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Abstract

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Alkylation of Phenol with Isobutylene Using Homogeneous and Heterogeneous Catalysts

It is known that the alkylation of phenol with olefins, with good results, is carried out with the aid of acid catalysts (H_2SO_4, H_3PO_4) and aluminum chloride at a temperature of 80–100°. The authors investigated the comparative effectiveness of acid catalysts in the alkylation of phenol with isobutylene, and also studied the alkylating ability, in this process, of a number of oxide heterogeneous catalysts.

The reaction was conducted at 100° and at a molar ratio phenol : isobutylene = 1 : 1, since these conditions are optimal for obtaining monobutylphenol. Alkylation with homogeneous catalysts, soluble in phenol or powdery and forming a good mixture with phenol, was carried out in a flask with a stirrer; isobutylene was fed beneath the layer of phenol. Alkylation of phenol with granulated heterogeneous catalysts was carried out in a reactor consisting of a column about 600 mm high, in which a layer of catalyst and phenol was placed; isobutylene was fed underneath the phenol. For alkylation, 98% isobutylene was used, obtained by dehydration of isobutyl alcohol over aluminum oxide at 400°, and phenol with m.p. +41° and n_D^{45}1.5401.

The alkylate obtained at a molar ratio phenol : isobutylene = 1 : 1 was an oily crystalline mass, which was transferred to a glass filter to separate the liquid portion. The results of the experiments are given in Table 1.

After separation of the alkylate, solid and liquid reaction products are obtained. The former, after treatment, is pure *n*-tert.-butylphenol; in the liquid products, di-tert.-butylphenol predominates (up to 75–85%), with an admixture of *o*-tert.-butylphenol and other reaction products (see Table 4).

The liquid products obtained in alkylation with $H_3PO_4 \cdot BF_3$, BF_3, H_3PO_4, $AlCl_3$, and $Al_2O_3 \cdot 4SiO_2 \cdot nH_2O$ consist entirely only of alkylphenols. The alkylation reaction may be represented as follows, where the yield of the reaction products depends on the catalyst used.

$$\text{phenol} + \text{iso-}C_4H_8 \longrightarrow \begin{cases} p\text{-tert.-butylphenol,} & 50\text{–}80\%, \\ \text{liquid alkylphenol fraction,} & 15\text{–}45\%. \end{cases}$$

In the liquid alkylphenol fraction:

di-tert.-butylphenol	75–85%,
tri-tert.-butylphenol	20–25%,
o-tert.-butylphenol	2–3%.

Table 1

Alkylation of phenol with isobutylene with various catalysts at atmospheric pressure and 100°
(molar ratio phenol : isobutylene = 1 : 1, phenol 47 g)

Catalyst	Amount of catalyst, g	Composition of crude alkylate, %: phenol	Composition of crude alkylate, %: *p*-tert.-butylphenol	Composition of crude alkylate, %: liquid products	Yield of reaction products, % of theory: *p*-tert.-butylphenol	Yield of reaction products, % of theory: liquid products	Yield of reaction products, % of theory: total
$H_3PO_4 \cdot BF_3$	3.7	4.0	81.0	15.0	81	15	96
BF_3	3.7	4.2	83.0	12.8	83	13	96
$AlCl_2 \cdot HSO_4$	7.5	28.0	40.7	31.3	41	11	52
H_2SO_4	7.5	15.7	65.7	18.6	65	19	84
H_3PO_4	7.5	13.7	59.6	26.7	60	28	88
$AlCl_3$	3.7	4.1	71.2	24.7	70	24	94
$Al_2O_3 \cdot 4SiO_2 \cdot nH_2O$*	69	13.5	42.5	44.0	43	44	87
TiO_2	69	Alkylation proceeds poorly, 4–5 g of alkylate is formed	Alkylation proceeds poorly, 4–5 g of alkylate is formed	Alkylation proceeds poorly, 4–5 g of alkylate is formed	Alkylation proceeds poorly, 4–5 g of alkylate is formed	Alkylation proceeds poorly, 4–5 g of alkylate is formed	Alkylation proceeds poorly, 4–5 g of alkylate is formed

