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Acenaphthene and Fluorene Hydrogenation on Industrial Aluminum Oxide Catalysts in a Flow System

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Abstract—Hydrogenation of the tricyclic aromatic hydrocarbons acenaphthene and fluorene on industrial aluminum oxide catalysts in a flow system has been studied. It has been found that total these hydrocarbons are exhaustively hydrogenated in the presence of a nickel–chromium catalyst at 200°C and a pressure of 100 atm to give isomer mixtures of the corresponding perhydroaromatic hydrocarbons decahydroacenaphthene and dodecahydrofluorene. The liquid products obtained can be of interest as components of hydrocarbon fuels with increased density. Certain conformational features of the stereoisomers obtained have been considered. It has been assumed that some spatial isomers of decahydroacenaphthene have six-membered rings in the boat conformation.

Keywords: solid polycyclic aromatic hydrocarbons, acenaphthene, fluorene, hydrogenation, industrial alumina catalysts, perhydroacenaphthene, perhydrofluorene, spatial isomer structure, coal tar, liquid components of hydrocarbon fuels

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Polycyclic saturated hydrocarbons are valuable components of hydrocarbon fuels with increased density and, hence, a higher volumetric calorific value. For example, the high-energy fuels RJ-4 and JP-10 designed for use in aircrafts with a limited volume of fuel tanks are based on hydrogenated dimers of cyclopentadiene and methylcyclopentadienes. A further progress in this area was made with the use of unique natural sources, gas condensates containing alkyldiamondoids, higher cyclic homologues of the adamantane hydrocarbon series, namely, alkyldiamantanes and alkyltriamantanes. High-energy fuels such as RF-1 and RF-3 were designed on their basis [1].

A process for preparing alkyladamantanes by isomerization of hydrogenated tricyclic aromatic hydrocarbons under conditions of heterogeneous catalysis on solid alumina and aluminosilicate catalysts was designed at the Topchiev Institute of Petrochemical Synthesis [2, 3]. Along with the use as fuel components, adamantane derivatives are of interest as valuable chemicals, a variety of pharmaceuticals, and other products important for the national economy. The first step of this process is the hydrogenation of appropriate aromatic hydrocarbons to obtain saturated polycyclic hydrocarbons. Along with petroleum fractions, cokemaking byproducts which have found limited application are a source of aromatic hydrocarbons and other valuable chemicals.

In this paper, we present the results of study of the hydrogenation in a flow system of tricyclic aromatic hydrocarbons acenaphthene and fluorene contained in coal tar, a byproduct of coke production.

EXPERIMENTAL

The reactant chemicals were technical-grade acenaphthene (AN) of 98% purity (mp 91–92°C; bp 277.5°C; density, 1.029 (99°C); flash point, 158°C; fire point, 162°C) with a sulfur content of 0.3–0.4% and biphenyl, diphenylene oxide, as methylnaphthalenes as impurities and reagent-grade fluorene (FL) of 99.5% purity, mp 115°C. Hydrogenation was carried out in a modified standard laboratory flow unit and a pilot flow unit both consisting of a feed tank, a pump, a coil heater, a reactor, a condenser, a separator, a filter, a hydrogen pressure and flow rate control system, and a process control panel. The units were provided with external heating of the feed tank and feedstock solutions, the feed pump head, and all the pipelines before the reactor. Feedstock from the tank was pumped to the heater. A hydrogen supply line was connected to the feed line before the heater. After the heater, the mixture of hydrogen and feedstock was fed to the top (bottom) of the reactor. Reaction products and hydrogen-containing gas were sent from the reactor to the condenser, and condensed liquid hydrogenation products and gases were separated in the gas separator. The liquid products were periodically bypassed to the receiver marinated under a pressure close to the atmospheric one.

