



Short communication

## Efficient catalysts for benzene alkylation with olefins



I.M. Kolesnikov, V.A. Vinokurov, P.A. Gushchin\*, E.V. Ivanov, S.I. Kolesnikov, V.A. Lyubimenko

Federal State Budgetary Educational Institution of Higher Education "Gubkin Russian State University of Oil and Gas (National Research University)", Leninskii Prospekt, 65/1, Moscow 119991, Russia

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### ABSTRACT

The experimental data of benzene alkylation with ethylene and propylene in the presence of methyl and ethylchlorosilanes are presented in this article. The catalytic activity series are determined for the methyl and ethylchlorosilanes. These compounds are found to demonstrate high catalytic activity and selectivity in the alkylation reactions and can be used in place of aluminum chloride. The computational study reveals the linear dependence between the charges, acceptor capacities and activities of the catalysts in the alkylation reactions.

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Investigations on benzene alkylation with ethylene and propylene were started in the classical papers of C. Friedel, J. M. Crafts and G. Gustavson [1,2]. Thus, complexes of aluminum chloride and aromatic molecules have been used as catalysts since the second half of the 19th century.

These catalytic complexes were used to design commercial units for the synthesis of alkyl benzenes by alkylation of benzene with olefins [1–5]. The catalyst is obtained on the commercial scale by the interaction of aluminum chloride with alkyl benzene in the liquid state. However, the liquid complex hardly dissolves in the liquid reaction mixture. Therefore, the process is carried out in an emulsion state, where the catalyst is a dispersed phase.

The colloidal state of the reaction mixture has disadvantages because aluminum chloride complexes participate in alkylation reaction only at the surface layer, but a significant part of the catalyst is in the volume of the drops and is inaccessible to benzene, ethylene and propylene. This fact dramatically decreases the alkylation reaction rate and selectivity. Moreover, the aluminum chloride complex is easily hydrolysable by moisture and cannot be recycled.

Therefore, the development of technology projects for the alkylation of benzene with olefins in the presence of new high-performance catalysts is carried out continuously [3–9].

Recently, ionic liquids [10,11] and  $\text{H}_3\text{PO}_4$  [12] were used as catalysts for benzene alkylation. Organic compounds of transition metals (Rh, Cu, and Co) were applied for the oxidative alkylation of benzene with ethylene with formation of styrene [13]. For benzene alkylation with olefins, HF [14] and ion-exchange resins [15] can also be used. However, HF shows a high toxicity, and the resins have a low thermal stability.

Studies of alkylation processes catalyzed by solids such as zeolites and silicates with functionalized surfaces are intensively being developed [16,17]. A significant number of studies [18–25] dedicated to complexes of the transition metals: Ir, Rh, Cu and Pd for activation of the C–H bonds of aromatic compounds, and in the presence of  $\text{O}_2$ , alkylation with olefins proceeds with the formation of alkyl arenes [26]. All of these catalysts have advantages and disadvantages. For commercial applications, it would be useful to employ alkyl chlorosilanes as catalysts for homogeneous alkylation processes.

Results of benzene alkylation with ethylene and propylene in the presence of new alkyl chlorosilane catalysts are presented in this paper. Furthermore, we discuss experimental and theoretical results on the investigation of the catalytic activity of alkyl chlorosilane compounds depending on the number of chlorine atoms and alkyl groups in a molecule. Mechanistic studies are also given. The main advantage of alkyl chlorosilanes is that they fully dissolve in liquid hydrocarbons, resulting in the formation of a true solution. The alkylation process is carried out on the molecular level in the presence of the organochlorosilanes. This causes increasing activity and selectivity of the catalysts. Alkylchlorosilanes together with benzene are extracted from the reaction mixture via rectification and then recycled. Experimental data of the alkylation process and theoretical computation of catalysis features with mechanistic investigations are presented below.

### 1. Benzene alkylation with ethylene

In the experiments benzene with the following properties was used:  $n_D^{20} = 1.5011$ ,  $\rho_4^{20} = 0.879 \text{ g/cm}^3$ , b. p. = 353 K. Ethylene and propylene with purities of 98.88% and 99.5%, respectively, were used. The properties of the catalysts are presented in Table 1.

\* Corresponding author.

**Table 1**  
Physicochemical properties of the alkyl chlorosilanes.

Formula	Mol. weight	$n_D^{20}$	$\rho$ , g/cm <sup>3</sup>	T, K
(CH <sub>3</sub> ) <sub>3</sub> SiCl	108.05	1.3888	0.8581	330.85
(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	129.06	1.4052	1.0715	343.25
CH <sub>3</sub> SiCl <sub>3</sub>	149.48	1.4129	1.2765	338.85
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> SiCl	150.73	1.4213	0.8970	419.94
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SiCl <sub>2</sub>	157.11	1.4309	1.1060	403.55
C <sub>2</sub> H <sub>5</sub> SiCl <sub>3</sub>	163.50	1.4257	1.2449	371.95

From Table 1 data one can note the following peculiarities in the properties of the methyl- and ethylchlorosilanes. The highest boiling point of methylchlorosilanes is observed for dimethyldichlorosilane. The boiling point of ethylchlorosilanes regularly decreases in the specified table row. The density of these compounds increases due to packing density increasing of molecules in the volume of liquid alkylchlorosilanes in the sequence from trialkylsilanes to dialkyl- and monoalkylsilanes.

Catalytic benzene alkylation was carried out in the autoclave with a constant volume of the reaction mixture and in a feed-batch reactor with the continuous feed of ethylene and propylene into liquid benzene with stirring. At first we used only dimethyldichlorosilane (DMDCS) with 99.9% purity as a catalyst.

