Fischer—Tropsch Synthesis with Cobalt Catalyst and Zeolite Multibed Arrangement

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Abstract—The role of zeolite in transformations of hydrocarbons produced from CO and H_2 over a Fischer– Tropsch cobalt catalyst under the conditions of multibed arrangement of the cobalt catalyst and the zeolite has been determined. Hydrocarbon conversion over the HBeta zeolite occurs via the bimolecular mechanism, as evidenced by a low methane yield and a high yield of unsaturated gaseous and liquid hydrocarbons. The conversion over the CaA zeolite obeys the unimolecular mechanism, as evidenced by the formation of increased amounts of methane and saturated gaseous C_2-C_4 hydrocarbons.

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Synthetic zeolites are used as catalysts in many chemical and petrochemical processes because they exhibit unique properties, such as acidity and specific structure and shape of the cavities and channels. The Fischer–Tropsch (FTS) synthesis is no exception; this process is a key stage of the technology for the production of high-quality synthetic oil from syngas (mixture of CO and H₂), which is derived from nonpetroleum carbonaceous raw materials [1–3]. The development of alternative methods for the production of fuel hydrocarbons is an important problem in view of the limited reserves of oil [4, 5].

Typically, the active metal used in FTS is cobalt or iron. It is believed that cobalt catalysts exhibit higher selectivity and provide the formation of a product that hardly contains any aromatic and oxygenated hydrocarbons [6]. Supported cobalt catalysts prepared by impregnating the support with a cobalt salt are most commonly used. A promising alternative is the use of skeletal cobalt, which provides additional removal of heat generated in the reaction owing to intrinsic heat conductivity [7].

In the last decade, the one-step production of synthetic oil from CO and H₂ has attracted the attention of many scientists around the world [8–11]. It is known that hydrocarbons formed in the FTS can undergo transformation in the presence of zeolites or other solid acids. The introduction of a zeolite into the catalyst composition provides a significant deviation from the classical Schulz–Flory–Anderson distribution and facilitates the production of synthetic oil with a boiling point below 400°C [12–14].

Studying the mechanisms of conversion of hydrocarbons formed in the FTS on the acid sites of zeolites is a quite important task, since the preparation and optimization of these systems requires understanding of the processes that occur on the surface. The knowledge of the mechanisms will make it possible to design more sophisticated systems that will provide the selective production of synthetic oil with a desired group and fractional composition. The effect of H-form zeolites on the composition of the resulting hydrocarbons was studied in detail by many investigators [8, 10-11,13–14]. Lee et al. [15] proposed to use zeolites in the cationic form for the formation of cobalt clusters of a certain size; however, the relationship between the performance of zeolites in this form and the composition of synthesis products was not studied.

Examination of discrete beds of a cobalt catalyst and a zeolite can facilitate the understanding of the hydrocarbon conversion mechanism and their contribution to the product composition and encourage the future development of zeolite-containing FT catalysts. The aim of this study was to determine the effect of the type of the zeolite as part of a multilayer catalyst bed containing skeletal cobalt on the composition of the synthesis products.

EXPERIMENTAL

The test samples were multicomponent beds composed of discrete beds of a cobalt catalyst and a zeolite. The cobalt catalysts to be studied were prepared via physically mixing an ultrafine aluminum powder to

| | Content, wt % | | | |
|----------|-----------------|----|--------------------------------|-----------|
| Sample | cobalt catalyst | | | zeolite |
| | Со | Al | Al ₂ O ₃ | HBeta/CaA |
| Со | 22 | 55 | 23 | _/_ |
| Co–HBeta | 20 | 50 | 20 | 10/— |
| Co–CaA | 20 | 50 | 20 | -/10 |

Total composition of the multicomponent bed

provide heat removal, utlrafine skeletal cobalt active in syngas conversion, and precalcined boehmite (i.e., Al_2O_3). An individual HBeta or CaA zeolite bed separated by a silica interlayer of 5 mm thickness was loaded to the reactor below the cobalt catalyst; the beds were. One of the samples (reference) was composed of the cobalt catalyst only and did not contain the additional zeolite bed. All powders were diluted with silica in a weight ratio of 1 : 4. The composition of the multicomponent catalyst beds and the arrangement of the beds are shown in the table and Fig. 1, respectively.

