

# HYBRID CATALYSTS FOR THE HYDROCARBON SYNTHESIS PROCESS FROM CO AND H<sub>2</sub>

Suxrob Ro'ziyev

Master, Karshi Engineering and Economic Institute,  
Republic of Uzbekistan, Karshi

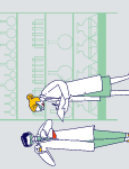
## Abstract

The strategy for creating a low-energy and consequently efficient GTL technology is to improve the hydrocarbon synthesis step by adjusting the selectivity of the process for the desired products by choosing catalysts and conditions that allow obtaining fuel fractions. one stage.

## Introduction

Recently, significant efforts have been made in this direction to create catalysts for "dual" use, that is, systems with the functions of hydrocarbon synthesis and hydrotreating. To solve this problem, it was proposed to combine FT synthesis catalyst with acid catalysts [1]. The combination of catalysts (hydrocarbon synthesis component and acid component) in one system makes it possible to eliminate the dependence of synthesis products on ACF distribution and obtain hydrocarbon fuel fractions with high selectivity. In the literature, such catalysts are called bifunctional or hybrid. Synthesis of hydrocarbons in the presence of hybrid catalysts can be conditionally divided into primary and secondary processes. The primary process, the synthesis of hydrocarbons itself, takes place in the active sites of the FT synthesis catalyst. Synthesized products spread to acid centers, where hydrofining reactions (cracking, isomerization, etc.) occur, i.e., a secondary process occurs. By tuning secondary conversions, high selectivity for C<sub>5</sub>-C<sub>18</sub> liquid hydrocarbons can be expected. As the most active catalysts for cracking and isomerization, which are widely used in industrial processes for hydrocarbon processing, it is proposed to use zeolites as an acid component, for example, HZSM-5, HY, Hb, etc. According to the method of preparation, hybrid catalysts can be divided into three main groups: mixed catalysts (a mixture of FT synthesis catalyst and zeolite); encapsulated catalysts (zeolite is a shell covering the FT synthesis catalyst); supported catalysts (in this case, zeolite is a carrier for the active component of the synthesis). In order to carry out the selective synthesis of hydrocarbons in the presence of hybrid catalysts, the following is necessary:

- for hydrocarbon synthesis and hydroprocessing processes selection of optimal technological conditions;
- selection of catalyst components exhibiting high activity and stability in catalyzed processes;
- providing close contact between active centers of hydrocarbon synthesis and acid centers of zeolite;



### Conducting catalytic tests

The study of the catalytic properties of the samples during the synthesis of hydrocarbons from CO and H<sub>2</sub> was carried out at a temperature of 240°C, a pressure of 2.0 MPa, a volumetric gas velocity of 1000 s<sup>3</sup>at<sup>-1</sup> and a ratio of H<sub>2</sub>/CO=2. The reference catalyst was FT - synthesis catalyst Co-Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> incorporated into the composite catalyst. The obtained experimental data are presented in Figure 1 and Table 1.

