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# Alkylation of Aromatic Hydrocarbons with 2-Methyl-2-Vinyl-*gem*-Dichlorocyclopropane over Zeolite Catalysts

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**Abstract**—It has been found as a result of the investigation of the catalytic properties of various microporous zeolites (of FAU, BEA, MOR, and MFI structural types) and a micro—meso—macroporous H-Ymmm zeolite (FAU) in the alkylation reaction of arenes (benzene (**II**) and toluene (**III**)) with the unsaturated compound 2-methyl-2-vinyl-*gem*-dichlorocyclopropane (**I**) that the reaction proceeds with the formation of chloroalkylarenes [1-(2,2-dichloro-1-methylcyclopropyl)ethyl]benzene (**IV**) and 1-[1-(2,2-dichloro-1-methylcyclopropyl)ethyl]-4-methylbenzene(**V**). Compounds **IV** and **V** are the most selectively formed over H-Beta (up to 82%) and H-Ymmm (up to 79%) zeolite catalysts with a high conversion of **I** (from 90% to full). It has been shown that high selectivity for chloroalkylarenes **IV** and **V** is achieved at 100°C, an arene : unsaturated compound molar ratio of 8 : 1, a catalyst concentration of 20 wt % of the reaction mass, and a reaction time of 2 h.

*Keywords*: alkylation, arenes, vinyl-*gem*-dichlorocyclopropane, zeolites

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Vinyl-*gem*-dichlorocyclopropanes, which are of significant interest as intermediates for organic synthesis, are readily formed in quantitative yields during the dichlorocarbenylation of commercially available dienes (divinyl and isoprene) [1–4].

The alkylation of aromatic structures with vinyl-*gem*-dichlorocyclopropanes can be successfully used for preparing a wide range of low-production-volume chemicals containing the *gem*-dichlorocyclopropane moiety. The resulting substituted benzenes are of significant interest as additives for fuels, oils, and polymers [5].

Acid-catalyzed alkylation of benzene and toluene with vinyl-*gem*-dichlorocyclopropanes in the presence of concentrated sulfuric acid has been studied earlier. The corresponding alkyl arenes have been obtained in a low yield (up to 34%). It has been shown that the ratio of *o*- and *p*-isomers in the case of alkylation of toluene with vinyl-*gem*-dichlorocyclopropanes is 1 : 4 in favor of the *p*-isomer [6]. In addition to the low yield of the desired product, the procedure used is characterized by tarring, need for expensive organic solvents, and the multistage nature—it includes the reaction mixture neutralization and washing steps. An alternative method eliminating all the above disadvantages is catalysis with the use of heterogeneous catalysts. As it has been acknowledged in recent years, zeolite catalysts are the most efficient heterogeneous catalyst systems for the alkylation of aromatic hydrocarbons (HCs) with olefins including the industrial processes [7–11].

Thus, in this work we studied the reaction of arenes (benzene and toluene) with 2-methyl-2-vinyl-*gem*-dichlorocyclopropane in the presence of various zeolite catalysts, namely, microporous zeolites, such as H-Y (FAU structural type), H-Beta (BEA), H-MOR (MOR), and H-ZSM-5 (MFI), and micro—meso—macroporous H-Ymmm (FAU) catalysts.

## EXPERIMENTAL

Benzene and toluene of the reagent grade (EKOS-1) were used in this work. The initial aromatic hydrocarbons (HCs) were thoroughly purified and dried according to a procedure described in [12].

The unsaturated compound 2-methyl-2-vinyl-*gem*-dichlorocyclopropane (**I**) was obtained according to a procedure given in [4].

The H-Y zeolite (a molar ratio $SiO_2/Al_2O_3 = 5$ and a degree of decationation $\alpha_{Na} = 0.95$) was obtained via ion exchange in a solution of $NH_4NO_3$ at 70°C from Na-Y zeolite synthesized at the Institute of Petroleum Chemistry and Catalysis, Russian Academy of Sciences, according to a procedure described in [13]. The

Beta zeolite ($SiO_2/Al_2O_3 = 18$) manufactured by the Angarsk Catalyst and Organic Synthesis Plant in the $NH_4^+$ form was converted into the H-form by thermal treatment in air at 540°C for 3 h. The H-ZSM-5 zeolite ($SiO_2/Al_2O_3 = 30$) was purchased from the Ishimbai Specialty Catalyst Plant. The Na-MOR zeolite ($SiO_2/Al_2O_3 = 5.0$) was synthesized at the Institute of Petroleum Chemistry and Catalysis, according to a procedure described in [14] and converted into the H-form by ion exchange of $Na^+$ for $NH_4^+$ cations followed by the thermal treatment of the obtained ammonium form.