Hydrocarbons were synthesized in a steel flow reactor with an inner diameter of 10 mm. Prior to testing, the FT catalyst as part of the multicomponent bed was activated in a hydrogen stream supplied at a space velocity of 3000 h^{-1} at 400°C and 0.1 MPa for 1 h.

After activation, the FT catalyst as part of the multicomponent bed was conditioned in a stream of syngas containing 5 mol % H₂ as an internal standard (H₂/CO molar ratio, 2; space velocity, 1000 h⁻¹; pressure, 2 MPa) with a stepwise increase in temperature from 170 to 225°C (by 3–10°Cevery 6 h) to achieve the best possible performance with the given parameters. Catalyst efficiency was calculated as the amount (in grams) of liquid hydrocarbons produced from the syngas per kilogram of catalyst per hour. After that, the synthesis conditions were optimized with respect to temperature via increasing it by 3–5°C and with



Fig. 1. Diagram of the multibed arrangement of (a) Co, (b) Co–HBeta, and (c) Co–CaA samples.

respect to space velocity via increasing it to 6000 h^{-1} in increments of 1000 h^{-1} (every 6-12 h) to achieve the best possible performance at each space velocity of syngas.

Analysis of the feed mixture of syngas and gaseous synthesis products was conducted by gas-solid chromatography using a thermal conductivity detector, helium as a carrier gas, and temperature programming (60–200°C). A column with CaA molecular sieves was used to separate CO and CH₄, and a HayeSeppacked column was employed to separate CO₂ and C₂-C₄ hydrocarbons. The rest of the 100% gas by weight was hydrogen.

The composition of liquid C_{5+} hydrocarbons was determined by gas–liquid chromatography using a flame ionization detector; helium as a carrier gas (flow rate of 30 mL/min); a 50-m capillary column; a DB-Petro stationary phase; and temperature programming (50–270°C; heating rate, 4°C/min).

RESULTS AND DISCUSSION

All the test samples were active in FTS and exhibited a CO conversion of 40-60% (comparison was conducted at a syngas space velocity of 6000 h^{-1} and an optimum temperature for each of the samples: at 269, 274, and 241°C for Co, Co-HBeta, and Co-CaA, respectively). The reference Co and Co-HBeta samples exhibited the C5+ hydrocarbon selectivity of 39 and 37%, respectively; the introduction of a separate CaA zeolite bed (Co-CaA sample) led to a decrease in this parameter to 31%. The selectivity for the main byproduct methane was 32 or 31% in the presence of the Co or the Co-HBeta sample, respectively, and significantly increased-to 40%-in the presence of the Co-CaA sample. Considerable differences between the Co-HBeta and Co-CaA zeolitecontaining samples suggest that the hydrocarbons formed from syngas on the active sites of the cobalt catalyst undergo conversion on the acid sites of the zeolites via different mechanisms. Thus, it is evident



Fig. 2. Composition of (a) saturated and (b) unsaturated gaseous C_2-C_4 hydrocarbons.

than the presence of the CaA zeolite leads to the formation of an additional amount of methane.

The most commonly assumed mechanisms of hydrocarbon conversion on zeolite acid sites are the bimolecular (carbocationic) [16, 17] and unimolecular (protolytic) mechanisms [18, 19]. Both of them are chain mechanisms and include three steps: chain initiation, propagation, and termination. The main products formed via the bimolecular mechanism are lower hydrocarbons, mostly unsaturated; in this case, the production of methane, ethane, and ethylene is thermodynamically unfavorable, and the main products formed via the unimolecular mechanism are saturated hydrocarbons, in particular methane and ethane [20].

