ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 4, pp. 706−710. © Pleiades Publishing, Ltd., 2009.
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TECHNOLOGY OF ORGANIC AND INORGANIC CHEMISTRY

The Processes of Benzene Alkylation with *n*-Alkenes on the Sulfocation Exchangers

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Received August 1, 2008

Abstract—-The processes of benzene alkylation with *n*-alkenes C_2–C_3 on sulfocation exchangers are developed. The processes are deprived of the strong corrosion aggressiveness, characteristic of the industrial processes with use of $AlCl_3$ or BF_3, and do not need the periodic burning out of the formed contaminants, that is characteristic of the processes with application of zeolites. Alkylation proceeds in the liquid phase at moderate temperatures: 70–90°C in the case of alkylation with propene and *n*-butenes, and 130°C for the alkylation with ethylene. With the use of alkane–alkene fractions C_2–C_3 the conversion of alkenes process exceeds 99%, the alkylbenzene to dialkylbenzenes ratio reaches 20–25%. Peralkylation of dialkylbenzenes it not required.

DOI: 10.1134/S1070427209040338

In the industry are widespread the processes of obtaining of ethylbenzene, isopropyl benzene (*i*-PrPh) and alkylbenzenes with the longer hydrocarbon group. Designation of the products is the synthesis of monomers (styrene, α-methylstyrene) by dehydrogenation, synthesis of phenol and acetone by oxidation *i*-PrPh and subsequent decomposition of isopropylbenzene hydroperoxide, producing of surfactants.

Synthesis of these alkylbenzenes is based on the following reactions:

$$C_6H_6 + CH_2{=}CH_2 \rightarrow C_6H_5\text{–}CH_2CH_3, \quad (1)$$

$$C_6H_6 + CH_2{=}CH\text{–}CH_3 \rightarrow C_6H_5\text{–}CH(CH_3)_2, \quad (2)$$

and other.

Partially further alkylation occurs:

$$C_6H_5\text{–}CH_2CH_3 + CH_2{=}CH_2 \rightarrow CH_3CH_2\text{–}C_6H_4\text{–}CH_2CH_3, \quad (3)$$

$$C_6H_5\text{–}CH(CH_3)_2 + CH_2{=}CH\text{–}CH_3 \rightarrow (CH_3)_2CH\text{–}C_6H_4\text{–}CH(CH_3)_2. \quad (4)$$

The formation of dialkylbenzenes (diethylbenzene [DEB], diizoropylbenzene [DIPB]) commonly is undesirable. In the presence of some strong catalysts it is possible to carry out disproportion, for example:

$$(CH_3)_2CH\text{–}C_6H_4\text{–}CH(CH_3)_2 + C_6H_6 \rightarrow 2C_6H_5\text{–}CH(CH_3)_2. \quad (5)$$

The reactions of alkylation are strongly exothermic: 100–108 kJ/g-mole in the case of EtPh or *i*-PrPh. As the catalysts are used [1–3]: $AlCl_3$ (in particular in Russia), BF_3, phosphoric acid on a carrier. Recently was enlarged (possibly, temporary) the use of zeolites. All these catalysts have the essential deficiencies: $AlC1_3$ and BF_3 display the strongest corrosion aggressiveness and tendency toward the formation of the large number of harmful drains, phosphoric acid (on a carrier) is relatively weak, it requires high temperature and therefore is insufficiently selective, zeolites also require higher temperatures, they do not "let out" large molecules (alkene oligomers, etc.) and therefore need periodic regeneration by burning out and calcination. For the purpose of the decrease of formation of dialkylbenzenes the alkylation is conducted with the significant molar excess of benzene with its subsequent isolation from the reaction mixture and recirculation. When the processes with $AlCl_3$ or BF_3 is is carried out with the benzene –alkene mole ratio 3.0–3.5, the processes with zeolites requires the ratio over 10.

The disproportion reactions proceed at the temperature by 30–40°C higher than the alkylation reaction. At the arranging a technology for the producing EtPh and *i*-PrPh in the presence of $AlCl_3$ (in particular utilized in Russia) the processes of alkylation and disproportionation are combined in one reactor, where they are necessarily carried out at a high temperature required for the disproportion. This, apparently, should be considered as a disadvantage, since such process is less selective.

A study showed that application of sulfocation exhcanger makes it possible to carry out alkylation of benzene at moderate temperatures: 70–80°C for obtaining *i*-PrPh and ~ 130°C for obtaining EtPh.

Tables 1 and 2 give some kinetic data in the reactors of periodic loading on the alkylation of benzene with propene (in the propene-propane fraction) and by ethylene. As the catalyst is used Amberlyst-36 [4] with the particle size from 0.3 to 1.3 mm and static exchange capacity 5.2 mg-equiv per 1 g of the catalyst. The catalyst quantity was 20–21% of the mass of liquid mixture.