The procedure for preparing the micro–meso–macroporous Ymmm zeolite in the H-form ($SiO_2/Al_2O_3 = 7.2$) is described in [15, 16] and is based on the selective crystallization of pellets, made of finely divided Na-Y zeolite and amorphous binder (metakaolin), in sodium silicate solutions at 96–98°C. A sample of H-Ymmm zeolite with $\alpha_{Na} = 0.95$ was prepared via ion exchange of the Na-Ymmm zeolite.

Prior to catalyst testing, zeolite samples were subjected to thermal treatment in air at 350°C for 4 h.

The zeolite catalysts were characterized using X-ray phase (XPA) and X-ray diffraction (XRD) analysis techniques, adsorption methods, low-temperature adsorption of nitrogen, mercury porosimetry, and temperature-programmed adsorption–desorption of ammonia ($NH_3$-TPD) [17–20].

### *General Procedure for C-Alkylation of Benzene and Toluene with 2-Methyl-2-Vinyl-gem-Dichlorocyclopropane*

A calculated amount of zeolite, a reactant aromatic (benzene (**II**) or toluene (**III**)), and the unsaturated reactant 2-methyl-2-vinyl-*gem*-dichlorocyclopropane (**I**) in a molar ratio of 2 : 1–8 : 1 were charged into a glass ampoule. After sealing, the ampoule was placed in a 17-mL “finger-type” metal autoclave which was heated at a preset temperature with continuous rotation in a thermostated cabinet for a certain time. Then the reaction mixture was cooled, separated from the catalyst by filtering, and analyzed by GLC. The reaction products were isolated by vacuum distillation. Compounds **IV** and **V** were obtained according to this procedure.

The chromatographic analysis of the products was performed on a chromatograph equipped with a flame ionization detector (25 m glass capillary column coated with SE-30; column temperature, 50–280°C programmed for a heating rate of 8°C/min; detector temperature, 250°C; evaporator temperature, 300°C; carrier gas (helium) flow rate, 30 mL/min). Mass spectra were obtained on a SHIMADZU GCMS-QP2010Plus instrument (SPB-5 capillary column 30 m × 0.25 mm; helium as the carrier gas, temperature programming from 40 to 300°C at a heating rate of 8°C/min; evaporator temperature, 280°C; ion source temperature, 200°C; ionization energy, 70 eV). $^1H$ and $^{13}C$ NMR spectra and homo- and heteronuclear procedures, such as COSY, HSQC, and HMBC, were recorded on Bruker Avance-400 instruments (operating frequencies of 400.13 and 100.62 MHz for $^1H$ and $^{13}C$, respectively) using $CDCl_3$ as the solvent.

The compounds had the following characteristics:

**[1-(2,2-dichloro-1-methylcyclopropyl)ethyl]benzene IV**. Colorless liquid. $T_b$ 106°C (2 mmHg). $^1H$ NMR, δ, ppm ($CDCl_3$): 1.31 (d, 3H, $CH_3$(5)), 1.79 (s, 3H, $CH_3$(6)), 2.45–2.65 (m, 2H, $CH_2$(2)), 2.99–3.08 (m, H, CH(4)), 7.24 (s, H, CH(10)),7.32 (s, H, CH(8,12)), 7.34 (s, H, CH(9,11)). $^{13}C$ NMR, δ, ppm ($CDCl_3$): 20.37 (C(5)), 21.17 (C(6)), 38.11 (C(4)), 38.21 (C(3)), 44.05 (C(2)), 126.36 (C(10)), 126.88 (C(8,12)), 128.44 (C(9,11)), 133.96 (C(7)), 146.11 (C(1)). Mass spectrum, *m/e* ($I_{rel}$, %): 228 (8) [$M^+$], 201 (8), 199 (13), 165 (16), 163 (46), 157 (10), 129 (10), 115 (10), 105 (100), 103 (9), 91 (17), 77 (16).