Table 1. Results of acenaphthene hydrogenation in a cyclohexane solution (weight ratio is 1 : 18) on the nickel catalyst at 80 atm

Temperature, °C	Solution space velocity, h^{-1}	Run time, h	Isomers PHAN, wt %				Total
			1	2	3	4	
150	1.5	4.5	2	2	3	93	100
150	0.5	4	40	4	48	4	96
150	0.5	5	20	14	22	40	96
200	0.5	4	45	4	47	4	100
200	1.0	1.5	32	2	61	5	100
200	1.5	1	22	4	61	13	100
200	2.0	1	30	4	59	7	100
200	2.0	4.5	23	2	70	3	98

The hydrogenation of acenaphthene was studied both in both its pure form (in melt) and solution. Cyclohexane, a mixture trimethylcyclohexanes, the crude perhydronaphthalene fraction, and still bottoms remaining after distilling crude perhydroacenaphthene off were used as a solvent. The best results were obtained with the use of the trimethylcyclohexane (TMCH) mixture prepared preliminarily by hydrogenating the industrial mesitylene fraction. The hydrogenation process was studied at 150–300°C and a hydrogen pressure of 30–100 atm. The catalysts used in the study were the commercial platinum–alumina catalyst AP-56 an industrial nickel catalyst, and the nickel–molybdenum–alumina catalyst manufactured at the Pikalevo integrated alumina plant according to the Topchiev Institute's method.

RESULTS AND DISCUSSION

Hydrogenation of Acenaphthene

Autoclave hydrogenation of acenaphthene (I) was studied by many investigators, including that on oxide catalysts [4]. Running the hydrogenation in a flow system is fraught with additional difficulties due to the solid state of the material, although these difficulties have been overcome by means by selecting and using a suitable solvent.

The acenaphthene hydrogenation process in a flow system on a fixed catalyst bed proceeds stepwise, a manner that is especially clear under mild process conditions. The aromatic hydrocarbon molecule adds two hydrogen molecules to give tetrahydroacenaphthene (THAN) (II) in the first step and three more molecules to give decahydroacenaphthene (perhydroacenaphthene, PHAN (III) in the second step. In the presence of the nickel–molybdenum–alumina catalyst, the hydrogenation of acenaphthene at a temperature of 250–300°C and a pressure of 30–100 atm proceeds quite selectively to give mainly tetrahydroacenaphthene (II). Under optimal conditions, the AN conversion reaches 95–100%.

The results obtained in the experiments with the industrial catalyst AP-56 showed that the catalyst also does not exhibit a sufficiently high activity: the degree of AN hydrogenation under the given conditions (150–200°C) was no more than 30%, with THAN being the main product. The industrial nickel catalyst appeared to be the most efficient, the 100% conversion of the reactant hydrocarbon was attained to give exclusively decahydroacenaphthene in the hydrogenation of AN in a cyclohexane or trimehylcyclohexanes solution over this catalyst. Table 1 presents the conditions of the process and the results of some of the most representative experiments.

The data in Table 1 show that the conditions of the process have a considerable effect on both its progress and the product composition. In the optimal temperature range of 150–200°C, the complete hydrogenation of AN to PHAN is achieved at all the space velocities studied, with the degradation products being actually absent, which appear at higher temperatures, as found in addition experiments. Changes in the process conditions considerably affect the PHAN isomer composition (Table 2). For example, an increase in the space velocity, especially, at a lower temperature facilitates the predominant formation of one of the isomers, isomer 4, which, being instable, isomerizes to more stable isomers 1 and 3 with an increase in the catalyst contact time or temperature. The product compounds were identified by elemental analysis and mass spectra data. The spatial structure of the isomers, some conformational features of the PHAN molecule structure, and chromatographic parameters of the PHAN isomers are also given in Table 2. The boiling points of the stereoisomers were calculated from the relative chromatographic retention times on Apiezon L; they differ somewhat from the published data obtained on another stationary phase [5] and agree with the data given by Grosse et al. [6].

