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A study of intermolecular hydrogen transfer from naphthenes to 1-hexene over zeolite catalysts

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ABSTRACT

The mechanism of hydrogen transfers from naphthenes (methylcyclohexane, cyclohexane) or their deuterated derivatives to 1-hexene was specified over model acid zeolite catalysts (HREY or HZSM5). The composition of products is determined by two reactions-cracking and intermolecular hydrogen transfer. The monomolecular cracking reaction proceeds mostly on HZSM-5 zeolite, whereas the bimolecular hydrogen transfer reactions are catalyzed by the wide-pore HREY zeolite. It was found that during the hydrogen transfer from the naphthene molecule (hydrogen donor) to the olefin molecule (hydrogen acceptor) only one hydrogen atom is transferred, whereas the second hydrogen atom comes from the Brønsted acid site of the catalyst.

1. Introduction

Intermolecular hydrogen transfer reactions were first reported by Zelinsky and Glinka [1], Wallach [2] and Wieland [3]. These researchers have thoroughly studied the transformations of cyclohexene over Pd-containing catalysts by the reaction displayed in Scheme 1.

Later, Gryaznov [4] and Linstead et al. [5] investigated intermolecular hydrogen transfer reactions involving other hydrocarbons (olefins and cycloolefins) on various catalytic systems: metal catalysts for hydrogenation/dehydrogenation and acid-base oxide catalysts. In the case of metal catalysts, the transfer reaction includes the formation of molecular hydrogen or superficially adsorbed hydrogen atoms under relatively mild conditions (at a temperature below 200 °C). Of special interest are the transformations of hydrocarbons on metal catalysts not accompanied by the release of molecular hydrogen; they formed a basis for the development of palladium-containing membrane catalysts [6,7]. In the case of acid catalysts (alumina and aluminosilicate), hydrogen transfer proceeds without the formation of molecular hydrogen due to redistribution of hydrogen between starting olefins and hydrocarbons-hydrogen donors. According to Petrov, Frost, and Blue [8,9], in the transformations of olefins and cycloolefins on alumina and aluminosilicate, hydrogen transfer proceeds via consecutive polymerization and cracking reactions. Multiple cycles of the indicated reactions lead to the formation of two hydrocarbons—with a low (arene, coke) or high (paraffin, naphthene) hydrogen content. However, this mechanism is acceptable only for the catalysts with a relatively large pore size that enables the formation of olefin dimers and trimers. For example, the authors of Ref. [10] studied the transformations of butanes and butenes over a narrow-pore HZSM-5 zeolite and demonstrated that such a mechanism is not implemented.

Hydrogen transfer reactions strongly contribute to the transformations of hydrocarbons in various oil refining processes: catalytic cracking, isomerization, alkylation, and particularly the catalytic upgrading of gasoline (without molecular hydrogen) — the process that has been developed by the authors and reported in Ref. [11–13]. Hydrogen transfer reactions imply the intermolecular transfer of hydrogen from hydrogen donors (paraffinic and naphthenic hydrocarbons) to hydrogen acceptors (unsaturated hydrocarbons and thiophene compounds) proceeding over zeolite catalysts. Joint transformations of organosulfur compounds and hydrocarbons are described in detail in Ref. [12]. A general scheme of such refining is presented in Ref. [13].

Hydrogen transfer reactions on oxide catalysts proceed with the involvement of Brønsted acid sites. The authors of [14–16] studied the H/D exchange between molecules of butanes and acid sites of HZSM-5 zeolite (Scheme 2). Hydrogen exchange reactions between hydrocarbons and Brønsted acid sites of the catalyst are one of the steps in intermolecular hydrogen transfer between hydrogen donor hydrocarbons and hydrogen acceptor hydrocarbons. So, the

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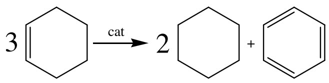


Scheme 1. Redistribution of hydrogen with the participation of cyclohexene.

exchange reactions affect the results of experiments on transformations of the mixtures of protium and deuterium forms of hydrocarbons.

To elucidate the mechanism of intermolecular hydrogen transfer between hydrocarbons (as hydrogen donors) and olefins (as hydrogen acceptors) on the acid-base catalysts, the transformations of the mixtures of model hydrocarbons (in particular their deuterated species) on zeolite catalysts were investigated.

2. Experimental

2.1. Catalyst preparation

Investigated in this work catalyst samples are multicomponent catalysts. The experiments were carried out with the model catalysts consisting of HREY zeolite, HZSM-5 zeolite, and a matrix comprising amorphous aluminosilicate, alumina, bentonitic clay and mixed magnesium-aluminum oxide. Base components of catalyst defining catalytic properties are zeolites Y and ZSM-5. A method used for the catalyst synthesis was described in Ref. [21]. The synthesized samples were formed as microspheres 0.05 ÷ 0.25 mm in diameter, dried at 100 °C for 12 h, calcined at 550–750 °C, and subjected to steam stabilization in 100 % water vapor at 788 °C for 5 h. The catalytic properties of pure zeolites, HREY (SiO_2/Al_2O_3 = 5, Na_2O = 1.46 wt.%, RE_2O_3–10 wt.%) and HZSM-5 (SiO_2/Al_2O_3 = 30, Na_2O = 0.051 wt.%), were also studied.