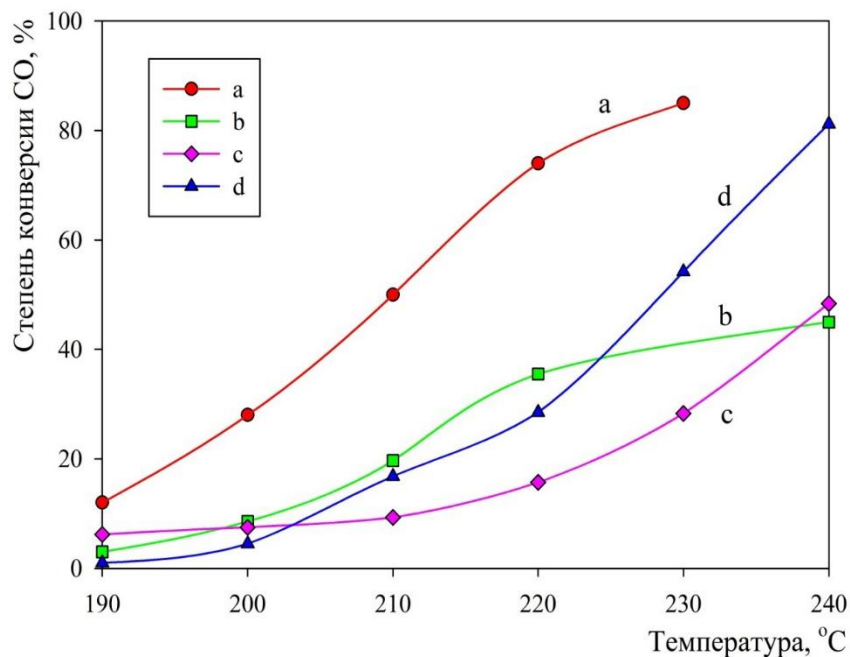


Fig. 1 - the dependence of the level of conversion of CO on the synthesis temperature for catalysts: a - Co-Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>; b and c - absorbent, containing 17.3% and 6.5% cobalt; d - composite

The analysis of the dependence of the conversion rate of CO on the synthesis temperature shows that the composite catalyst exhibits higher activity in FT-synthesis than absorption catalysts. The reasons for the low catalytic activity of the impregnating catalysts in the investigated temperature range (190-240 °C) may be the effect of diffusion limitations, for example, blocking the pores of the zeolite with cobalt during impregnation, as well as cobalt and aluminum oxides. due to the formation of compounds that are difficult to reverse. The difference in the activity of the absorption catalysts is probably due to the different composition and distribution of cobalt.

Despite a 3-fold decrease in cobalt concentration, increasing the temperature of FT-synthesis to 240°C in the presence of a composite catalyst allows to achieve CO conversion levels of 74.2% and hydrocarbon C<sub>5</sub>+ efficiency of 91.7 kg/m<sup>3</sup>cat·h. FT-synthesis catalyst is comparable with similar figures for Co-Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> (Table 1).

Table 1. Catalyst test results

Catalyst	C <sub>co</sub> , %	T, °C	X <sub>co</sub> , %	selectivity, %				G <sub>C5+</sub> , floor-h	kg/m <sup>3</sup>
				CH <sub>4</sub>	C <sub>2</sub> -C <sub>4</sub>	CO <sub>2</sub>	C <sub>5+</sub>		
Co-Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	20,8	225	76,2	16,1	10,4	1,4	72,1	115,0	
Absorbent	17,3	240	36,8	24,3	15,4	1,8	58,5	50,5	
	6,5	240	43,3	18,6	14,8	7,0	59,6	58,0	
Composite	6,3	240	74,2	19,1	11,8	2,6	66,5	91,7	

Note: X<sub>SO</sub> is the degree of conversion of CO; Performance for GC<sub>5</sub> + - C<sub>5</sub> + hydrocarbons.

Samples of hybrid catalysts are characterized by a decrease in the selectivity of C<sub>5</sub>+ hydrocarbon formation to the level of 58-66% compared to the Co-Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalyst. This is due to the increase of intermediate processes - the formation of methane and hydrocarbons S<sub>2</sub>-S<sub>4</sub>, the reaction of water gas.

On the one hand, the increase in selectivity in methane formation can be caused by the acceleration of the hydrogenation reaction of CO in the centers of methane formation due to the increase in synthesis temperature; in hand, this carbon may be the result of various CO and H<sub>2</sub> diffusions through the zeolite pores on the surface of the active component of hydrocarbon synthesis.

The maximum selectivity in methane formation was established for the absorption catalyst containing 17.3% cobalt. It can be seen that the effect of changing the content of CO and H<sub>2</sub> on the surface of the active component of hydrocarbon synthesis is more pronounced due to the blocking of pores due to the formation of a catalyst structure with a high content of cobalt, this is indicated by low values of the specific surface area. In some works, an increase in the selectivity for methane is also associated with cracking reactions of hydrocarbons in the presence of zeolites. The increase in selectivity for gaseous hydrocarbons (S<sub>2</sub>-S<sub>4</sub>) is probably due to the cracking of high molecular weight hydrocarbons at the acid sites of the zeolite. The increase in selectivity in the formation of SO<sub>2</sub> may be due to the reaction of the conversion of CO with water vapor, which is accelerated by increasing the synthesis temperature.

