



Alkylation of benzene with ethylene in the presence of dimethyldichlorosilane



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ABSTRACT

The kinetics of the alkylation of benzene with ethylene in the presence of dimethyldichlorosilane (DMDCS) are studied and a kinetic equation for this homogeneous irreversible reaction of the second order is created. The circulation of the DMDCS catalyst does not reduce its initial activity in relation to the formation of ethylbenzene and diethylbenzenes. The presence of moisture in the initial $C_6H_6 + C_2H_4 + DMDCS$ mixture reduces the catalyst activity. The dehydration of the starting mixture by removal of moisture from benzene was carried out using an azeotropic distillation. A reaction mechanism for the benzene alkylation with ethylene in the presence of DMDCS is formulated based on the generalized quantum-chemical principle and the theory of groups. The participation of DMDCS in the process of hydrocarbon conversion is confirmed experimentally and theoretically for the first time.

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1. Introduction

Ethylbenzene (ETB) is a product that is manufactured in excess of several million tons per year. It is used for the production of styrene, its polymers and copolymers, as well as chlorine- and oxygen-containing compounds, and other products [1]. Scientists worldwide have carried out research aimed at the improvement of the production process of ETB through the development of new catalysts and technologies for the alkylation of benzene with ethylene.

The industrial alkylation process of benzene with ethylene, outlined in 1877 by the studies of Friedel, Crafts, and Gustavson, is conducted on polyalkylbenzene in the presence of an aluminum chloride complex.

Approximately 50% of ethylbenzene is produced in the presence of the $Al_2Cl_6 \cdot nArR$ complex. This technology has been implemented and described in articles and monographs by several research groups [1–5].

An important direction of the work of both research groups and educational institutions is the development of effective aluminosilicate zeolites as catalysts for benzene alkylation [6,7].

The number of scientific publications reflects the great deal of research work that has been performed on the alkylation of benzene with ethylene in the presence of homogeneous and heterogeneous catalytic systems [8–22].

The investigation of the alkylation of benzene with ethylene over the faujasite zeolite by the ONIOM method has been described [8]. Beta, MCM-22, USY-1, and USY-2 zeolites have been shown to efficiently activate the C_6H_6 and C_2H_4 molecules for the alkylation of benzene with ethylene in the liquid phase, under pressure and at low temperatures [9]. It has been established that the zeolite activity increases in the order $MCM-22 > Beta > USY-1 > USY-2$ [18].

In another study, the usage of tablets of clay mixed with aluminum oxide as active catalyst has been described [10].

It has also been established that the reasonable processing of the zeolites MCM-49 and MCM-22 in a 0.025 N sodium hydroxide solution increases the selectivity of the catalyst to ETB up to 97% at $P = 3.5$ MPa and $T = 493$ K in the liquid phase [11].

In another reports, the authors postulated that the weak and strong catalytic centers of the MCM-56 zeolite might participate in the catalytic alkylation process [12,13].

The zeolite β exhibits an enhanced catalytic activity [14]. The zeolite MCM-49 possesses a high selectivity, and a correlation has been found between the activity and the content of the Brønsted centers on the zeolite surface and in its lattice [15].

The oxidative alkylation of benzene with ethylene is effective over the ZSM-5 zeolite. [16]. The ETB selectivity in the liquid phase

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alkylation of benzene with ethylene over the H-TMP-16 zeolite at 200–260 °C reaches 99% [17,18].

An interesting study on the alkylation of benzene with ethylene in the presence of MCM-49 zeolites was also carried out [19]. The mesoporous zeolites are more active (2–10 wt%) in the alkylation of benzene with ethylene in the liquid phase and more selective towards ETB (90–97%), compared to conventional zeolites [20–22,16].

A catalyst based on MCM-22 was used in technology, and named as EBMax™ by Mobil–Raytheon. In this application, the alkylation is performed in the liquid phase. The first industrial application was realized in 1997 [23,24].

In different studies [18–22,16], the mechanism of the alkylation of benzene with ethylene was explained by the presence of $\{\text{AlO}_4\cdot\text{SiO}_4\}$ tetrahedral ensembles in the lattice of zeolites [25–27]. The reaction over the aluminosilicate catalyst surface occurs at the centers of the $\{\text{AlO}_4\cdot\text{SiO}_4\}$ tetrahedral ensembles [28–31]. The ensembles of $\{\text{AlO}_6\cdot\text{SiO}_4\}$ are catalytically inactive. The basic understanding of the catalysis over zeolites is presented in the theory of catalysis by polyhedra [29–33].

The objective of this work is to develop a new catalyst that is non-toxic, completely soluble in liquid aromatic hydrocarbons, easily separated from the alkylation products during its circulation in the system, and capable of forming environmentally friendly products of hydrolysis.

2. Experimental methods

Experiments involving the alkylation of benzene with ethylene were carried out in an autoclave at elevated pressure (up to 10 atm) and temperatures up to 573 K. The ethylene used in the experiments was of 98.88 wt% purity, while benzene was of chemical purity grade. DMDCS was used as catalyst.

