer-Tropsch synthesis, and considering the demand for these products, the study of new catalytic properties of Co-containing catalysts and the localization of these catalysts is currently one of the most pressing issues [2].

Currently, hydrocarbons Fe- and Co-catalysts are used in industry to obtain an aliphatic mixture from CO and H_2 . Co-composite catalysts of Fisher-Tropsch synthesis increase the yield of alkanes as a result of the reaction.

Increasing the amount of high-molecular-weight hydrocarbons in the Co catalyst and reducing the concentration of gaseous products is one of the important tasks for the development of the Fischer-Tropsch synthesis.

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

RESULT: Cobalt catalysts are active in the synthesis of hydrocarbons from CO and H at temperatures of 150-240 °C₂. As the temperature increases, their activity and selectivity change. Increasing the temperature leads to an increase in CO conversion and an increase in the yield of the synthesis products. If the total yield of hydrocarbons C₁-C₄ and CO₂ increases with increasing temperature, the yield of liquid hydrocarbons will exceed the maximum corresponding to the optimal 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 hydrocarbon synthesis process from CO and H₂. The optimal synthesis temperature is their individual characteristic and is determined by the catalyst composition, as well as the conditions for its preliminary purification. The results of studying the influence

of the nature of a wide range of supports (aluminum oxides and aluminosilicates of various porosities) 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 on Co/carrier catalysts

T=190 °C, R=1 atm

catalyst	X _{CO} %	Output g/m ³				Selectivity %			
So/Al ₂ O ₃ (1)	47	6.	4.	87	3.	5.	4.	90	1.
So/Al ₂ O ₃ (2)	58	15	10	96	4.	11.	8.	80	1.
So/Al ₂ O ₃ (3)	67	19	17	104	4.	12	12	75	1.
So/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

10Co/AC (1-5) samples exhibited high selectivity for target synthesis products (83-91%), low profitability (29-58 g/m³), and low CO conversion (16-34%).

The 10Co/Al₂O₃ (1-4) systems showed high activity: X_{CO} 51-67%, and the yield of liquid hydrocarbons was 76-104 g/m³; therefore, the study of the properties of co-catalysts in hydrocarbon synthesis was carried out using samples prepared on the basis of Al₂O₃, which possess structural properties similar to bases 1-4 from CO and H₂. (Table 1) The properties of the Co-system catalysts prepared for the Fisher-Tropsch synthesis based on SiO₂ were also studied. To increase

catalyst activity, the cobalt content in $\text{Co}/\text{Al}_2\text{O}_3$ and Co/SiO_2 samples was increased to 20%.

We studied the influence of the base nature (Al_2O_3 and SiO_2) on the properties of the catalysts $20\text{Co}-1\text{K} / \text{Al}_2\text{O}_3$ and $20\text{Co}-1\text{SiO}_2$. A comparison of these series of samples at a synthesis temperature of 200°C showed that the addition of 1% potassium led to a significant decrease in CO conversion for the aluminum oxide-based Co-system: from 94 to 67% (Fig. 1).

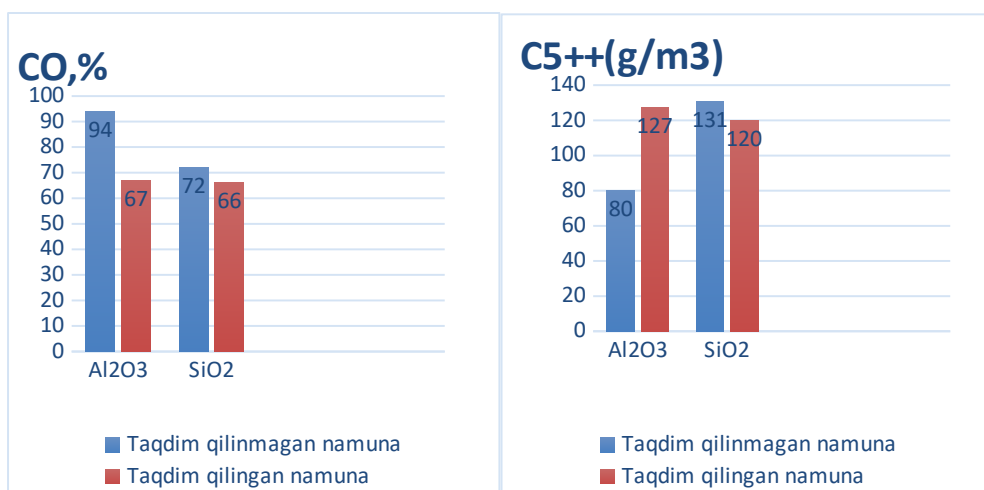


Figure 1. Influence of catalyst nature on the conversion of $20\text{Co} (0-1) \text{K}/\text{Al}_2\text{O}_3 (\text{SiO}_2)$ into CO and the yield of C_{5+} products during the synthesis of hydrocarbons from CO and H_2 at $T=200^\circ\text{C}$.