**1-[1-(2,2-dichloro-1-methylcyclopropyl)ethyl]-4-methylbenzene V**. Colorless liquid. $T_b$ 131°C (2 mmHg). $^1H$ NMR, δ, ppm ($CDCl_3$): 1.28 (d, 3H, $CH_3$(5)), 1.79 (s, 3H, $CH_3$(6)), 2.36 (s, 3H, $CH_3$(13)), 2.45–2.65 (m, 2H, $CH_2$(2)), 2.96–3.02 (m, H, CH(4)), 7.06 (s, H, CH(9,11)), 7.28 (s, H, CH(8,12)). $^{13}C$ NMR, δ, ppm ($CDCl_3$): 20.21 (C(5)), 21.20 (C(6)), 21.28 (C(13)), 37.77 (C(4)), 38.11 (C(3)), 44.06 (C(2)), 126.72 (C(9,11)), 127.08 (C(8,12)), 134.00 (C(10)), 143.77 (C(1)).Mass spectrum, *m/e* ($I_{rel}$, %): 242 (2) [$M^+$], 206 (8), 191 (2), 171 (3), 141 (2), 119 (51), 103 (19), 91 (9), 77 (4).

## RESULTS AND DISCUSSION

### *Characteristics of Zeolite Catalysts*

The catalytic properties of the zeolite catalysts differing in the crystal lattice structure, acidic properties, and porosity have been studied. The H-Y, H-Beta, H-MOR, and H-ZSM-5 zeolites have a microporous structure, and the H-Ymmm zeolite has a hierarchal structure formed not only by micro-, but also meso- and macropores [21, 22].

In the series of microporous zeolites, zeolites Y (cavities with the entrance window of 0.74 × 0.74 nm) and Beta (straight channels with a size of 0.66 × 0.67 nm and tortuous channels with a size of 0.56 × 0.56 nm) possess the widest pores. Pentasil ZSM-5 is characterized by narrower pores are (straight channels of a 0.51 × 0.55 size nm and tortuous channels of a 0.53 × 0.56 nm size). The H-MOR zeolite has a unidimensional channel structure (two types of channels with sizes of 0.70 × 0.65 and 0.26 × 0.57 nm) [23].

The physicochemical properties of the zeolite catalysts studied are presented in Table 1.

**Table 1.** Physicochemical characteristics of the zeolites

| Catalyst | Crystallinity, rel. % | Equilibrium adsorption capacity (20°C and $P/P_s = 0.8$), $cm^3/g$, for vapor of | | $S_{sp}$, $m^2/g$ | Acidic properties* | | |
|---|---|---|---|---|---|---|---|
| | | | | | concentration of acid sites, μmol $g^{-1}$ | | |
| | | $H_2O$ | $C_6H_6$ | | $C_I$ | $C_{II}$ | $C$ |
| H-Y | 100 | 0.30 | 0.30 | 870 | 610 | 520 | 1130 |
| H-Beta | 100 | 0.26 | 0.32 | 470 | 530 | 340 | 870 |
| H-MOR | 100 | 0.18 | 0.16 | 393 | 651 | 349 | 1000 |
| H-ZSM-5 | 100 | 0.14 | 0.15 | 320 | 270 | 190 | 460 |
| H-Ymmm | 93 | 0.25 | 0.30 | 741 | 515 | 460 | 975 |

* $C_I$, $C_{II}$, and $C$ are the concentrations of "weak" and "strong" acid sites and their total concentration, respectively.

According to the XPA data and values of the adsorption characteristics of the zeolites, the degree of crystallinity is close to 100% for all the samples of microporous zeolites. For the H-Ymmm zeolite, the crystallinity is 93%, which is associated with the incomplete crystallization of its amorphous component.

According to the data of the low-temperature adsorption–desorption of nitrogen and mercury porosimetry for an H-Ymmm zeolite sample, the "apparent" BET specific surface area of the samples is 741 $m^2/g$, and the specific surface area of the secondary porous structure determined using mercury porosimetry is 12.1 $m^2/g$. The volumes of micro-, meso-, and macropores are 0.28, 0.15, and 0.15 $cm^3/g$, respectively.

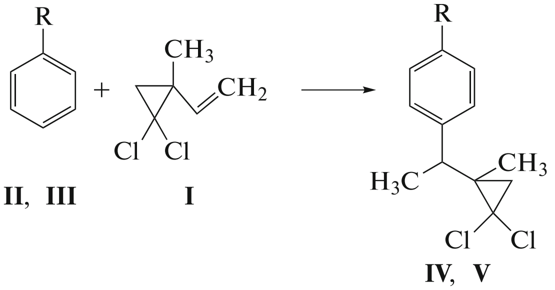
The $NH_3$-TPD spectra of the microporous zeolites exhibit two peaks, the low-temperature peak with a maximum at 250–300°C and the high-temperature peak with a maximum in the range of 410–480°C. Their presence suggests that there are acid sites of two types in the samples under study, namely, weak sites characterized by the low-temperature peak and strong sites characterized by the high-temperature peak [18]. The concentration of strong acid sites, which are the most important for catalytic transformations, decreases in the order H-Y > H-MOR ≥ H-Beta > H-ZSM-5. The total concentration of the acid sites varies in a similar manner.

