DETERMINATION OF PROCESS CONDITIONS FOR ALKYLATION OF TOLUENE WITH ETHYLENE AND PROPYLENE ON Al_2O_3 PROMOTED WITH BORON FLUORIDE

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UDC 542.952.53

It had been shown previously [1-3] that commercial Al_2O_3 promoted with boron fluoride is an active catalyst for the alkylation of aromatic hydrocarbons with olefins. In this article, we are presenting results from a study of the alkylation of toluene with ethylene and propylene, directed toward the production of ethyltoluenes and cymenes.

EXPERIMENTAL

In this study, we used a dried toluene having $\rho_4^{20} = 0.8670$ and $n_D^{20} = 1.4970$, and ethylene and propylene with respective purities of 99.6 and 99.8%. The catalyst consisted of Al_2O_3 that had been calcined at 450° for 5 h, with boron fluoride in amount of 13% by weight deposited on the alumina. The boron fluoride used in this work was technical grade, with a content of 99.63% principal substance. The experiments were performed in a previously described [3] flow-type pilot unit, in a 1-liter reactor. The alkylates were analyzed in a KhT-63 IK chromatograph with a column length of 4 m, packed with Celite 545 with 10% Apiezon M. The analysis was performed with a column temperature of 180°C and a carrier-gas (hydrogen) feed rate of 50 ml/h. The isomer composition of the ethyltoluene was determined in an UKh-2 chromatograph with a flame ionization detector, using a column 2.3 m in length with Bentone 34 and dinonyl phthalate, taken in 60 : 40 ratio and deposited on Celite 545 in amount of 15%. The analysis was performed with a column temperature of 80°C and a carrier-gas (nitrogen) flow rate of 30 ml/min. The isomer composition of the isopropyltoluene was determined in a KhT-63 IK chromatograph with a flame ionization detector,

TABLE 1. Alkylation of Toluene with Ethylene on Al_2O_3 Promoted with Boron Fluoride

Alkylation conditions				Ethylene conversion, %	Ethyltoluene yield (calc. on ethylene), mole %	Ethyltoluene/polyethyltoluene ratio, moles/mole	Isomer comp. of ethyltoluenes, %		
pressure, kg/cm²	temp., °C	space velocity (toluene), h-1	toluene/ethylene ratio, moles/mole				o-isomer	m-isomer	p-isomer
1,5	125	1,50	4:1	87,0	42,4	1:0,19	51	25	24
3,0	125	1,50	4:1	92,3	52,6	1:0,24	49	27	24
6,0	125	1,50	4:1	95,3	53,6	1:0,24	—	—	—
3,0	50	1,50	4:1	31,1	22,5	1:0,12	52	24	24
3,0	100	1,50	4:1	81,6	45,6	1:0,25	50	25	25
3,0	150	1,50	4:1	96,9	56,9	1:0,25	48	28	24
3,0	125	0,75	4:1	94,6	56,7	1:0,24	44	31	25
3,0	125	3,00	4:1	71,8	42,5	1:0,20	50	25	24
3,0	125	4,50	4:1	64,8	40.1	1:0.17	50	26	24
3,0	125	1,50	1:1	35,6	13,9	1:0,34	50	25	25
3,0	125	1,50	2:1	61,4	29,6	1:0,34	50	25	25
3,0	125	1,50	8:1	94,2	69,1	1:0,16	51	25	24

Krasnodar Branch, VNIIneftekhim (All-Union Scientific-Research Institute of Petrochemical Processes). Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 12, pp. 5-8, December, 1973.

