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INVESTIGATION OF CATALYTIC CONVERSION OF FISCHER-TROPSCH WAX ON Pt/AlSBA-15 AND Pt/BETA ZEOLITE CATALYSTS

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Because of the more serious problems with the environment (e.g. greenhouse effect) and the crude oil supply (e.g. import dependence) the use of fuels and lubricants produced from renewable feedstocks have come to the front nowadays. The Fischer-Tropsch wax (60–80% of the Fischer-Tropsch products) which is produced on synthesis gas from different sources (biological or waste), is a mixture of high molecular weight (C_{20}-C_{60}) n-paraffins, which are in solid state (high pour point) at normal conditions. The products (fuels and base oils) which can be produced from this paraffin mixture have high quality and have fewer negative effects on the environment (practically zero sulphur- and nitrogen content, low aromatic content, excellent application properties) thus they do not demand changes in the fuel supply infrastructure and in the engine constructions. The isomerization of high molecular weight n-paraffins can be effectively carried out on bifunctional catalysts. There are only a few indications about the application of metal catalysts on mesoporous carrier in the literature. Consequently our objective was to investigate some Pt/AlSBA-15 (SBA: Santa Barbara Amorphous) catalysts which have not been investigated in detail in this reaction system yet, and compare its properties with a Pt/beta zeolite catalyst which has been recommended for this reaction earlier. The applicability and catalytic activity of Pt/AlSBA-15 and Pt/beta zeolite catalysts of 0.5% platinum content for the selective isomerization of Fischer-Tropsch wax was investigated in the present experiment. The experiments were carried out in a high-pressure microreactor system in continuous operation and on a catalyst with steady-state activity. The main properties of the feedstock which was a mixture of paraffin produced by Fischer-Tropsch synthesis (the synthesis gas was produced from biomass) were: n-paraffin content (C_{18}-C_{57}): 97.4%, sulphur content: <5 mg/kg, pour point: 72 °C. In the experiment the following process parameters were applied: T = 275–375 °C, P = 40–80 bar, LHSV = 1.0–3.0 h^{-1}, H_2/hydrocarbon ratio: 400–800 Nm^3/m^3. The composition of the products was determined by gas chromatography. From the catalysts with different support the best results were gained on the catalysts with AlSBA-15 support, and with increasing temperature the yield of liquid products (C_{5+}) decreased, but until 325 °C this value was above 93% in every case. In case of the beta zeolite high amount of cracking took place. Increasing the pressure shifted back the hydrocracking reactions (with the increasing number of moles) so it had a decreasing effect on the volume of the gas products and the lower contact time (higher liquid hour space velocity) had the same effect. In the gas products mainly branched isobutane was identified, which indicated that the cracking enacted partly after the isomerization reactions. The isoparaffin contents of the liquid products in the function of process parameters increased with increasing temperature and decreased with increasing pressure and LHSV in every case while other parameters were kept constant. Based on the isoparaffin contents of the different fractions it can be concluded that on Pt/AlSBA-15 catalyst at advantageous process parameter combinations (T = 300–325 °C (C_{11}-C_{20})/ 275–300 °C (C_{21}-C_{30}), P = 40–80 bar, LHSV = 1.0–2.0 h^{-1}) the catalyst was applicable to produce C_{11}-C_{20} and C_{21}-C_{30} fractions with high isoparaffin content (63.5–85.6% and 34.1–58.7%) with adequate yields (29.9–36.6% and 46.2–58.8%). We experienced that the gas oil fractions having the lowest pour point were obtained in the case of high concentrations of 5-methyl isomers. The C_{21}-C_{30} fraction is a high viscosity index (VI ≥ 125) base oil. The selectivity of the target product fractions was high, and based on these facts the selective isomerization of the Fischer-Tropsch wax can be a new application area of the Pt/AlSBA-15 catalyst.