The acidity spectra of the H-Ymmm zeolite display two peaks due to weak acid sites with a temperature maximum $T_{max}$ at 250–280°C and strong acid sites with $T_{max}$ in the temperature range of 350–420°C. The concentration of the strong acid sites in the H-Ymmm zeolite is lower than that in the H-Y zeolite.

### *Catalytic Properties of Microporous Zeolites in Synthesis of Alkylarenes*

The alkylation of arenes **II** and **III** with unsaturated compound **I** in the presence of the studied zeolite catalysts proceeds with the formation of chloroalkylarenes **IV** and **V** (see Scheme 1). In addition to them, products of transformation of unsaturated reactant **I** denoted as "light" were identified in the reaction mixture.

Note that in the case of alkylation of toluene with vinylcyclopropane **I** in the presence of the studied zeolites, only the *p*-isomer is produced. Due to presence of two chiral centers in **IV** and **V**, two diastereomers with the (*R**,*R**)- and (*R**,*S**)-configurations can be formed. The presence of the diastereomeric pair in the products is confirmed by the appearance of a twinned set of signals with a 2 : 3 ratio in the $^{13}C$ NMR spectrum. Unfortunately, it is difficult to perform direct identification of the prevalent isomer because compounds **IV** and **V** lack functional groups capable of selective binding of derivatizing shift agents.



R = H (**II**, **IV**), R = $CH_3$ (**III**, **V**)

**Scheme 1.** Scheme of the reaction of benzene and toluene with 2-methyl-2-vinyl-*gem*-dichlorocyclopropane.

The alkylation proceeds most selectively in the presence of the microporous H-Beta zeolite or the micro–meso–macroporous H-Ymmm zeolite (Table 2). The values of selectivity for alkylarenes **IV** and **V** are close, being 73–82%. The highest conversion of vinylcyclopropane **I** was observed over the same catalysts (H-Beta and H-Ymmm).

The high catalytic activity and selectivity of the H-Beta and H-Ymmm zeolites is apparently determined

**Table 2.** Synthesis of [1-(2,2-dichloro-1-methylcyclopropyl)ethyl]benzene **IV** and 1-[1-(2,2-dichloro-1-methylcyclopropyl)ethyl]-4-methylbenzene **V** in the presence of zeolite catalysts. Synthesis conditions: 20 wt % catalyst, $T = 100°C$, molar ratio arene : **I** = 8 : 1, 2 h

| Catalyst | Arene | Conversion of **I**, % | Selectivity, % | |
|---|---|---|---|---|
| | | | **IV** and **V** | light |
| H-Y | Benzene | 70 | 39 | 61 |
| H-MOR | | 35 | 57 | 43 |
| H-Beta | | 100 | 82 | 18 |
| H-ZSM-5 | | 0 | 0 | 0 |
| H-Ymmm | | 90 | 79 | 21 |
| H-Y | Toluene | 86 | 29 | 71 |
| H-MOR | | 15 | 52 | 48 |
| H-Beta | | 97 | 81 | 19 |
| H-ZSM-5 | | 0 | 0 | 0 |
| H-Ymmm | | 96 | 73 | 27 |

by their porous structure characteristics providing good accessibility of catalyst active sites for the reacting molecules and not creating diffusion limitations for the transport of the reactant and product molecules. The lower values of the selectivity of the H-Ymmm zeolite for alkylarenes in comparison with the H-Beta zeolite (73 versus 81%, respectively, in reaction with toluene) can be explained by a higher acidity of the H-Ymmm zeolite, which leads to the intensification of the reactions of transformation of vinylcyclopropane **I**, resulting in an increase in concentration of the "light" compounds in the products.

The same factor, a high concentration of acid sites, also explains the results obtained over H-Y and H-MOR zeolites. The reaction mixture obtained in the presence of these catalysts contained a significant amount of the "light" compounds, because of which the selectivity for alkyl arenes **IV** and **V** is lower than over the H-Beta zeolite. At the same time, the significant difference in the values of the vinylcyclopropane **I** conversion observed over the H-Y and H-MOR samples is apparently due to particular features of the crystal lattice structure of these zeolites. The three-dimensional wide-pore structure of the H-Y zeolite provides better accessibility of active sites for the reactants than does the unidimensional porous structure of H-MOR; therefore, the conversion of vinylcyclopropane **I** over the H-Y zeolite is two- to fivefold higher tan that on the H-MOR zeolite.