Catalyst	Amount of catalyst, g	Composition of crude alkylate, %: phenol	Composition of crude alkylate, %: p-tert.-butylphenol	Composition of crude alkylate, %: liquid products	Yield of reaction products, % of theory: p-tert.-butylphenol	Yield of reaction products, % of theory: liquid products	Yield of reaction products, % of theory: total
TiO_2 + Al_2O_3	69	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed
MoO_3 + SiO_2	69	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed
SiO_2 + MoO_3	69	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed
SiO_2	69	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed	Alkylation proceeds poorly, 2–5 g of alkylate is formed

Catalyst	Amount of catalyst, g	Composition of crude alkylate, %: phenol	Composition of crude alkylate, %: *p*-tert.-butylphenol	Composition of crude alkylate, %: liquid products	Yield of reaction products, % of theory: *p*-tert.-butylphenol	Yield of reaction products, % of theory: liquid products	Yield of reaction products, % of theory: total
CuO	69	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed
Al_2O_3	69	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed
PbO	69	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed
Fe_2O_3	69	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed	The alkylation reaction does not proceed

* Industrial aluminosilicate catalyst.

From the data presented in Table 1, the following conclusions may be drawn. Phenol is alkylated with isobutylene in the presence of catalysts containing boron fluoride most successfully in comparison with the other catalysts studied. Under the conditions of the experiments with $H_3PO_4 \cdot BF_3$ and BF_3, the yield of *p*-tert.-butylphenol is respectively 80 and 83%, whereas with $AlCl_3$ it reaches only 70%. The yield of liquid products in the alkylation of phenol by means of $H_3PO_4 \cdot BF_3$ and BF_3 (15 and 13%) is lower than with $AlCl_3$ (24%). The increase in the yield of *p*-tert.-butylphenol in the case of catalysts containing boron fluoride occurs at the expense of a decrease in the formation of liquid products.

It follows from the foregoing that the most effective of the catalysts studied for the reaction of alkylation of phenol with isobutylene in the direction of formation of *p*-tert.-butylphenol is the complex of boron fluoride with orthophosphoric acid, and especially boron fluoride; under these same conditions, with such oxide catalysts as titanium oxide, silicon oxide, and aluminum oxide, this reaction essentially does not proceed. To increase the yield of alkylation products, it is probably necessary to select other reaction conditions. Apparently, one should proceed in the direction of increasing the pressure and temperature.

Of the other compounds examined, an industrial aluminosilicate catalyst shows good results in carrying out the reaction of alkylation of phenol with isobutylene; its use in industry would considerably cheapen and simplify this process. By carrying out the process at the appropriate phenol : isobutylene ratios, phenol can be completely brought into the reaction. The di-tert.-butylphenol formed in this case is not a waste product of the process, since it finds various applications. The use of a solid catalyst—aluminosilicate, taking into account what has been stated—eliminates the need for water and alkaline washing of the reaction mass. The availability of a ready-made catalyst, whose production has been mastered on an industrial scale, is in itself a substantial positive factor in recommending it for industrial use as a catalyst for the alkylation of phenol.

The considerations presented above served as the basis for carrying out a further investigation of the reaction of alkylation of phenol with isobutylene on an aluminosilicate catalyst. Our subsequent experiments were carried out with this catalyst in order to determine the optimum temperature of the process at a molar ratio phenol : isobutylene = 1 : 1, with 47 g of phenol in each experiment and 69.3 g of catalyst, which was used in 8 successive experiments. The data obtained are summarized in Table 2.