As we mentioned above, the FT-synthesis Co-Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalyst was developed for the synthesis of high molecular hydrocarbons (S<sub>19</sub>+), so their content in C<sub>5</sub> + hydrocarbons reaches 46.7% (Table 3.5). The group composition of S<sub>5</sub>+ hydrocarbons is represented by paraffins of normal composition, the amount of isoparaffins and olefins does not exceed 3%. The molecular mass distribution of hydrocarbons corresponds to the distribution of AShF (Fig. 1). In the diagram showing the distribution of the amount of hydrocarbons obtained by the number of carbon atoms in the molecule, the main part of the obtained hydrocarbons includes up to 25 carbon atoms, and the important part - 25-35.

The fractional composition of S<sub>5</sub>+ hydrocarbons obtained with the presence of hybrid catalysts is mainly represented by liquid hydrocarbons (S<sub>5</sub>-S<sub>18</sub>), their content is 83% for absorbing catalysts and 95% for composite catalysts. This is mainly due to the cracking of S<sub>19</sub>+ hydrocarbons at the acid center of the zeolite. Against the background of a decrease in the

amount of S19+ and partially S11-S18 hydrocarbons, an increase of S5-S10 hydrocarbons by 24-34%, compared to their content, a redistribution of the synthesis products of the products obtained with the presence of the FT-synthesis catalyst Co-Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> was noted.

Table 2. The composition of the resulting S5+ hydrocarbons

Catalyst	Hydrocarbon	Total, %			total	iso/n
		C5-C10	C11-C18	C19+		
Co-Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	n-paraffin	17,2	34,7	45,5	97,4	0,02
	isoparaffin	0,4	0,6	0,8	1,8	
	olefin	0,1	0,3	0,4	0,8	
	total	17,7	35,6	46,7	100	
composition, 17.3% Co	n-paraffin	28,4	20,2	13,6	62,2	0,4
	isoparaffin	11,9	13,1	3,6	28,6	
	olefin	7,1	2,1	-	9,2	
	total	47,4	35,4	17,2	100	
composition, 6.5% Co	n-paraffin	12,7	19,8	13,2	45,7	0,4
	isoparaffin	4,5	11,4	4,0	19,9	
	olefin	25,2	9,1	0,1	34,4	
	total	42,4	40,3	17,3	100	
composites	n-paraffin	15,1	24,1	4,1	43,3	0,6
	isoparaffin	10,8	14,3	0,7	25,8	
	olefin	26,7	4,2	-	30,9	
	total	52,6	42,6	4,8	100	

Note: iso/n is the ratio of isoparaffins:paraffins

A large number of products of secondary changes (cracking, isomerization) - isoparaffins and olefins - was found in all fractions of hydrocarbons synthesized with the presence of hybrid catalysts. The largest amount of isoparaffins was recorded for the composite catalyst - the iso/n parameter is equal to 0.6, which indicates that it has increased activity compared to the catalysts absorbed in the hydroimprovement reactions. A higher concentration of olefins was found for catalysts with low cobalt content, which is due to their low hydrogenation capacity compared to unsaturated hydrocarbons. An increase in the content of cobalt in the impregnation catalyst to 17.3% leads to a decrease in the concentration of olefins.