The alkylation process was carried out at various temperatures, pressures and contact times ( $\tau$ ). The results of the experiments are given in Table 2.

The obtained results show that the main product of benzene alkylation with ethylene under increasing temperature and contact time is ethylbenzene (EB). However, there are hexenes and diethylbenzene (DEB) in the reaction mixture. The alkylation process is carried out with a high DMDCS selectivity for EB formation. The high selectivity of the catalyst can be accounted for by the following: DMDCS fully dissolves in liquid hydrocarbons, forms a true solution and single molecules participate in the reaction. Additionally, there are no triple collisions between catalyst and substrate molecules.

The activity of DMDCS molecules increases in the presence of stoichiometric or a stoichiometric additives. Ethylchloride (C<sub>2</sub>H<sub>5</sub>Cl) was added to the reaction mixture as a stoichiometric component. The yields of benzene, EB and DEB are 69.6 wt.%, 29.6 wt.% and 4.61 wt.%, respectively, under the following conditions:  $P = 10$  atm,  $C_{DMDCS} = 0.5$  wt.%,  $C_{C_2H_5Cl} = 0.5$  wt.% and  $T = 533$  K. The DEB yield increased by 27 wt.% in the presence of a stoichiometric additive compared to the alkylation process without a stoichiometric component.

The influence of the temperature on the alkylation product yields at  $P = 10$  atm,  $\tau = 3$  h, benzene/ethylene molar ratio = 3:1 and  $C_{DMDCS} = 0.5$  wt.% is presented in Table 3.

From the data obtained in the temperature range of 513–573 K, it can be observed that there is a maximum yield of EB at  $T = 533$  K. This result may be explained by the appearance of thermodynamic

**Table 3**  
The influence of the temperature on product yields, wt.%.

T, K	$P_{fin}$ , atm	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>12</sub> (hexene)	EB	DEB
513	6.6	89.53	1.21	15.90	0.32
533	7.0	76.23	1.94	21.18	0.62
553	7.5	81.254	2.08	15.3	0.86
573	6.7	82.68	2.42	14.10	0.80

restrictions when the temperature of the reaction mixture rises or by the formation of dimers and trimers of ethylene.

The benzene alkylation was also carried out with propylene in the presence of ethylchlorosilanes at various temperatures. The obtained results are given in Table 4.

Ethylchlorosilanes are arranged in the following series according to their activity in the alkylation reaction: C<sub>2</sub>H<sub>5</sub>SiCl<sub>3</sub> > (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SiCl<sub>2</sub> > (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>SiCl. As will be shown below, the same trend exists for the charges of the silicon ions in the ethylchlorosilanes (see Fig. 2).

Benzene alkylation with propylene in the presence of methylchlorosilanes was also studied in an autoclave at an initial pressure of 10 atm. The experimental data are presented in Table 5.

Table 5 data show that with increasing the number of methyl groups in molecules of methylchlorosilanes their activity in the alkylation reaction decreases and with the temperature increasing their catalytic activity increases.

Experimental data obtained allow arrange methylchlorosilanes in the following series according to their activity: CH<sub>3</sub>SiCl<sub>3</sub> > (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> > (CH<sub>3</sub>)<sub>3</sub>SiCl. The highest alkyl benzenes yield was obtained in presence of methylchlorosilane at 423 K. We note the difference in the data presented in Table 2 with the data in Tables 4 and 5. Table 2 includes data on the alkylation of benzene in the presence of dimethyldichlorosilane, while Tables 4 and 5 in the presence of ethylchlorosilanes and methylchlorosilanes. However, the alkylation activity of alkylchlorosilanes in series for the process of benzene alkylation with olefins following from Table 2 match the data given in Tables 4 and 5. To clarify the action mechanism of catalysts on the molecules of the reagents quantum-chemical calculations were carried out with the formulation of the mechanism of alkylation. Quantum chemical computations were performed to determine the structures of the molecules of alkylchlorosilanes, charge distribution in these molecules and their activity and selectivity in benzene alkylation reactions.

## 2. Quantum chemical computations of the structure and properties of reactants and catalysts for benzene alkylation with propylene

The computation of energetic and geometric parameters of methyl- and ethylchlorosilanes was performed by means of the DFT and TDDFT using B3LYP functional with aug-cc-pVDZ basis set in the program complex GAMESS [27–29]. The computation was carried out for molecules

**Table 2**  
Kinetics of benzene alkylation with ethylene in the presence of DMDCS ( $P_{in}$ ,  $P_{fin}$  – initial and final pressure of the reaction mixture).

$\tau$ , hours	$C_{DMDCS}$ , wt.%	$P_{in}$ , atm	$P_{fin}$ , atm	Hexenes	Benzene	Ethylbenzene	Diethylbenzene
$T = 513$ K							
2	10	10	9.0	0.52	93.66	5.63	–
3	10	10	8.4	0.89	88.15	11.85	–
5	10	10	6.8	2.34	81.61	15.89	0.13
0.5	20	10	9.5	0.20	95.75	3.47	0.06
1.0	20	10	7.5	0.43	93.80	5.68	0.09
2.0	20	10	7.3	0.46	86.21	13.14	0.10
3.0	20	10	6.2	3.34	72.69	23.57	0.21
$T = 553$ K							
0.5	0.5	10	7.6	0.60	86.92	12.13	0.12
3.0	0.5	10	4.5	0.75	75.61	23.30	0.32
5.0	0.5	10	3.0	1.92	65.64	32.80	1.64

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