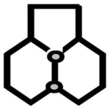
To determine the spatial structures of the PHAN stereoisomers and their chromatographic elution order from column, were used the results of the detailed comprehensive stereochemical analysis of PHAN isomers by Shabanova [5].

The stereochemistry of perhydroacenaphthene has some specific features that are worth noting. Theoretically, decahydroacenaphthene can have six stereoisomers:


trans,
trans,
trans-
III-A


cis,
trans,
trans-
III-B


cis,
cis,
trans-
III-C


trans,
trans,
cis-
III-D


trans,
cis,
cis-
III-E


cis,
cis,
cis-
III-F

It might seem that the structure of individual PHAN stereoisomers, their thermodynamic stability, and the elution order from chromatographic column with a nonpolar phase would be determined on the basis of the structures of isomers of their nearest bicyclic analogs, methyldecalin derivatives (methylbicyclo[4.4.0]decanes), whose stereochemistry had been studied in [7–9]. Thus, it was found that among 2-substuted methyldecalins, the isomer with the *trans*-junction of the six-membered cycles, namely, *trans,trans*-2-methyldecalin, is the most stable thermodynamically, its content in the equilibrium mixture at 160°C is more than 80% of total 2-substuted methyldecalin derivatives. In the case dimethylbicyclo[4.4.0]decanes as compounds that are the closest in structure to PHAN isomers,, the isomers having the *trans*-decalin configuration also considerably prevails at equilibrium (usually their content is more than 90%) among all the 2,X-dimethylated derivatives. It might be assumed that the most stable PHAN isomers, i.e., isomers 1 and 3, making in total more than 90% in the PHAN mixture close to equilibrium also have the *trans*-junction of the six-membered cycles.

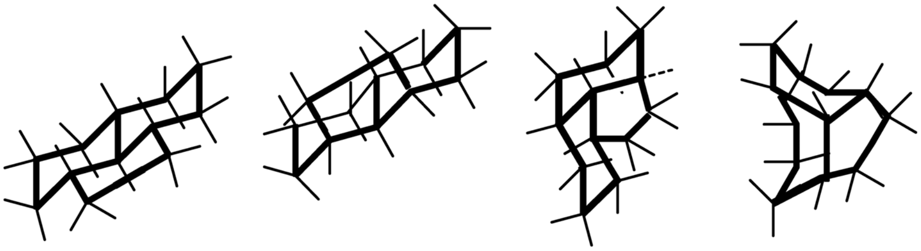
At the same time, it was unambiguously found [5] that the most thermodynamically stable PHAN isomer is the *trans,cis,cis*-isomer (III-E), i.e., the isomer having the *cis*-configuration of the decalin moiety of the molecule; in equilibrium at 613 K, its content was 38.7%. The equilibrium concentrations of other stereoisomers are arranged in the following order: *trans,trans,trans* (III-A), 30.4%; *cis,cis,trans* (III-C), 25.2%; *cis,trans,trans* (III-B), 3.4%; and *cis,cis,cis* (III-F), 2.3%. The *trans,trans,cis*-isomer (III-D) seems to exist only theoretically. Comparison of these results with published data on the thermodynamic stability and on the elution order of PHAN stereoisomers made it possible to determine the structure and chromatographic characteristics of the PHAN stereoisomers obtained in hydrogenation, which are given in Table 2.

Of no less of interest are the conformations of units making the tricyclic structure of perhydroacenaphthene. The presence of the additional cycle in the decalin structure, which rigidly joins the six-membered rings, considerably impedes conformational transitions in PHAN isomer molecules. This results in the situation when stabilization of the six-membered cycle in the "boat" conformation is significantly favored. In this case, the existence of several conformers with approximately equal strain energies is possible for some stereoisomers. Thus, isomers with the *trans*-decalin moiety—*trans,trans,trans* and *cis,cis,trans*—have rather limited possibilities to form conformers and mainly exist as the conformers shown below, whereas isomers with the *cis*-decalin unit, for example, the *trans,cis,cis*- and *cis,cis,cis*-PHAN isomers, can have several conformations with a nearly equal strain of the five-membered cycle, in which one or both of six-membered ring will be in the boat conformation (Scheme 2).

