Hydrocracking of Fischer−Tropsch Paraffin Mixtures over Strong Acid Bifunctional Catalysts to Engine Fuels

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ABSTRACT: Biomass-based Fischer−Tropsch paraffin mixtures, having C_16−C_46 and C_11−C_45 carbon number range, were hydrocracked over platinum-supported beta, ZSM-5, and mordenite catalysts. The aim of the study was to investigate the effects of the feedstock composition, the process parameters, and the catalyst properties (acidity and zeolite structure) on the C_21+ conversions, the product yields, and the isoparaffin contents. It was stated that lower C_21+ conversions and higher JET and diesel fuel yields can be obtained for feedstock comprising C_11−C_45 hydrocarbons. Under identical reaction conditions, the activity order of the catalysts was Pt/H-beta > Pt/H-ZSM-5 > Pt/H-mordenite. This order corresponds to the relative number of accessible acid sites. Among the tested catalysts, platinum-supported beta zeolite showed the highest hydrosisomerization activity; meanwhile, in the pores of Pt/ZSM-5 and Pt/H-mordenite, diffusion constraints were observed. As the product of hydrocracking valuable gasoline, JET and diesel fuels having high hydrogen content and excellent burning properties were produced.

1. INTRODUCTION

Nowadays, 80−85% of the world’s growing energy demand is covered by conventional, petroleum-based fuels that contribute to serious environmental problems and depletion of oil reserves.1−4 The global concerns and political targets promote the research and development of environmentally friendly alternative fuels.

Fischer−Tropsch synthesis is a promising and increasingly popular way of producing alternative fuels.5−8 The synthesis product is rich in aliphatic hydrocarbons and does not contain sulfur and aromatics.9−12 It is compatible with the current vehicles and can be used in the existing refueling infrastructure.13,14

Fischer−Tropsch synthesis follows a polymerization-like reaction mechanism, including reactants adsorption, chain formation, chain propagation, chain termination, and product desorption.15 The product formation is difficult to control; thus, 20−45 wt % of the synthesis product can be a higher boiling point than 360 °C.16 The formation of high-molecular-weight Fischer−Tropsch paraffin wax reduces the cost-effectiveness of the technology and results in the limitation of the fulfillment of the market requirements.17,18

To increase the economics of the Fischer−Tropsch technology, hydrocracking of the high-molecular-weight paraffin mixtures was proposed in the literature.19−23 According to the most accepted reaction mechanism of paraffin hydrocracking, n-paraffin is first dehydrogenated on the metallic sites to n-olefins. After diffusion to the Brønsted acidic sites, they are protonated and transformed to a carbocation. The carbocation is isomerized and/or cracked and an olefin and a lighter carbocation are formed. After deprotonation, the olefinic products diffuse to the metallic sites and are hydrogenated.24,25 Presumably, the classical mechanism is valid only for alumina-supported platinum catalysts operating at higher temperatures. In the case of strong acid-supported catalysts, the nonclassical protonated cyclopropane ring formation is the more generally accepted.

Ideally, hydrocracking selectively converts the high-molecular-weight paraffins into middle distillates. The metallic and acidic functions of the catalyst are in balance to minimize the cracking of C_{10}−C_{21} hydrocarbons already present in the feedstock and to favor the formation of isoparaffins, having excellent cold flow properties.26−28 The metallic function of bifunctional catalysts can be provided by transition metals (Mo, W, Co, and Ni) or noble metals (Pt and Pd). As a support, amorphous silica−alumina, MoO_3-modified amorphous silica−
alumina, anion-modified (tungstated and sulfated) zirconia, and zeolites can be used.20,22,30–32

