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Abstract

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INVESTIGATION OF THE ALKYLATION REACTION OF AROMATIC HYDROCARBONS

ALKYLATION OF NAPHTHALENE WITH PROPYLENE ON AN ALUMINOSILICATE CATALYST AT LOW TEMPERATURES

Alkylation of hydrocarbons with olefins, carried out with the aid of various catalysts, is, as a rule, accompanied by side reactions: isomerization, disproportionation, destruction, etc. The occurrence of these reactions is governed by the nature of the catalyst used and by the conditions of the alkylation reaction. Suppression of side reactions can be accomplished by selecting a catalyst possessing a definite complex of properties and by choosing optimal alkylation conditions.

Such catalysts may be aluminosilicates, when they are used in the alkylation reaction of hydrocarbons, in particular aromatic ones, with olefins at acceptably low temperatures. The lower limit of the alkylation temperature is determined by the temperature conditions for suppressing the polymerization reaction—the reaction having the lowest activation energy among the side reactions. The upper limit is determined by the maximum yield of the desired monoalkylaromatic hydrocarbon.

The use of aluminosilicates in the alkylation reaction of aromatic hydrocarbons has long been discussed (⁀1). The named catalysts are successfully used (⁀2) in the alkylation of benzene and toluene with propylene, butylenes, and amylenes at 450–480° and 140–160 atm. Benzene can be alkylated with ethylene in the presence of a synthetic aluminosilicate at atmospheric pressure and 400° (⁀3). On diatomite, naphthalene is alkylated at 250° with olefins having six or more carbon atoms (⁀4). Heating ethylnaphthalene (⁀5) with activated gumbrin at 230–240° and atmospheric pressure causes redistribution of the alkyl group: naphthalene and di- and tri-ethylnaphthalenes were found in the reaction products. At 275° deeper transformations occur; ethylbenzene, ethane, tetrahydronaphthalene, and $(C_{10}H_7)_2$ are formed. Activation of gumbrin with hydrogen chloride (⁀6) makes it possible to lower the temperature of the alkylation reaction of aromatic hydrocarbons to 70°; but even under these conditions side reactions are observed: isomerization of alkylaromatic hydrocarbons. We (⁀7) have shown that the alkylation of aromatic hydrocarbons such as benzene and toluene with propylene on an industrial aluminosilicate catalyst proceeds, respectively, at +20° and 0° with high rates. Study of the process of alkylation of aromatic hydrocarbons on aluminosilicate catalysts at low temperatures appears interesting from the point of view of the possibility of investigating a reaction minimally complicated by side processes.

In the present work, using as an example the reaction of naphthalene with propylene, the study of low-temperature alkylation on aluminosilicate catalysts has been continued.

It has been established that isopropylnaphthalene, obtained on aluminosilicate at 50° (in solvent) and 100°, is identical in isomeric composition to isopropylnaphthalene obtained with the aid of $H_3PO_4 \cdot BF_3$ (^8) at 20 and 50°. The alkylation temperature of naphthalene of 100° on an aluminosilicate catalyst is the lowest for a reaction minimally complicated by side ···

processes. In this case about 80% 1-isopropylnaphthalene and 20% 2-isopropylnaphthalene are formed. Raising the alkylation temperature increases the rate of alkylation of naphthalene, but at the same time a considerable intramolecular isomerization of isopropylnaphthalene begins to be observed. At 150°, in addition, disproportionation of the isopropylnaphthalenes formed also occurs. As a result of this reaction naphthalene is formed: at 100° 1–2%, at 200° about 4%, and at 250° about 9%.

Data on the isomeric composition of the alkylates obtained at various temperatures with an aluminosilicate catalyst are given in Table 1.

With an increase in the alkylation temperature, an increase is observed in the content of 2-isopropylnaphthalene in the alkylate. It may be assumed that, during the alkylation of naphthalene, the isopropyl group enters position 1, while the formation of 2-isopropylnaphthalene should be explained by isomerization of 1-isopropylnaphthalene.