Figure 2 shows the yields of saturated and unsaturated gaseous C_2-C_4 hydrocarbons formed in the presence of the test discrete beds. The Co sample was characterized by the lowest concentration of ethane, propane, and butane (5.1, 2.5, and 2.7 g/m³, respectively; Fig. 2a). The introduction of an HBeta zeolite bed resulted in a slight increase in the yield of saturated C_2-C_4 hydrocarbons, up to 5.3 g/m³ of ethane, 2.8 g/m³ of propane, and 3.3 g/m³ of butane. The introduction of a CaA zeolite bed caused a considerable increase in the yield of saturated hydrocarbons: the ethane yield was 9.8 g/m³, while the yield of propane and butane increased almost threefold to 8.4 and 7.3 g/m³, respectively.

The presence of the Co sample resulted in the formation of 0.5 g/m^3 of ethylene, 5.4 g/m^3 of propylene, and 3.9 g/m^3 of butylene (Fig. 2b). The introduction of a separate bed of the HBeta zeolite had no significant effect on the formation of unsaturated gaseous C_2-C_4 hydrocarbons: the yields of ethylene and propylene were 0.5 and 5.6 g/m³, respectively; the butylene yield decreased to 2.9 g/m³. In the presence of a discrete Co–CaA bed, a substantially lower amount of unsaturated hydrocarbons was produced: the yields of ethylene, propylene, and butylene were 0.2, 3.7, and 2.2 g/m^3 , respectively.

The data are in good agreement with the assumption of different mechanisms of conversion over the HBeta and CaA zeolites. The low yield of methane and the high yield of unsaturated gaseous C_2-C_4 hydrocarbons in the presence of the HBeta zeolite suggest that the hydrocarbons undergo transformation via the bimolecular mechanism. The formation of larger amounts of methane and saturated gaseous C_2-C_4 hydrocarbons in the presence of the CaA zeolite suggests that the conversion of the hydrocarbons follow the unimolecular mechanism.

The molecular weight distribution of linear saturated C_{5+} hydrocarbons characterizes the fractional composition of the resulting hydrocarbons (Fig. 3a). In the case of the Co sample, the maximum of distribution of alkanes was at a carbon number of 8. The amounts of *n*-alkanes of the C_5-C_{10} and $C_{11}-C_{18}$ fractions were 29.4 and 36.5 wt %, respectively; the amount of C_{19+} heavy *n*-alkanes was 10.9 wt %; and the total *n*-alkane content was 76.8 wt %. The introduction of the HBeta zeolite did not lead to a shift of the maximum of distribution of linear saturated hydrocarbons. In this case, the amounts of *n*-alkanes of the C_5-C_{10} and $C_{11}-C_{18}$ fractions decreased to 24.4 and 29.4 wt %, respectively; the amount of C_{19+} heavy *n*-alkanes slightly decreased to 9.3 wt %; and total *n*-alkanes made the lowest values of 63.1 wt %. Thus, the introduction of the HBeta zeolite bed leads to a decrease in the amount of *n*-alkanes. The introduction of the CaA zeolite resulted in a shift of the distribution maximum toward lighter hydrocar-



Fig. 3. Molecular weight distribution of (a) *n*-alkanes, (b) isoalkanes, and (c) alkenes.

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bons corresponding to carbon number 7. The amounts of *n*-alkanes of the C_5-C_{10} and $C_{11}-C_{18}$ fractions increased to 39.9 and 27.4 wt %, respectively; the amount of C_{19+} heavy *n*-alkanes increased to 8.8 wt %; and total *n*-alkanes made 76.1 wt %. The introduction of a zeolite bed, regardless of the zeolite type, leads to a decrease in the amount of *n*-alkanes of the $C_{11}-C_{18}$ fraction, whereas the introduction of the CaA zeolite leads to a significant increase in the amount of saturated normal hydrocarbons of the C_5-C_{10} fraction.