Among the possible bifunctional catalysts, oxide-supported transition metal or noble metal catalysts were also widely studied in Fischer–Tropsch wax hydrocracking.23–26 Despite the favorable results of experiments carried out with model compounds,27–29 about the effects of strong solid acid supports on Fischer–Tropsch wax hydrocracking, only limited information is available.30,31 Zeolites have higher activity than amorphous-based catalysts;37 thus, they may be suitable to decrease the energy demand of the hydrocracking. Moreover, the lower reaction temperatures can minimize the extent of the secondary hydrocracking. Nonetheless, Pt/H-beta, Pt/H-ZSM-5, and Pt/H-mordenite catalysts were not previously studied in hydrocracking of high-molecular-weight Fischer Tropsch paraffin waxes, particularly belonging to C16−C46 and C11−C45 carbon number ranges. As a result, there is no available information about the effects of the zeolite structure, the acidity, and the carbon number distribution on the conversions of C21+ hydrocarbons as well as on the yield and the composition of the C21 fraction.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. Strong acid Pt/H-beta, Pt/H-ZSM-5, and Pt/H-mordenite bifunctional catalysts were applied. The Fischer–Tropsch paraffin mixtures contained C16−C46 and C11−C45 hydrocarbons and were designated as WAX A and WAX B. Conversions of C21+ hydrocarbons, product yields, and isoparaffin contents were studied in the function of process parameters, feedstocks, acidity, and structure of the zeolite catalysts.

2.2. Characteristics of Feedstocks. The Fischer–Tropsch waxes were characterized by composition, C21+ hydrocarbon content, molecular weight, densities, and congealing points (Table 1). The latter two properties were measured by 1183:2013 and 2176:1996 analytical methods approved by the European Standards (EN) and International Organization for Standardization.

To determine the carbon number distribution and the hydrocarbon composition, gas chromatography (GC) was used. The Shimadzu 2010-type GC fitted with an Rxi-Sil MS (30 m × 0.25 mm × 0.25 μm) column and also with a Shimadzu QP2010 SE-type mass spectrometer. The injector and the detector were heated to 260 °C.

The heating program was as follows:
• at 35 °C for 8 min.
• Heating to 240 °C with a heating rate of 8 °C/min.
• Heating from 240 to 350 °C with a heating rate of 10 °C/min.
• At 350 °C for 15 min.

2.3. Catalyst Preparation. Beta and mordenite zeolites were the products of Zeolyst International, commercially designated as CP814E and CBV-21A, respectively. The patented method of Mobil Oil18 was modified to prepare ZSM-5 zeolite. It was found that a quarter of the prescribed amount of proplyamine (C6H11N) template was sufficient for the synthesis of ZSM-5 samples having a silica/alumina (Si/Al) molar ratio of 20–50. In the hydrothermal synthesis, silica (SiO2) gel and aluminum sulfate octadecahydrate [Al2(SO4)3·18 H2O] (both obtained from Reanal Plc., Hungary) were the sources of silicon (Si) and aluminum (Al), respectively. The molar composition of the synthesis gel was 2.3 SiO2:0.1 alumina (Al2O3):0.3 sodium oxide (Na2O):0.6 sodium sulfate (Na2SO4):1.8 C6H11N:94.9 water (H2O). The synthesis gel was hydrothermally treated for 40 h in an oven at a temperature of 180 °C, the products were recovered, thoroughly washed with deionized H2O to neutral pH, dried at 100 °C, and then calcined in air at 550 °C to remove the template molecules from the zeolite structure.

Catalysts, containing 1 wt % platinum (Pt), were prepared by wet impregnation of the zeolites with a solution of tetraammineplatinum(II) hydroxide (Pt(NH3)4(OH)2·H2O). After overnight impregnation, the material was dried at 120 °C and finally air-calcined at 480 °C for 4 h.

2.4. Catalyst Characterization. Al and Na contents of the zeolites were determined by atomic absorption spectroscopy after dissolving the solid in hydrofluoric acid using a Varian Spectra A-20 spectrometer.

The specific surface area (SSA) was calculated by the B-point method from nitrogen (N2) adsorption isotherms measured at −196 °C using a Thermo Fisher Scientific “Surfer” instrument. Before the measurement, the samples were evacuated for 3 h at 200 °C.