The H-ZSM-5 zeolite was inactive in the reaction. It can be supposed that the lack of activity is due to the low concentration of acid sites in it or spatial hindrances created by the narrow channels of H-ZSM-5 zeolite to the reactants and the products.

The obtained results show that in order to obtain alkylarenes **IV** and **V** with a high yield, it is necessary that a zeolite catalyst have both a wide-pore structure and an optimum concentration of acid sites. Neither low nor high acidity is desirable because the catalyst is inactive in the former case and predominantly catalyzes the transformations of vinylcyclopropane **I** in the latter case.

The influence of the reaction parameters (temperature, molar ratio of the reactants, catalyst concentration, reaction time) on the conversion of vinylcyclopropane **I** and the product composition has been studied in the presence of H-Beta, the most active of the zeolite catalysts.

It has been shown that a high conversion of vinylcyclopropane **I** (from 90% to complete) is achieved at 70–150°C (Fig. 1). The maximum selectivity for alkylarene **V** is observed at 100°C, a further increase in temperature leads to an increase in the yield of the side products.

Increasing the concentration of toluene in the initial reaction mixture from 2 : 1 to 8 : 1 leads to an increase in selectivity for desired product **V** (Fig. 2). At the minimum concentration of toluene in the reaction mixture, the alkylarene selectivity is low because of the predominant occurrence of side reactions of transformation of vinylcyclopropane **I**. The high alkylarene selectivity with an almost complete conversion of vinylcyclopropane **I** is achieved at a toluene : **I** molar ratio of 8 : 1.

The conversion of vinylcyclopropane **I** and the selectivity for alkylarene **V** are also affected by the concentration of the zeolite catalyst (Fig. 3). The alkylation proceeds most selectively and with a high conversion of vinylcyclopropane **I** in the presence of the catalyst in an amount of 20% of the mass of the reactants.

Figure 4 illustrates the influence of the reaction time on the degree of conversion of unsaturated compound **I** and the selectivity for 1-[1-(2,2-dichloro-1-methylcyclopropyl)ethyl]-4-methylbenzene **V**. The maximum conversion of the unsaturated compound

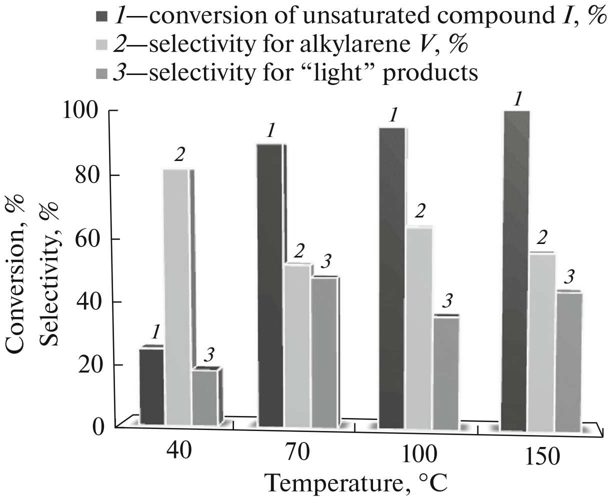


**Fig. 1.** The influence of temperature on the conversion of **I** and the selectivity for 1-[1-(2,2-dichloro-1-methylcyclopropyl)ethyl]-4-methylbenzene **V**. Synthesis conditions: a molar ratio of toluene : **I** = 5 : 1, 20 wt % catalyst, 2 h.

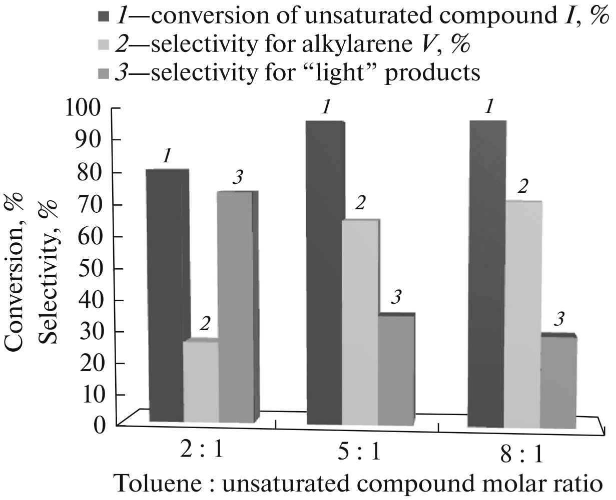


**Fig. 2.** The influence of the molar ratio of the reactants on the conversion of **I** and the selectivity for 1-[1-(2,2-dichloro-1-methylcyclopropyl)ethyl]-4-methylbenzene **V**. Synthesis conditions: 100°C, 20 wt % catalyst, autoclave, 2 h.