Table 2. Characterization of perhydroacenaphthene (tricyclo[7.2.1.$0^{5.12}$]dodecane) isomers

Name		RRT*	Bp, °C	Bp, K [5]	Conformation
1,3,5-TMCH		1.0	136–141	–	
PHAN, isomers:	1	4.3	235	499	*trans*, *trans*, *trans*
	2	5.0	239	503	*cis*, *trans*, *trans*
	3	5.9	243	507	*trans*, *cis*, *cis* + *cis*, *cis*, *trans*
	4	7.0	246	513	*cis*, *cis*, *cis*
Tetrahydroacenaphthene		19.0	252	–	–
Acenaphthene		36.0	278	–	–

Relative retention time, Apiezon L, 200°C.



trans, *trans*, *trans*- III-A

cis, *cis*, *trans*- III-C

trans, *cis*, *cis*- III-E

cis, *cis*, *cis*- III-F

Scheme. Preferred conformations of some PHAN isomers.

However, one of the six-membered cycles of the third isomer with the *trans*-junction of the decalin moiety, namely, *cis,trans,trans*-PHAN (III-B), should also have a slightly deformed boat conformation.

The isomer composition of perhydroacenaphthene prepared by AN hydrogenation has a considerably effect on its physicochemical parameters and, hence, performance characteristics of the product. For example, *cis,cis,cis*-PHAN at room temperature is a solid, whereas an isomer mixture containing 75% of this isomer has the pour point of 15°C (density of 0.950 g/cm^3, a refractive index n n_D^{20} 1.4995).

Hydrogenation of Fluorene

Under conditions similar to those for acenaphthene hydrogenation (150–160°C, 100 atm, fluorene WHSV 0.08–0.12 h^{-1}), fluorene is exhaustively hydrogenated to dodecahydrofluorene to give three stereoisomers, of which one having the highest boiling point makes 70–80% of the total mixture. Most likely, it is the *cis,syn,cis*-PHFL isomer. Perhydrofluorene (tricyclo[7.3.1.$0^{5.13}$]tridecane) is a transparent, colorless or slightly yellowish liquid with an odor characteristic of naphthene hydrocarbons, bp 132°C (12 mm Hg) or 254–258°C (760 mm Hg), pour point below –60°C (at a certain isomer composition), density of 0.945–0.950 g/cm^3, and refractive index of 1.5002. Thus, perhydroacenaphthene and perhydrofluorene correspond to kerosene-cut hydrocarbons in their physicochemical characteristics. They can be used as components of hydrocarbon fuels with an increased density.

Thus, in this study we have determined the conditions and processing parameters for the process of acenaphthene and fluorene hydrogenation on industrial alumina catalysts to allow the process to be run in the continuous mode to produce their fully hydrogenated derivatives with a desired isomer composition. The catalyst activity loss remained unchanged during the time on stream of 200 h.

Based on the results of the study, we can propose an area of focus in the integrated use of coal by chemical processing the liquid products of coke byproducts plants, which represent valuable chemical and energy-generation feedstock that has not found wide practical use to date. It is evident that extending the range of feedstock resources by involving other components of coal tar and petroleum fractions with a high amount of polycyclic aromatic hydrocarbons will help somewhat to resolve the solubility problem, although it will be necessary to modify the catalysts in the line of enhancement of their stability to catalytic poisons present in tar and to adjust the processing conditions.

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Development and validation of the technology of hydrogenation of solid polycyclic hydrocarbons to liquid fuels on the pilot scale and production of an enlarged batch of the product were performed on a petrochemical plant. The energy characteristics of fuels were obtained at the level of those of JP-10.

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