



Hydrogen transfer in transformations of olefin and thiophene compounds for the refining of gasoline fractions



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ABSTRACT

Hydrogen transfer reactions in the transformations of mixtures of model hydrocarbons (hydrogen donors and acceptors) on zeolite catalysts were studied. Hydrogen donors were represented by various classes of hydrocarbons, and acceptors—by unsaturated (olefin) and thiophene compounds. The [H]-donor activity series of hydrocarbons was revealed. Strong differences in the transformation pathways of 1-hexene and 1-octene under the conditions of catalytic refining were demonstrated. A new method for the refining of low-rank gasoline fractions was proposed. The method is based on the hydrogen transfer reactions between hydrogen donor hydrocarbons and hydrogen acceptor hydrocarbons, which proceed without molecular hydrogen. The proposed method allows the simultaneous removal of sulfur (more than 95%) and unsaturated (more than 90%) compounds.

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1. Introduction

Investigation of intermolecular hydrogen transfer reactions has started at the beginning of the 20th century [13]. The mechanisms of such reactions on various catalytic systems were compared in [14]. The occurrence of hydrogen transfer reactions on the catalysts with high concentration of acid sites (in particular, on aluminosilicates) was shown to differ strongly from that on metallic systems (Pt, Pd, Ni). It was demonstrated that hydrogen transfer in the transformations of hydrocarbons on aluminosilicate catalysts proceeds mainly via the transfer of hydride ions [15,16]. In our opinion, this mechanism is most reasonable. Intermolecular hydrogen transfer reactions play a significant part in the transformations of hydrocarbons in the course of catalytic cracking, alkylation and isomerization.

Intermolecular hydrogen transfer reactions can be used as a method for processing the thermal cracking gasolines in the absence of molecular hydrogen. Low-rank gasoline fractions, first of all the coke and viscosity breaking gasolines, should often be involved in processing at refineries. Having a low octane number and a high content of unsaturated and sulfur compounds, such gasoline fractions can be used as components of motor fuels only in small amounts or after additional refining. Conventional hydrotreatment is complicated by a substantial thermal effect of the hydrogenation of unsaturated compounds and by a high consumption of hydrogen [1,2], which strongly increase the capital and operating costs for the process. The saturation of unsaturated and partially aromatic compounds during hydrotreatment decreases the octane number of such gasolines [3].

The transformations of gasoline fractions under the conditions of catalytic cracking were discussed in [5–12]. The production of light olefins with a maximum yield by cracking of gasoline fraction hydrocarbons over ZSM-5 zeolites was studied in [5–9]. The authors of [10,11] suggested that low-rank gasoline fractions should be blended into vacuum gasoil, which is a classical feedstock for cracking. Cracking of such blended feedstock disturbs the lift reactor hydrodynamics, decreases the yield of gasoline fraction referred to vacuum gasoil, and increases the load on a unit for separation of cracking products.

A. Corma et al. [12] investigated the transformations of straight-run gasoline fraction, cracking gasoline, and their blends with vacuum gasoil on a Y zeolite cracking catalyst, an additive containing ZSM-5 zeolite, and their mixtures. It was shown that the regenerated catalyst is most suitable for cracking of gasolines, while the partially deactivated catalyst—for cracking of vacuum gasoil. When studying the transformations of the indicated feedstock, the authors paid particular attention to the effect of hydrogen transfer reactions. However, they did not consider joint transformations of gasolines with a high content of unsaturated hydrocarbons and gasolines containing hydrogen donor hydrocarbons.

Investigation of the effect of hydrogen transfer reactions on the joint transformations of hydrocarbons and sulfur-containing compounds [4] made it possible to develop a process for gasoline refining without molecular hydrogen. The essence of the method consists in joint processing of two low-rank gasolines (coke gasoline and straight-run gasoline fraction) using a setup that is similar to the catalytic cracking unit (without vacuum gasoil, at close temperatures and catalyst-to-oil ratios). The ($t_{b,r} \approx 62\text{--}85\text{ }^\circ\text{C}$) fraction of straight-run gasoline, containing more than 40 wt.% of naphthenic $C_5\text{--}C_8$ compounds that are highly capable of donating hydrogen (hydride ions), can serve as a hydrogen donor. The indicated method can simultaneously remove the sulfur

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and unsaturated compounds, thus providing an increase in the antiknock value of the produced gasolines. Among the advantages of this process is the low total thermal effect caused by conjugation of endo- and exothermic reactions [17]. The proposed methods can be considered as an alternative to classical hydrofining of thermal gasolines.

The contribution of hydrogen transfer reactions can be increased in two ways [4]: by improving the catalyst activity in the reactions of intermolecular hydrogen transfer or by changing the feedstock composition, i.e. by increasing the content of paraffinic and naphthenic hydrocarbons that possess a high [H]-donor activity.

The present work was aimed to study the joint transformations of unsaturated hydrocarbons and thiophene compounds in the presence of hydrogen donors under the conditions of catalytic refining over a zeolite catalyst.

