

# Fischer-Tropsch synthesis in the presence of bifunctional catalysts based on hierarchical zeolite MFI

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## Abstract

The effect of the hierarchical pore structure of ZSM-5 zeolites obtained by alkali modification on the composition of the synthesized products and the catalytic properties of bifunctional cobalt catalysts for the Fischer-Tropsch synthesis was studied. The bifunctional catalysts were prepared by mechanically mixing the Co-Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalyst, HZSM-5 zeolite and boehmite binder. The HZSM-5 zeolite was preliminarily subjected to alkali modification with different alkali concentrations (0.1, 0.25, 0.5, and 1.0 M) to create a hierarchical porous structure and change the acidic properties of the zeolite. The samples of ZSM-5 zeolites and the bifunctional catalysts prepared on their basis were characterized by SEM, low-temperature nitrogen adsorption-desorption, X-ray diffraction and H<sub>2</sub> TPR. Catalytic tests were carried out in a tubular reactor with a fixed catalyst bed at a pressure of 2.0 MPa, a temperature of 250 °C and a gas space velocity of 1000 h<sup>-1</sup>. The tests were performed for 70–80 h of continuous operation. The fractional composition of the Fischer-Tropsch synthesis products was studied at a temperature of 250 °C. It was shown that preliminary treatment of zeolite ZSM-5 with a 0.5 M alkali solution contributed to an increase in the yield and productivity of branched hydrocarbons to 62% and 70.3 kg/(m<sup>3</sup><sub>cat</sub>·h) compared to a similar bifunctional catalyst based on the industrial microporous zeolite HZSM-5.

## Key findings

- Alkaline modification of zeolite HZSM-5 with 0.1–1 M alkali solution resulted in the formation of additional mesopores and nonlinear change in the number of weak and strong acid sites.
- The use of hierarchical zeolite HZSM-5 pre-treated with 0.5 M alkali solution in the hybrid catalyst contributed to the selective formation of hydrocarbons with a branched structure.
- The developed hybrid catalyst can be used in the chemical and petrochemical industries.

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## 1. Introduction

To obtain high-quality synthetic fuel with a large content of branched hydrocarbons at the stage of Fischer-Tropsch synthesis (FTS), bifunctional catalysts are used, containing a metal component – cobalt and an acidic component – zeolite [1, 2]. The presence of zeolite in the composition of the bifunctional catalyst promotes the formation of branched hydrocarbons, which, in turn, increases the octane number of the gasoline fraction and improves the low-temperature characteristics of the diesel [3]. MFI type zeolites, such as

ZSM-5, have become widely used as catalysts for hydrocarbon isomerization, since they have a developed surface area, a sufficient number of Brønsted acid sites, and high hydrothermal and chemical stability [4–6]. However, the structural features of zeolite systems impose some restrictions on their use in FTS. In the processes of hydrocarbons hydrofining, access of reagents to acidic centers of zeolite is of great importance. It is known that the microporous structure of aluminosilicates (pore size 0.5–2.0 nm) prevents the mass transfer of large hydrocarbon molecules to acidic centers inside the zeolite volume. As a

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result, the catalytic reaction occurs only on the outer surface, which leads to the formation of unwanted by-products, blocking of micropores and rapid deactivation of aluminosilicate [7–9]. This issue can be resolved by forming a hierarchical (micro-mesoporous) structure in the zeolite, which will improve mass transfer and open access to the acidic centers located inside the zeolite volume [10–12]. Synthesis methods for hierarchical zeolites can be divided into two main groups: the bottom-up approach and the top-down approach. The bottom-up approach (or primary synthesis) is carried out directly during the synthesis of zeolites and includes hard templating, soft templating, and zeolitization [13–15]. The top-down approach (or post-synthesis modification) is applied to the finished microporous material, which is then subjected to post-synthetic modification to obtain a hierarchical zeolite and includes dealumination, desilylation, recrystallization, and irradiation [16–19]. Desilylation is one of the cheap and universal methods for creating secondary porosity in zeolites. It is based on the selective removal of Si atoms in the zeolite structure in an alkaline medium. Alkaline modification of zeolites takes into account the ratio of various Brønsted and Lewis acid sites and can also take into account their localization and ratio. In addition, the removal of silicon improves molecular diffusion by creating additional pores. The desilicization method has been well studied and has long been used in industrial conditions for the processing of zeolites. Most fundamental studies on the creation of a hierarchical structure were carried out for ZSM-5 zeolites with a silicate module of 25–50 as a commercially in-demand product [20]. At the same time, when using zeolites with a hierarchical porous structure as bifunctional catalysts, there are no unambiguous ideas, since the structure and topological characteristics of zeolites are based on the Fischer-Tropsch synthesis. It should be taken into account that the optimal conditions for alkaline treatment largely depend on the properties of a specific zeolite manufacturer. Based on the above, this work was recognized as a universal hierarchical structure of ZSM-5 zeolite obtained by alkaline modification with different concentrations of NaOH on the selectivity and productivity of hydrocarbons of a branched element. This work generalizes scientific knowledge about the influence of the physicochemical properties of acid components of hybrid catalysts on their catalytic characteristics in the Fischer-Tropsch synthesis [21, 22].