The Bronsted acid site concentration of zeolites was determined by measuring the temperature-programmed ammonia evolution from the NH4+ zeolite forms. To prepare the ammonium form, the conventional ion-exchange process was applied using a 1 M ammonium chloride (NH4Cl) solution at room temperature. The zeolite samples were heated up at a rate of 10 °C/min from 180 to 650 °C in N2 flow. The released ammonia (NH3) was absorbed in H2O and titrated continuously with a 0.1 M hydrogen chloride (HCl) solution. The molar amount of NH3 released was taken as equivalent with the Bronsted acid site concentration of the sample.

The Bronsted and Lewis acidity of the catalysts was characterized by the infrared (IR) spectra of the adsorbed pyridine (C5H5N) using a Nicolet Compact 400 type spectrometer. In the first step of the IR measurement, a self-supporting pellet was made from the zeolites and activated in situ in the IR cell in oxygen (O2) flow at 450 °C. After the evacuation of the cell, the spectrum was recorded at room temperature (Figure 1, Section A, spectrum a). After recording the spectrum, the sample was contacted with 5 mbar of C5H5N vapor for 0.5 h at 200 °C and then the cell was evacuated at 100 °C for 0.5 h. The spectrum was recorded again at room temperature (Figure 1, Sections A, spectrum b, and Section B, spectrum b’), and then the temperature was increased from 100 to 500 °C. In every step, 0.5 h of evacuation time was applied and the spectrum was recorded at room temperature (Figure 1, Section B, spectra c–f).

The number of surface Pt atoms was determined by the carbon monoxide (CO) chemisorption method, and the dispersion of the Pt particles was calculated. The catalyst sample

Table 1. Main Characteristics of the Paraffin Waxes

| characteristics          | WAX A | WAX B |
|--------------------------|-------|-------|
| congealing point, °C     | 78    | 60    |
| molecular weight, g/mol  | 375   | 300   |
| density (25 °C), kg/m³   | 910   | 846   |
| C21+ hydrocarbon content, wt % | 79.7  | 41.4  |
| n-paraffin content, wt % | 97.6  | 96.5  |
| isoparaffin content, wt %| 2.1   | 2.5   |
| cycloparaffin content, wt %| 0.06  | 0.06  |
| n-olefin content, wt %   | 0.2   | 0.9   |
was placed in a flow-through quartz microreactor, heated up to 450 °C in a hydrogen (H₂) flow of 30 cm³/min, and kept at this temperature for 1 h. The heating rate was 10 °C/min. The samples were then flushed with a 20 cm³/min helium (He) flow at 450 °C and cooled to room temperature in the He flow. At room temperature, CO pulses were sequentially injected into the He flow from a 10 μL loop volume using a loop valve. The effluent gas of the microreactor was analyzed by a thermal conductivity detector (TCD). The pulses were repeated in 3−5 min intervals until the TCD signal indicated that all the chemisorption sites of the catalyst became saturated. The molar amount of chemisorbed CO was considered as equivalent to the number of surface Pt atoms.

### 2.5. Catalytic Experiments

A flow-through high-pressure microreactor system was used. About 1 cm³ of the catalyst was placed into the reactor and activated in situ by reduction at 450 °C in H₂ flow. The experiments were carried out in the temperature range of 225−350 °C. The liquid hourly space velocity (LHSV) was varied between 0.5 and 2.0 h⁻¹ cm⁻³ cm⁻³ catalyst⁻¹. Based on preliminary experimental results, the total pressure (P = 40 bar) and H₂/hydrocarbon volume ratio (600) were not changed.

### 2.6. Analytical Methods

The gas product was analyzed by GC equipped with a flame-ionization detector and an Equity-1 column. The composition of the liquid product was determined by GC−mass spectrometry (MS) (the conditions were the same as shown in chapter 2.2). The C_{21}−hydrocarbon conversions, the gas (C_1−C_4), gasoline (C_5−C_9), JET (C_{10}−C_{14}), and diesel fuel (C_{15}−C_{21}) yields, and the isoparaffin contents of the liquid.

