Deactivation of the catalytic complex of obtaining alkylbenzenes by oxygenate compounds

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Abstract. The possibility of environmentally safe and energy-saving deactivation of the catalytic complex based on aluminum chloride used in the process of alkylation of benzene with olefins, oxygenate compounds – epoxy soybean oil, propylene oxide and isopentane oxidation products is shown. It has been established that the deactivating ability increases in the series: oxygenates → propylene oxide → epoxidized soybean oil (ESBO).

1. Introduction
The sources of many environmental problems associated with the formation of wastewater are industrial enterprises [1-8].

Production of ethyl- and isopropyl benzene is one of the most large-scale commercial processes in terms of consumption and processing of benzene. Almost 75% of the petrochemical benzene produced in the world is consumed in the production of ethylbenzene and isopropyl benzene. Almost all ethylbenzene is used in the production of styrene, the most important monomer for polymers production[9].

The technology of alkylation of benzene with ethylene (propylene) in the presence of liquid-phase acid catalysts has been introduced at many petrochemical enterprises in Russia and in the world. Aluminum chloride is widely used as an active component of the catalyst system because of its following advantages: use of a smaller molar excess of benzene relative to olefin; ability to catalyze both alkylation and transalkylation reactions, mild conditions of the process[10-14]. However, the use of aluminum chloride has a number of disadvantages: equipment corrosion; formation of a large amount of wastewater at the stage of the catalytic complex deactivation [15-19].

Traditionally, deactivation of AlCl₃-based catalyst complexes is carried out by aqueous-alkaline treatment of the reaction products. This produces a large amount of wastewater. In the production of 1 ton of ethylbenzene, 10 tons of wastewater is formed. Disposing 1 ton of wastewater costs 6000 rubles. If the company produces 100 thousand tons of ethylbenzene per year, then the approximate cost of wastewater disposal will be 6 billion rubles. Thus, the technology of producing alkyl benzenes in the presence of AlCl₃ is energy-intensive and environmentally hazardous. Solving the problem of reducing the amount and even eliminating the formation of polluted wastewater is an urgent task.

In recent years, the use of epoxy compounds, in particular, olefin oxides [20], for example, propylene oxide (PO) for deactivation of catalyst systems based on metal chlorides has been described.

Along with non-technological PO, more high-boiling epoxy compounds, such as epoxy resins, are used. [21-23].
It is worth noting that the use of epoxy compounds for the deactivation of catalyst systems based on Lewis acids is described only for the polymeric petroleum resin synthesis processes, but for deactivation of catalytic systems in alkylation processes, with the exception of our published results [24], there is no information available. Oxygen-containing organic compounds formed during the oxidation of saturated hydrocarbons, in particular isopentane, were used as deactivating agents for the first time. [25-29].

The purpose of the study - the development of environmentally friendly process of deactivating the catalyst complex used in industrial processes for the alkylation of benzene with ethylene or propylene with oxygenate compounds.

To assess the possibility of deactivating the catalyst complex used in industrial processes for the alkylation of benzene with ethylene or propylene with oxygenate compounds, the model reaction of benzene alkylation with hexene-1 was chosen. Gustavson liquid complex, obtained on the basis of aluminum chloride, propyl chloride and benzene, was used as a catalyst ($\text{AlCl}_3 : \text{C}_7\text{H}_7\text{Cl} : \text{C}_6\text{H}_6 = 1 : 0.5 : 2$ mol.). As a deactivating agent, propylene oxide, epoxidized soybean oil, and products of liquid-phase oxidation of isopentane were used.

2. Experimental part

The physical and chemical characteristics of the epoxidized soybean oil are presented in table 1.

| Indicator                          | Value   |
|------------------------------------|---------|
| Colorsaturation (Pt-Co)            | 120     |
| Density, g/cm$^3$                  | 0.993   |
| Epoxy oxygen content, % wt.       | 6.2     |
| Acid index, mg KOH/g              | 0.5     |
| Iodine index, g I$_2$/100 g       | 1.6     |
| Flash point, °C                    | 300     |
| Refraction index, 20 °C            | 1.47    |

Isopentane oxidation is carried out in the liquid phase at a batch plant, in the metal reactor, equipped with a tank jacket, a cooler, systems for hydrocarbon dosing and loading, and a cooled sampling instrument. A porous ceramic plate is installed at the bottom of the reactor to form a stream of small gas bubbles. The process is carried out at a temperature of 120 °C and a pressure of 30 kgf/cm$^2$.