## 2. Experimental

For the studies, synthetic zeolite ZSM-5 of the MFI type with a silicate modulus of 40.5 in the proton form was used. It was obtained by calcining the ammonia form of zeolite (Zeolyst International) for 6 h at a temperature of 550 °C. The modification of the zeolite was carried out according to the method given in work [23]. When preparing modified samples, a weighed portion of zeolite ( $m = 10$  g) was treated

with a NaOH ( $V = 100$  cm<sup>3</sup>) solution having a molar concentration of 0.1, 0.25, 0.5 and 1.0 M for 1 h at a temperature of 70 °C. Then the zeolite samples were washed with distilled water at room temperature, dried for 8 h at a temperature of 100–120 °C and calcined for 3 h at 300 °C. The H-form of zeolites was obtained by treating the samples with a 1 M solution of NH<sub>4</sub>NO<sub>3</sub> ( $V = 100$  cm<sup>3</sup>) for 1 hour at a temperature of 70 °C, after which they were dried for 8 h at a temperature of 100–120 °C and calcined for 6 h at 550 °C. The samples of zeolite HZSM-5 were designated as follows: initial – Z, modified – x Z, where x is the molar concentration of the NaOH solution used in the processing, x: 0.1, 0.25, 0.5 and 1.0 M.

Bifunctional cobalt catalysts for SFT were obtained in the form of a mixture of components [24]. The metal component was the Co-Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalyst for the selective synthesis of long-chain hydrocarbons [25] with a silica gel carrier KSKG (LLC «Salavat Catalyst Plant»), the acid component was the initial or modified samples of zeolite HZSM-5, and the binder was boehmite (Sasol, TH 80).

The catalysts were prepared by mixing powders (fraction < 0.1 mm), % by weight: catalyst Co-Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> – 35, zeolite HZSM-5 – 30, boehmite – 35 [2]. To plasticize the boehmite binder, a water-alcohol solution of triethylene glycol and nitric acid was used (the nitric acid solution was prepared by adding 1–2 ml of nitric acid with a concentration of 65% by weight to 90–100 ml of distilled water per 100 g of the powder mixture; triethylene glycol was added based on the volume ratio of nitric acid triethylene glycol in the mixture of 1:3). The catalyst granules were formed by extrusion. They were dried for 24 h at room temperature, 4–6 h at 80–100 °C, 2–4 h at 100–150 °C and calcined for 5 h at 400 °C. The catalysts were designated as follows: initial – Cat, with modified zeolite – x Cat, where x is the concentration of the NaOH solution, x: 0.1, 0.25, 0.5 and 1.0 M.

The microstructure of the zeolites was studied by scanning electron microscopy with field emission (FE-SEM) on a Hitachi Regulus SU8220 scanning electron microscope. The images were taken in the secondary electron recording mode at an accelerating voltage of 4 kV.

The parameters of the porous structure of zeolites and catalysts were studied by the nitrogen adsorption-desorption method using a Nova 1200e device (Quantachrome, USA). The specific surface area was calculated by the BET (Brunauer-Emmett-Teller) method at a relative partial gas pressure of  $P/P_0 = 0.20$ . The pore volume was determined by the BJH (Barrett-Joyner-Halenda) method at a relative partial pressure  $P/P_0 = 0.95$ ; the pore size distribution was calculated using the BJH desorption curve, and the micropore volume in the presence of mesopores was measured using the t-method (de Boer and Lippens). The samples were preliminarily subjected to vacuum treatment for 5 h at a temperature of 350 °C.

The acidic properties of the zeolites were assessed using the temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) method on a ChemiSorb 2750 device. The zeolite

samples were pre-degassed in a helium stream at 550 °C for 1 h. Ammonia adsorption was carried out for 1 h at room temperature in a flow of ammonia-helium mixtures. (5% ammonia by volume). The removal of physically adsorbed ammonia was carried out in a helium stream at 100 °C for 1 h. Ammonia desorption was carried out in a helium stream in the temperature range of 100–550 °C, with a heating rate of 20 °C min<sup>-1</sup>. The gas flow at all stages was equal to 20 ml min<sup>-1</sup>.

X-ray phase analysis of the zeolites and the catalysts was carried out using a Thermo Scientific ARLX'TRA Powder Diffractometer (Thermo Fisher Scientific, Switzerland) with Cu K $\alpha$  radiation using the point scanning method (step 0.02°, accumulation time 1 s) in the 2 $\theta$  range of 5°–90°. The phase composition was identified using the electronic database of diffraction standards ICDD PDF-2 in the Crystallographica software package. The X-ray diffraction patterns were processed using the FullProf program; the average particle size of cobalt oxide for the characteristic line with a 2 $\theta$  value of 36.8° was calculated using the Scherrer equation [26]:

$$d(\text{Co}_3\text{O}_4) = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \quad (1)$$

where  $d(\text{Co}_3\text{O}_4)$  is the average particle size, nm;  $K$  is the dimensionless particle shape factor ( $K = 0.89$ );  $\lambda$  is the X-ray wavelength, nm;  $\theta$  is the Bragg angle, rad;  $\beta$  is the half-height width of the reflection, rad.

The average particle size and dispersion of metallic cobalt were calculated in accordance with [27]:

$$d(\text{Co}^0) = d(\text{Co}_3\text{O}_4) \cdot 0.75, \quad (2)$$

where  $d(\text{Co}^0)$  is the size of cobalt particles, nm;  $d(\text{Co}_3\text{O}_4)$  is the size of cobalt oxide particles, nm.

The calculation of the relative degree of crystallinity of zeolites was performed taking into account the integral degree of characteristic reflections of zeolite ZSM-5 in the angular range from 22.5° to 25.0° [28, 29]. Untreated zeolite ZSM-5 was used as a sample with a degree of standard crystallinity equal to 95%.