It is evident from Table 1 that the conversion of propene is sufficiently high, and the formation of propene dimers and trimers is insignificant. The ratio of *i*-PrPh/*i*-$Pr_2C_6H_4$ (selectivity) raises with an increase in the benzene : propene mole ratio and falls with increase in the propene conversion. Therefore it is reasonable to conduct alkylation with the moderate conversion of propene for one pass (74–80%). This is acceptable completely when propane–propene fraction is used as a raw material at the alkylation due to the possibility to increase propene concentration by rectification of light fraction distilled off from the reaction mixture.

The distillate is returned to the reaction zone. In this case the conversion of propene more than 99% is achieved. The alkylation of benzene with ethylene is proceeds with a somewhat greater formation of dimers and of trimers. In this case reaching high selectivity EtPh/$Et_2C_6H_4$ (~ 20:1) more easily. Use as the raw material of concentrated ethylene makes it possible to carry out the

Table 1. Kinetics of benzene alkylation with propene on the sulfocation exchanger Amberlyst-36

Hydrocarbons, conversion, selectivity, duration	Initial benzene – propene mole ratio 4.5, 80°C. Concentrations, wt %					Initial benzene – propene mole ratio 7: 1, 80°C. Concentrations, wt %				
Duration, h	Initial	0.5	1.0	2.0	4.0	Initial	0.5	1.0	2.0	4.0
Propane	2.6	2.6	2.6	2.6	2.6	1.82	1.82	1.82	1.82	1.82
Propene[a]	10.3	4.6	2.7	0.7	0.06	7.02	2.79	1.58	0.18	0.01
Hexenes[a]	–	0.03	0.04	0.04	0.1	–	0.02	0.04	0.2	0.1
Nonenes[a]	–	0.04	0.16	0.2	0.2	–	0.05	0.2	0.3	0.2
Benzene	87.1	76.2	73.0	69.3	68.1	91.16	82.5	80.06	77.92	77.84
Isopropylbenzene	–	15.6	20.5	25.3	26.2	–	11.37	14.61	17.89	18.31
Diisopropylbenzene	–	0.6	0.98	1.83	2.63	–	0.45	0.73	1.45	1.64
Heavy alkylbenzenes	–	–	0.02	0.03	0.05	–		0.02	0.04	0.05
Diisopropyl ether	–	–	–	–	–	–	1.0	0.9	0.2	0.02
Propene conversion,%	–	55.0	73.5	92.9	99.4	–	60.2	77.5	97.5	99.8
Contribution to,%	–	95.5	94.4	92.2	89.5	–	93.7	93.5	92.5	
Isopropylbenzene/ diisopropylbenzene selectivity, wt	–	26.0	20.9	14.4	9.9	–	25.1	20.0	12.3	11.2

[a] Propene dimers and trimers.

Table 2. Kinetics of benzene alkylation on the sulfocation exchanger Amberlyst-36

Hydrocarbons, conversion, selectivity, duration	Initial benzene – ethylene mole ratio 3.1, 140°C. Concentrations, wt%		Initial benzene – ethylene mole ratio 6:1, 130°C. Concentrations, wt%			Initial benzene – ethylene mole ratio 8.6:1, 130°C. Concentrations, wt%	
Duration, h	Initial	4	Initial	2	4	Initial	5.0
Ethylene	10.4	2.7	5.5	2.2	1.4	4.0	0.9
Butenes[a]	–	0.1	–	0.1	0.1	–	0.1
Hexenes[a]	–	2.7	–	1.7	1.8	–	0.8
Octenes[a]	–	1.0	–	0.1	0.2	–	0.1
Benzene	89.3	78.7	94.5	88.5	87.5	96.0	89.1
Ethylbenzene	–	33.4	–	6.9	8.5	–	7.8
Diethylbenzenes	–	0.9	–	0.3	0.4	–	0.3
Heavy alkylbenzenes	–	0.6	–	0.2	0.3	–	0.1
Ethylene conversion, %	–	75.0	–	60.0	74.5	–	77.5
Contribution to ethylbenzene, %	–	–	–	–	–	–	–
Ethylbenzene/diethylbenzene selectivity, wt	–	15:1	–	23:1	20:1	–	26:1

[a] Ethylene dimers, trimers and tetramers.

process with ethylene conversion ~75% for one passage that with the use of a recycle does not exclude reaching the total conversion of ethylene in the process more than 99%.

Due to high enough selectivity alkylbenzene/dialkylbenzene (≥ 20: 1) it is possible to carry out the process without the disproportion of dialkylbenzene (with the benzene) and to conduct alkylation in the optimum temperature conditions.