Table 1

Isomeric composition of isopropylnaphthalene obtained at various alkylation temperatures

Alkylation temperature, °C	1-Isopropylnaphthalene	2-Isopropylnaphthalene
100	80	20
100	79	21
150	63	37
200	56	44

When comparing the isomeric compositions of isopropylnaphthalenes obtained at low temperatures in the presence of different catalysts, it is seen that in all cases they are identical (the alkylation is carried out under conditions in which side processes are reduced to a minimum).

It seems to us that sufficiently convincing facts confirming what has been stated may be provided by data obtained in the isomerization of 1-isopropylnaphthalene of about 96 mol. % purity. The isomeric composition of the reaction products was determined by the spectral method.

The isomerization was carried out in the reactor used for the alkylation of naphthalene. The isomerization conditions for isopropylnaphthalene (contact time, temperature, etc.) were selected so that they corresponded exactly to the conditions for alkylation of naphthalene with propylene over an aluminosilicate catalyst. The change in the isomeric composition of isopropylnaphthalene with the isomerization temperature is given in Table 2. Initially the experiments were carried out with 1-isopropylnaphthalene, and then with a mixture of isopropylnaphthalenes obtained in the alkylation of naphthalene at 100°. In both the first and the second cases identical results were obtained after the reaction.

Table 2

Composition of isopropylnaphthalene after isomerization over an aluminosilicate catalyst at various temperatures

Composition of the initial isopropylnaphthalene	Isomerization temperature, °C	Composition of isopropylnaphthalene after isomerization
1-Isopropylnaphthalene 96%	100	1-Isopropylnaphthalene 80%2-Isopropylnaphthalene 20%
1-Isopropylnaphthalene 79%2-Isopropylnaphthalene 21%	150	1-Isopropylnaphthalene 64%2-Isopropylnaphthalene 36%
1-Isopropylnaphthalene 80%2-Isopropylnaphthalene 20%	200	1-Isopropylnaphthalene 54%2-Isopropylnaphthalene 46%

Comparison of the isomeric compositions of the isopropylnaphthalenes obtained after alkylation (Table 1) and isomerization (Table 2) gives grounds to think that the addition of the alkyl group in the first case takes place at position 1. 2-Isopropylnaphthalene is formed as a result of intramolecular migration of the alkyl group to the adjacent 2-position.

The formation of isomers in these reactions, carried out with an aluminosilicate catalyst, can be well explained by taking into account the structure of aluminosilicates, using a carbonium mechanism. The propylene molecule on the surface of the catalyst forms a carbonium ion

$$CH_2{=}CH{-}CH_3 + HO{-}Si{-}O{-}Al{-}O{-}Si{-}O^{-}H^{+} \longrightarrow CH_3{-}\overset{+}{CH}{-}CH_3,$$

which interacts with a naphthalene molecule, giving 1-isopropylnaphthalene

$$C_{10}H_8 + \overset{+}{CH}(CH_3)_2 \longrightarrow 1\text{-}C_{10}H_7{-}CH(CH_3)_2 + H^{+}\cdot$$

Further, 1-isopropylnaphthalene forms a complex on the catalyst surface by adding a proton

$$1\text{-}C_{10}H_7{-}CH(CH_3)_2 + H^{+} \rightleftharpoons [C_{10}H_8{-}CH(CH_3)_2]^{+}\cdot$$

Next the alkyl group migrates to the neighboring position 2.

$$[C_{10}H_8{-}CH(CH_3)_2]^{+} \longrightarrow 2\text{-}C_{10}H_7{-}CH(CH_3)_2 + H^{+}\cdot$$

The proton attaches to the aluminum complex of the catalyst surface. Thus, in the alkylation of naphthalene with propylene on aluminosilicate, 1-isopropylnaphthalene is formed, while the 2-isomer is obtained upon isomerization of 1-isopropylnaphthalene on the aluminosilicate catalyst.