The studies of catalysts by the temperature-programmed reduction method with hydrogen (TPR H<sub>2</sub>) were carried out on a Micromeritics ChemiSorb 2750 analyzer (Micromeritics, USA) with a thermal conductivity detector (TCD). The catalysts were preliminarily kept in a helium flow (20 ml min<sup>-1</sup>) for 1 h at a temperature of 200 °C. Then they were cooled to room temperature and a mixture of 10% hydrogen and 90% nitrogen (20 ml min<sup>-1</sup>) was supplied. The studies were carried out in the temperature range of 20–800 °C with a heating rate of 20 °C min<sup>-1</sup>.

The study of catalytic properties in FTS was conducted in an isothermal reactor with a diameter of 16 mm and a fixed catalyst bed. The reactor was loaded with 5–10 cm<sup>3</sup> of the catalyst (fraction 1–2 mm) mixed with 15–30 cm<sup>3</sup> of quartz. The catalyst was reduced with hydrogen for 1 h at a

temperature of 400 °C and a gas hourly space velocity of 3000 h<sup>-1</sup>. Activation of samples with synthesis gas with a ratio of H<sub>2</sub>/CO = 2 and the catalytic tests were carried out at a pressure of 2.0 MPa and a gas volumetric velocity of 1000 h<sup>-1</sup>, raising the temperature from 180 °C to 250 °C at a rate of 2.5 °C h<sup>-1</sup>. Balance experiments were carried out for 70–80 hours, analyzing the composition and quantity of gas at the outlet of the installation every 2 h. The activity of the catalysts was judged by the conversion of CO, selectivity and productivity of the catalysts, and the fractional and hydrocarbon composition of the synthesis products. The total error in calculating the results of catalytic tests did not exceed 2.5%.

The following equations were used to calculate CO conversion values  $X_{\text{CO}}$  and selectivities:

$$X_{\text{CO}} = \frac{(\text{moles of CO at inlet}) - (\text{moles of CO at outlet})}{(\text{moles of CO at inlet})} \cdot 100\%. \quad (3)$$

CO<sub>2</sub> selectivity:

$$S_{\text{CO}_2} = \frac{(\text{moles CO at outlet})}{(\text{moles of CO inlet}) - (\text{moles CO at outlet})} \cdot 100\%. \quad (4)$$

Gaseous hydrocarbons C<sub>n</sub> ( $n = 1-4$ ) selectivity:

$$S_{C_n} = \frac{n \cdot (\text{moles of C}_n \text{ at outlet})}{(\text{moles of CO at inlet}) - (\text{moles of CO at outlet}) - (\text{moles of CO}_2)} \cdot 100\%. \quad (5)$$

C<sub>5+</sub> selectivity:

$$S_{C_{5+}} = 100\% - \sum_{n=1}^4 S_{C_n} \quad (6)$$

The productivity of C<sub>5+</sub> hydrocarbons was calculated as:

$$G_{C_{5+}} = \frac{m_{C_{5+}}}{V_{\text{cat}} \cdot \tau} \cdot 100\%. \quad (7)$$

where  $m_{C_{5+}}$  is the mass of C<sub>5+</sub> hydrocarbons, kg;  $V_{\text{cat}}$  is the volume of the catalyst, m<sup>3</sup>;  $\tau$  is the time, h.

The composition of the initial gas and gaseous synthesis products was analyzed using a Crystal 5000 gas chromatograph (Chromatec, Russia) equipped with a thermal conductivity detector and two columns (active phase Haysep R and molecular sieves NaX). The analysis mode was temperature-programmed with a heating rate of 8 °C min<sup>-1</sup>.

The condensed synthesis products were separated by distillation at atmospheric pressure, isolating fuel fractions with boiling points: gasoline – up to 180 °C, diesel – 180–330 °C, bottoms – above 330 °C. The composition of C<sub>5+</sub> hydrocarbons was determined using an Agilent 7890A chromatograph mass spectrometer (Agilent Technologies, USA) equipped with an MSD 5975C detector (Agilent, USA) and an HP-5MS capillary column.

## 3. Results and Discussion

### 3.1. Physicochemical properties of zeolites

Table 1 presents the designations of alkali-modified HZSM-5 zeolites and bifunctional catalysts prepared on their basis.

According to the electron microscopy data (Figure 1), changes in the surface morphology of alkali-modified zeolites are observed compared to the original zeolite. Zeolite Z has intergrowths of elongated prismatic crystals from 100 to 700 nm. After post-synthetic treatment of zeolite Z with alkali, small particles measuring 100–200 nm dissolve. As a result, voids are formed in their place (Figure 1 b, c). It should be noted that when treated with a 0.25 M NaOH solution in zeolite 0.25 Z, small particles of 100–200 nm in size are still observed. However, a further increase in the NaOH concentration to 0.5 M leads to their almost complete dissolution.

A study of the textural characteristics of alkali-modified HZSM-5 zeolites showed a change in the porous structure after treatment with alkali solutions of different concentrations. It is noteworthy that with an increase in the alkali concentration from 0.1 to 0.5 M there is no significant change in the specific surface area of the modified zeolites (345–307 m<sup>2</sup>/g), whereas the external specific surface area (106–155 m<sup>2</sup>/g), the total pore volume and mesopore volume increase (Table 2). Treatment with a higher concentration of alkali resulted in the of zeolite 1.0 Z being 2 times less than that of the original Z.