The composition of oxidation products is given in table 2.

| S No. | Components   | Content,% mass |
|-------|--------------|----------------|
| 1     | Isopentane   | 85.48          |
| 2     | Alcohols     | 4.29           |
| 3     | Ketones      | 6.85           |
| 4     | Esters       | 1.71           |
| 5     | Ethers       | 0.15           |
| 6     | Heterocycles | 1.17           |
| 7     | Diols        | 0.29           |
| 8     | Acids        | 0.07           |
| Total |              | 100            |

Propylene oxide is a colorless liquid with an etheric odor. It is mixed with water in a volume ratio of 1:1.5 (20 °C), ether and alcohol.

The physical and chemical characteristics of the propylene oxide are presented in table 3.
The catalyst complex is prepared in a vessel with a hermetically-sealed plug to prevent the ingress of moisture. The calculated amounts of toluene and aluminum chloride are loaded, and then propyl chloride is added. The resulting mixture is kept for at least 6 hours at a temperature of 60°C. The resulting catalyst complex is a homogeneous system.

Alkylation is carried in a three-neck glass flask equipped with a mixing device and a back flow condenser. The flask is loaded with feed materials – benzene and catalyst complex. Then, hexane-1 is added via the addition funnel while stirring intensively. Alkylation reaction is carried out at a temperature of 60°C for 3 hours. The concentration of the aluminum chloride catalyst complex is 2% of the mass.

| Table 3. The physical and chemical characteristics of the propylene oxide |
|-------------------------------------------------|
| Indicator                        | Value               |
|----------------------------------|---------------------|
| Melting point, $T_M$, °C         | 104.4               |
| Boiling point, $T_B$, °C         | 34.5 - 34.9         |
| Flashpoint, °C, higher than      | -30                 |
| Density, 20 °C, $\rho$, g/cm³    | 0.859               |
| Refraction index, $n^20_D$       | 1.3667              |

The process of the catalyst complex deactivation is carried out by adding the calculated amount of the deactivating agent to the alkylation reaction mass. During the deactivation process, samples of reaction mass, in which the amount of free AlCl$_3$ and the degree of the catalyst complex deactivation are determined, is taken according to the methodology given in the work [10].

IR spectra were obtained by FTIR spectroscopy on a Thermo Scientific Nicolet iS10 spectrometer.

The aluminum content in the bottom product was determined by burning samples of the bottom product in a muffle furnace at a temperature of 800 °C until constant mass was reached [30].

3. Results and its discussion

Since aluminum chloride is particularly dangerous in terms of the release of aggressive HCl, deactivation can be carried out by transferring it to a compound that does not have acidic properties and is not capable of producing HCl.

In general, the scheme of a catalyst complex deactivation with an epoxy compound can be represented as follows [11]:

$$3 \text{ R} \text{CHCH}_2 + \text{AlCl}_3 \rightarrow \text{AlO} \left( \text{CHCHClCHR}_3 \right)$$

Thus, during the deactivation reaction, the termination no free aluminum chloride occurs with the formation of a stable organic compound and thereby the release of free hydrogen chloride is prevented.

Initially, the deactivation process was studied on a model system, which was a solution of a catalyst complex in toluene. Epoxidized soybean oil was used as a deactivating agent.

In the course of the work, the influence of temperature, the molar ratio of aluminum chloride and epoxy groups (EG) [AlCl$_3$]:[EG], and the nature of the deactivating agent on the degree of deactivation was studied.
Figure 1. Dependence of AlCl₃-containing catalyst complex degree of deactivation on molar ratio of [AlCl₃]:[EG] in the reaction mass at temperature $T=50\, ^\circ\text{C}$ (1), $60\, ^\circ\text{C}$ (2), $70\, ^\circ\text{C}$ (3).

