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Abstract

Full Text

Chemistry

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LIQUID-PHASE ALKYLATION OF BENZENE WITH PROPYLENE ON ALUMINOSILICATE AT LOW TEMPERATURES

(+20, +50, +80°)

For the alkylation of aromatic hydrocarbons with olefins, a number of catalysts are used, among which the following have found the widest application:

1. Acids—hydrogen fluoride, sulfuric acid, phosphoric acid, boron fluoride compounds such as boron fluoride hydrate, and a molecular compound of boron fluoride with phosphoric acid. 2. Metal halides—aluminum chloride, zinc chloride, and others. 3. Synthetic and natural aluminosilicates.

Fig. 1. Batch alkylation apparatus: **1**—gas clock; **2**—intermediate vessel; **3**—ultrathermostat; **4**—reactor; **5**—dryers; **6**—cylinder with propylene.

Alkylation of aromatic hydrocarbons with olefins in the presence of acid catalysts is carried out at low temperatures of 20-50°, with phosphoric acid on supports at 180-200° and 15-20 atm, and with $AlCl_3$ at $+50 \div +80°$.

As is known from the literature ([1–4]), alkylation on natural and synthetic aluminosilicates proceeds under the following conditions. Hydrosilicates: 250-400° and 25-40 atm; silica gel + alumina: 400° and 100 atm, 380° and 5 atm, 350° and 35 atm; synthetic aluminosilicate: 350-380° and 30 atm.

Recently ([5]), the kinetics of the reaction of alkylation of benzene with propylene on aluminosilicate at 325° and atmospheric pressure in the vapor phase has been studied. Thus, a characteristic feature of alkylation on aluminosilicates is the use of a comparatively high temperature and, in most cases, pressure.

In the present work the authors have shown for the first time that alkylation of aromatic hydrocarbons with olefins is possible in the liquid phase at low temperatures $+20, 50$, and 70°, with rates customary for acid catalysis.

The alkylation experiments on industrial aluminosilicate were carried out in a vertical reactor (Fig. 1) 34 mm in diameter, filled with a bed of spherical catalyst 68 cm high; the catalyst volume was 450 ml, weight 300 g. The activity index of the catalyst was 34, the specific surface area by BET was 305 m^2/g, and the pore volume was 0.501 cm^3/g. Propylene was passed into the lower part of the column, into a charge of 230 g of benzene. For alkylation, a propane-propylene fraction containing 83% propylene and 17% propane was used. Alkylation with liquid acid catalysts was carried out in a three-necked flask with a stirrer according to the procedure described in our previous works ([6]). The alkylation products were treated by the usual method and distilled into fractions corresponding to the boiling points of mono-, di-, tri-, and tetraisopropylbenzenes.

Table 1

Composition of the mixture of alkylbenzenes (in mole percent) obtained by alkylation of benzene with propylene over various catalysts ($C_6H_6 : C_3H_6 = 1 : 1$ at 50°)

	Equilibrium composition $AlCl_3$ ([7])	Aluminosilicate*	$AlCl_2 \cdot HSO_4$**	$H_3PO_4 \cdot BF_3$**
Monoisopropylbenzene	70.0	53.2	57.5	83.5
Diisopropylbenzene	24.0	36.7	24.0	10.5
Triisopropylbenzene	4.6	7.8	10.2	4.9
Tetraisopropylbenzene	1.5	2.3	8.3	1.1
Benzene content in the crude alkylate (before rectification)	34	49	36.4	14.8

* Space velocity 35 h^{-1}.
** Space velocity 10-20 h^{-1}.

On aluminosilicate, monoisopropylbenzene and diisopropylbenzene are obtained in almost equal amounts, together with an appreciable yield of tri- and tetraisopropylbenzenes. For comparison, Table 1 gives the results of alkylation of benzene with propylene using the catalysts $AlCl_3$, $AlCl_2 \cdot HSO_4$, and $H_3PO_4 \cdot BF_3$. Although the composition of the reaction products on aluminosilicate differs from that with other catalysts in the direction of formation of a larger amount of di- and polyisopropylbenzenes, the rate of the alkylation reaction is of the same or a higher order.

On aluminosilicate the yield of alkylbenzenes is high; moreover, mono- and diisopropylbenzenes are formed in approximately equal amounts (see Table 2),

Table 2

Yield of alkylbenzenes (as percent of theoretical) in the alkylation of benzene with propylene over various catalysts
($C_6H_6 : C_3H_6 = 1 : 1$ at 50°)

Alkylbenzenes	Aluminosilicate	$H_3PO_4 \cdot BF_3$	$AlCl_2 \cdot HSO_4$	$AlCl_3$
Monoisopropylbenzene	29.3	67	31	46—57
Diisopropylbenzene	26.6			
Triisopropylbenzene	6.7	22	46	26
Tetraisopropylbenzene	3.4			

Table 3 gives the results of experiments on the alkylation of benzene with propylene on aluminosilicate at 20, 50°, and 70–80°. The yield of monoisopropylbenzene increases with increasing temperature, while that of diisopropylbenzene decreases.

Table 3

Composition of alkylbenzenes (in wt. percent) obtained in the alkylation of benzene with propylene at various temperatures on aluminosilicate (space velocity 35 h^{-1})

Alkylbenzenes	At 20°	At 50°	At 70–80°
Monoisopropylbenzene	33	44	54
Diisopropylbenzene	49	41	25
Triisopropylbenzene	10	11	16
Tetraisopropylbenzene	8	4	5

Propylene conversion 60%.

Table 4 gives the physicochemical characteristics of the alkylbenzenes obtained by alkylation on aluminosilicate. In their physicochemical characteristics, the alkylbenzenes correspond to literature data and contain no polymer impurities.

Table 4

Characteristics of the physicochemical properties of alkylbenzenes obtained in alkylation on aluminosilicate at $+20 \div +50°$

Characteristic	Isopropylbenzenes*	Isopropylbenzenes*	Isopropylbenzenes*
	mono-	di-	tri-

Characteristic	Isopropylbenzenes*	Isopropylbenzenes*	Isopropylbenzenes*
Boiling point, °C	154 (152.5)	206–216** (206)	220–240*** (239)
d_4^{20}	0.862 (0.862)	0.8604 (0.8608)	0.8619
n_D^{20}	1.4905 (1.4913)	1.4899 (1.4898)	1.4922
Mol. wt.	120 (120)	162	202
Bromine number	0	0	0

* Constants according to literature data are given in parentheses.
** The main portion boils at 204°.
*** The main portion boils at 239°.

The possibility of alkylating benzene with propylene at low temperatures with a high degree of conversion is evident if one considers the free energy of formation of isopropylbenzene at atmospheric pressure according to the reaction:

$$C_6H_6 + C_3H_6 \rightleftharpoons C_6H_5 - C_3H_7,$$

$$\Delta F = -23376 + 34{,}01T.$$

The value of ΔF has a large negative value at low temperatures.

Aluminosilicate is an acidic catalyst, in the presence of which a number of reactions proceed, apparently by a carbonium mechanism both at low and at high temperatures. Low-temperature reactions include the polymerization of olefins. Thus, isobu-

ethylene polymerizes on natural aluminosilicates over a wide range of temperatures, beginning at −80°.

It is known that in a number of cases polymerization and alkylation reactions proceed with analogous catalysts and under similar conditions. Low-temperature alkylation of benzene with propylene on aluminosilicate catalysts should be assigned to this type of reaction.

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Note: Figure translations are in progress. See original paper for figures.