Effects of SiO₂/Al₂O₃ Ratio in ZSM-5 Zeolite on the Activity and Selectivity of a Bifunctional Cobalt Catalyst for Synthesis of Low-Pour-Point Diesel Fuels from CO and H₂

R. E. Yakovenko^{a,*}, I. N. Zubkov^a, V. G. Bakun^a, O. P. Papeta^a, and A. P. Savostyanov^a

^a *Platov South Russian State Polytechnic University, Novocherkassk, 346428 Russia*

**e-mail: jakovenko39@gmail.com*

Received September 2, 2021; revised October 21, 2021; accepted January 27, 2022

Abstract—This study investigates the production of diesel fuels by integrated Fischer–Tropsch synthesis over a bifunctional cobalt catalyst consisting of a cobalt component (Co–Al₂O₃/SiO₂) and a zeolite-containing component (ZSM-5). The catalytic properties were tested in a continuous-flow reactor with a stationary catalyst bed at 240–250°C, 2 MPa, and gas WHSV 1000 h^{–1}. The effects of the SiO₂/Al₂O₃ ratio in a HZSM-5 zeolite on the catalytic performance, catalyst deactivation rate, and hydrocarbon and fractional compositions of the synthetic product were identified. The low-temperature properties of the synthesized diesel fuel satisfy the current requirements for winter fuels.

Keywords: Fischer–Tropsch synthesis, bifunctional cobalt catalyst, catalytic performance, HZSM-5, diesel fuel

DOI: 10.1134/S0965544122010157

The development of remote Arctic and northern territories—with their tremendous hydrocarbon reserves, harsh climatic conditions, and complex ecosystems—calls for green technology innovations. Among green technologies, of particular interest are GTL (gas-to-liquid) processes designed to produce high-value-added environmentally friendly fuels and chemicals from natural gases and associated petroleum gases (APG) [1, 2]. Current GTL technologies involve Fischer–Tropsch (FT) synthesis integrated into a single process step with the hydroprocessing of the synthetic product [3–5]. The mobile version of the process design is particularly promising. This design is favorable for processing not only natural gas but also flared APG and low-pressure gas from abandoned gas fields in remote territories [6]. At the same time, this approach could effectively solve the challenge of providing a stable supply of low-pour-point fuels to remote regions.

The particular interest in integrated FT synthesis is driven by the opportunity to produce diesel fuels with improved environmental and operating characteristics. In contrast to oil refining products, synthetic fuels are free of carcinogenes, sulfur and nitrogen compounds,

aromatics, and solids, and show very low ecotoxicity [7, 8]. To synthesize diesel fuels in industrial GTL process facilities, FT synthesis generally occurs under low-temperature conditions over a cobalt catalyst, with long-chain hydrocarbons (HCs) being produced and then hydrocracked [9]. Such fuels exhibit high storage stability, a high cetane number, and a low density [10]. The quality of low-pour-point diesel fuels is determined by the content of C₁₈₊ *n*-alkanes in their optimum ratio to C₁₀–C₁₅ *n*-alkanes, and by the presence of isomeric HCs [11, 12].

The components of initial syngas (CO and H₂), as well as their products, undergo a complex of transformations on the surface of a bifunctional hybrid catalyst. The catalyst (generally based on zeolites or zeolite-like structures) ensures effective contact and interaction of the FT metal sites with the acid sites of HC cracking and isomerization [13–20]. The synthesis selectivity largely depends on the balance between the probability of chain growth and the HC cracking level [14, 21, 22], as well as on the properties of the catalyst components. For zeolite components of the catalysts, the selectivity-decisive

factors are the chemical composition, crystal structure, pore structure, and surface acidity [23–30].

One promising type of zeolite-based bifunctional systems is a physical mixture of an FT catalyst and zeolite (powdered or pelletized) [31, 32] with a binder (represented by an acid component, usually alumina). In a previous work, we synthesized a similar cobalt catalytic system for direct synthesis of HC fuels in the form of extruded particles that consist of a mixture of a pre-generated Co–Al₂O₃/SiO₂ catalyst for the selective synthesis of long-chain HCs [33], a ZSM-5 zeolite in the form of HZSM-5, and a binder [34].

The purpose of this study was to investigate the effects of the SiO₂/Al₂O₃ ratio in HZSM-5 on the catalytic performance of the bifunctional FT cobalt catalyst and on the low-temperature properties of the synthesized diesel fuel.

EXPERIMENTAL

Samples of cobalt-based bifunctional FT catalysts with ZSM-5 zeolite in the H-form and a boehmite binder were prepared as a mixture of components. We used a Co–Al₂O₃/SiO₂ catalyst for the selective synthesis of long-chain hydrocarbons (20.0 wt % Co and 1.0 wt % Al₂O₃) [33] on a *KSKG* grade silica gel support (manufactured by the Salavat Catalyst Plant, Republic of Bashkortostan, Russia) as a cobalt-containing component; HZSM-5 zeolites with SiO₂/Al₂O₃ molar ratios of 40.5 (manufactured by the Ishimbay Specialized Chemical Catalyst Plant, Republic of Bashkortostan, Russia), 59.5, 84.7, and 307 (the last three manufactured by Zeolyst International) as an acid component; and Al(OH)O boehmite TH 80 (manufactured by Sasol) as a binder.