As the figure shows, the degree of deactivation increases with the increase of molar ratio and temperature of deactivation. A further increase in the molar ratio and temperature was impractical, since no increase in the degree of deactivation of the catalyst complex was observed.

Thus, the optimal conditions for the deactivation of the catalyst complex were selected: molar ratio $[\text{AlCl}_3]:[\text{EG}]=1:3$; temperature $70\, ^\circ\text{C}$; time 45 minutes, at which the degree of deactivation reaches 98%.

Then the deactivation process was studied on a model reaction of benzene alkylation with hexene-1.

As deactivating agents, compounds containing oxirane rings, which are propylene oxide and epoxidized soybean oil (ESBO), and oxygenates were used. Their composition is given in table 2.

Deactivation was carried out for 60 minutes at a temperature of $70\, ^\circ\text{C}$ and a molar ratio of $[\text{AlCl}_3]:[\text{EG}]=1:3$.

Study in the process of the AlCl₃-containing catalyst complex deactivation in the reaction mass of benzene alkylation with hexene-1 by time (Fig. 2) showed that the most effective deactivating agent was ESBO. In this case, the degree of the catalyst complex deactivation (the degree of AlCl₃ conversion to a neutral compound) was 98%. The products of isopentane oxidation turned out to be the least effective, which may be due to the fact that they contain oxygen-containing groups of a different nature.

Figure 2. Dependence of AlCl₃-containing catalyst complex degree of deactivation on time of deactivation of benzene alkylation with hexene-1. 1 – ESBO, 2 – propylene oxide, 3 – isopentane oxidation products.

When an excess of epoxidized soybean oil is used for catalyst complex deactivation, a sufficiently large amount of the product of its interaction with AlCl₃ may be formed. As a result, the problem of finding ways for its qualified use arises. After deactivation, the reaction mass was subjected to vacuum
distillation, and after the fractionation in the temperature range of 90-100 °C and a vacuum of 15 Mmhg the bottom product was obtained, which was a gel-like homogeneous mass of a dark yellow color.

According to IR spectroscopy, the transmission band in the region of 820 cm\(^{-1}\), typical for epoxy groups and present on the spectrum of epoxidized soybean oil (Fig. 2, curve 2), is absent in the spectrum of the bottom product (Fig. 2, curve 1). This indicates that the deactivation process is carried out with the opening of the epoxy ring. In addition, a wide band is observed in the spectrum of the bottom product in the region of 3400 cm\(^{-1}\), which may be due to the presence of hydroxyl groups in it. There is also a wide band in the region of 1600 cm\(^{-1}\), which may indicate the presence of aromatic compounds with unsaturated group [30].

![Figure 3. IR spectra of the bottom product obtained during the deactivation of aluminum chloride by epoxidized soybean oil (1), epoxidized soybean oil (2).](image)

The fact that aluminum passes into a bound state and remains in the bottom product after the process of deactivation can determine further uses of the bottom product.

### Table 4. Aluminum content in the bottom product

| Molar ratio [ESBO] : [AlCl\(_3\)] | Al content in the bottom product, % |
|----------------------------------|----------------------------------|
|                                  | Theoretical | Experiment |
| 6:1                              | 1.18        | 0.50       |
| 6:1                              | 1.18        | 0.55       |
| 3:1                              | 1.50        | 0.60       |
| 3:1                              | 1.50        | 0.60       |

As the table shows, the Al content in the bottom product is 0.5-0.6% by weight.

The presence of various functional groups and aluminum in the composition of the bottom product allows us to consider the possibility of using it as a modifying, multifunctional additive to polymers.

### 4. Conclusion

For the first time, the laws of deactivation of an AlCl\(_3\)-containing catalyst system for the alkylation of benzene with olefins with oxygen-containing compounds have been established. It was established that the deactivating ability increased in the series: oxygenates C\(_5\) → propylene oxide → ESBO. The degree of deactivation increases with increasing molar ratio [AlCl\(_3\)] : [EG], temperature, and process duration.

Using the technology of the AlCl\(_3\)-based catalyst system deactivation with oxygenate compounds gives a positive environmental effect and reduces waste disposal costs.
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