### Table 2. Main Characteristics of the Platinum-Supported Zeolite Catalysts

| characteristics          | Pt/H-beta | Pt/H-ZSM-5 | Pt/H-mordenite |
|--------------------------|-----------|------------|---------------|
| Pt content, wt %         | 1.0       | 1.0        | 1.0           |
| Pt dispersity, %         | 17.8      | 17.7       | 9.8           |
| micro- and mesopore volume, cm³/g | 0.37⁺ | 0.21       | 0.25⁺         |
| micropore volume, cm³/g  | 0.14      | 0.13       | 0.18          |
| SSA, m²/g                | 566       | 383        | 470           |
| Al content, mmol/g       | 1.21      | 0.69       | 1.52          |
| Na content, mmol/g       | 0.013     | N/A        | 0.013         |
| no. of ring members/pore size, nm | 12/0.66 × 0.67 | 10/0.51 × 0.55 | 12/0.65 × 0.70 |
| ion-exchange capacity, mmol NH₄⁺/g | 1.21 | 0.64 | 1.36 |
| Si/Al molar ratio        | 12.9      | 23.1       | 10.0          |

⁺Gurvich pore volume for the beta, ZSM-5, and mordenite catalysts determined from the N₂ adsorption capacity at p/p₀ 0.8, 0.95, and 0.9, respectively.  
⁻Micropore volume calculated from Alfa-s-plot.
products were calculated from the data of the gas chromatographic analysis.

3. RESULTS AND DISCUSSION

The activity differences were related to the acidity and the structural properties of the catalysts (Table 2). The NH₄⁺-exchange capacity of zeolites gives the concentration of the framework Al atoms that must be equal to the possible highest Bronsted acid site concentration of the zeolite. The ion-exchange capacity of zeolite H-beta and H-mordenite zeolites was nearly twice as high as that of zeolite H-ZSM-5. Despite its similar acidity, about 50 °C higher reaction temperature was needed for the mordenite catalyst to reach about the same conversion (∼50%) than on the Pt/H-beta. The micropore system of mordenite consists of two pore channels. The 12- and 8-membered ring entrances have a pore opening of 0.65 × 0.70 and 0.26 × 0.57 nm; ¹⁰ meanwhile, the molecular size of C₃−C₄ n-paraffins is between 0.45 and 0.49 nm. ⁴¹,⁴² Based on the aforementioned discussion, it was concluded that only pores having 12-membered ring apertures are accessible to the paraffin molecules; therefore, the micropore system of mordenite is one-dimensional regarding the paraffin transport.

In contrast, the whole three-dimensional channel system of zeolite beta, having 0.46 × 0.67 and 0.56 × 0.56 nm pore openings, is freely accessible for the reactant paraffin molecules. The difference in the accessibility of the acid sites is reflected by the catalytic activities of these zeolite catalysts. Zeolite ZSM-5 has 10-membered ring channels, establishing a two-dimensional network of pores characterized by 0.51 × 0.55 and 0.53 × 0.56 nm openings. ⁴⁰

The accessibility of this pore system for the straight-chain paraffins is similar to that of zeolite beta, but the acid site concentration of this zeolite is significantly lower. The latter property must be responsible for the relatively low cracking activity. The reaction temperature had to be raised to 350 °C to attain the activity of the Pt/H-beta catalyst at 300 °C.

The amount, the nature, that is, Lewis or Bronsted acidity, and the accessibility of the acid sites can be determined by analyzing the IR spectrum of C₅H₅N adsorbed on acidic solid.⁴³

Figure 2. Integrated absorbance of the band at 1546 cm⁻¹ as a function of the evacuation temperature (cf. the legend of Figure 1).