For the initial zeolite Z, a weakly expressed hysteresis loop is observed (Figure 2). The isotherms of the modified zeolites have a more noticeable hysteresis loop in the pressure range of  $0.5 < P/P_0 < 0.95$ , the area of which increases significantly with increasing concentration of the alkali

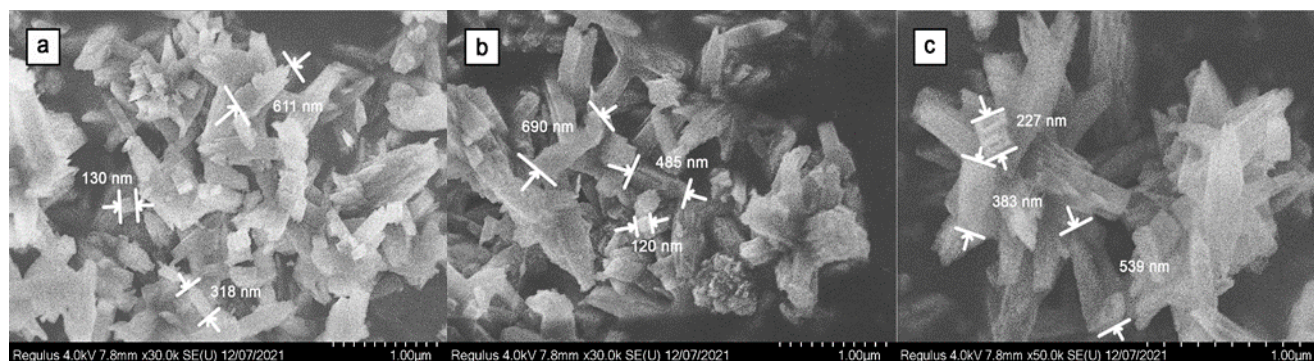
solution used to modify the zeolite. The pore size of the alkali-modified zeolites 0.1 Z and 0.25 Z does not exceed 2 nm. For the 0.5 Z sample, the pore size is from 2 to 8 nm, with maxima of 4 and 6 nm.

Analysis of the acidic properties of alkali-modified zeolites showed that the original zeolite Z has two clear peaks (Figure 3). The first of them is located in the low-temperature region (Peak 1) at 150–300 °C and refers to weak acidic centers. The second peak (Peak 2) is found in the high-temperature region at 370–440 °C [30]. It is usually associated with the desorption of ammonia from Brønsted acid sites and is classified as a strong acid site. It was determined that the acidity of zeolites has a complex dependence on the concentration of the NaOH solution with which the zeolite Z was treated (Table 2). For zeolite 0.1 Z, a decrease in the concentration of weak and strong acidic centers is observed. Zeolite 0.25 Z has comparable values of acidic properties with zeolite Z.

**Table 1** Designations of the obtained zeolites and catalysts.

Concentration of NaOH, <sup>a</sup> M	Zeolite	Catalyst
–	Z	Cat
0.1	0.1 Z	0.1 Cat
0.25	0.25 Z	0.25 Cat
0.5	0.5 Z	0.5 Cat
1.0	1.0 Z	1.0 Cat

<sup>a</sup> Concentration of NaOH solution used to obtain hierarchical zeolite xHZ.



**Figure 1** Micrographs of the surface of zeolites: Z (a), 0.25 Z (b), 0.5 Z (c).

**Table 2** Parameters of the porous structure and acid characteristics of zeolites.

Zeolite	$S_{\text{BET}}$	$S_{\text{BH}}$	$V_{\text{meso}}$	$V_{\text{total}}$	Pore size, nm	Acidity, $\mu\text{mol/g}$			Relative degree of crystallinity (%)
	m <sup>2</sup> /g	m <sup>2</sup> /g	cm <sup>3</sup> /g	cm <sup>3</sup> /g		Peak 1	Peak 2	Total	
Z	345	106	0.13	0.25	>2	454	316	770	95
0.1 Z	307	115	0.14	0.24	2	413	287	700	93
0.25 Z	347	145	0.21	0.31	2	448	324	772	88
0.5 Z	327	155	0.32	0.41	2-8	552	383	935	79
1.0 Z	178	n/a	n/a	n/a	n/a	685	249	934	67

$S_{\text{BET}}$  – specific surface area according to BET;

$S_{\text{BH}}$  – external specific surface area;

$V_{\text{meso}}$  – specific volume of mesopores;

$V_{\text{total}}$  – total specific pore volume.

