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Abstract

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Some Questions Concerning the Use of the KU-2 Cation-Exchange Resin in the Alkylation of Phenols with Higher Olefins

Cation-exchange resins as catalysts for the alkylation reaction of phenols have substantial advantages over other catalysts (aluminum chloride, sulfuric acid, benzenesulfonic acid), among which should be included the possibility of repeated use. Phenomena observed in practice indicate that the catalytic activity of cation exchangers is not a constant quantity, but is a function of the operating time of the cation exchanger as a catalyst ($^{1-6}$). An analysis of the literature data gives no idea of the causes of the decrease in the catalytic activity of cation exchangers in alkylation processes. At the same time, the question of the fundamental possibility of prolonged operation of a cation exchanger cannot be resolved without confidence that, during alkylation, no changes occur in the structure of the cation exchanger that lead to the loss of free functional sulfo groups, which, according to the reaction mechanism, are the source of the catalytic activity of the cation exchanger.

Among the causes producing a decrease in the catalytic activity of cation exchangers, the following appear to be the most realistic: 1) partial decomposition of the polymer structure of the cation exchanger and dissolution of low-molecular-weight fragments in the alkylate, which leads to the removal of functional sulfo groups; 2) possible chemical reactions between the functional groups of the cation exchanger and the reacting components—phenols, alkylphenols, and olefins; 3) adsorption of resinous particles on the catalytic surface of the cation exchanger.

In order to determine the predominant causes of the loss of catalytic activity of cation exchangers, which is of great importance in choosing the method and conditions for catalyst regeneration, we carried out experimental work comprising the alkylation of phenol and a technical mixture of cresols (b.p. 180–205°, molecular weight 108, refractive index 1.5314) with propylene trimer (b.p. 130–160°, molecular weight 132, refractive index 1.4325) in the presence of KU-2 cation exchanger in the H-form, dried to constant weight, and subsequent investigation of the reaction products and the spent cation exchanger.

The alkylation reaction was carried out in a vertical reaction column provided with heating and filled with KU-2 cation exchanger (100 g). A mixture of phenol (or technical cresols) with propylene trimer was introduced into the feed heater; in the reaction column the temperature was raised to 120°, and by means of a stopcock a uniform rate of flow of the mixture of reagents through the cation-exchanger bed was established. In all experiments the rate was maintained at 1 ml of reaction mixture per 1 g of KU-2 per hour. The reaction products were separated by vacuum distillation.

The alkylation process was continued until the beginning of a decrease in the catalytic activity of the catalyst, which was detected from the decrease in the yield of alkylphenols. A decrease in the catalytic activity of the cation exchanger was observed after obtaining 40–45 g of alkylphenols from 1 g of KU-2 in the case

alkylation of pure phenol and 25–30 g with 1 g of KU-2 in the case of alkylation of a technical mixture of cresols.

Owing to the presumed cleavage of the polymer structure of the cation exchanger under the conditions of the alkylation process, low-molecular-weight compounds containing functional groups SO_3H should be formed and washed out by the liquid phase, as a result of which sulfur would be found in the latter. In fact, as analysis of the products of alkylation of phenol and technical mixtures of cresols with propylene trimer showed, they contain no sulfur. From this it may be concluded that cleavage of the cation exchanger under the conditions of the alkylation process, and the washing out of low-molecular-weight destruction fragments, either does not occur at all or occurs to a very insignificant extent.

The chemical interaction of the functional groups of the cation exchanger with the reacting components may be represented, on the one hand, by the formation of sulfoesters of olefins:

$$\text{cationite}\text{—}SO_3H + CH_2{=}C(R)(CH_3) \longrightarrow \text{cationite}\text{—}SO_2\text{—}O\text{—}C(CH_3)_2\text{—}R,$$

and, on the other hand, by the formation of sulfones with phenols and alkylphenols:

$$\text{cationite}\text{—}SO_3H + HO{-}C_6H_4{-}(R_1) \longrightarrow \text{cationite}\text{—}SO_2{-}C_6H_3(OH){-}(R_1).$$

The formation of sulfones and sulfoesters in the alkylation process would, along with a decrease in the catalytic activity of the cation exchanger, cause a reduction in its exchange capacity. To verify this fact, after its use in the alkylation reaction by the method described, the KU-2 cation exchanger was washed in the same column with alcohol to remove resinous particles and reaction components adsorbed on the active surface, and was then dried. No sulfur was found in the eluate, which indicates the absence in it of low-molecular-weight fragments of cation-exchanger destruction containing functional groups. The weight of the cation exchanger after elution and drying remained unchanged; its exchange capacity in all experiments approached the initial value (Table 1). Consequently, it may be considered that in the process of alkylation of phenols with higher olefins the functional SO_3H groups are preserved almost quantitatively in the unsubstituted state. Apparently, the polymer structure of KU-2 cation exchanger greatly diminishes the reactivity of the SO_3H groups and thereby reduces to a minimum their sulfonating action with respect to phenols and olefins.

Table 1

Material balance and exchange capacity of the initial and spent KU-2 cation exchanger

Specimen No.	Anhydrous KU-2 cation exchanger	Exchange static capacity, mg-eq/g	Weight of cation exchanger, g
1	Initial, before alkylation	4.68	100.00
2	After alkylation of phenol with propylene trimer	4.60	100.06
3	After alkylation of technical cresols with propylene trimer	4.58	100.13

On the basis of the fact that the cation exchanger used in the alkylation reaction, when washed with solvent, exhibits the initial exchange capacity, and that the liquid phase (alkylate and eluate) contains no destruction products

the cation exchanger, and the material balance for the cation exchanger (Table 1) indicates the absence of any substantial changes in the weight of the cation exchanger; of all the above-mentioned causes leading to a decrease in the catalytic activity of the KU-2 cation exchanger, the predominant one should be considered to be adsorption of resinous particles on the catalytic surface.

It has been established that the rate of decline of the catalytic activity of the cation exchanger depends on the starting material. As noted above, in the alkylation of a technical mixture of cresols, which are more prone than phenol to oxidation and resinification, the catalytic activity of the cation exchanger begins to decrease almost twice as fast as in the alkylation of pure phenol. This fact also points to the decisive importance of adsorption of resinous particles in the phenomenon of decreased catalytic activity of the KU-2 cation exchanger.

It follows from the foregoing that, when selecting a method for regenerating the catalyst, attention must be paid to the most complete possible freeing of the surface of the cation exchanger from resinous particles.

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