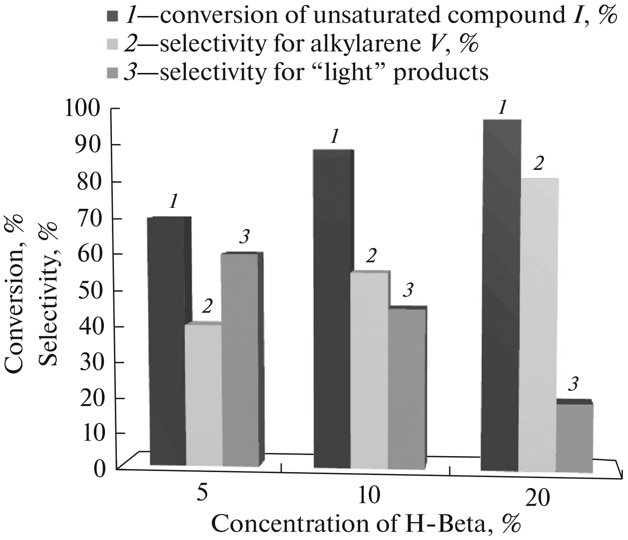


**Fig. 3.** The influence of the concentration of the catalyst on the conversion of unsaturated compound **I** and the selectivity for 1-[1-(2,2-dichloro-1-methylcyclopropyl)ethyl]-4-methylbenzene **V**. Synthesis conditions: 100°C, a molar ratio of arene : **I** = 8 : 1, autoclave, 2 h.

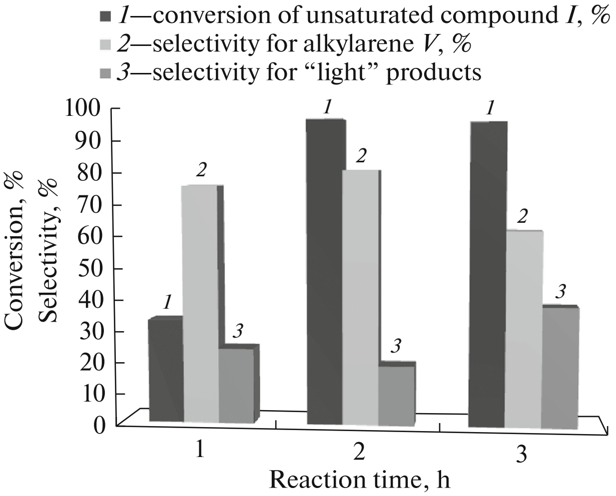


**Fig. 4.** The influence of the reaction time on the conversion of unsaturated compound **I** and the selectivity for 1-[1-(2,2-dichloro-1-methylcyclopropyl)ethyl]-4-methylbenzene **V**. Synthesis conditions: 100°C, a molar ratio of arene : **I** = 8 : 1, 20 wt % catalyst.

and selectivity for the desired product are achieved after 2 h. Further running the synthesis leads to a decrease in selectivity for **V**.

In summary, it has been found as a result of the investigation of the catalytic properties of various zeolites in the alkylation reaction of benzene and toluene with 2-methyl-2-vinyl-*gem*-dichlorocyclopropane, that zeolites H-Beta (microporous) and H-Ymmm (micro–meso–macroporous) are the most active and selective catalysts for the synthesis of alkylarenes. The selectivity for [1-(2,2-dichloro-1-methylcyclopropyl)ethyl]benzene **IV** and 1-[1-(2,2-dichloro-1-methylcyclopropyl)ethyl]-4-methylbenzene **V** over these catalysts reaches 82% at a conversion of vinylcyclopropane **I** of 90–100%.

It has been shown that the maximum yield of alkylarenes is achieved at a molar ratio of arene : **I** = 8 : 1

and a temperature of 100°C in the presence of 20 wt % catalyst within the reaction time of 2 h.

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