Table 2

Temperature, °C	Composition of crude alkylate, %	Composition of crude alkylate, %	Composition of crude alkylate, %	Yield of reaction products, % of theory	Yield of reaction products, % of theory	Yield of reaction products, % of theory
	phenol	*p*-tert.-butylphenol	liquid products	*p*-tert.-butylphenol	liquid products	total
100	13.5	42.5	44.0	43	44	87
130	13.3	56.2	30.5	56	31	87
160	16.6	46.7	36.7	47	37	84

The amount of catalyst was selected so as to ensure a satisfactory rate of absorption of isobutylene. From the data given in Table 2 it is evident that the optimum temperature of the process at atmospheric pressure is 130°. Under these conditions the maximum yield of *p*-tert.-butylphenol is attained (56% of theory) and a minimum of liquid reaction products is formed. At temperatures of 100 and 130° phenol is practically not carried off by the unreacted isobutylene; at 160° about 2–3 g are lost from 49 g of phenol. In the reaction of 49 g of phenol and 28 g of isobutylene (100–150°), about 0.4–0.7 g of carbonaceous deposits is formed on the catalyst.

Further study of the process of alkylation of phenol with isobutylene was carried out at 130°, at a molar ratio phenol : isobutylene = 1 : 1, and on a single charge (69.3 g) of catalyst, which was subjected to periodic regeneration. Working cycles, lasting on average about 90 hours, alternated with regeneration cycles of 3 hours' duration.

Table 3

Change in the activity of the aluminosilicate catalyst in the process of alkylation of phenol with isobutylene

Experiment Nos.	Duration of working cycle, h	Duration of regeneration cycle (air purge), h	Yield of tert.-butylphenol per cycle, g	Yield of tert.-butylphenol per cycle, g
			mono-	di-
9—21	96	3	464	209
22—32	80	3	388	175
33—42	72	3	349	157
43—52	72	3	349	157
9—52	320	–	1550	698

A working cycle is a series of experiments carried out with one and the same portion of catalyst at a molar ratio phenol : isobutylene = 1 : 1. One charge (one experiment) of phenol into the reactor amounted to 47 g; the amount of isobutylene passed through was 28 g, and the amount of catalyst participating in the reaction was 69 g. After completion of the experiment (28 g of isobutylene had entered into reaction), the crude alkylate was separated from the catalyst and treated in the usual manner.

The operating cycle was considered complete when the absorption rate of isobutylene decreased under various conditions from 1.5 l/h to 0.5 l/h. During the regeneration cycle, the reactor with the catalyst was heated to 500°, after which air was blown through the catalyst for 3 h, ensuring complete removal of coke deposits. Table 3 gives data characterizing the activity of the catalyst in the alkylation of phenol with isobutylene.

From the data presented in Table 3 it is evident that the activity of the aluminosilicate catalyst changed relatively little during operation. In the first experiments before regeneration it operated for 96 h; in subsequent runs, after regeneration, for 80–72 h. During catalyst operation lasting 320 h, 1550 g of mono-tert-butylphenol and 698 g of di-tert-butylphenol were obtained, which, calculated per 1 g of catalyst, amounts to 22.4 g of mono-tert-butylphenol and 10.1 g of di-tert-butylphenol. The complete composition of the products of alkylation of phenol with isobutylene using an aluminosilicate catalyst at 130° and a molar ratio phenol : isobutylene = 1 : 1 is given in Table 4.

Table 4

Composition of the alkylate (in weight percent) obtained by alkylation of phenol with isobutylene at 130° on an aluminosilicate catalyst

	p-tert-Butylphenol	*o*-tert-Butylphenol	Di-tert-butylphenol	Phenol	Tributylphenol	Butyl ether of butylphenol
Crude alkylate	65.4	4.6	15.5	13.3	0.8	0.4
Alkylate	75.4	5.3	17.8	–	1.0	0.5

The obtained *o*-tert-butylphenol had the following constants: b.p. 114–116°/16, m.p. $-6.2°$, n_D^{20} 1.5212, d_4^{20} 0.9791, MW = 150, OH 11.2% (literature data: b.p. 120°/30 mm, m.p. $-6.8°$, n_D^{20} 1.5239, d_4^{20} 0.982).

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