The catalyst samples were prepared by mixing powders (<0.1 mm) of Co–Al₂O₃/SiO₂ (35 wt %), HZSM-5 (30 wt %), and boehmite (35 wt %) [34, 35]. To plasticize the boehmite binder, an aqueous-alcoholic solution of triethylene glycol with nitric acid was used. A nitric acid solution was prepared by introducing 1–2 mL of 65 wt % nitric acid into 90–100 mL of distilled water per 100 g of the powder mixture. Triethylene glycol was then added based on a nitric acid to triethylene glycol volumetric ratio of 1 : 3.

Catalyst pellets were molded by extrusion, successively dried at room temperature for 24 hours, at 80–100°C for 4–6 h, and at 100–150°C for 2–4 h, and calcined at 500°C for 5 h.

The cobalt content in the catalysts was identified by X-ray fluorescence (XRF) on an ARL QUANT'X energy-dispersive spectrometer (Thermo Scientific, USA) under the following conditions: air environment, Teflon support, effective irradiation area 48.9 mm².

The BET specific surface area was measured on a Micromeritics ChemiSorb 2750 analyzer (Micromeritics, USA) at –196°C using an argon–helium mixture (10 vol % argon). The catalysts were preliminarily held in helium at 200°C for 1 h.

The catalysts were analyzed by X-ray diffraction (XRD) on a Thermo Scientific ARL X'TRA powder diffractometer (Thermo Fisher Scientific, Switzerland) with monochromated CuK_α radiation using point-to-point scanning (step 0.01°, counting time 2 s) in the 2θ range of 5° to 90°. The qualitative phase composition was identified using Crystallographica software and the PDF-2 database involved [36].

The X-ray patterns were processed using FullProf software. The mean size of Co₃O₄ particles for the characteristic line with 2θ = 36.8° was derived from the Scherrer equation [37]:

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

where $d(\text{Co}_3\text{O}_4)$ is the mean particle size (nm); K is the dimensionless particle shape factor ($K = 0.89$); λ is the X-ray wavelength (nm); θ is the Bragg angle (rad); and β is the line broadening at half the maximum intensity (rad).

The mean size of cobalt metal particles $d(\text{Co}^0)$ was calculated by the formula [38]:

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

The dispersion of the metal component D (in %) was evaluated by the formula [39]:

$$D = \frac{96}{d(\text{Co}^0)}. \quad (3)$$

Hydrogen temperature-programmed reduction (H₂–TPR) of the catalysts was carried out using a Micromeritics ChemiSorb 2750 analyzer equipped with a thermal conductivity detector (TCD). Prior to starting the H₂–TPR procedure, the catalyst sample was held in

Table 1. Physicochemical properties of bifunctional catalysts

Catalyst sample	HZSM-5			Cobalt concentration, wt %	XRD data		
					particle size, nm		<i>D</i> ^a , %
	SiO ₂ /Al ₂ O ₃ molar ratio	crystallinity, %	surface area, m ² /g		Co ₃ O ₄	Co ⁰	
Z40	40,5	95	405	7.4	14.5	10.8	8.9
Z60	59.5	96	445	7.5	15.0	11.3	8.5
Z80	84.7	94	463	7.4	14.6	11.0	8.7
Z300	307	88	396	7.4	17.0	12.8	7.5

^a *D* (%) is the dispersion.

helium (20 mL/min) at 200°C for 1 h. It was then cooled to room temperature, and a 10% H₂/90% N₂ mixture was introduced at 20 mL/min. The examination was performed in the range of 20–800°C at a heating rate of 20°C/min.

The catalysts were examined by ammonia temperature-programmed desorption (NH₃–TPD) on a Quantachrome Autosorb analyzer (Quantachrome, USA). Prior to starting the adsorption, the samples were degassed in helium at 600°C for 5 h and purged to remove physically adsorbed ammonia. The ammonia adsorption was carried out at 100°C in an ammonia–helium mixture flow (10 vol % NH₃) for 2 h. The desorption occurred in the range of 100–600°C at a linear heating rate of 10°C/min, with helium as a carrier gas.

The FT catalytic properties were tested in a 16 mm dia. isothermal reactor with a stationary catalyst bed. The catalyst (1–2 mm particles) in an amount of 5–10 cm³ mixed with 15–30 cm³ of quartz was introduced into the reactor. The catalyst was reduced with hydrogen at 400°C and a gas hourly space velocity (WHSV) of 3000 h^{−1} for 1 h. The activation of the samples with syngas (H₂/CO = 2) and the catalytic tests were carried out at 2.0 MPa and WHSV 1000 h^{−1} by stepwise heating (2.5°C/h) from 180°C to 240°C. The balance tests were run during 20–100 h, with the gas composition and flow rate at the test unit outlet being analyzed every 2 h. The catalyst activity was assessed by measuring the CO conversion degree, the selectivity and productivity of the catalyst, and the fractional and hydrocarbon compositions of the synthetic product.

The compositions of the starting gas and the gaseous synthetic product were identified on a Crystal 5000 gas

chromatograph (*Chromatec*, Russia) equipped with a thermal conductivity detector and two columns (Haysep R active phase and NaX molecular sieves). The heating was programmed at a rate of 8°C/min.

The condensed synthetic product was separated, by distillation at atmospheric pressure, into a gasoline fuel (<180°C), a diesel fuel (180–330°C), and a bottom residue (>330°C). The C₅₊ HC composition was identified by chromatography-mass spectrometry using an Agilent 7890A instrument (Agilent Technologies, USA) equipped with a mass-selective detector (MSD) and an HP-5MS capillary column. The low-temperature properties of the diesel hydrocarbons were evaluated using a *TPZ-LAB-12* instrument designed to measure the cloud and pour points of petroleum products (in compliance with ASTM D6749-02, ASTM D7683-11, GOST 20287-91, and GOST 5066-91).