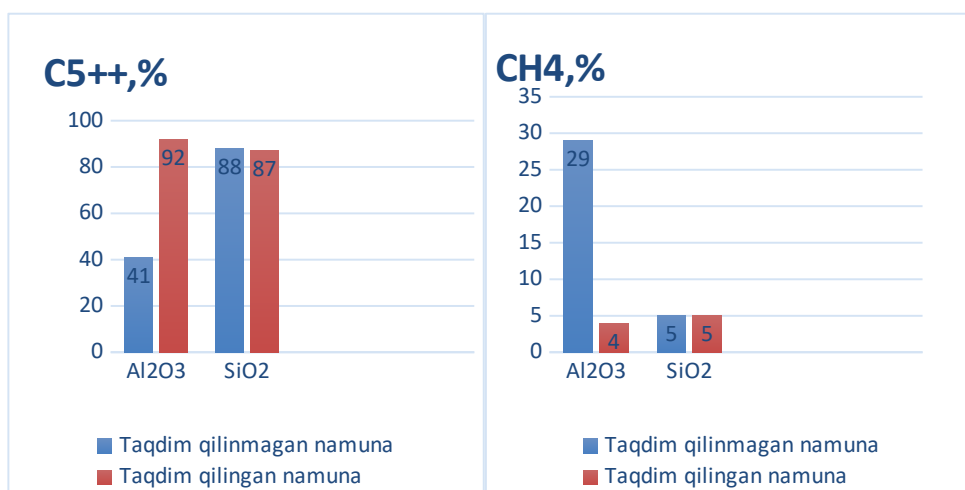


Fig. 2. Influence of the catalyst $20\text{Co} (0-1) \text{K}/\text{Al}_2\text{O}_3 (\text{SiO}_2)$ on the selectivity of C_{5+} and CH_4 in the synthesis of hydrocarbons from CO and H_2 at $T=200^\circ\text{C}$.

The yield of liquid products increased from 80 to 127 g/m³ simultaneously with a sharp increase in the probability of hydrocarbon chain growth from 0.68 to 0.91. The introduction of potassium into the 20Co/SiO₃2 catalyst led to a decrease in HCO₃ from 72 to 66%, while the yield of liquid hydrocarbons decreased from 131 to 120 g/m³.

The selectivity of liquid synthesis products for the aluminum oxide-based sample decreased from 41 to 92% with the addition of a potassium catalyst, while the selectivity of methane formation decreased from 29 to 4% (Fig. 2). The introduction of the potassium additive into the 20Co/SiO₂ catalyst did not lead to a change in these selectivity indicators, which amounted to 87-88% and 5%, respectively.

A 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 catalyst activity (Table 2). The addition of potassium to the aluminum oxide-based co-catalyst contributed to an increase in CO conversion from 72 to 82%, while simultaneously 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 cityl 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	11 2	17	75	12	9.	4.	0.86
Co-1K/Al ₂ O ₃	210	82	16	10	13 8	24	81	8.	6.	5.	0.87
Co/SiO ₂	210	86	18	17	14 0	21	79	9.	9.	4.	0.83
Co-1K/ SiO ₂	220	87	13	14	14	24	82	6.	7.	4.	0.82

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

DISCUSSION: For the first time, it was found that activating a co-catalyst with Group I metals (Li, Na, K, Rb, Cs) increases the yield of liquid hydrocarbons in the Fisher-Tropsch synthesis and increases their average molecular weight. A correlation was established between the nature of the catalytic activity and selectivity of the alkali metal 20Co-M/Al₂O₃ (SiO₂). The method for preparing the catalyst is based on the sequence of activated metal impregnation, which increases the yield of hydrocarbon synthesis from CO and H₂ in the process, along with CO conversion and the formation of C₅₊ products.

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

CONCLUSION: In conclusion, as a result of the conducted research, catalysts for the synthesis of hydrocarbons from CO and H on Co/carrier catalysts were studied for samples 10Co/AC (1-5) and it was found that the selectivity of liquid synthesis products for the aluminum oxide-based sample decreases from 41 to 92%, and the selectivity of methane formation from 29 to 4% when a potassium catalyst is added.

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