Keywords: Fischer-Tropsch wax, Pt/AlSBA-15, hydroisomerization, hydrocracking

Introduction

Nowadays, the application of fuels and lubricants produced from renewable feedstocks has come to the front because of serious environmental problems (e.g. greenhouse effect) and ambiguity of crude oil supply (e.g. import dependence). In the integrated Fischer-Tropsch synthesis *(Fig. 1)* liquid hydrocarbons („synthetic crude") and subsequently fuels, base oils, paraffins and other special products are produced from natural gas, coal, crude oil derivates, biomass and wastes through synthesis gas in three main steps. The base process is the Fischer-Tropsch synthesis which forms the hydrocarbon molecules – significantly simplified – from $-CH_2-$ units. The Fischer-Tropsch wax (60–80% of the Fischer-Tropsch products) produced of synthesis gas of different sources is a mixture of high molecular weight (C_{20}-C_{60}) n-paraffins, which is practically free of sulphur, nitrogen and aromatics, but which is a solid at ambient conditions (high pour point). These paraffin mixtures can be excellent feedstocks of catalytic processes which can produce high quality products (fuels and base oils), less harmful to the environment (practically zero sulphur- and nitrogen content, low aromatic content), with excellent application properties and their use does not call for changes in the fuel supply infrastructure and in the engine constructions [1-6].

The final step of the integrated Fischer-Tropsch technology is product upgrading and separation to get fractions having required compositions and quality. The Fischer-Tropsch paraffin mixture is upgraded by hydrocracking or hydroisomerization to get lower pour point product. The product comprises of lower and/or branched hydrocarbons *(Fig. 2)*. The volume of the gaseous and naphta products formed over conventional hydrocracking catalysts is significant (6–8% and 10–20%), however, the selectivity for the target fraction (middle distillate) is relatively low. Therefore, it is very important to develop new catalytic systems for selective isomerization (skeletal arrangement) (reactor, feedstock, reaction mixture, process parameters) that can produce the appropriate mixture of gas oils and base oils (target product mixture) with high iso-paraffin content, and also to develop the suitable catalysts and application parameters [7-11].

The isomerization of high molecular weight n-paraffins can be effectively carried out over bifunctional catalysts. The metal component is responsible for the hydrogenation-dehydrogenation activity. The activation of C–C and C–H bonds proceeds on the acidic active sites of the support that is usually zeolite or mesoporous alumino-silicate. There are only a few data in the literature about the application of noble metal on mesoporous support for the hydroisomerization of high molecular weight paraffins [12, 13]. Consequently, our objective was to investigate mesoporous aluminosilicate Pt/AlSBA-15 catalyst which has not been studied in details in the above reaction yet, and to compare with a Pt/Beta catalyst which was highly recommended earlier for the same purpose [4, 14].