RESULTS AND DISCUSSION

The bifunctional catalysts prepared from industrial samples of MFI-type aluminosilicate zeolite (pentasil group), specifically ZSM-5 in the H-form with SiO₂/Al₂O₃ ratios of about 40, about 60, about 80, and about 300 [3, 40] were labeled Z40, Z60, Z80, and Z300, respectively. Their characteristics and XRD data are presented in Table 1 and Fig. 1. In high-silica zeolites, the SiO₂/Al₂O₃ molar ratio may vary within a wide range; for the HZSM-5 samples under study, this ratio varied from 40.5 to 307. The residual Na₂O content did not exceed 0.04–0.05 wt %. The crystallinity was 94–96%, except for the lowest degree (88%) in Z300. The ZSM-5 crystalline structure consists of a three-dimensional network of channels with cavities formed

Fig. 1. X-ray patterns of bifunctional catalysts: (1) Z40; (2) Z60; (3) Z80; and (4) Z300.

Fig. 2. H_2 -TPR curves for catalysts: (1) Z40; (2) Z60; (3) Z80; and (4) Z300.

by intersecting straight and zigzag 10-membered rings [41]. The channels are of two types, 0.51×0.55 and 0.53×0.56 nm in size [42, 43]. The zeolite has a medium-pore structure with a mean pore diameter of 0.6 nm. The specific surface area is in the range of 396–463 m^2/g , depending on the silica to alumina molar ratio in the HZSM-5.

The cobalt concentration in the catalysts (7.4–7.5 wt %) was determined by using one cobalt-containing component ($Co-Al_2O_3/SiO_2$) to prepare these samples. According to XRD, the oxide precursor of the $Co-Al_2O_3/SiO_2$ active component, and of the catalyst samples derived therefrom, contains Co_3O_4 with a cubic spinel structure (Fd3m). The size of cobalt crystallites calculated by the Scherrer equation from the evaluated average size of Co_3O_4 particles varies from 10.8 to 14.2 nm. SiO_2 is X-ray-amorphous; the reflections in the range of $2\theta \approx 7^\circ$ – 30° are attributed to ZSM-5 with an orthorhombic crystalline structure [36], and a higher reflection intensity corresponds to a higher SiO_2/Al_2O_3 ratio. Alumina is represented by reflections at $2\theta \approx 47^\circ$ – 70° . Weak reflections indicate low crystallinity of the Al_2O_3 phase generated under the heat treatment of the boehmite binder.

The H_2 -TPR curves of the catalysts are similar (Fig. 2). The reduction of the cobalt-containing component follows a sequential mechanism ($Co_3O_4 \rightarrow CoO \rightarrow Co^0$ [33]), as confirmed by the presence of two reduction

peaks. For these catalysts, the ratio of the peak areas of hydrogen—which is required to ensure the $Co^{3+} \rightarrow Co^0$ stepwise transformation—differs from the theoretical value (3) calculated in accordance with the cobalt oxide reduction stoichiometry. This value is 2.70 for Z40, and declines from 2.87 to 2.54 for Z60 to Z300. The lack of H_2 absorption peaks in the high-temperature range indicates that the main portion of cobalt, which is fixed during the calcination of the $Co-Al_2O_3/SiO_2$ oxide form at up to $400^\circ C$ [33], undergoes no significant interaction with the zeolite or the alumina binder that could form hard-to-reduce compounds. This implies that the catalyst preparation technology under study differs from the Chevron catalytic system production technology. The Chevron technology, designed for single-reactor production of liquid hydrocarbons, involves extrusion molding of zeolite and alumina binder followed by impregnating the extrudates with a cobalt solution. Using this method, cobalt particles are selectively dispersed on the alumina matrix to produce a bifunctional catalyst in which the FT component (Co/Al_2O_3), although separated from zeolite particles, resides in a nanoscale proximity to them [44, 45].

Aluminum content is a critical parameter to measure the number of various acid sites both on the internal and external surfaces of zeolite crystals; moreover, this parameter is responsible for the activity, selectivity, and deactivation rate of these sites in acid-catalyzed

Table 2. Catalyst surface acidity

Catalyst sample	Acidity, $\mu\text{mol NH}_3/\text{g}$			
	weak sites ^a	medium sites ^b	strong sites ^c	total
Q	50	7	0	57
Z40	70	31	5	106
Z80	61	20	4	85
Z300	54	14	1	69

^a Amount of NH₃ desorbed in the range of 100–250°C.^b Amount of NH₃ desorbed in the range of 250–400°C.^c Amount of NH₃ desorbed in the range of 400–550°C.**Table 3.** Activity of FT catalysts

Catalyst sample	Temperature, °C	CO conversion, %	Selectivity, %				C ₅₊ productivity, kg/(m ³ _{cat} ·h)
			CH ₄	C ₂ –C ₄	C ₅₊	CO ₂	
Q (reference)	240	77.0	18.5	11.8	67.3	2.4	117.1
Z40	240	75.6	18.7	11.9	67.1	2.3	107.1
	250	85.9	15.8	8.2	72.8	3.3	132.0
Z60	240	85.6	17.8	7.3	70.7	4.2	129.1
	250	91.1	19.4	5.4	70.4	4.8	140.2
Z80	240	85.5	15.9	6.6	74.7	2.8	141.0
	250	91.9	18.0	7.3	70.8	3.9	143.6
Z300	240	84.1	19.1	6.9	70.2	3.8	131.4
	250	89.4	23.0	7.9	64.5	4.6	128.1

reactions [23]. The protonic (decationated) form of HZSM-5 utilized for the catalyst preparation exhibits high Brønsted acidity; the specific number of acid sites depends on various characteristics such as aluminum content, aluminum distribution over the crystals, SiO₂/Al₂O₃ ratio, presence of compensating cations, etc. [24]. The individual acidity parameters of zeolites and catalysts can be evaluated by various methods.