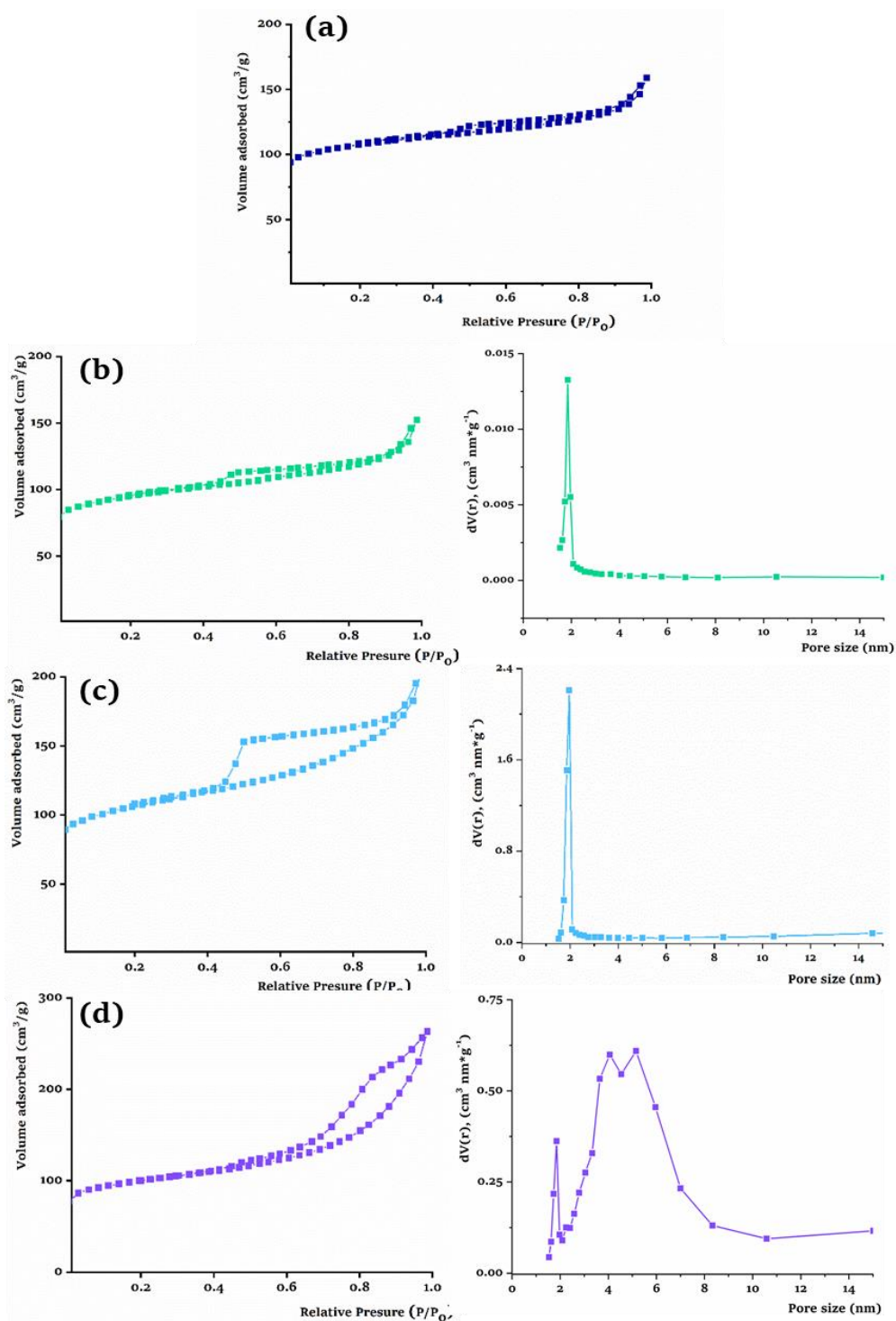


Figure 2 N<sub>2</sub> adsorption/desorption isotherms and pore size distribution for zeolites: Z (a), 0.1 Z (b), 0.25 Z (c), 0.5 Z (d).

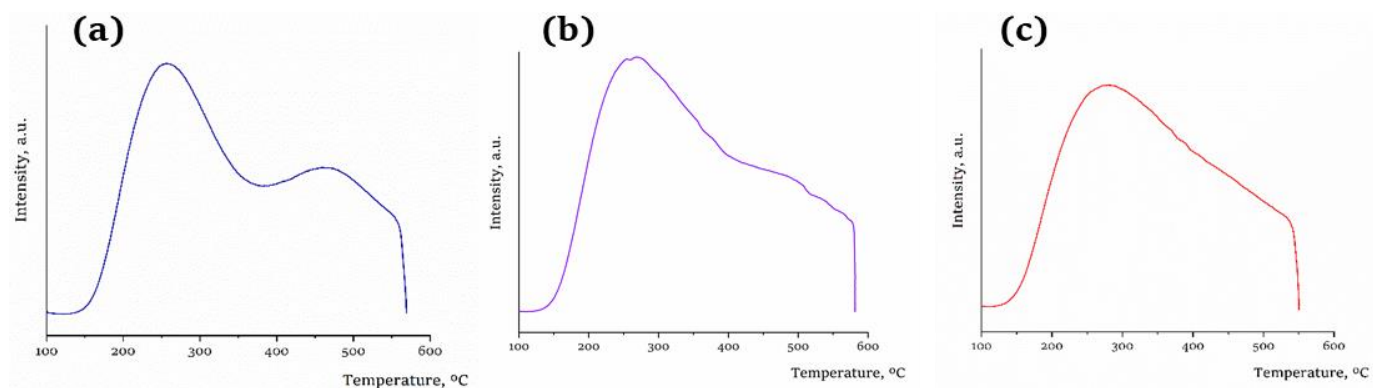


Figure 3 TPD spectra of NH<sub>3</sub> zeolites: Z (a), 0.5 Z (b), 1.0 Z (c).

However, the treatment of zeolite Z with a higher concentration of alkali 0.5–1.0 M led to the opposite effect. Thus, zeolite 0.5 Z has the maximum concentration of strong acidic centers (383  $\mu\text{mol/g}$ ), and zeolite 1.0 Z has the highest content of weak acidic centers (685  $\mu\text{mol/g}$ ). Moreover, the concentration of total acidic centers in zeolites 0.5 and 1.0 Z is comparable.

