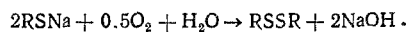


with feedstock of the central gas-fractionating unit. The mercaptide-saturated CTC is withdrawn from the still of K-7 (governed by interface level) and passes through the heat exchanger T-17, where it is heated with steam to 40°C, after which it enters the regenerator tower K-8. This tower was reconstructed; the S-channel trays were removed, and the tower was packed with 25 × 25 × 3 mm Raschig rings in a single bed with a height of 6 m. The still of the tower K-8 was fed with process air in amount of 300-350 m³/h, preheated to 40°C in the heat exchanger T-22. The tower K-8 operates under flooded conditions in a regime of emulsification; at 40°C with a pressure of 2-4 kgf/cm², the caustic is regenerated in accordance with the reaction



The spent air from the upper part of the tower K-8, passing through the separator/spray trap E-19, is directed to a furnace P-2 for combustion. The catalyst complex with the disulfides passes from the still of K-8 to the disulfide separator tank E-20, where the disulfides are washed out of the CTC with a hexane cut (1 metric ton/h). From E-20, the upper layer (hexane cut with disulfides) passes to a clarifier and then is pumped to hydrotreating. The bottom layer in E-20, consisting of regenerated CTC, is withdrawn (governed by interface level) and refed by the pump N-32 as the liquid wash in the extractor K-7.

The content of mercaptan sulfur in the wide cut after treating is less than 0.001% by weight, and the hydrocarbons in the exhaust air amount to no more than 0.1% by volume. The expected service life of the catalyst complex is 3-4 months.

LITERATURE CITED

1. R. Ya. Barashkov, N. A. Gorechenkova, M. M. Emel'yanov, et al., *Neftepererab. Neftekhim.*, No. 7, 18 (1974).
2. A. M. Mazgarov, A. G. Akhmadullina, et al., *Neftepererab. Neftekhim.*, No. 5, 28 (1975).
3. A. M. Mazgarov, N. R. Vorob'ev, A. V. Neyagov, et al., *Neftepererab. Neftekhim.*, No. 10, 24 (1975).
4. S. I. Krichmar and V. E. Stepanenko, *Zh. Anal. Khim.*, No. 12, 1874 (1969).
5. E. N. Konstantinov, V. A. Kuznechikov, et al., *Gazov. Prom.*, No. 5, 11 (1973).

ALKYLATION OF BENZENE WITH PROPYLENE OVER PROMOTED BORON FLUORIDE-CONTAINING CATALYSTS

V. A. Sidorov and E. V. Lazareva

UDC 665.652.4

Earlier reports [1, 2] dealt with studies aimed at improving the quality of boron fluoride-containing catalysts, consisting of boron fluoride on various types of porous solid supports. One of the important performance characteristics in rating these catalysts is their stability in alkylation reactions, since boron fluoride in the presence of traces of promoters (moisture, Bronsted acids, Lewis acids, etc.) manifests a rather high activity.

The present article is devoted to investigation of the process technology for manufacturing isopropylbenzene on one of the catalysts that have been developed, this catalyst being promoted with fluorine and saturated with boron fluoride [1]. This particular catalyst is more stable than unpromoted, boron fluoride-saturated specimens of aluminum oxide or other supports [1, 2].

The alkylation of benzene with propylene was studied in a flow-type unit with a fixed bed of catalyst, at various pressures, temperatures, specific feedstock space velocities, and molar ratios of reactants. The basic flow plan of the alkylation unit is for the most part similar to one described previously [3].

The experimental procedure was as follows. A reactor, designed for 150 kgf/cm², was fed with the required quantity of benzene (from a feed buret, pumped), and the propylene was fed from a calibrated high-pres-

Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 12, pp. 9-11, December, 1976.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50.

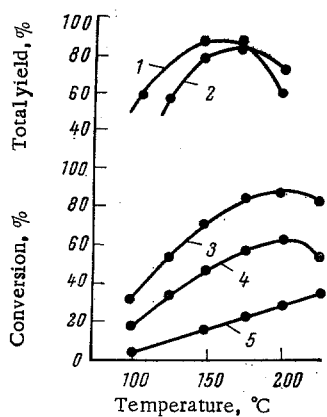


Fig. 1

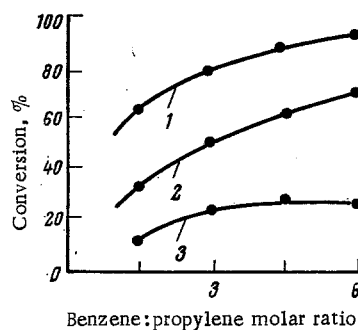


Fig. 2

Fig. 1. Influence of temperature on propylene conversion and total yield of products from alkylation of benzene (4-day run, benzene:propylene molar ratio 4:1, specific benzene feedstock space velocity 1 h^{-1}): 1, 2) total yield of products at respective pressures of 30 and 1 kgf/cm^2 ; 3, 4, 5) propylene conversion at respective pressures of 30, 20, and 1 kgf/cm^2 .