During the acidity investigation by NH₃–TPD (Table 2) and the catalytic test runs (Table 3)—intended to confirm and characterize the zeolite effects on the active surface condition and on the secondary synthesis reactions—a reference catalyst (Q) was tested in addition to the bifunctional catalysts. The Q catalyst contained 35 wt % Co–Al₂O₃/SiO₂, 30 wt % inert quartz (instead of zeolite), and 35 wt % boehmite, and had an average Co⁰ particle size of 12 nm (according to XRD) and a narrow nanoparticle size distribution. The average particle size of the catalysts under study was 10.8 to 12.8 nm [34]. At the same time, we took into account the results of

extensive research on the acidity of HZSM-5 samples (purchased from Alfa Aesar, a China-based company) with SiO₂/Al₂O₃ ratios of 23, 30, 50, 80, and 300, and specific surface areas of 400–425 m²/g [46, 47]. For the referenced research, various examination methods were employed, such as elemental analysis, IR spectroscopy, NMR, and temperature-programmed desorption of pyridine and collidine (to quantify the total number of acid sites and the numbers of sites on the external surface or at the pore mouth).

The Q catalyst surface, represented by weak and medium acid sites, had a total acidity of 57 $\mu\text{mol NH}_3/\text{g}$. The total acidity of the assayed samples ranged between 69 and 106 $\mu\text{mol NH}_3/\text{g}$. The number of strong acid sites did not exceed 2–5%. Like HZSM-5, the catalysts based thereon exhibited relatively high Brønsted acidity. The strength, concentration, location, and accessibility of the sites are the parameters critical for the catalyst efficiency in the hydroisomerization of *n*-alkanes, including those with a high molecular weight. As the SiO₂/Al₂O₃ ratio

Fig. 3. Degree of CO conversion vs. FT synthesis time at 240°C (a) and 250°C (b) for catalyst samples: (1) Z40; (2) Z60; (3) Z80; and (4) Z300.

grows and the total Al concentration declines, the Brønsted acidity of the zeolite and catalysts derived therefrom decreases, and the percentage of medium acid sites (which reduce the probability of a cracking reaction) drops from 30 to 25%. In this case, the total aluminum concentration per zeolite's unit cell drops from 7.7 to 3.7 for samples with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 23–50, and from 2.3 to 0.6 for samples with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 80 and 300 [46, 47]. The Al concentration in the zeolite, associated mostly with Brønsted acid sites, decreases from 6.2 ± 0.6 to 2.4 ± 0.3 and from 2.0 ± 0.2 to 0.5 ± 0.1 , respectively. The concentration of extra-framework cationic and neutral Al varies from 1.1 ± 0.3 to 0.1 ± 0.3 as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio grows from 23 to 300.

Table 3 shows the high activity of the catalysts during FT synthesis. The variation in performance parameters indicates the effects of zeolite introduction, of its $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and, therefore, of its surface acidity. For example, increasing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from 40 to 80 at 240°C enhanced the main performance parameters such as CO conversion, selectivity, and C_{5+} HC productivity. Elevating the reaction temperature to 250°C intensified the FT process. The variations in CO conversion and C_{5+} productivity as functions of the zeolite structure are similar, but they are also accompanied by an increase in the generation of CO_2 and methanation. The C_{5+} productivity lies between 128.1 and 143.6 $\text{kg}/(\text{m}^3_{\text{cat}} \cdot \text{h})$.

Z80 proved to be the most active FT catalyst. Z300 was the least active at 250°C.

The catalyst activity variation over time is graphically illustrated in Fig. 3 as a CO conversion trend. At 240°C, the degree of CO conversion grew monotonically for the initial 10 h followed by a gradual decline. During the initial period, the catalyst activation likely continues under the influence of the reaction medium, which may change both the reduction degree and the cobalt particle size. At 250°C, the CO conversion trend follows a different pattern. After the initial 15 h of CO conversion growth, the catalysts went into stable operation. Further on, over the course of gradual catalyst deactivation, the CO conversion predictably began, over time, to decrease.

The catalyst deactivation rate R_d (in $\% \cdot \text{h}^{-1}$) was calculated by the formula:

$$R_d = \frac{X_{\text{CO}}^{\text{init}} - X_{\text{CO}}^{\text{fin}}}{\tau}, \quad (4)$$

where $X_{\text{CO}}^{\text{init}}$ is the initial degree of CO conversion (after 10–15 h), %; $X_{\text{CO}}^{\text{fin}}$ is the final degree of CO conversion, %; and τ is the time, h.