2. Experimental

2.1. Catalytic system

All the experiments were carried out with a model refining catalyst comprising HREY (18 wt.%) and ZnHZSM-5 (4 wt.%) zeolites and a matrix (78 wt.%) made of amorphous aluminosilicate, aluminum hydroxide and bentonitic clay. The catalyst of such composition provides a maximum selectivity of the hydrogen transfer reactions from hydrogen donor hydrocarbons to thiophene ring [4]. ZSM-5 zeolite exerts a pronounced effect on the catalyst activity and composition of resulting products. As shown in [17.1], HZSM-5 zeolite changes the composition of gaseous products, decreases the yield of liquid products, and increases the octane number of gasoline by 3–4 points. The method of catalyst preparation was reported in [18]. The synthesized sample was formed as microspheres with the diameter of 0.05–0.25 mm, dried at 100 °C for 12 h, and calcined at 550–750 °C. Before testing, the sample was treated in 100% water vapor at 760 °C for 5 h. The choice of such heat treatment conditions was caused by the low content of microcrystalline (0.3–0.8 micron) zeolite in the catalyst.

2.2. Feedstock

The feedstock was represented by mixtures of model hydrocarbons: 1-hexene (Alfa Aesar, 99%), 1-octene (Alfa Aesar, 99%), n-octane (Alfa Aesar, 99%), cyclohexane (Alfa Aesar, 99%), methylcyclohexane (Alfa Aesar, 99%), decalin (cis + trans, Aldrich, 99%), isooctane (Alfa Aesar, 99%) and methylcyclopentane (Alfa Aesar, 99%), and by a mixture of coke gasoline and straight-run gasoline fraction with $t_{b.r.} \approx 62\text{--}85$ °C (the gasolines were blended in a 1:2 weight ratio, respectively). The group composition of the gasolines is shown in Table 1.

In all the experiments, a thiophene compound was represented by 2-methylthiophene (Merck, 98%), which was introduced into the model feedstock in the amount of 5000 ppm.

2.3. Catalytic testing and analysis of the resulting products

Catalytic testing was performed at a lab-scale unit with a fixed-bed catalyst (21 g) in the temperature range of 350–500 °C at a catalyst-to-oil mass ratio equal to 4. The feedstock was metered for 120 s.

Table 1
Composition of gasoline fractions, wt.%.

Naphtha source (process)	Delayed coking	62–85 °C fraction
Paraffin	29.8	23.6
Isoparaffin	23.6	21.7
Olefin	24.8	0.0
Naphthene	16.1	53.3
Arene	5.7	1.4
Sulfur content	0.26	<0.0050

The composition of gaseous cracking products was analyzed on a Chromos GH-1000 gas chromatograph equipped with: a) capillary column (SiO₂, 30 m × 0.32 mm) and flame-ionization detector to determine the composition of hydrocarbon gases (C₁–C₅₊); b) packed column (2 m × 3 mm, CaA zeolite) and thermal conductivity detector to measure the content of inorganic components in the gas.

Analysis of liquid products was made on a chromato-mass spectrometer 6890/5973N (Agilent Technologies) with a chromatographic column HP-5 ms (30 m × 0.25 mm × 0.25 μm). In addition, the quantitative composition of the liquid products was determined using a Kristallux 4000 M gas chromatograph equipped with a capillary column ZB-5 (60 m × 0.32 mm × 1.00 μm) and a FPD/FID module including flame photometric detector (FPD) to analyze sulfur compounds and flame ionization detector (FID) to analyze the hydrocarbon moiety. Total sulfur content in the initial feedstock and liquid cracking products was estimated by X-ray fluorescence spectroscopy on an ARL OPTIM'X WD-XRF spectrometer (Thermo Techno). Octane numbers were estimated in compliance with ASTM D 5134 (chromatographically, from the component composition).

The distribution of protons among components of the liquid cracking products, C_{arene}-H, C_{olefin}-H and C_{paraffin_ or _naphthene}-H, was found by analysis of the ¹H NMR spectra. The ¹H NMR spectra were recorded using a Bruker Avance-400 (9.4 T) spectrometer with a PARBO BB broadband polycyclic detector in a single-pulse experiment at the Larmor frequency of 400 MHz, a pulse time of 12 μs, and a pulse spacing of 3 s. Tetramethylsilane was employed as the internal standard.

A residual content of olefins was determined in two ways: 1) chromatographically from the component composition of resulting products, and 2) from changes in the fraction of protons at the C=C double bond (with the chemical shift of 4–6 ppm measured from the ¹H NMR spectra) with respect to the total number of protons in the feedstock. The relative residual content of olefins and the degree of their removal were calculated by the formulas:

$$Ost, \% = \frac{Z_{liquid} \cdot \varpi_{liquid}}{Z_{feed}} \cdot 100\%,$$

$$Ste, \% = 100 - Ost,$$

where Z_{liquid} and Z_{feed} are the concentrations of olefins (determined by chromatographic analysis or from the ¹H NMR spectra) in the liquid cracking products and in the feedstock, respectively; and ϖ_{liquid} is the yield of liquid cracking products.

The amount of coke deposits on the catalyst was determined from a loss in the sample weight after its calcinations in air at 550 °C. The composition of solid cracking products (coke) was examined using a Vario el cube Elementar Analysensysteme GmbH CHNOS analyzer.

Losses in experiments did not exceed 5 rel.%. In all the experiments, material balance (in particular with respect to sulfur content in the products) was within 95–105%. In further calculations, data were normalized to 100% by the equation:

$$Yield_i, \% = \frac{m_i}{\sum m_j} \cdot 100\%,$$

where $Yield_i$ is the yield of the i-th product, %; m_i is the weight of the i-th product, g; and $\sum m_j$ is the sum of all the products, g.

3. Results and discussion

3.1. The effect of temperature on the transformation pathways of the mixture of gasoline fractions

Transformations of the gasoline mixture over the model catalyst were studied over a temperature range of 350–500 °C. Material balance

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