The molecular weight distribution and fractional composition of the resulting saturated branched hydrocarbons were significantly different in the presence of the test samples (Fig. 3b). The Co sample was characterized by a diffused maximum of distribution corresponding to carbon numbers of 8-12. The amounts of isoalkanes of the C_5-C_{10} and $C_{11}-C_{18}$ fractions were 3.0 and 5.2 wt %, respectively; the amount of C_{19+} heavy isoalkanes was 0.4 wt %; and total isoalkanes made 8.6 wt %. The Co-HBeta sample was characterized by a pronounced distribution maximum corresponding to carbon number 10. The amount of C_5-C_{10} isoalkanes increased to 5.8 wt %; the amount of C_{11} - C_{18} isoalkanes remained almost unchanged at a level of 4.9 wt %; C_{19+} heavy isoalkanes were not detected in the analysis; and the amount of total isoalkanes increased to 10.7 wt %. The molecular weight distribution of isoalkanes in the presence of the Co-CaA sample was characterized by the lowest carbon number of 7. The amount of C_5-C_{10} isoalkanes increased to 7.9 wt %; the amounts of $C_{11}-C_{18}$ isoalkanes and C_{19+} heavy isoalkanes were 5.4 and 0.5 wt %, respectively; and total isoalkanes increased to 13.8 wt %. Thus, the amount of isoalkanes increased after the introduction of a zeolite bed regardless of the zeolite type; the presence of CaA led to the formation of lighter isoalkanes.

Figure 3c shows the molecular weight distributions of unsaturated hydrocarbons. The Co sample was characterized by a distribution maximum corresponding to carbon number 7. The amount of alkenes of the C_5-C_{10} and $C_{11}-C_{18}$ fractions were 12.7 and 2.1 wt %, respectively, and total unsaturated hydrocarbons made 14.8 wt %. The introduction of the HBeta zeolite led to a shift of the maximum of distribution of unsaturated hydrocarbons to carbon number 8. The amount of C_5-C_{10} alkenes increased to 23.1 wt %; the amount of $C_{11} - C_{18}$ alkenes was 3.2 wt %; and total alkenes made 26.3 wt %, the highest value among all the test samples. The introduction of the CaA zeolite led to a shift of the distribution maximum toward lighter hydrocarbons corresponding to carbon number 6. The amounts of alkenes of the C_5-C_{10} and $C_{11}-C_{18}$ fractions decreased to 9.4 and 0.6 wt %, respectively, and total alkenes made the lowest quantity of 10 wt %. Thus, the introduction of the HBeta or CaA zeolite led to a 1.5-fold increase or about a 1.5-fold decrease in the amount of alkenes, respectively. It is interesting that the alkenes produced in the presence of the HBeta zeolite had higher molecular weights compared with the alkenes formed in the presence of the CaA zeolite.

Consequently, the introduction of a zeolite, irrespective of its type, leads to an increase in the yields of C_5-C_{10} hydrocarbons and isoalkanes; with the formation of alkenes being enhanced only in the presence of the HBeta zeolite. This fact also confirms the assumption that the conversion of hydrocarbon on zeolite acid sites occurs via different mechanisms depending on the zeolite type, either the bimolecular or the unimolecular mechanism the presence of the HBeta or CaA zeolite, respectively.

CONCLUSIONS

Thus, based on the foregoing, we can reveal the role of zeolite in the transformations of hydrocarbons produced over a Fischer–Tropsch cobalt catalyst under conditions of multibed arrangement of the cobalt catalyst and the zeolite.

Hydrocarbons produced from CO and H_2 over cobalt undergo conversion on zeolite acid sites. In the presence of the HBeta zeolite, cracking and isomerization occur in accordance with the bimolecular mechanism, which leads to an increase in the yield of C_5-C_{10} hydrocarbons and gaseous and liquid alkenes and isoalkenes; in the presence of the CaA zeolite, the reactions follow the unimolecular mechanism, which results in an increased yield of C_5-C_{10} hydrocarbons and alkanes, particularly methane and C_{5+} isoalkanes.

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