The calculated catalyst deactivation rates are presented in Table 4. Z40 showed the highest stability of catalytic properties under the FT conditions imposed. At 240–250°C, its R_d value varied between 0.14 and 0.11 $\% \cdot \text{h}^{-1}$. At 240°C, the deactivation rates of Z60,

Z80, and Z300 were higher by factors of 1.5 to 1.9. An increase in the reaction temperature accelerates hydrocracking and other secondary reactions of long-chain hydrocarbons, which may block the active surface of the catalyst, thus suppressing the catalyst deactivation. In this manner, obviously, elevating the temperature (in our case to 250°C) slowed down the catalyst deactivation, thus serving as an effective method for intensifying the entire process and maintaining the stable operation of the catalysts.

The synthetic C_{5+} hydrocarbons consist of various components pertaining to the $\text{C}_5\text{--C}_{10}$, $\text{C}_{11}\text{--C}_{18}$, and C_{19+} fractions, and are represented by normal and isomeric alkanes and alkenes (Table 5). No naphthenics or aromatics were detected; unsaturated hydrocarbons were mostly represented by branched alkenes; and C_{11+} alkenes were present in minor amounts. Increasing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in HZSM-5 affected the cracking ability of the catalysts regardless of the temperature, markedly reducing the amount of n -alkanes involved in the secondary reactions on the zeolite's acid sites. Clearly, the content of n -alkanes in C_{5+} hydrocarbons is determined by the zeolite acidity. Similar results were obtained in [32] for zeolite effects on the properties of a composite catalyst. In the presence of the Q catalyst, the synthetic product consisted mostly of n -alkanes (78.0%) and n -alkenes (10.8%), as well as a relatively small amount of *iso*-alkanes and traces of branched alkenes [34].

The highest amount of isomeric and branched hydrocarbons is formed at 250°C , which likely results from

Table 4. Deactivation rate of FT catalysts

Catalyst sample	Deactivation rate at different FT temperatures, $\% \cdot \text{h}^{-1}$	
	240°C	250°C
Z40	0.14	0.11
Z60	0.26	0.23
Z80	0.21	0.18
Z300	0.24	0.11

the migration of resultant longer-chain HCs onto acid sites and into zeolite channels to initiate hydrocracking and isomerization, including the oligomerization of methane molecules [3, 45]. The variations in the ratios of isomeric to normal HCs and of alkenes to alkanes (expressed as *iso/n* and O/P, respectively) as functions of the zeolite's $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and of the reaction temperature are graphically illustrated in Fig. 4. The highest content of isomeric hydrocarbons was observed for Z60.

The composition of the synthetic hydrocarbons has a decisive effect on the amounts and properties of resultant fuel components. Table 6 clearly demonstrates that the share of the gasoline fraction ($\text{C}_5\text{--C}_{10}$) in the product synthesized at 240°C drops with an increase in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in HZSM-5—i.e., in the series of Z40, Z60, Z80, and Z300—and similarly rises at 250°C . The content of the diesel fraction ($\text{C}_{11}\text{--C}_{18}$) at 240°C increases

Fig. 4. Isomeric to normal HC ratio (*iso/n*) and olefin to paraffin ratio (O/P) in FT synthesis product as functions of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio at 240°C (a) and 250°C (b).

Table 5. HC composition of FT synthesis product

Catalyst sample	<i>T</i> , °C	HC group	Group composition of C ₅₊ HCs, wt %			Total	<i>iso/n</i> ^a	O/P ^b
			C ₅ –C ₁₀	C ₁₁ –C ₁₈	C ₁₉₊			
Z40	240	<i>n</i> -Alkanes	12.54	18.39	5.23	36.16	0.76	0.72
		<i>iso</i> -Alkanes	9.53	10.82	1.68	22.03		
		Alkenes	18.25	2.34	–	20.59		
		Branched alkenes	13.96	7.26	–	21.22		
		Total	54.28	38.81	6.91	100.00		
	250	<i>n</i> -Alkanes	9.39	13.11	3.68	26.18	1.06	0.99
		<i>iso</i> -Alkanes	11.51	10.48	2.11	24.10		
		Alkenes	20.34	2.05	–	22.39		
		Branched alkenes	20.94	6.39	–	27.33		
		Total	62.18	32.03	5.79	100.00		
Z60	240	<i>n</i> -Alkanes	14.2	18.0	5.5	37.70	1.11	0.6
		<i>iso</i> -Alkanes	8.8	15.1	2.8	26.70		
		Alkenes	9.3	1.7	–	11.00		
		Branched alkenes	12.1	12.5	–	24.60		
		Total	44.4	47.3	8.3	100.00		
	250	<i>n</i> -Alkanes	11.4	14.2	3.8	29.40	1.67	0.7
		<i>iso</i> -Alkanes	10.7	16.4	2.6	29.70		
		Alkenes	7.5	2.2	–	9.70		
		Branched alkenes	18.2	12.8	0.2	31.20		
		Total	47.8	45.6	6.6	100.00		
Z80	240	<i>n</i> -Alkanes	18.4	22.1	14.4	54.90	0.56	0.4
		<i>iso</i> -Alkanes	8.4	7.4	2.1	17.90		
		Alkenes	8.8	1.0	–	9.80		
		Branched alkenes	13.3	4.1	–	17.40		
		Total	48.9	34.6	16.5	100.00		
	250	<i>n</i> -Alkanes	20.7	17.6	6.2	44.50	0.77	0.4
		<i>iso</i> -Alkanes	9.7	12.4	2.5	24.60		
		Alkenes	12.3	0.7	0.1	13.10		
		Branched alkenes	15.0	2.8	–	17.80		
		Total	57.7	33.5	8.8	100.00		
Z300	240	<i>n</i> -Alkanes	26.4	37.8	13.8	78.00	0.19	0.1
		<i>iso</i> -Alkanes	3.7	6.9	2.8	13.40		
		Alkenes	4.9	0.9	–	5.80		
		Branched alkenes	1.9	0.9	–	2.80		
		Total	36.9	46.5	16.6	100.00		
	250	<i>n</i> -Alkanes	36.7	26.1	10.6	73.40	0.26	0.1
		<i>iso</i> -Alkanes	4.5	8.4	5.1	18.00		
		Alkenes	5.5	0.3	–	5.80		
		Branched alkenes	2.3	0.5	–	2.80		
		Total	49.0	35.3	15.7	100.00		

^a Isomeric to normal HC ratio.^b Alkene to alkane (olefin to paraffin) ratio.