2.2. Catalyst characterization

Porous structure of the samples was examined by low-temperature nitrogen adsorption (an ASAP-2020 instrument, Micromeritics), specific surface area being determined by the BET method, and total adsorption pore volume—from the nitrogen adsorption at P/P_0 = 0.99. Samples were degassed at 300 °C for 5 h prior to analysis.

The acidic properties of the components surface identified by IR spectroscopy of adsorbed pyridine on FTIR spectrometer FTIR-8400 (Shimadzu).

2.3. Catalytic tests

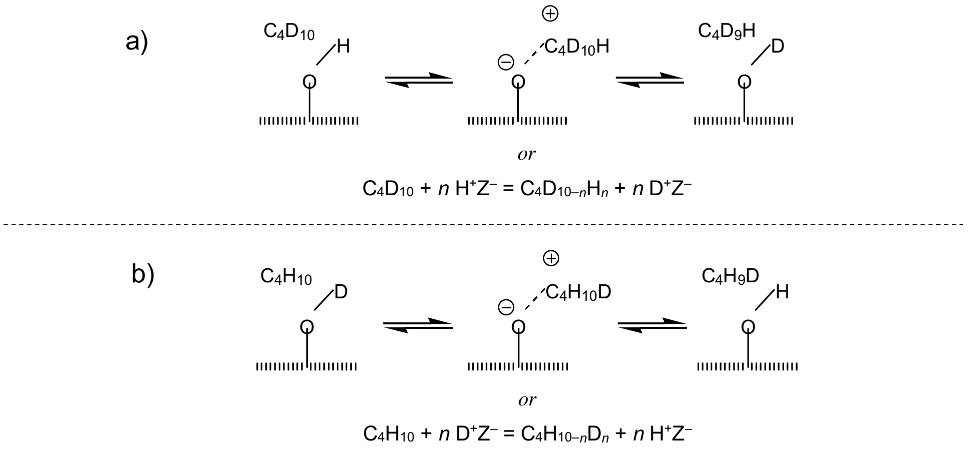
Catalytic testing was performed in a setup with a fixed-bed catalyst (21 g) over the temperature range of 350–550 °C, at a catalyst to hydrocarbons weight ratio of 1–5, and a weight hourly space velocity of 10 h^{-1}.

The starting reactants were the mixtures of model hydrocarbons in the protium form and deuterated hydrocarbons. 1-Hexene (Alfa Aesar, 99 %), cyclohexane (Alfa Aesar, 99 %), and methylcyclohexane (Alfa Aesar, 99 %) were used as model hydrocarbons. Cyclohexane-D_{12} (99.5 %) and methylcyclohexane-D_{14} (99.5 %) (ABCR GmbH & Co. KG) without additional purification served as deuterated compounds. The model mixture consisted of 1-hexene and a hydrogen donor hydrocarbon (cyclohexane or methylcyclohexane) taken in a weight ratio of 1:3. 1-Hexene was chosen as a hydrogen acceptor due to its relatively low reactivity toward cracking as compared to olefins with a chain length of more than 8 carbon atoms. In the case of 1-hexene, olefin transforms mostly via bimolecular hydrogen transfer reactions rather than monomolecular cracking reactions [13]. Deuterated hydrocarbon is introduced into the reaction mixture by replacing protium form completely or partially.

The composition of gaseous cracking products was analyzed on a Chromos GH-1000 gas chromatograph equipped with: (a) a capillary column (SiO_2, 30 m × 0.32 mm) and a flame-ionization detector for determining the composition of hydrocarbon gases (C_1–C_{5+}); (b) a packed column (2 m × 3 mm, CaA zeolite) and a thermal conductivity detector for measuring the content of inorganic components in the gas.

Analysis of the liquid products was carried out on a 6890/5973 N chromato-mass spectrometer (Agilent Technologies) with an HP-5MS chromatographic column (30 m × 0.25 mm × 0.25 μm). In addition, the quantitative composition of liquid products was determined on a Kristallux-4000 M gas chromatograph equipped with capillary columns (ZB-5, 60 m × 0.32 mm × 1.00 μm and DB-PETRO, 100 m × 0.25 mm × 0.5 μm).

The isotopic composition of hydrogen (the H/D ratio) was estimated by isotope ratio mass spectrometry on a DELTA V Advantage (Thermo Fisher Scientific) magnetic mass spectrometer combined with a gas chromatograph and high-temperature pyrolysis reactor (GC–TC–MS), at a constant flow rate. At first, the initial gaseous or liquid sample was separated chromatographically. After elution, components of the sample were consecutively delivered from the column to the pyrolysis reactor, which was designed as a hollow ceramic tube. A complete pyrolysis of substances took place in the reactor at a temperature of 1420 °C. The generated hydrogen passed through a membrane trap (a semipermeable Nafion membrane) for



Scheme 2. H/D exchange between molecules of butanes and acid sites of a zeolite: (a) HZSM-5 and (b) DZSM-5.