Experimental Part

The experiments were carried out in a laboratory unit of periodic operation (7). The catalyst was an industrial aluminosilicate catalyst, which had: bulk density 0.634 g/cm^3, specific surface area 490 m^2/g, specific pore volume 0.44 cm^3/g, activity index (9) 34. The freshly charged catalyst was activated with air (1000 ml of air per 1 ml of catalyst per hour) at 380° for 3 hours. The spent catalyst, after removal from it of the adsorbed alkylate (0.347 g per 1 g of catalyst), was regenerated by blowing with air at 400° for 30 min., then with steam for 5 min. (0.8 ml of water per 1 ml of catalyst), again with air, etc., until absence of CO_2 in the exit gases. After regeneration the catalyst had practically the same activity index as the original one.

For an experiment, 350 ml of catalyst was taken; the ratio of the height of the catalyst bed to the internal diameter of the reactor cross section (wall thickness 1.5 mm) was 14, which ensured satisfactory conversion of propylene (84% at a propylene feed rate of 12 l/hour).

The feedstocks used were: naphthalene conforming to TU MKhP 1571-47, and propylene of 99% purity. The influence of various factors on the yield and composition of the reaction products was studied: the influence of the molar ratio of the reacting components (naphthalene : propylene) was investigated at 100° (Table 3) and the experimental temperature (Table 4). The propylene feed rate in all cases was maintained at 12 l/hour. The composition of the alkylate was determined by its threefold distillation on a vacuum column with an efficiency of 24 theoretical plates and by spectral investigations; it was established that, depending on the conditions, the alkylate consists of mono-, di-, tri-, and tetraisopropylnaphthalenes. The physicochemical properties of the synthesized alkylnaphthalenes are given in Table 5.

Table 3

Composition of alkylates (wt. %) obtained at different molar ratios of naphthalene : propylene (experiment temperature 100°)

Naphthalenes	1 : 2 crude alkyl	1 : 2 alkylate	1 : 1 crude alkyl	1 : 1 alkylate	2 : 1 crude alkyl	2 : 1 alkylate
Naphthalene	21.4	–	28.8	–	50.5	–
Isopropylnaphthalene	22.9	29.2	29.4	41.3	37.4	75.6
Diisopropylnaphthalene	27.2	34.6	23.9	33.5	9.3	18.8
Triisopropylnaphthalene	20.0	25.4	11.5	16.2	2.0	4.0
Tetraisopropylnaphthalene	8.5	10.8	6.4	9.0	0.8	1.6

Yield from theory

	1 : 2 crude alkyl	1 : 2 alkylate	1 : 1 crude alkyl	1 : 1 alkylate	2 : 1 crude alkyl	2 : 1 alkylate
Isopropylnaphthalene	29%	–	42%	–	66%	–

Table 4

Composition of alkylates (wt. %) obtained at different experiment temperatures (molar ratio naphthalene : propylene = 1 : 1)

Naphthalenes	50°	100°	150°	200°
Naphthalene	30.0	29.0	28.0	24.0
Monoisopropylnaphthalene	30.0	30.0	37.0	44.0
Diisopropylnaphthalene	23.6	24.0	23.0	18.0
Triisopropylnaphthalene	10.8	11.0	2.0	6.0
Tetraisopropylnaphthalene	5.6	6.0	5.0	8.0

Yield from theory

	50°	100°	150°	200°
Isopropylnaphthalene	43%	42%	52%	58%

Table 5

Properties of isopropylnaphthalenes synthesized with an aluminosilicate catalyst

Alkylnaphthalene	B.p., °C	M.p., °C	n_D^{20}	d_4^{20}	Mol. wt.
1-Isopropylnaphthalene	264–266	–	1.5751	0.9009	171
2-Isopropylnaphthalene	267–260	–	1.5770	0.9798	172
Isopropylnaphthalene	264–270	–	–	–	170
Diisopropylnaphthalene	165–170/2	–	1.5700	0.9636	215
Triisopropylnaphthalene	190–195/2	–	1.5620	0.9610	253
Tetraisopropylnaphthalene	–	128–129	–	–	296

We have studied the reaction of alkylation of naphthalene with propylene at atmospheric pressure and at various temperatures over an aluminosilicate catalyst and have established that the alkylation of naphthalene proceeds according to position 1. In the course of the reaction, intramolecular migration of the alkyl group occurs, leading to the formation of a mixture of isomeric products.

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