Table 6. Fractional composition of FT synthesis product

Catalyst sample	T, °C	Fractional composition of C ₅₊ , wt %			Cloud point ^a , °C	Pour point ^a , °C
		< 180°C	180–330°C	bottom residue		
Z40	240	58.2	35.1	6.7	–12.8	–21.0
	250	60.7	31.9	7.4	–20.8	–32.0
Z60	240	57.8	39.5	2.7	–7.6	–17.0
	250	61.2	36.5	2.3	–9.6	–28.0
Z80	240	54.7	41.5	3.8	–4.6	–12.0
	250	63.1	33.8	3.1	–2.5	–15.0
Z300	240	47.7	42.1	10.2	+1.9	–4.0
	250	56.2	35.7	8.2	+0.1	–6.0

^a For 180–330°C distillate.

in the same series by a factor of about 1.2, and fluctuates between 31.9 and 36.5 wt % at the elevated temperature.

As the SiO₂/Al₂O₃ ratio in HZSM-5 increases, and regardless of the reaction temperature, the viscosity/temperature properties of the diesel distillate (180–330°C) decline. The diesel fuel distilled from the product synthesized over catalyst Z300 (above 70% *n*-alkanes) exhibited positive cloud points and slightly negative pour points. Thus, bifunctional catalysts with SiO₂/Al₂O₃ ratios of 40 and 60 in HZSM-5 showed high potential for the production of low-pour-point diesel fuels. The products synthesized in the presence of these catalysts exhibited the highest content of *iso*-alkanes and branched alkenes in combination with the lowest concentration of C₁₉₊ HCs. The cloud point and pour point of the diesel distillate for Z40 reached –20.8 and –32.0°C, respectively, which complies with the regulations applicable to winter diesel fuels.

CONCLUSIONS

The study comparatively assessed the catalytic performance of FT bifunctional cobalt catalysts prepared from HZSM-5 zeolites with different SiO₂/Al₂O₃ molar ratios. We demonstrated the high activity and selectivity of these catalysts in the synthesis of C₅₊ hydrocarbons. At 250°C, the catalysts exhibited productivity of 128.1–143.6 kg/(m³_{cat}·h). The SiO₂/Al₂O₃ molar ratio in HZSM-5 has a decisive effect on the hydrocarbon composition of the resultant C₅₊ product.

An HZSM-5 zeolite with a SiO₂/Al₂O₃ molar ratio of 40.5 was found to be preferable as an acidic component in a bifunctional catalyst for the purposes of producing high-quality synthetic low-pour-point diesel fuels. The viscosity/temperature properties of the synthetic diesel fuel produced in the presence of this catalyst are in compliance with the regulations applicable to winter diesel fuels.

AUTHOR INFORMATION

R.E. Yakovenko, ORCID: <https://orcid.org/0000-0001-9137-7265>

I.N. Zubkov, ORCID: <https://orcid.org/0000-0003-0828-3159>

V.G. Bakun, ORCID: <https://orcid.org/0000-0002-0971-8145>

O.P. Papeta, ORCID: <https://orcid.org/0000-0002-7334-1821>

A.P. Savostyanov, ORCID: <https://orcid.org/0000-0002-5319-2443>

FUNDING

This study was carried out within the framework of the national project “Science and Universities” with financial support from the Ministry of Sciences and Higher Education of the Russian Federation (project no. 075-03-2021-016/4), in the laboratory “New composite and functional materials with special properties” using equipment of the Nanotechnology Center for Collective Use, South Russian State Polytechnic University.

CONFLICT OF INTEREST

The authors declare no conflict of interest requiring disclosure in this article.