Pt/H-mordenite catalyst. As a result, carbenium ions, which are common surface intermediates of paraffin hydroisomerization and hydrocracking reactions, could form in the lowest concentration over the Pt/H-mordenite.

In the applied range of parameters, such as reaction temperature and LHSV, the conversions of C₂₁⁺ hydrocarbons of WAX A and WAX B feedstocks were 2.5−73.0 and 0.2−55.3%, respectively (Figure 3). In hydrocracking of WAX A feedstock—containing longer chain hydrocarbons in higher amount—higher conversions were observed than in the case of lower average molecular weight WAX B feedstock. The reason was attributed to the higher reactivity of longer-chain paraffins and their stronger adsorption at the active sites.

Over the tested catalysts, gaseous hydrocarbons were produced with significant yields (Table 3). The gas yields were significantly influenced by the C₂₁⁺ conversions and the reaction temperatures. At the same reaction temperature, for instance, at 300 °C, the order of gas yields strictly followed the order of C₂₁⁺ conversions. The gas contained mainly propane (C₃H₈) and butanes (C₄H₁₀) and virtually no methane (CH₄) and ethane (C₂H₆). C₄H₁₀ were present in higher concentration than C₃H₈. This product distribution can be interpreted with the protonated cyclopropene mechanism suggested by Sie. ⁷⁶−⁷⁸ According to this mechanism, the acid-catalyzed hydroconversion of normal paraffins proceeds through secondary carbenium ion intermediate. Before its β-scission, the carbenium ion is transformed to a nonclassical protonated cyclopropane carbocation. The β-scission results in an olefin and a tertiary carbenium ion. The latter has a methyl branch because of the opening of the cyclopropane ring. Hydride-transfer and hydrogenation steps result in methyl-branched and straight-chain paraffin products from the carbenium ion and the olefin, respectively. The shortest paraffin that can transform by this mechanism is heptane (C₇H₁₆). The gas products obtained from C₇H₁₆ are principally C₃H₈ and isobutane (i-C₄H₁₀). Hydrocarbons C₃ and C₄ can be formed by a single way of scission, whereas the longer-chain hydrocarbons can be formed by different ways of scissions, explaining the lower C₄ concentration than the C₃ concentration of the gas products. ⁴⁸ If the hydrocracking proceeds in 12-membered ring zeolite channels, as in the zeolite, beta, and mordenite catalysts, the isobutane (i-C₄H₁₀) concentration exceeds that of the n-butane (n-C₄H₁₀). Interestingly, n-C₃H₈ is the dominating species in the gas product obtained from the hydrocracking in the 10-membered ring channels of the ZSM-5 zeolite catalyst.

The preferential
formation of straight-chain product suggests that shape-selective cracking proceeds.

The product selectivity within the relatively narrow pores of zeolite ZSM-5 did not favor the formation of branched hydrocarbons having larger critical diameter than the straight-chain paraffin molecules. In one-dimensional channels of mordenite, the isomer diffusion was presumably much slower than in beta and ZSM-5 zeolite having a three-dimensional pore system. The pores of Pt/H-mordenite allowed the formation of branched isomers, but the isomers were cracked before leaving the pores. As a result, the gas yield was a bit higher over this catalyst, while the yield of branched isomers was slightly lower.

The role of Pt metal in the catalyst must be mentioned here. The primary product of \( \beta \)-scission is olefin. Olefin must be

Figure 3. \( C_{21} \) conversions in the function of the process parameters (\( P = 40 \) bar and \( H_2/\)hydrocarbon volume ratio = 600).