TABLE 2. Alkylation of Toluene with Propylene on Al_2O_3 Promoted with Boron Fluoride

Alkylation conditions				Propylene conversion, %	Yield of cymenes (calc. on propylene), mole %	Ratio of cymene to polyisopropyltoluene, moles/mole	Isomer comp. of cymenes, %		
pressure, kg/cm²	temp., °C	space velocity (toluene), h⁻¹	toluene/propylene ratio, moles/mole				o-isomer	m-isomer	p-isomer
0,1	75	8	4:1	83,8	54,9	1:0,24	25	34	41
1,0	75	8	4:1	91,5	61,6	1:0,23	26	32	42
2,0	75	8	4:1	90,0	60,0	1:0,22	28	30	42
3,0	75	8	4:1	89,0	60,5	1:0,23	—	—	—
2,0	50	8	4:1	88,0	57,3	1:0,26	38	19	43
2,0	100	8	4:1	87,5	66,5	1:0,15	18	43	39
2,0	125	8	4:1	85,0	65,7	1:0,14	21	38	41
2,0	140	8	4:1	66,0	52,5	1:0,11	21	37	42
2,0	75	4	4:1	100,0	72,3	1:0,20	21	35	44
2,0	75	6	4:1	95,0	65,3	1:0,22	23	32	45
2,0	75	12	4:1	84,5	51,6	1:0,22	32	23	45
2,0	75	8	2:1	78,4	38,3	1:0,48	—	—	—
2,0	75	8	6:1	91,0	64,6	1:0,17	30	26	44
2,0	75	8	8:1	94,0	74,0	1:0,09	31	27	42

in a capillary column 40 m in length and 0.25 mm in diameter. The liquid phase used in this column was squalane with 13.5 wt. % 7,8 benzoquinoline. The analysis was performed with a column temperature of 80°C and a carrier-gas (nitrogen) flow rate of 10 ml/min.

ALKYLATION OF TOLUENE WITH ETHYLENE

It can be seen from the data of Table 1 that, under the indicated conditions, the ethylene conversion and the ethyltoluene yield increase with increasing pressure, temperature, or molar ratio of toluene to ethylene, and with decreasing space velocity. The yield of polyethyltoluenes (di- and triethyltoluenes)* amounts to 0.12 to 0.34 mole/mole ethyltoluene. With increasing pressure and temperature, the yield of polyethyltoluenes increases, but decreases with increasing space velocity or molar ratio of toluene to ethylene. From these data, it follows that the optimal conditions for producing ethyltoluenes by alkylation of toluene with ethylene are as follows:

Pressure, kg/cm²	1.5—3
Temp., °C	125—150
Space velocity (toluene), h⁻¹	1.5
Toluene/ethylene ratio, moles/mole	4,8:1
Ethylene conversion, %	96.9
Ethyltoluene yield, mole %	69.1
Quantity of polyethyltoluenes, mole/mole ethyltoluene	0,16

The properties of the ethyltoluene obtained under these conditions are as follows:

Density, ρ_4^{20}	0,8720
Refractive index n_D^{20}	1,5005
Fractional composition, Kramer, °C	
IBP	161,6
10%	162,5
30%	163,1
50%	163,4
70%	163,6
90%	163.7
EP	164,1
Bromine No.	0
Isomer content, %	
o-	51
m-	25
p-	24

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* Tetraethyltoluenes were detected only in the alkylate obtained with a 1:1 mole ratio of toluene to ethylene.

It is also evident from Table 1 that, under these conditions, o-ethyltoluene is the primary isomer of ethyltoluene, amounting to about 50%. The meta and para isomers are present in approximately equal quantities. The content of para isomer is practically independent of the alkylation process conditions. For the ortho and meta isomers, increasing the temperature or decreasing the space velocity produces a drop in the content of the former and an increase in the latter.

ALKYLATION OF TOLUENE WITH PROPYLENE

As the pressure or temperature is increased, the conversion of propylene and the yield of cymenes reach a maximum. In the case of pressure increases, this behavior is apparently due to the increase in concentration of dissolved propylene in the reaction mixture [4] and the decreased degree of agitation of the reaction mixture caused by the curtailment of the undissolved propylene volume. The effect of temperature also involves an increase in the reaction rate constant and a decrease in the concentration of dissolved propylene in the reaction mixture.

The propylene conversion and cymene yield increase as the space velocity is decreased or the mole ratio of toluene to propylene is increased. The yield of polyisopropyltoluenes, which consist only of di- and triisopropyl derivatives, amounts to 0.09-0.48 mole/mole isopropyltoluene. The pressure and space velocity have practically no effect on the yield of polyisopropyltoluenes. However, increases in mole ratio and temperature will reduce the yield of polyisopropyltoluenes.