### 3.2. Physicochemical properties of catalysts

Bifunctional catalysts are a complex multiphase system. In this regard, the total acidity and specific surface area of the components of bifunctional catalysts were investigated (Table 3). It is important to note that during the preparation of the catalyst, during calcination, boehmite ( $\text{Al}(\text{OH})\text{O}$ ) is converted into aluminum oxide  $\gamma\text{-Al}_2\text{O}_3$ . Therefore, in order to measure the acidity and specific surface area of the resulting  $\gamma\text{-Al}_2\text{O}_3$ , the initial boehmite was molded, dried and calcined, as was the bifunctional catalyst. From the data obtained, it was found that the specific surface area of the  $\text{Co-Al}_2\text{O}_3/\text{SiO}_2$  and  $\gamma\text{-Al}_2\text{O}_3$  components is 205 and 204  $\text{m}^2/\text{g}$ . In the presence of the  $\text{Co-Al}_2\text{O}_3/\text{SiO}_2$  catalyst, linear alkanes are obtained with high selectivity, while branched hydrocarbons are very few in number [31]. The value of its acidity of 349  $\mu\text{mol g}^{-1}$  is explained by the adsorption of ammonia on the surface of silica gel ( $\text{SiO}_2$ ). Obviously, in addition to the zeolite, the secondary transformations of linear hydrocarbons are also affected by the contribution of  $\gamma\text{-Al}_2\text{O}_3$ . It was found [24] that the presence of  $\gamma\text{-Al}_2\text{O}_3$  in the catalyst in which inert quartz chips were used instead of zeolite promotes the initiation of the hydrocracking/isomerization reaction of the primary products of the Fischer-Tropsch synthesis.

The diffraction patterns of the bifunctional catalysts are shown in Figure 4. The zeolites retained their peak intensity in the range of angles  $2\theta = 7\text{--}30^\circ$ . At the same time, for catalysts 0.5 Cat and 1.0 Cat in the range of angles  $2\theta = 22\text{--}27^\circ$ , a broadening and decrease in the intensity of zeolite reflections are observed, which is associated with partial destruction of its crystalline structure under the action of alkali. The relative degree of crystallinity was calculated for the original and modified zeolites (Table 2). The reflections of aluminum oxide  $\text{Al}_2\text{O}_3$  are in the range of angles  $2\theta = 47\text{--}70^\circ$ . It is formed during the heat treatment of the binding component boehmite. The weak intensity of the  $\text{Al}_2\text{O}_3$  reflections is due to its low crystallinity.  $\text{SiO}_2$  is X-ray amorphous. The cobalt oxide phase  $\text{Co}_3\text{O}_4$  is in the range of angles  $2\theta = 18\text{--}65^\circ$ .

**Table 3** Parameters of the porous structure and acid characteristics of catalyst components.

Component	Acidity, $\mu\text{mol/g}$	$S_{\text{BET}}$ , $\text{m}^2/\text{g}$
$\text{Co-Al}_2\text{O}_3/\text{SiO}_2$	349	205
$\gamma\text{-Al}_2\text{O}_3^*$	639	204

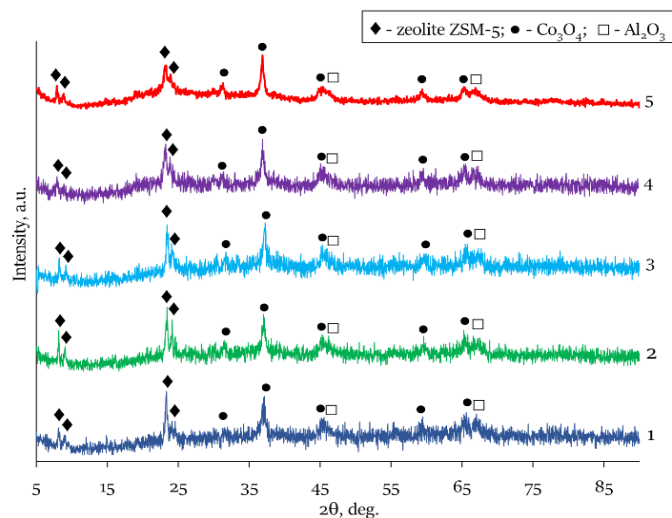
\* precursor – boehmite ( $\text{Al}(\text{OH})\text{O}$ );

$S_{\text{BET}}$  – specific surface area according to BET.

Analysis of the porous structure of the granules of the obtained hybrid catalysts (Table 4) showed that the total specific surface area and the specific surface area of the micropores of catalyst Cat and catalysts 0.25 Cat, 0.5 Cat differ insignificantly. At the same time, the total specific surface area of the catalyst 1.0 Cat has the smallest value, which is due to a decrease in this parameter for 1.0 Z. Catalysts 0.25 Cat, 0.5 Cat show an increase in the mesopore volume from 0.55 to 0.59  $\text{cm}^3/\text{g}$  and the total pore volume ( $V$ ) from 0.59 to 0.62  $\text{cm}^3/\text{g}$  with an increase in the concentration of the alkali solution used to modify the zeolite, which correlates well with the change in the porosity of the zeolites included in the obtained catalysts.

The particle size of  $\text{Co}_3\text{O}_4$  calculated using the Scherrer equation is 13–16 nm, which corresponds to the size of the metallic cobalt crystallites that should form after reduction, 10–12 nm (Table 4).

For all the studied hybrid catalysts, the reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$  (Peak 1) occurs in the range from 250 to 400  $^\circ\text{C}$  (Figure 5). In turn,  $\text{Co}^{2+}$  is converted to  $\text{Co}^0$  in the temperature range of 400–600  $^\circ\text{C}$  (Peak 2) [32]. The ratio of the corresponding peak areas (Peak 2/Peak 1) varies within the range of 2.7–2.8 and tends to the stoichiometric value of 3.