Table 3. Gas Product Yields and the Compositions (\( P = 40 \) bar, \( H_2/\)hydrocarbon Volume Ratio of 600)

| denomination | Pt/H-beta T = 225–300 °C | Pt/H-ZSM-5 T = 275–350 °C | Pt/H-mordenite T = 275–350 °C |
|--------------|----------------------------|-----------------------------|-------------------------------|
| Feedstock    | WAX A                      | WAX A                       | WAX A                         |
| yield, wt %   | 0.9–27.0                   | 7.9–44.0                    | 0.5–31.3                      |
| composition, wt % | 0.8–25.0                   | 5.0–42.0                    | 0.4–29.0                      |
| CH₄           | 0.0–0.2                    | 0.0–0.6                     | 0.1–0.6                       |
| C₂H₆          | 0.0–0.2                    | 0.1–2.0                     | 0.8–2.2                       |
| C₃H₈          | 4.0–13.2                   | 42.5–45.0                   | 21.5–27.0                     |
| i-C₄H₁₀       | 76.0–83.5                  | 78.2–85.1                   | 41.1–51.4                     |
| n-C₄H₁₀       | 10.5–12.5                  | 35.9–38.9                   | 20.4–34.0                     |

The measured minimum and maximum values of yields and selectivities.

Table 4. Liquid Product Yields (\( P = 40 \) bar, \( H_2/\)hydrocarbon Volume Ratio of 600)

| denomination | Pt/H-beta T = 225–300 °C | Pt/H-ZSM-5 T = 275–350 °C | Pt/H-mordenite T = 275–350 °C |
|--------------|----------------------------|-----------------------------|-------------------------------|
| Feedstock    | WAX A                      | WAX A                       | WAX A                         |
| product yields, wt % |                      |                             |                               |
| gasoline     | 3.8–42.1                   | 4.7–35.0                    | 0.5–31.0                      |
| JET          | 0.8–9.0                    | 0.1–1.2                     | 0.0–2.5                       |
| diesel fuel  | 6.4–16.8                   | 2.0–15.1                    | 7.7–22.0                      |
| middle distillates | 7.2–25.8                   | 2.1–16.3                    | 7.7–24.5                      |
| gasoline/middle distillate ratio | 0.5–1.6                   | 2.2–2.1                     | 0.1–1.3                       |

Ratio of yields, obtained at identical temperatures.
Table 5. Isomer Contents of Gasoline, JET, and Diesel Fuels (P = 40 bar, H₂/Hydrocarbon Volume Ratio of 600)

| catalyst                  | Pt/H-beta | Pt/H-ZSM-5 | Pt/H-mordenite |
|---------------------------|-----------|------------|---------------|
| temperature, °C           | 300       | 300        | 350           | 350           | 350           |
| LHSV, cm⁻³ wax/cm⁻³ catalyst h⁻¹ | 2.0       | 0.5        | 2.0           | 0.5           | 0.5           |
| feedstock                 | WAX A     | WAX B      | WAX A         | WAX B         | WAX A         | WAX B         |
| gasoline                  | 48.4      | 48.1       | 50.1          | 50.8          | 63.0          | 53.6          |
| JET                       | 59.0      | 65.5       | 20.0          | 22.0          | 59.1          | 36.0          |
| diesel fuel               | 77.5      | 81.8       | 38.8          | 43.0          | 74.1          | 79.9          |
| C₂₁ - conversion, wt %    | 93.0      | 91.0       | 37.0          | 38.0          | 91.0          | 37.0          |
| isoparaffin content, wt % | C₁₆−C₂₁  | C₁₆−C₂₁  | C₁₆−C₂₁      | C₁₆−C₂₁      | C₁₆−C₂₁      | C₁₆−C₂₁      |

The yields of gasoline, JET, and diesel fuel are summarized in Table 4. The sum amount of the JET and diesel fuel corresponds to the middle distillate yield (C₁₆−C₂₁). The ratio of the gasoline fraction to middle distillates for WAX A was at least equal to the same ratio for WAX B or higher because of the stronger adsorption of heavier n-paraffins of WAX A. That explains deeper fragmentation, resulting in higher gasoline, lower middle fraction formation. Among the investigated feedstocks, WAX B was the more suitable feedstock for middle distillate production.