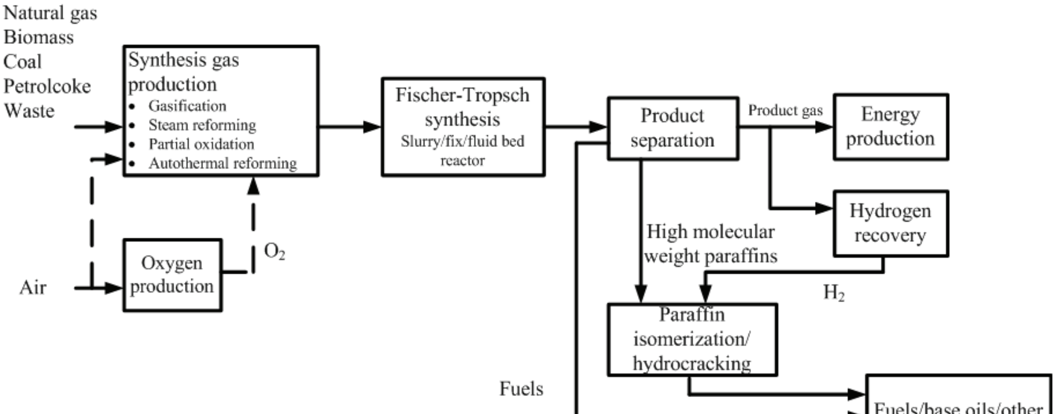

Figure 1: The integrated Fischer-Tropsch synthesis

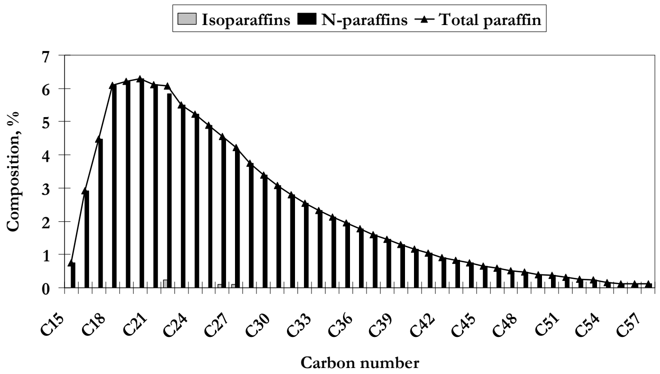

Figure 2: The paraffin composition of the feedstock

Experimental

Objectives

The aim of our experiments was to investigate 0.5% Pt containing AlSBA-15 and beta zeolite catalysts catalyst applicable for hydroisomerization and hydrocracking of Fischer-Tropsch wax to produce high quality gas oil and base oil fractions. The catalysts having 0.5% platinum were investigated because they were found based on our pre-experiments advantageous in the view of activity and economics for the selective isomerization of Fischer-Tropsch wax. The activity and selectivity of the catalysts and the effect of the process parameters (pressure, temperature, liquid hour space velocity, H_2/hydrocarbon volume ratio) on the yield and on the product compositions were also studied.

Feedstock

The feedstock of our experiments was a paraffin mixture produced from biomass-based synthesis gas with Fischer-Tropsch synthesis. The main properties and the paraffin composition of the feedstock are shown in *Table 1* and Fig. 2.

Table 1: The main characteristics of the feedstock

Properties	**Value**
N-paraffin content (C_{18}-C_{57}), %	99.6
Sulphur content, mg/kg	2.5
Nitrogen content, mg/kg	12
Pour point, °C	72

Catalysts

We used as catalyst AlSBA-15 and beta zeolite carrier materials prepared by us. Beta zeolite was prepared from 1 SiO_2 : 0.028 Al_2O_3 : 0.89 Na_2O : 0.38 tetra-ethyl ammonium hydroxide : 36.2 H_2O synthesis mixture by hydrothermal synthesis at 135 °C for 5 days. AlSBA-15 catalyst were synthesized according to the procedure of Vinu et al. [15] with reaction mixture composition of 1 SiO_2 : 0.04 Al_2O_3 : 0.016 P123 : 0.46 HCl : 127 H_2O, and aluminum isopropoxide as Al source. 0.5 wt.% of Pt was loaded by incipient wetness impregnation method on both supports in the form of tetraammineplatinum(II) hydroxide hydrate precursor. The catalysts were loaded into the reactor after forming. In order to assure the appropriate liquid distribution the reactant and the hydrogen was fed on a bed of quartz beads placed above the catalyst bed in the reactor tube. Catalysts were activated by reduction at 450 °C in hydrogen flow. Main properties of the catalysts are presented in *Table 2*.

Table 2: Main properties of the applied catalysts

Properties	**β zeolite**	**AlSBA-15**
Pt content, %	0.5	0.5
Brønsted acidity, mmol NH_3/g	0.83	0.6–0.65
BET area, m^2/g	280	470
Average pore diameter, nm	0.76 x 0.64	3.6
Si/Al ratio	19.2	17.8

Experimental equipment

Catalytic experiments were carried out in a high-pressure microreactor system *(Fig. 3)* at continuous operation and on steady-state catalyst. Minimum 80 °C temperature was maintained in the reactor system to avoid condensation (the feedstock was solid at room temperature).

Process parameters

The process parameters of the experiments were determined by our pre-experiments, which were the followings: Temperature: 275–375 °C, Pressure: 40–80 bar, Liquid hour space velocity: 1.0–3.0 h^{-1}, H_2/hydrocarbon volume ratio: 400–800 Nm^3/m^3

Analytical methods

The composition of the gas and liquid products was analyzed on-line gas chromatograph (GC) with FID detector. The main properties and the analytical parameters are shown in *Table 3*.