OPEN ACCESS

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

REFERENCES

1. Dry, M.E., *Catal. Today*, 2002, vol. 71, nos. 3–4, pp. 227–241.
[https://doi.org/10.1016/S0920-5861\(01\)00453-9](https://doi.org/10.1016/S0920-5861(01)00453-9)
2. Wood, D.A., Nwaoha, C., and Towler, B.F., *J. Natural Gas Sci. Eng.*, 2012, vol. 9, pp. 196–208.
<https://doi.org/10.1016/j.jngse.2012.07.001>
3. Adeleke, A.A., Liu, X., Lu, X., Moyo, M., and Hildebrandt, D., *Rev. Chem. Eng.*, 2020, vol. 36, no. 4, pp. 437–457.
<https://doi.org/10.1515/revce-2018-0012>
4. Sartipi, S., Makkee, M., Kapteijn, F., and Gascon, J., *Catal. Sci. Technol.*, 2014, vol. 4, pp. 893–907.
<https://doi.org/10.1039/C3CY01021J>
5. Chunxiang, Z. and George, M.B., *Appl. Catal. B: Environmental*, 2018, vol. 235, pp. 92–102.
<https://doi.org/10.1016/j.apcatb.2018.04.063>
6. Arutyunov, V.S., Savchenko, V.I., Sedov, I.V., Nikitin, A.V., Troshin, K.Ya., Borisov, A.A., Fokin, I.G., Makaryan, I.A., and Strekova, L.N., *Euras. Chem.-Technol. J.*, 2017, vol. 19, no. 3, pp. 265–271.
<https://doi.org/10.18321/ectj662>
7. Gill, S., Tsolakis, A., Dearn, K., and Rodríguez-Fernández, *Progr. Energy Combust. Sci.*, 2011, vol. 37, no. 4, pp. 503–523.
<https://doi.org/10.1016/j.pecs.2010.09.001>
8. Fu, T., Jiang, Y., Lv, J., and Li, Z., *Fuel Proc. Technol.*, 2013, vol. 110, pp. 141–149.
<https://doi.org/10.1016/j.fuproc.2012.12.006>
9. Khodakov, A.Y., Wei, C., and Fongarland, P., *Chem. Rev.*, 2007, vol. 107, no. 5, pp. 1692–1744.
<https://doi.org/10.1021/cr050972v>
10. Leckel, D., *Fuel Proc. Technol.*, 2011, vol. 92, no. 5, pp. 959–969.
<https://doi.org/10.1016/j.fuproc.2010.12.017>
11. Englin, B.A., *Primenenie zhidkikh topliv pri nizkikh temperaturakh* (Application of Liquid Fuels at Low Temperatures), Moscow: Khimiya, 1980.
12. Kinzul', A.P., Khandarkhaev, S.V., Pisarenko, N.O., Buryukin, F.A., and Tverdokhlebov, V.P., *Mir Nefteprodukt.*, 2012, no. 8, pp. 7–11.
13. Lipin, P.V., Doronin, V.P., and Gulyaeva, T.I., *Petrol. Chem.*, 2010, vol. 50, no. 5, pp. 362–367.
<https://doi.org/10.1134/S0965544110050075>
14. Sartipi, S., Parashar, K., Valero-Romero, M., Santos, V., Linden, B., Makkee, M., Kapteijn, F., and Gascon, J., *J. Catal.*, 2013, vol. 305, pp. 179–190.
<https://doi.org/10.1016/j.jcat.2013.05.012>
15. Gerasimov, D.N., Fadeev, V.V., Loginova, A.N., and Ly-senko, S.V., *Catal. Industr.*, 2015, vol. 7, pp. 128–154.
<https://doi.org/10.1134/S2070050415020051>
16. Li, J., He, Y., Tan, L., Zhang, P., Peng, X., Oruganti, A., Yang, G., Abe, H., Wang, Y., and Tsubaki, N., *Nature Catal.*, 2018, vol. 1, pp. 787–793.
<https://doi.org/10.1038/s41929-018-0144-z>
17. Sineva, L.V. and Mordkovich, V.Z., *Nauch. Zh. Ross. Gaz. O-va*, 2019, no. 2 (21), pp. 56–68.
18. Sadek, R., Chalupka, K.A., Mierczynski, P., Rynkowski, J., Millot, Y., Valentin, L., Casale, S., and Dzwigaj, S., *Catal. Today*, 2020, vol. 354, pp. 109–122.
<https://doi.org/10.1016/j.cattod.2019.05.004>
19. Přech, J., Strossi Pedrolo, D.R., Marcili, N.R., Gu, B., Peregudova, A.S., Mazur, M., Ordonsky, V.V., Valtchev, V., and Khodakov, A.Y., *ACS Catal.*, 2020, vol. 10, pp. 2544–2555.
<https://doi.org/10.1021/acscatal.9b04421>
20. Maddi, B., Davidson, S., Job, H., Dagle, R., Guo, M., Gray, M., and Ramasamy, K.K., *Catal. Lett.*, 2021, vol. 151, pp. 526–537.
<https://doi.org/10.1007/s10562-020-03324-7>
21. Sineva, L.V., Gorokhova, E.O., Pushina, E.A., Kulchakovskaya, E.V., and Mordkovich, V.Z., *Mendeleev Commun.*, 2020, vol. 30, pp. 362–365.
<https://doi.org/10.1016/j.mencom.2020.05.034>
22. Wang, Y., Yu, J., Qiao, J., Sun, Y., Jin, W., Zhang, H., and Ma, J., *J. Energy Institute*, 2020, vol. 93, pp. 1187–1194.
<https://doi.org/10.1016/j.joei.2019.11.002>
23. Koval', L.M., Korobitsyna, L.L., and Vosmerikov, A.V., *Sintez, fiziko-khimicheskie i kataliticheskie svoystva vyso-*