If as the raw material is used not concentrated alkene, but its mixture with alkane (propane-propylene or ethane-ethylene fraction), then it is expedient to conduct rectification of these fractions distilled off from the reaction mixture, and to recirculate into the reaction the flow enriched by alkene.

There is an opinion that it is formidable difficultly to separate propene from propane by rectification because the propene–propane system is deflected significantly from the ideal one in the sense of Raul's law. This, however, concerns only obtaining highly concentrated propene, when the coefficient of the relative volatility (a) of propene and propane in the colum head is ~1.065. A study of phase equilibrium in the propene – propane system and their separation by rectification showed that enrichment of the mixture to propene concentration 60–65% is an inexpensive procedure, which is illustrated by Table 3.

It is evident in part from the Table 3 that on the column with the effectiveness of 50 theoretical plates the concentration of propene to 60% is reached at the reflux ratio $R = 0.9$, on the column of 30 theoretical plates with $R = 1.2$. Concentration to 70% is reached at $R = 2.8$. At the same time in the cases of use in the dephlegmator of usual recirculating water (temperature in the dephlegmator 44–45°C) the pressure in the column does not exceed 18 atm(abs.). These conditions are sufficiently soft, being not large power consumption.

Alkylation can be carried out in the direct-flow reaction zones or in the vapor-liquid reaction zones (preferably with the countercurrent of liquid and vapor) with the evaporation of the part of reaction mixture (in essence of propane and propene) for the heat removal.

The second version requires the use of coarse-grained (for example, molded) catalysts, that with their today's

Table 3. Parameters of rectification of propene (1)–propane (2) mixture

Propylene concentration, wt %		α_{12} in the column head	Number of theoretical plates	Reflux ratio	Temperature at the pressure 18 atm	
in the distillate	in the bottom (residual propane)				head	bottom
60	2.5	1.18	30	1.2	45	54
70	2.5	1.15	30	3.7	44	53
80	2.5	1.12	60	11.0	49	53
60	2.5	1.18	50	0.9	45	58
70	2.5	1.15	50	2.7	44	57
80	2.5	1.12	50	5.1	43	56
99.5	2.5	1.065	120	18–20	43	63

quality should be recognized as been risky.

With the use of the direct-flow sequential reaction zones (they can be located in one or several apparatuses) the flows are cooled in the space between the reaction zones. It is very useful a discrete feeding with the initial propene-propane or ethylene-ethane fraction, or ethylene, into the different sequential points, moreover, between the reaction zones the hydrocarbons are supplied cold and are fulfilled simultaneously the function of the refrigerant at the mixing. This method makes it possible to reduce the necessary quantity of recirculating benzene.

The second version requires the use of coarse-grained (for example, molded) catalysts, that with their today's quality it follows to recognize as that been risky. At the use of the direct-flow sequential reaction zones (they can be placed in one or several apparatuses) the flow cooling is conducted between the reaction zones. It is very useful the application of the discrete supply initial propane–propylene, ethane–ethylene or respectively ethylene into the different sequential points, moreover between the reaction zones the hydrocarbons will be given in a cool state and simultaneously is fulfilled the function of the refrigerant of mixing. This method makes it possible to reduce the necessary recirculation of benzene.

In the scheme is depicted synthesis of isopropylbenzene or ethylbenzenne at the direct-flow reaction zones with the intermediate cooling and the discrete feeding with alkene-containing raw material. The names of the flows which relate to the synthesis of ethylbenzene are given in the parentheses.