Fig. 2. Propylene conversion as a function of benzene:propylene molar ratio, with alkylation temperature 175°C and benzene space velocity 1 h^{-1} : 1, 2, 3) respective pressures 30, 20, and 1 kgf/cm^2 .

sure buret in the required molar ratio, both feed rates being calculated to give the desired space velocity. The reactor was prepressurized with nitrogen from a cylinder. The alkylation products, together with excess benzene and gases, passed to a water-cooled, high-pressure receiver and then to a low-pressure receiver, where the gases were separated from the liquid products, measured by means of a gas meter, and vented to an exhaust system after withdrawing the required samples for analysis.

The temperature in the reactor was monitored by means of thermocouples, and the system pressures were monitored by means of gauges on the reactor, nitrogen system, pump, high-pressure receiver, and pump line.

The feedstock used in this work was a petroleum benzene with a refractive index n_D^{20} of 1.5010, crystallization temperature $+5.4^\circ\text{C}$, relative density ρ_4^{20} of 0.879, and a mercaptan sulfur content of 1 ppm. The propylene that was used was 99.6–99.8% pure; also used were propane/propylene cuts containing 30–72% propylene. The boron fluoride used in saturating the supports was commercial technical-grade material, with a purity of 99.5–99.6%. The quantity of boron fluoride was determined by the weight gain of the sorbent [2] and by the difference between the total quantity of fluorine in the catalyst and the quantity of fluorine promoter. The alkylates were analyzed chromatographically.

The specimens of catalyst used to obtain isopropylbenzene were prepared from a commercial aluminum oxide that had been calcined at 500°C , impregnating this support with a 2–8% solution of hydrofluoric acid and drying for 4–6 h at $175\text{--}300^\circ\text{C}$ in a stream of nitrogen or air, and then saturating with boron fluoride [1, 2].

The fluorine contents of the catalyst specimens varied from 0.59% to 6.4% after promotion of the aluminum oxide, and from 9.93% to 17.1% after saturation of the promoted support with boron fluoride [2].

The vapor-liquid phase alkylation of benzene with propylene was performed at temperatures from 50° to 200°C , pressures from 1 to 30 kgf/cm^2 , molar ratios of benzene to propylene from 1.5:1 to 6:1, and specific feedstock (benzene) space velocities from 0.5 to 3.0 h^{-1} . The total time of the experiments was 6 to 150 h.

The influence of temperature and pressure on propylene conversion and total yield of isopropyl derivatives of benzene is shown in Fig. 1. These data were obtained after a 24-h run in order to account for the stability factor.

The conversion increased with increasing pressure and temperature; in the case of a benzene space velocity of 1 h^{-1} , the conversion reached a maximum at a temperature of 200°C , pressure of 30 kgf/cm^2 , and a ben-

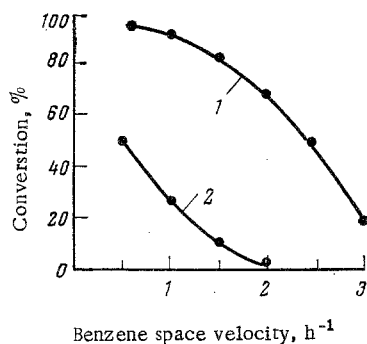


Fig. 3

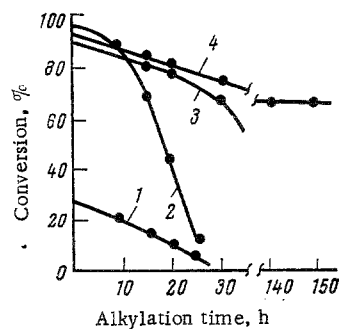


Fig. 4

Fig. 3. Propylene conversion as a function of specific feedstock (benzene) space velocity, with benzene:propylene molar ratio 4.5:1 and alkylation temperature 175°C: 1, 2) respective pressures 30 and 1 kgf/cm².

Fig. 4. Influence of support type, temperature, and pressure on stability of catalyst in alkylation of benzene with propylene (benzene:propylene molar ratio 4:1, benzene space velocity 1 h⁻¹): 1) 175°C, 1 kgf/cm²; 2) 50°C, 1 kgf/cm²; 3) 175°C, 30 kgf/cm², commercial aluminum oxide support without promoter; 4) 175°C, 30 kgf/cm², support promoted with fluorine.

zene:propylene molar ratio of 4:1. The maximum yields of alkylated products were obtained at temperatures of 150–175°C, the influence of pressure on yield (as calculated on the olefinic hydrocarbon reacted) being less pronounced than the influence on the propylene conversion.

The influence of the benzene:propylene molar ratio and the benzene space velocity is illustrated in Figs. 2 and 3, respectively. An increase in molar ratio from 1.5:1 to 4.5:1 produced a large effect on the propylene conversion; further increases had less effect.