**Figure 4** Diffraction patterns of catalysts: 1 – Cat; 2 – 0.1 Cat; 3 – 0.25 Cat, 4 – 0.5 Cat, 5 – 1.0 Cat.

**Table 4** Parameters of the porous structure and particle size of cobalt bifunctional catalysts.

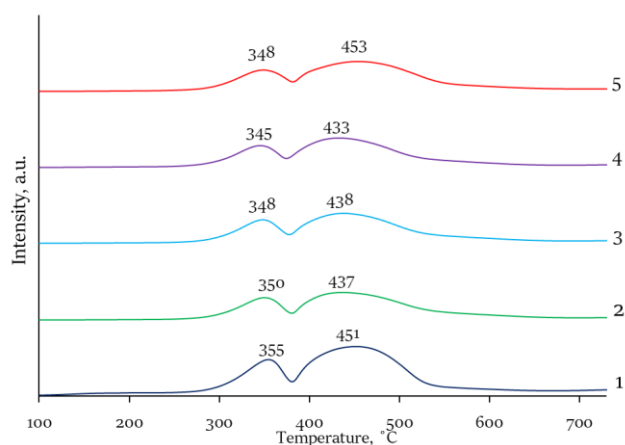
Catalyst	$S_{\text{BET}}$	$S_{\text{BH}}$	$V_{\text{meso}}$	$V_{\text{total}}$	CSR, nm	
	$\text{m}^2/\text{g}$		$\text{cm}^3/\text{g}$		$\text{Co}_3\text{O}_4$	$\text{Co}^0$
Cat	245	187	0.56	0.59	13±1.0	10
0.25 Cat	251	196	0.54	0.57	15±1.3	11
0.5 Cat	253	204	0.59	0.62	13±1.5	10
1.0 Cat	208	n/a	n/a	n/a	16±1.5	12

$S_{\text{BET}}$  – specific surface area according to BET;

$S_{\text{BH}}$  – external specific surface area;

$V_{\text{meso}}$  – specific volume of mesopores;

$V_{\text{total}}$  – total specific pore volume.



**Figure 5** TPR-H<sub>2</sub> spectra of catalysts: 1 – Cat; 2 – 0.1 Cat; 3 – 0.25 Cat; 4 – 0.5 Cat; 5 – 1.0 Cat.

### 3.3. Results of catalytic tests

The results of catalytic tests of the obtained bifunctional catalysts in the synthesis of hydrocarbons at 250 °C, a pressure of 2.0 MPa and a gas space velocity of 1000 h<sup>-1</sup> are presented in Table 5. From the obtained data it is evident that modification of zeolite with an alkali solution of 0.1 and 0.25 M for catalysts 0.1 Cat and 0.25 Cat does not affect the degree of CO conversion, selectivity and productivity for C<sub>5+</sub> hydrocarbons. However, when treated with a higher concentration of alkali, a decrease in these parameters is observed for 0.5 Cat and 1.0 Cat catalysts. Moreover, for all bifunctional catalysts, with an increase in the concentration of alkali, there is an increase in methane selectivity. The influence of zeolite on catalytic activity is not typical for FTS catalysts, since the main catalytic indicators are affected by the cobalt component of the bifunctional catalyst [33]. It should be noted that the hierarchical structure of the zeolite for our catalysts was obtained by the alkaline modification method. Even though the alkaline zeolites were treated in our industrial ion exchange of sodium for ammonia cations, the modified zeolites could retain residual sodium [23]. It is known from the literature that sodium reduces the catalytic activity of cobalt catalysts [34, 35]. We see that the decrease in the catalytic parameters for the 0.5 Cat and 1.0 Cat catalysts is probably due to the presence of sodium in the zeolite crystal lattice. In general, a slight influence of the structure and composition of zeolite in some bifunctional catalysts on the catalytic parameters was noted in other studies [36, 37].

The component composition of C<sub>5+</sub> hydrocarbons obtained in the presence of bifunctional catalysts (Table 6) is represented mainly by liquid hydrocarbons, 88–94% of which are: 48–62% is the gasoline fraction (C<sub>5</sub>–C<sub>10</sub>) and 32–40% is the diesel fraction (C<sub>11</sub>–C<sub>18</sub>). The content of C<sub>19+</sub> hydrocarbons does not exceed 11 %. A correlation is observed between the selectivity of the formation of branched hydrocarbons and the acidity of the zeolites included in the hybrid catalysts. Catalysts based on modified zeolites 0.1 Cat–0.25 Cat and 1.0 Cat showed reduced selectivity for

branched alkanes, linear and branched alkenes, in comparison with catalyst Cat. The iso/*n* parameter (the ratio of branched hydrocarbons to linear ones) was used to evaluate the isomerizing ability of the catalyst [38]. It was found that treatment with 0.1, 0.25, and 1 M alkali solution reduced the iso/*n* ratio compared to catalyst Cat., which is associated with a decrease in the number of strong acid sites in zeolites 0.1 Z, 0.25 Z, and 1.0 Z. On the contrary, modification with 0.5 M alkali solution for 0.5 Cat catalyst contributes to an increase in selectivity of 62%, productivity of 70.3 kg/(m<sup>3</sup><sub>cat</sub>·h) for branched hydrocarbons and a maximum value of the iso/*n* parameter of 1.6.