Table 3: Main properties of the gas chromatographs

Properties	**Liquid(solid) analysis**	**Gas analysis**
Type of column	Agilent Tech DB-1HT	Supelco EQUITY-1
Detector	Flame ionization	Flame ionization

Results and discussion

Our catalytic result showed that on the Pt/AlSBA-15 catalyst higher liquid product (C_{5+}) yield could be reached compared to Pt/Beta. With increasing temperature the yield of the liquid products (C_{5+}) decreased, but until 325 °C this value remained above 93% in case of the Pt/AlSBA-15 catalyst *(Fig. 4)*. On the Pt/Beta zeolite catalyst the C_{5-} product yield increased significantly above 300 °C. With increasing H_2 pressure the hydrocracking reactions were suppressed, the volume of the gas products decreased. Lower contact times had the same effect.

The yield of the C_{4-} fractions as a function of different process parameters is shown in *Fig. 5*. The produced amount of methane and ethane was very small or zero on both catalysts suggesting that hydrogenolysis did not proceed. Increasing temperature resulted in an increased yield of propane and higher molecular weight compounds. In the C_{5-} fractions on both catalysts mainly branched iso-butane could be identified which is probably formed by the β-scission of the branched carbenium ion intermediate.

The iso-paraffin content of the C_{5+} products increased with increasing temperature and decreased with increasing H_2 pressure and LHSV while other parameters were kept constant. It is important to be noted that the isomer content of the liquid products was significantly higher on the Pt/AlSBA-15 catalyst than on the other catalyst *(Fig. 6)*.

Based on the iso-paraffin content of the different fractions produced on the Pt/AlSBA-15 catalyst it can be concluded that at advantageous parameters (T = 300–325 °C, P = 40–80 bar, LHSV = 1.0–2.0 h^{-1}, and T = 275–300 °C, P = 40–80 bar, LHSV = 1.0–2.0 h^{-1}) the catalyst produce C_{11}-C_{20} and C_{21}-C_{30} fractions with high iso-paraffin content (63.5–85.6% and 34.1–58.7%) with reasonable yields (29.9–36.6% and 46.2–58.8%). It was found that the gas oil fractions having the lowest pour point were obtained with high concentrations of 5-methyl isomers. These gas oil boiling point range mixtures are excellent blending components having practically zero sulphur-, nitrogen- and aromatic content and can be used alone too. The C_{21}-C_{30} fraction can be used as environmentally friendly, high viscosity index (VI ≥ 125) base oil *(Table 4)*. It was also found that, the activity and isomerization selectivity of the AlSBA-15 catalyst having 0.5 wt.% of platinum did not change during the 240 hours time on stream experiment.

Table 4: The main characteristics of produced base oils and gas oils at the optimum process parameters

Properties	**Gas oils (C_{11}-C_{19})**	**Base oils (C_{21}-C_{29})**
Yield, %	29.9–36.6	46.2–58.8
Cetane number	>65	-
Viscosity index	-	125–135
Pour point, °C	(-16)–(-21)*	(-16)–(-10)
Sulphur content, mg/kg	<2	<3