The decrease in amount of polysubstituted derivatives with increasing temperature is apparently explained by the occurrence of the reaction of transalkylation of toluene with polyisopropyltoluenes. And in fact, in the transalkylation of toluene with a mixture of polyisopropyltoluenes containing 66.4 wt.% di-, 28% tri-, and 5.6% tetraisopropyltoluenes, at 95°C with a 3.8:1 mole ratio of toluene to polyisopropyltoluene, in the presence of Al_2O_3 with 5.7% BF_3, taken in amount of 0.75 volumes/volume of hydrocarbon, in the course of one hour the conversion of polyisopropyltoluenes and the yield of isopropyltoluene amounted to (respectively) 36 and 39.4% of theoretical.

The optimal conditions for the alkylation of toluene with propylene are: pressure 1-2 kg/cm^2, temperature 75°C, space velocity (toluene) 6-8 h^{-1}, mole ratio of toluene to propylene 4:1 to 6:1. Under these conditions, the propylene conversion is 95%, the yield of cymenes 60-62 mole % (of propylene taken), and the quantity of polyisopropyltoluenes is 0.2 mole/mole cymene. The properties of the cymene obtained under these conditions are as follows:

Density, ρ_4^{20}	0.8624
Refractive index n_D^{20}	1.4942
Fractional composition, Kramer, °C	
IBP	173.2
10%	174.2
30%	175.7
50%	176.1
70%	176.2
90%	176.2
EP	176.4
Bromine No.	0
Isomer content, %	
o-	22
m-	34
p-	44

Comparing the results, we see that there is a sharp increase in reaction intensity upon going from ethylene to propylene in the alkylation; under milder conditions, the production of cymenes per liter of catalyst is 11.7 moles/h, that of ethyltoluenes 2.4 moles/h.

It can be seen from the data of Table 2 that the quantity of p-isomer in the cymenes is almost independent of alkylation conditions. As the space velocity is decreased, the content of m-isomer increases, and the content of o-isomer decreases. With increasing temperature, the content of m-isomer in the cymene increases and reaches a certain maximum at a temperature of 100°C, while the o-isomer content falls to a minimum at this temperature.

The data on isomer composition of the ethyltoluene and cymene indicate that, in alkylation on Al_2O_3 promoted with boron fluoride, the rule of substituent orientation is not observed. The content of m-isomer in the ethyltoluene reaches 27.8% and that in the isopropyltoluene 42.8%. It is also evident from Table 2 that an increase in the content of m-isomer is usually accompanied by a decrease in the content of o-isomer, with relatively little change in the amount of p-isomer. Also, the concentration of p-isomer is close to the thermodynamic equilibrium concentration of the constituents at 100°C (29.2% for ethyltoluenes and 36.4% for cymenes) [5]. This points out the possibility of preferential isomerization of the o-isomer to the m-isomer.

And in fact, by the isomerization of p-cymene containing 1.4% m-cymene as an impurity, in the presence of Al_2O_3 with 5.8 wt.% BF_3 at a temperature of 75°C, volume ratio of catalyst to p-cymene of 0.75 : 1, and reaction time of one hour, the reaction products contained 5.9% m-, 0.2% o-, and 93.9% p-cymene; i.e., the conversion of p-cymene to m-cymene amounted to only 4.5%. In contrast, with 30-minute contacting of o-cymene containing 7.1 and 4.9% m- and p-isomers with Al_2O_3 modified with BF_3 in amount of 5.9 wt.%, under the same conditions, the reaction products contained 10.5% o-, 57.2% m-, and 32.2% p-cymene; i.e., the conversion of o-cymene to m-cymene was 57%.

In the case of alkylation with propylene, the yield of m-isomer is higher and o-isomer lower than in the alkylation of toluene with ethylene. This apparently can be explained by the ease of migration of the isopropyl group in comparison with the ethyl group, and also by the lower stability of the o-isopropyltoluene [6].

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