- kokremnezemnykh tseolitov* (Synthesis, Physicochemical, and Catalytic Properties of High-Silica Zeolites), Tomsk: TomGU, 2001.
24. Gábová, V., Dědeček, J., and Čejka, J., *Chem. Commun.*, 2003, no. 10, pp. 1196–1197.
<https://doi.org/10.1039/B301634J>
25. Sadek, R., Chalupka, K.A., Mierczynski, P., Rynkowski, J., Gurgul, J., and Dzwigaj, S., *Catalysts*, 2019, vol. 9, pp. 497–518.
<https://doi.org/10.3390/catal9060497>
26. Xing, C., Li, M., Zhang, G., Noreen, A., Fu, Y., Yao, M., Lu, C., Gao, X., Yang, R., and Amoo, C.C., *Fuel*, 2021, vol. 285, pp. 119233.
<https://doi.org/10.1016/j.fuel.2020.119233>
27. Li, X., Chen, Y., Liu, S., Zhao, N., Jiang, X., Su, M., and Li, Z., *Chem. Eng. J.*, 2021, vol. 416, pp. 129180.
<https://doi.org/10.1016/j.cej.2021.129180>
28. Horáček, J., *Monatshefte für Chemie-Chemical Monthly*, 2020, vol. 151, pp. 649–675.
<https://doi.org/10.1007/s00706-020-02590-w>
29. Li, Z., Wu, L., Han, D., and Wu, J., *Fuel*, 2018, vol. 220, pp. 257–263.
<https://doi.org/10.1016/j.fuel.2018.02.004>
30. Cheng, S., Mazonde, B., Zhang, G., Javed, M., Dai, P., Cao, Y., Tu, S., Wu, J., Lu, C., Xing, C., and Shan, S., *Fuel*, 2018, vol. 223, pp. 354–359.
<https://doi.org/10.1016/j.fuel.2018.03.042>
31. Asalieva, E.Y., Kul'chakovskaya, E.V., Sineva, L.V., and Mordkovich, V.Z., *Petrol. Chem.*, 2020, vol. 60, no. 1, pp. 69–74.
<https://doi.org/10.1134/S0965544120010028>
32. Sineva, L.V., Asalieva, E.Y., and Mordkovich, V.Z., *Russ. Chem. Rev.*, 2015, vol. 84, no. 11, pp. 1176–1189.
<https://doi.org/10.1070/RCR4464>
33. Narochnyi, G.B., Yakovenko, R.E., Savost'yanov, A.P., and Bakun, V.G., *Catal. Industr.*, 2016, vol. 8, no. 2, pp. 139–144.
<https://doi.org/10.1134/S2070050416020070>
34. Yakovenko, R.E., Savost'yanov, A.P., Narochnyi, G.B., Soromotin, V.N., Zubkov, I.N., Papeta, O.P., Svetogorov, R.D., and Mitchenko, S.A., *Catal. Sci. Technol.*, 2020, vol. 10, no. 22, pp. 7613–7629.
<https://doi.org/10.1039/D0CY00975J>
35. Savost'yanov, A.P., Narochnyi, G.B., Yakovenko, R.E., Saliev, A.N., Sulima, S.I., Zubkov, I.N., Nekroenko, S.V., and Mitchenko, S.A., *Petrol. Chem.*, 2017, vol. 57, no. 12, pp. 1186–1189.
<https://doi.org/10.1134/S0965544117060251>
36. PDF-2. The powder diffraction file TM. International Center for Diffraction Data (ICDD). PDF-2 Release 2012.
<https://www.icdd.com/>
37. Young, R.A., *The Rietveld Method*, Oxford University Press, 1995.
38. Schanke, D., Vada, S., Blekkan, E.A., Hilmen, A.M., Hoff, A., and Holmen, Ah., *J. Catal.*, 1995, vol. 156, no. 1, pp. 85–95.
<https://doi.org/10.1006/jcat.1995.1234>
39. Xu, D., Li, W., Duan, H., Ge, Q., and Xu, H., *Catal. Lett.*, 2005, vol. 102, nos. 3–4, pp. 229–235.
<https://doi.org/10.1007/s10562-005-5861-7>
40. Peng, G., Nana, Y., Lei, W., Xiaodong, Z., *Crystal Growth Design*, 2017, vol. 17, no. 12, pp. 6821–6835.
<https://doi.org/10.1021/acs.cgd.7b01410>
41. Akhmedov, V.M. and Al-Khowaiter, S.H., *Catal. Rev.*, 2007, vol. 49, no. 1, pp. 33–139.
<https://doi.org/10.1080/01614940601128427>
42. Weitkamp, J., *Solid State Ionics*, 2000, vol. 131, nos. 1–2, pp. 175–188.
[https://doi.org/10.1016/S0167-2738\(00\)00632-9](https://doi.org/10.1016/S0167-2738(00)00632-9)
43. Davis, T.M., Drews, T.O., Ramanan, H., He, C., Dong, J., Schnablegger, H., Katsoulakis, M.A., Kokkoli, E., McCormick, A.V., Penn, R.L., and Tsapatsis, M., *Nature Mater.*, 2006, vol. 5, pp. 400–408.
<https://doi.org/10.1038/nmat1636>
44. Kibby, C., Jothimurugesan, K., Das, T., Lacheen, H.S., Rea, T., and Saxton, R.J., *Catal. Today*, 2013, vol. 215, pp. 131–141.
<https://doi.org/10.1016/j.cattod.2013.03.009>
45. Rytter, E. and Holmen, A., *ACS Catal.*, 2017, vol. 7, no. 8, pp. 5321–5328.
<https://doi.org/10.1021/acscatal.7b0152>
46. Bräuer, P., Ng, P.L., Situmorang, O., Hitchcock, I., and D'Agostino, C., *RSC Adv.*, 2017, vol. 7, no. 3, pp. 52604–52613.
<https://doi.org/10.1039/C7RA10699H>
47. Bräuer, P., Situmorang, O., Ng, P.L., and D'Agostino, C., *Phys. Chem. Chem. Phys.*, 2018, vol. 20, no. 6, pp. 4250–4262.
<https://doi.org/10.1039/C7CP07826A>