In the alkylation of benzene without any excess pressure the propylene conversion decreased markedly even when the feedstock space velocity was increased to 1 h⁻¹, and at a velocity of 2 h⁻¹ the process became unfeasible. At a process pressure of 30 kgf/cm², the drop in propylene conversion with increasing feedstock space velocity was more gradual, and only at a velocity of 2.5 h⁻¹ did the conversion become equal to that at atmospheric pressure with a velocity of 0.5 h⁻¹.

The same sort of influence of these parameters was observed when a propane/propylene cut was used. In this case the yield with respect to benzene was 1–2% lower.

The influence of these parameters remained much the same when the changeover was made from conventional aluminum oxide to the fluorine-promoted specimens, but the stability of the two types of catalysts showed considerable differences. The catalyst stability and the propylene conversion were highly dependent on the temperature and pressure. Figure 4 illustrates the influence of promoter, pressure, and temperature on the changes in propylene conversion during alkylation. The poorest results were obtained at atmospheric pressure and high temperature, i.e., in the vapor phase. The total yield of alkylation products and the selectivity did not change greatly.

When the process temperature was reduced below the boiling point of benzene at atmospheric pressure, the initial propylene conversion was much higher, but the conversion dropped off quite rapidly as the experiment was continued. An increase in pressure to 30 kgf/cm² can slow down the drop in catalyst activity to a considerable extent. A greater effect was achieved when operating under pressure with boron fluoride-containing aluminum oxide catalyst that had been previously promoted with fluorine; without impregnation with boron fluoride, the catalyst activity dropped off gradually over 30–35 h (conversion decreased to 75–72%), and then the catalyst remained essentially stable for more than 150 h (see Fig. 4). When the catalyst bed was impregnated with boron fluoride dissolved in benzene or in the polyalkylated reaction products in amounts of 0.1–0.3% [1], the catalyst activity remained at the level of freshly prepared catalyst in an analogous run of the unit.

*As in Russian original; statements in this paragraph do not coincide with statements in Fig. 4, where catalysts with and without fluorine promoter are compared – Translator.

From the data obtained in this work, the catalyst and process technology that have been developed can be recommended for commercialization of this cumene synthesis process.

LITERATURE CITED

1. USSR Inventor's Certificate 338,246, Byull. Izobret., No. 16 (1972).
2. USSR Inventor's Certificate 269,155, Byull. Izobret., No. 15 (1970).
3. V. G. Telegin and V. A. Sidorov, Khim. Prom., No. 11, 807 (1961).

UPPER LIMIT OF UREA ADDUCT FORMATION WITH STRAIGHT-CHAIN 1-ALKENES IN BINARY AND MULTICOMPONENT MIXTURES

A. A. Krupina, Z. G. Borisova,
and V. A. Matishev

UDC 547.313:541.49

This is a continuation of work reported in [1], devoted to investigation of the upper limit of adduct formation (ULA) of urea with binary and multicomponent mixtures of straight-chain 1-alkenes. The work was performed in two consecutive stages. As noted in [1], 1-dodecene (fifth in the series of straight-chain 1-alkenes forming an adduct with urea) is the "borderline" hydrocarbon, for which the ULA temperature can be determined by a linear equation of the type

$$\theta = a(n - b) + \theta \quad (1)$$

and by a nonlinear equation of the type

$$\theta = \frac{t_b}{\frac{1}{a} + a'(n - b')}. \quad (2)$$

In a study of ULA relationships for binary mixtures of straight-chain alkanes, it was shown in [2] that, up to the "borderline" decane, all relationships for the binary mixtures are linear, and, beginning with n-decane, all are nonlinear. Hence the present communication is the result of the first stage of the investigations, the object of which was the straight-chain 1-alkenes from C₈ through C₁₁.

The same as in [1], the reagents used in this work were straight-chain 1-alkenes from USSR and foreign production, crystalline urea in ch.d.a. grade ["pure for analysis"], and distilled ethyl alcohol as an activator. The experiments were performed using a procedure given in [3].

In the binary mixtures of 1-alkenes, the main component was (in turn) undecene, decene, nonene, and octene, and the second components used with each of the main components were (in turn) all the 1-alkenes of lower molecular weight, including 1-heptene and 1-hexene, which do not form adducts and hence cannot be used as the main components of the binary mixtures.

As would be expected (Fig. 1), all the binary mixtures in the group under investigation do follow a linear relationship of the ULA in the interval of concentrations from 0 to 99% by mass, i.e., the same relationship obtained previously for binary mixtures of straight-chain alkanes [3]:

$$\theta_{\text{bin}} = \theta - c \cdot \Delta t. \quad (3)$$

In studying the values of the gradients Δt for the various binary mixtures of 1-alkenes, two more relationships were found, relationships that had not been established in analogous experiments with binary mixtures of straight-chain alkanes. As can be seen from Table 1, each of the main components of the binary mixtures has

Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 12, pp. 11-12, December, 1976.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50.