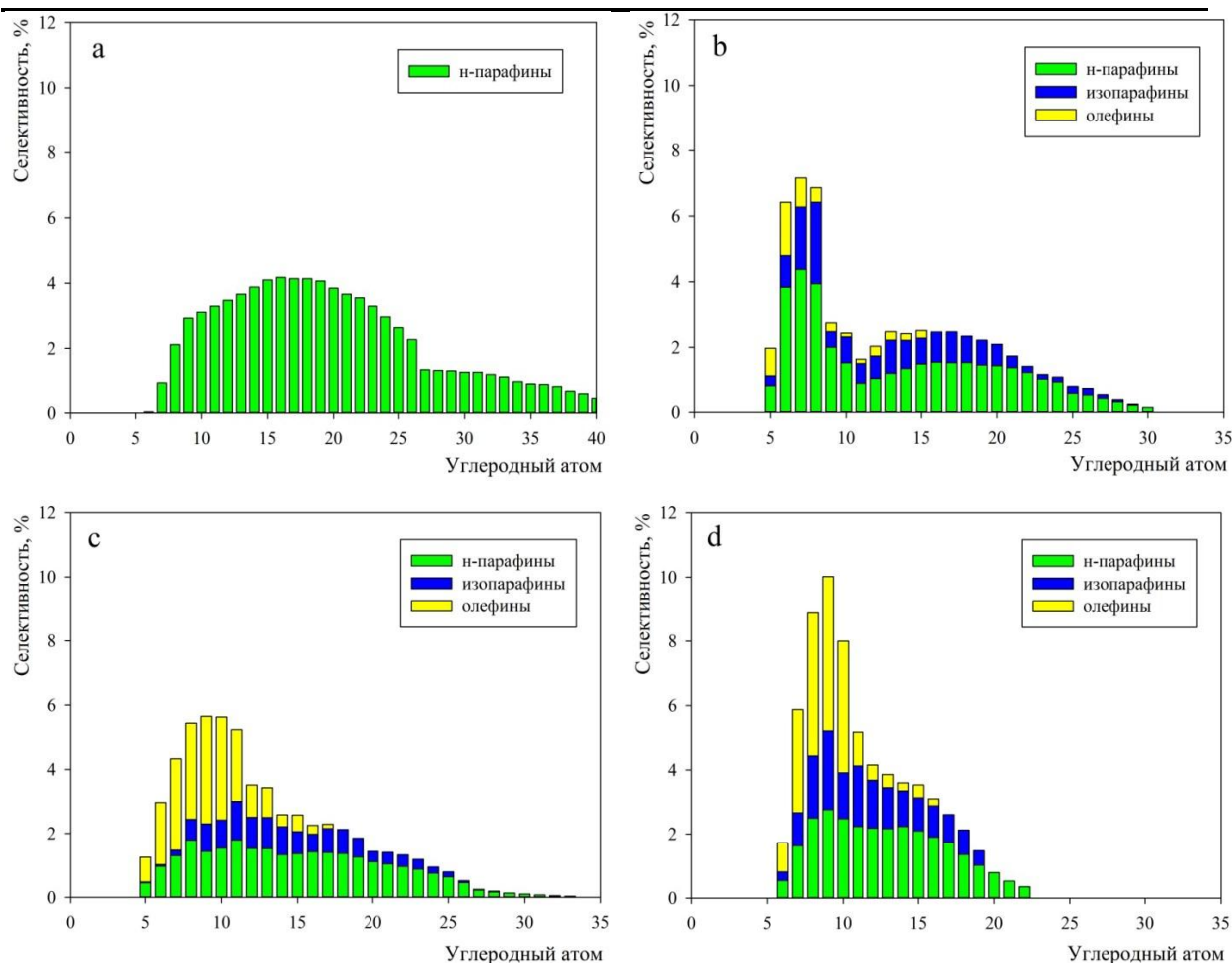


Figure 2. Molecular-mass distribution of S5+ hydrocarbons obtained in the presence of catalysts: a - Co-Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>; b and c - absorbent, containing 17.3% and 6.5% cobalt; d - composite

The use of zeolite in the composition of hybrid catalysts allows obtaining S5+ hydrocarbons whose molecular-mass distribution does not obey the AShF equation. Maximum MMD corresponds to C5-C10 hydrocarbons. The products consist mainly of liquid hydrocarbons. The selectivity in the formation of S5-S18 hydrocarbons for absorbing catalysts is 46-49%, for the composition is 62.6% (Fig. 2). Thus, it was found that mixing cobalt by impregnation into the formed carrier and using methods of cobalt precipitation have a significant effect on the physicochemical and catalytic properties of the hybrid catalysts.

The use of the absorption method for the preparation of hybrid catalysts produces a system that exhibits lower catalytic properties compared to the composite catalyst during the synthesis of hydrocarbons. This is probably due to both diffusion factors, pore blocking by precipitated cobalt, and the formation of compounds of cobalt and aluminum oxides that are difficult to recover from oxide-oxide interactions.

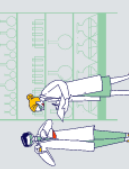


## Summary

Thus, in order to create a competitive GTL technology compared to traditional methods of obtaining engine fuel, it is necessary to activate the processes that occur at each stage. One way to solve this problem is to optimize the technological process by combining the hydrocarbon synthesis and hydrocracking stages in a single reactor. This requires the development of new efficient hybrid catalysts. Simplifying the hardware design of the technological process makes it possible to implement the GTL technology in a mobile block-module design, which allows to attract low-pressure gases from oil gases and waste gas fields attached to processing in field conditions.

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