* Cold Filter Plugging Point

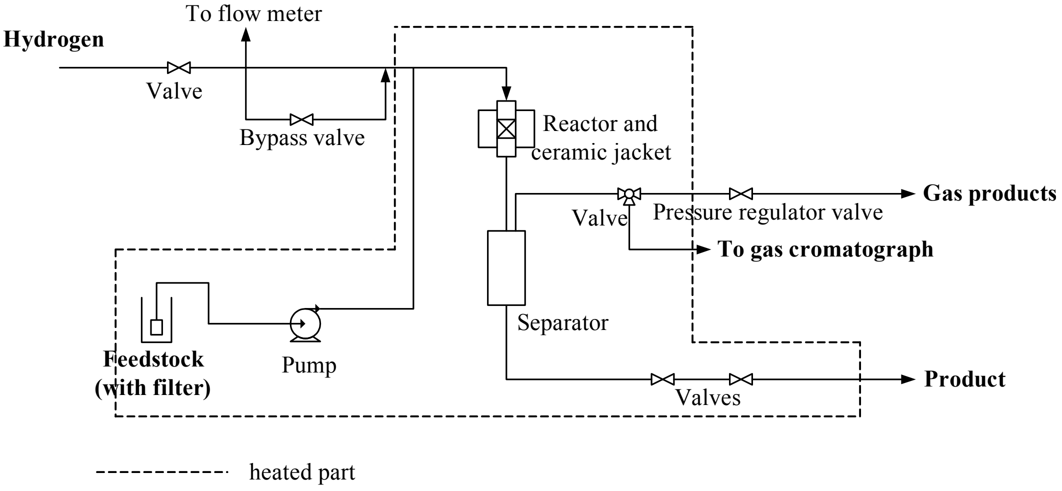

Figure 3: Scheme of the catalytic system

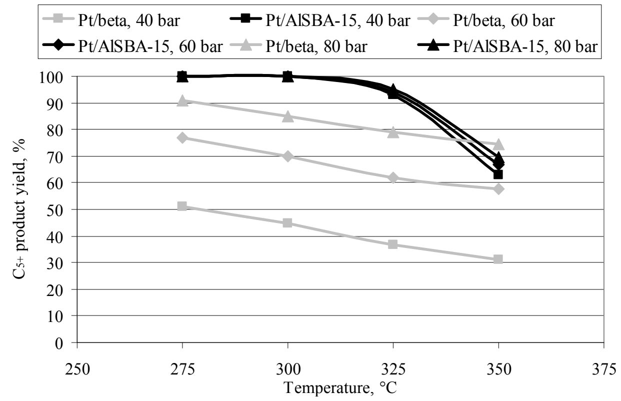

Figure 4: Changes in the yield of liquid product yield (C_{5+}) as a function of process parameters (LHSV = 1.0 h^{-1})

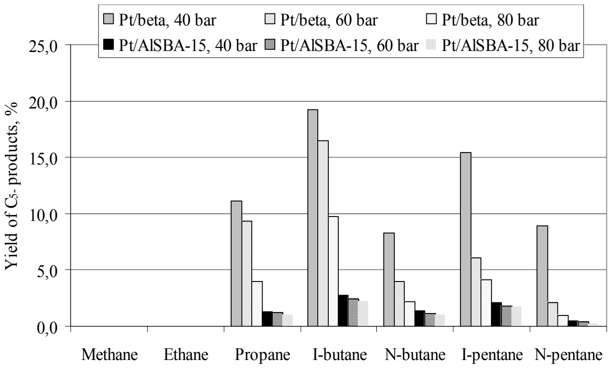

Figure 5: The composition of C_{5-} products as a function of process parameters (325 °C, LHSV = 1.0 h^{-1})

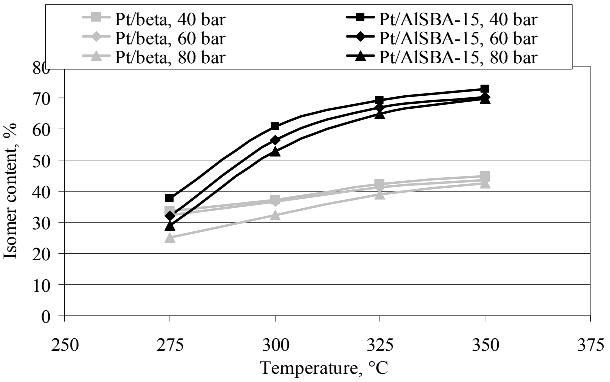

Figure 6: The effect of process parameters on the total isomer content of the products (LHSV = 1.0 h^{-1}).

Conclusions

In summary, the Pt/AlSBA-15 catalyst showed better results in the production of gas oil and base oil fractions with high isoparaffin content from Fischer-Tropsch wax than the Pt/Beta catalyst. The main cause of this is the higher isomerization and lower cracking activity of the previous catalyst. The yields of the target fractions (29.9–36.6% and 46.2–58.8%) adequately high. Our result supported that the mesoporous Pt/AlSBA-15 materials can be suitable catalyst for the selective hydroisomerization of the Fischer-Tropsch waxes.

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