### 4. Limitation

In this study, zeolites with a hierarchical porous structure were used to create bifunctional catalysts for Fischer-Tropsch synthesis. Hierarchical zeolites were obtained by alkaline treatment of microporous zeolite ZSM-5 with an aqueous NaOH solution. This approach allowed reducing diffusion limitations in the porous system of zeolite and increasing the number of strong acidic centers. As a result, the number of branched olefins in the composition of the synthesis products increased. However, isoalkanes are of great value as components of motor fuels. It is possible to increase the amount of isoalkanes by introducing a noble metal (Pt, Pd, Ru) promoting additive into the bifunctional catalyst. It is planned to conduct such studies in the future. It should be noted that after alkaline treatment of zeolite with NaOH, subsequent washing and ion exchange, a small amount of sodium may remain in its cationic positions. It is known that sodium can have a negative impact on the activity of cobalt catalysts for hydrocarbon synthesis. In the future, it is planned to conduct experiments in which sodium of different concentrations will be introduced into the zeolite, and its effect on the catalytic activity of the catalysts, as well as on the composition of the resulting products, will be studied.

### 5. Conclusions

Alkaline modification of zeolite HZSM-5 with 0.1–1.0 M NaOH solution leads to the formation of additional pores and a nonlinear change in the acidic properties of hierarchical zeolites HZSM-5. It was shown that the isomerizing capacity of the bifunctional catalyst is influenced not only by an increase in the number of pores, but also by the concentration of strong acidic centers. It was determined that modification of zeolite HZSM-5 0.5 M with an alkali solution promotes the formation of a regular mesoporous structure (2–8 nm) and increases the number of strong acidic centers by 383 μmol/g. The use of such a zeolite in the composition of a bifunctional catalyst for Fischer-Tropsch synthesis at a temperature of 250 °C increases the yield and productivity of branched hydrocarbons to 62% and 70.3 kg/(m<sup>3</sup><sub>cat</sub>·h) compared to a similar catalyst based on industrial microporous zeolite HZSM-5.

**Table 5** Catalytic activity of the catalysts.

Catalyst	$X_{CO}^b$ , %	Selectivity, %			$G_{C_{5+}}^c$ , kg/(m <sup>3</sup> <sub>cat</sub> ·h)		
		CH <sub>4</sub>	C <sub>2</sub> -C <sub>4</sub>	C <sub>5+</sub>	CO <sub>2</sub>	general	br. <sup>a</sup>
Cat	85.9	15.8	8.2	72.8	3.3	132.0	67.8
0.1 Cat	86.3	16.9	8.8	70.5	3.9	130.8	51.1
0.25 Cat	85.2	17.3	8.4	71.6	2.7	131.4	63.3
0.5 Cat	81.9	20.2	11.8	65.3	2.7	113.4	70.3
1.0 Cat	76.0	28.7	15.2	52.5	3.7	85.4	19.2

<sup>a</sup> br. – for branched hydrocarbons;<sup>b</sup> X(CO) – CO conversion rate in %;<sup>c</sup> G<sub>C<sub>5+</sub></sub> – productivity of hydrocarbons C<sub>5+</sub> in kg/(m<sup>3</sup><sub>cat</sub>·h).**Table 6** Composition of the synthesis products of C<sub>5+</sub> hydrocarbons.

Catalyst	Hydrocarbons	Group composition of hydrocarbons C <sub>5+</sub> , % wt.			Total	iso/n <sup>a</sup>
		C <sub>5</sub> -C <sub>10</sub>	C <sub>11</sub> -C <sub>18</sub>	C <sub>19+</sub>		
Cat	alkanes	9.4	13.1	3.7	26.2	
	branched alkanes	11.5	10.5	2.1	24.1	
	alkenes	20.3	2.1	–	22.4	1.1
	branched alkenes	20.9	6.4	–	27.3	
	<b>Total</b>	<b>62.1</b>	<b>32.1</b>	<b>5.8</b>	<b>100.0</b>	
0.1 Cat	alkanes	22.9	19.9	6.7	49.5	
	branched alkanes	8.3	14.0	4.4	26.7	
	alkenes	8.9	2.5	–	11.4	0.6
	branched alkenes	8.3	4.1	–	12.4	
	<b>Total</b>	<b>48.4</b>	<b>40.5</b>	<b>11.1</b>	<b>100.0</b>	
0.25 Cat	alkanes	22.7	12.4	3.9	39.0	
	branched alkanes	11.8	14.9	3.3	30.0	
	alkenes	11.4	1.4	–	12.8	0.9
	branched alkenes	13.7	4.5	–	18.2	
	<b>Total</b>	<b>59.6</b>	<b>33.2</b>	<b>7.2</b>	<b>100.0</b>	
0.5 Cat	alkanes	15.6	9.6	3.1	28.3	
	branched alkanes	7.8	9.4	2.7	19.9	
	alkenes	9.6	0.1	–	9.7	1.6
	branched alkenes	27.2	14.3	0.6	42.1	
	<b>Total</b>	<b>60.2</b>	<b>33.4</b>	<b>6.4</b>	<b>100.0</b>	
1.0 Cat	alkanes	33.6	28.0	7.2	68.8	
	branched alkanes	4.6	6.9	0.9	12.4	
	alkenes	7.4	1.3	–	8.7	0.3
	branched alkenes	7.1	3.0	–	10.1	
	<b>Total</b>	<b>52.7</b>	<b>39.2</b>	<b>8.1</b>	<b>100.0</b>	

<sup>a</sup> ratio of branched hydrocarbons to linear hydrocarbons.

## Supplementary materials

No supplementary materials are available.

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## Conflict of interest

The authors declare no conflict of interest.

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