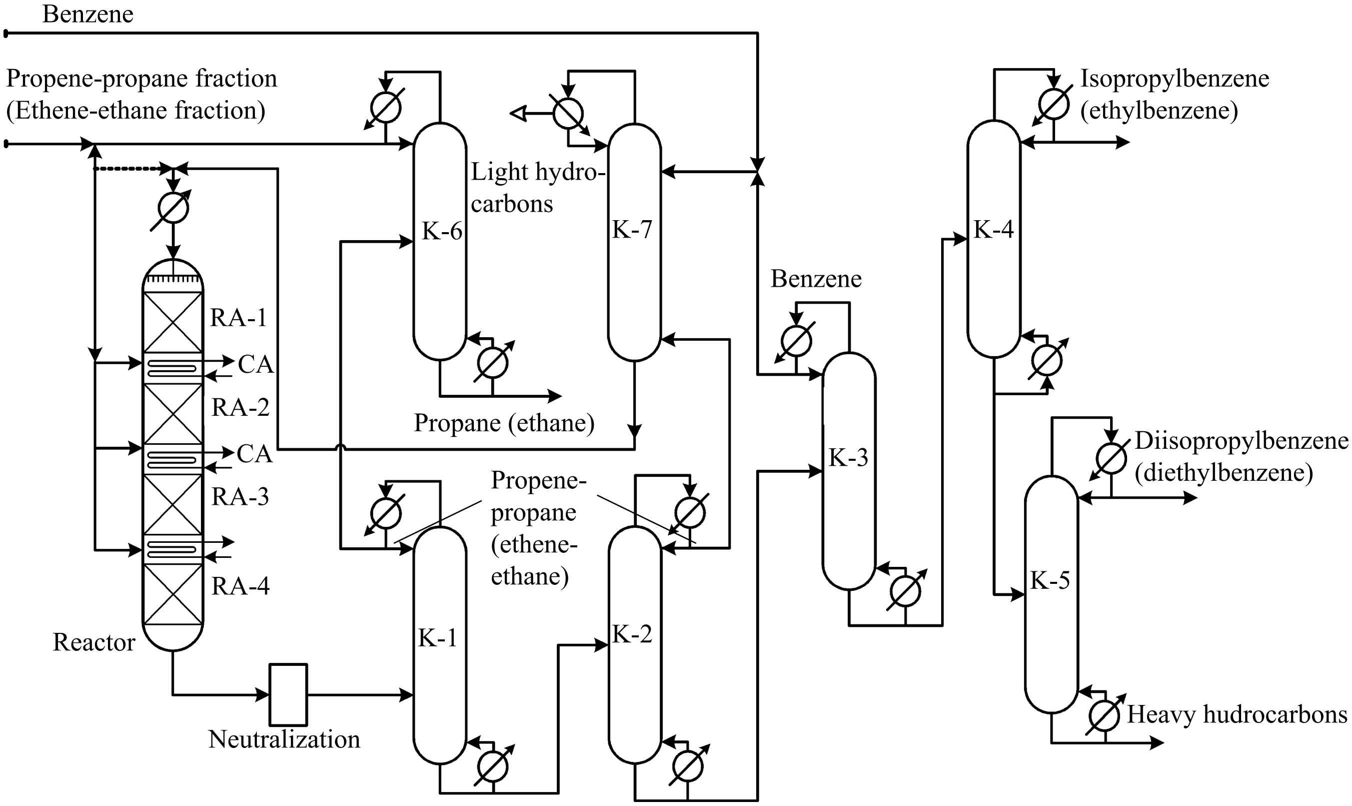
As a whole the scheme is intelligible without the special explanations. A problem at the development was distillation from the reaction mixture of the unreacted hydrocarbons C_3 (C_2) without the application of a special refrigerant for their condensation, i.e., with the use of usual recirculating water.

Distillation is achieved in two sequential apparatuses; first at the high pressure (in K-1), and then at smaller pressure (in K-2). The flow distilled from K-1 preferably (when a fraction rather than concentrated alkene is used as the raw material) is then separated by rectification in K-6 and the distillate enriched with alkene (for example. 60-65% of propene) is recirculated for the mixing with initial propylene – propane fraction (the same for ethylene–ethane fraction). The flow distilled form K-2 is passed for absorption with benzene in K-7 and is used for feeding to the reaction zone RZ-1.

The alkenes dimers and trimers are tertiary alkenes (C_4, C_6 and C_9); they interact enough actively with benzene and practically are not accumulated in the reaction unit or enter into EtPh or *i*-PrPh.

At the synthesis of *i*-PrPh from 1 ton of propene-propane fraction (80% propene) and 1.44 ton of benzene is produced 2.13 ton of *i*-PrPh with concentration 99.65% (~ of 0.1% of benzene, 0.2% of diisopropylbenzene, admixtures) and ~ 0.1 ton (2%) of the fraction of diisopropylbenzene with concentration 96%, and 2% of propene trimers and other more high-boiling admixtures).

By the energy consumption the process is somewhat better than the existing process with $AlCl_3$. The key advantage of process is the absence of highly aggressive medium, not necessary carefully remove of water from the raw material, no essential formation of harmful effluents (ecological purity).



Scheme of the synthesis of isopropylbenzene(ethylbenzene) by benzene alkylation with propene (ethylene) on the sulfocation exchangers. (RA) Reaction area, (CA) cooling agent.

At the synthesis of of EtPh from 1 ton of ethylene and 2.79 ton of benzene it is produced 3.5 ton of ethylbenzene with the concentration higher than 99% and 0.2 t of a fraction of diethylbenzenes with the concentration 97%.

By the analogous technology can be carried out the alkylation of benzene by *n*-butenes with obtaining of *sec*-butylbenzene. The latter is interesting because after its transformation into respective hydrogen peroxide and decomposition of the latter are formed not the phenol and acetone, but phenol and methylethylketone, which is more valuable than acetone.

The processes are protect by patent RU-2278102 [5] and by patent claims, which are now under examination.

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