Pre-estimated amounts of benzene and DMDCS were loaded into the autoclave, and ethylene was then injected under pressure.

Benzene was purified by shaking with concentrated H_2SO_4 to remove thiophene, then washed with distilled water, and dried in a desiccator over concentrated H_2SO_4 .

The reaction mixture was analyzed chromatographically. The mixture of benzene and DMDCS was distilled from the reaction mixture on a distillation column to be reused in further alkylation experiments.

3. Results and discussion

3.1. Effect of the DMDCS concentration on the yield of the alkylation products

The study of the alkylation of benzene with ethylene was carried out in an autoclave by varying the DMDCS concentration (10, 20, and 24 wt%) in the reaction mixture and according to the following experimental parameters: $T = 513 \text{ K}$, $\gamma = \frac{n_{\text{C}_6\text{H}_6}}{n_{\text{C}_2\text{H}_4}} = 3:1$, contact time τ from 0.5 to 5 h, and initial pressure of 10 atm. Ethylene was fed into the autoclave from a cylinder where it was enclosed under a pressure of 50 atm. The results of these experiments are presented in Table 1.

The composition of the products in the reaction mixture was determined chromatographically. Hexene was formed as a result of the ethylene polymerization reaction (trimerization).

According to Table 1, an increase in the yield of ethyl benzene occurs with increasing DMDCS concentrations in the reaction mixture under the initial pressure of 10 atm and temperature of 513 K. The highest yield of ethyl benzene of 28.78 wt% at $\gamma = \frac{n_{\text{C}_6\text{H}_6}}{n_{\text{C}_2\text{H}_4}} = 3:1$ was obtained at a concentration of DMDCS of 24 wt% and $\tau = 5 \text{ h}$.

These data are comparable with those obtained by using the aluminum chloride catalytic complex from the industrial alkylation installations.

The advantages of the alkylation process of benzene with ethylene in the presence of DMDCS are:

- complete DMDCS solubilization in aromatic hydrocarbons with the formation of a true thermodynamically stable solution;
- the alkylation takes place in a homogeneous mixture;
- the catalyst is non-toxic and the products of its hydrolysis are environmentally friendly;
- the boiling points of benzene and DMDCS are very close, thus these components can be distilled together out of the reaction mixture for their subsequent circulation through the alkylation unit;
- DMDCS is stable in the reaction mixture in the absence of moisture, and its high activity and selectivity remain unchanged.

In view of this, the DMDCS catalyst favorably differs from the aluminum chloride complex used with polyalkylbenzene.

3.2. Calculation of the equilibrium output

The process of benzene alkylation with ethylene generally occurs at temperatures up to 573 K and atmospheric pressure, and with a molar ratio of benzene to ethylene equal to 3:1. The experiments described in this study were carried out at temperatures ranging from 353 to 573 K, and the thermodynamic parameters were calculated for this range. The standard Gibbs free energy change was obtained according to the equation:

$$\Delta_r G_T^\circ = \Delta_r H_T^\circ - T \cdot \Delta_r S_T^\circ,$$

where $\Delta_r G_T^\circ$ is the standard Gibbs free energy change for the benzene alkylation reaction with ethylene, $\Delta_r H_T^\circ$ is the enthalpy of the reaction, and $\Delta_r S_T^\circ$ is the entropy change of this reaction. These thermodynamic characteristics of the reaction were calculated using the data from the standard heat of formation of benzene, ETB, and ethylene and their standard entropies [34]. The resulting equation is:

$$\Delta G_T^\circ = -103818 + 142.687 \cdot T,$$

in Joules.

The following values of the Gibbs free energy change were obtained:

$$T = 353 \text{ K}, \Delta G_{353}^\circ = -53449 \text{ J/mol};$$

$$T = 453 \text{ K}, \Delta G_{453}^\circ = -39180 \text{ J/mol};$$

$$T = 573 \text{ K}, \Delta G_{573}^\circ = -22058 \text{ J/mol}.$$

The calculated equilibrium constants were obtained according to the equation:

$$K_p = e^{\frac{-\Delta G_T^\circ}{RT}}.$$

The numerical values of the equilibrium constants at $T = 353, 453, \text{ and } 573 \text{ K}$ were equal to: $K_{p,353} = 1.23 \cdot 10^8$, $K_{p,453} = 32,960$, and $K_{p,573} = 102.53$.

Therefore, the equilibrium yield of ethylbenzene is 0.999 mol fraction at these temperatures. Consequently, the thermodynamic conditions do not limit the kinetics of the alkylation of benzene with ethylene, and the kinetics of the process reflect the occurring of a kinetically irreversible reaction.

3.3. Kinetics of the alkylation process

The kinetics of the benzene alkylation with ethylene in the presence of DMDCS at the initial pressure of 10 atm, $T = 513 \text{ K}$, and molar ratio of benzene to ethylene of 3:1 were studied at

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