On Pt/H-beta and Pt/H-mordenite catalysts, gasoline fractions were produced with nearly the same isoparaffin content (Table 5). Similarly, no significant differences were observed in the isoparaffin content of C₁₅−C₂₁ fractions. The isoparaffin content of JET fraction produced in hydrotreating of WAX B feedstock was lower than that from WAX A over each catalyst. The lower isoparaffin contents were attributed to the difference in feedstocks. However, the significantly lower isomerization activity found for the Pt/H-mordenite catalyst can also bear relation to the mordenite structure. In terms of results, it is clearly seen that the Pt/H-beta catalyst had the highest hydroisomerization activity. The pore size of the Pt/H-beta catalyst was large enough to allow the formation and fast diffusion of isoparaffins out of pores before the further transformation. The isomer selectivity of the Pt/H-ZSM-5 zeolite catalyst was significantly lower than that of Pt/H-beta and Pt/H-mordenite. This was caused by shape selectivity related to the limited diffusivity of branched isomers in the 10-membered ring zeolite channels.

The monobranched isomer concentration was always higher than the concentration of multibranched isoparaffins in the C₁₆−C₂₁ fraction. The phenomenon can be attributed to two reasons:

(I) In the first step of hydrotreating, monobranched isomers are formed,

(II) β-Scission of multibranched isomers takes place with higher reaction rate.

The thus-prepared environmentally friendly engine fuels have high hydrogen content and do not contain sulfur, olefins, and aromatic hydrocarbons. Because of the lack of aromatics, the burning properties are excellent, resulting in a lower flame temperature and NOₓ emission. The use of this highly valuable engine fuels is also advantageous from the point of view of engine structural material protection. As it was mentioned above, hydrotreating was accompanied by hydroisomerization; therefore, isoparaffin-containing engine fuels were produced. In the case of gasoline fractions, multibranched isoparaffins have high octane number; meanwhile, monobranched isoparaffins decrease the freezing and the cold filter plugging point of JET and diesel fuels.

4. CONCLUSIONS

Biomass-based Fischer–Tropsch paraffin mixtures, having C₁₆−C₄₅ and C₁₁−C₄₅ carbon number range (WAX A and WAX B), were hydrotreated over platinum-supported beta, ZSM-5, and mordenite catalysts. The experiments were carried out in the temperature range of 225−350 °C. The LHSV was varied between 0.5 and 2.0 cm⁻³ wax/cm⁻³ catalyst h⁻¹. The total pressure (P = 40 bar) and H₂/hydrocarbon volume ratio (600) were not changed. Conversions of C₂¹+ hydrocarbons, product yields, and isoparaffin contents were studied in the function of process parameters, feedstocks, acidity, and structure of the zeolite catalysts. It was stated that the feedstock composition influences the hydrotreating significantly because lower C₂₁+ conversions and higher JET and diesel fuel yields were obtained from hydrotreating of WAX B feedstock. The activity of Pt/H-ZSM-5 and Pt/H-mordenite zeolites was low at temperatures lower than 300 °C, whereas the Pt/H-beta zeolite catalyst was active already in the temperature range of 225−300 °C. Under the identical reaction conditions, the activity order of the catalysts was Pt/H-beta > Pt/H-ZSM-5 > Pt/H-mordenite. This order corresponds to the relative number of accessible acid sites. Among the tested catalysts, the Pt/H-beta zeolite had the highest hydroisomerization activity. The micropore dimensions of this catalyst were large enough to allow the formation and fast diffusion of isoparaffins out of pores before the further...
transformation. Hydrocracking/hydroisomerization reactions take place at lower temperatures on the Pt/H-beta catalyst than on Pt/H-ZSM-5 and Pt/H-mordenite zeolites, resulting in lower gas product and higher middle distillate yields. As the product of hydrocracking valuable gasoline, JET and diesel fuels having high hydrogen content and excellent burning properties were produced.

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**Notes**

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