

Effect of Binder on the Properties of MWW Zeolite Catalysts in Benzene Alkylation with Propylene

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Abstract—The effect of the nature of the binding component (Al_2O_3 , SiO_2 , kaolin) on the physicochemical and catalytic properties of catalysts based on a hierarchical zeolite of the MWW framework type in benzene alkylation with propylene has been studied. The best results have been obtained using $\text{Al}(\text{OH})_3$ as an Al_2O_3 precursor. This precursor does not have an adverse effect on the acidic properties of the catalyst and thereby provides an increase in the yield of the desired product, i.e., cumene. The addition of kaolin to this catalyst does not affect the strength characteristics; however, the presence of this binder leads to a decrease in the number of acid sites in the sample.

Keywords: zeolite MWW, hierarchical zeolite, binding component, benzene alkylation with propylene, cumene

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Isopropylbenzene (cumene) is an important intermediate in the production of phenol and acetone in the petrochemical industry. Most of cumene is produced by benzene alkylation with propylene. Conventional processes using solid phosphoric acid (SPA) catalysts and Friedel–Crafts alkylation (AlCl_3) for the commercial production of cumene cause many problems, in particular, a negative impact on the environment and corrosion of the equipment [1, 2]. Currently, interest in the study and development of new efficient environmentally friendly zeolite catalysts capable of operating at relatively low benzene/propylene ratios is constantly increasing in view of reducing the operating costs [2].

Catalytic activity in benzene alkylation with lower olefins is exhibited by zeolites BEA, MFI, and MWW [3]. Zeolites of the BEA framework type are the most active of the above zeolites; however, their catalytic activity is stable only at relatively high degrees of dilution of propylene with benzene (benzene/propylene molar ratio of 6–8). Zeolites of the MWW framework type are slightly less active; however, they preserve their catalytic properties at a benzene/propylene molar ratio of 3–4; therefore, the energy consumption for benzene recycling and the isolation of the target product can be significantly reduced [4].

Zeolite crystals of the MWW framework type have a layered structure; their 2.5-nm-thick individual plates comprise two independent micropore systems:

sinusoidal pores defined by 10-membered silicon–oxygen rings and hourglass-shaped pores defined by 12-membered rings. Benzene alkylation with lower olefins involves Brønsted acid sites (ASs) localized in 12-membered cavities. The diffusion of the reactants and products inside the crystal is limited to the inter-layer space of the zeolite; therefore, this study is focused on a hierarchical zeolite of the MWW framework type (MWW-HZ) comprising an additional mesopore system formed by the recrystallization method [5].

Since the catalysts used in industry are synthesized with a binder to provide the formation of samples with a high strength of the granules, an important task is to study the effect of the binding component on the physicochemical and catalytic properties of the samples. To date, data on this effect for MWW catalysts have not been reported.

This study is focused on the effect of the nature of the binding component (Al_2O_3 , SiO_2 , kaolin) on the physicochemical and catalytic properties of MWW zeolites in benzene alkylation with propylene.

EXPERIMENTAL

The original MWW zeolite was synthesized as described in [6] using hexamethylenimine (HMI) as a template from a $0.09\text{Na}_2\text{O} \cdot 0.033\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 0.5\text{HMI} \cdot 45\text{H}_2\text{O}$ reaction mixture. The precursors

were silica gel, sodium aluminate, sodium hydroxide, HMI (99%, Aldrich), and distilled water. Hydrothermal treatment was conducted at a temperature of 150°C under stirring for 5 days; after that, the resulting zeolite was washed on a Buchner funnel with distilled water and dried at 95°C.

Recrystallization was implemented by a hydrothermal treatment at 110°C in two stages. At the first stage, the zeolite structure is partially dissolved in an alkaline solution of (1-hexadecyl)trimethylammonium bromide. At the second stage, the zeolite dissolution products constitute a mesoporous phase to form a micro/mesoporous structure of the MWW-HZ.

The resulting MWW-HZ was calcined at 550°C in an air stream for 8 h; after that, it was subjected to five ion exchange runs in a 0.1 M NH_4NO_3 solution and subsequent calcining at 550°C to obtain the protonated form of the zeolite.

Several binders were used to synthesize the zeolite catalysts. Alumina is a conventional binder used for this purpose. Typically, the final form of alumina in the catalyst is $\gamma\text{-Al}_2\text{O}_3$, which is prepared using various precursors. To synthesize samples with a binder, boehmite AlOOH (SASSOL) and aluminum hydroxide $\text{Al}(\text{OH})_3$ (Promyshlennye katalizatory, Ryazan, Russia) were used as precursors for Al_2O_3 . Another binder was silica; silica sol—colloidal polysilicic acid—was used as the silica precursor. Natural layered aluminosilicate kaolin was used as an additive to control the strength and texture characteristics of the samples.

The zeolite catalysts were synthesized taking 70 wt % of the MWW-HZ and 30 wt % of a binder. Kaolin was taken in an amount of 20% of the weight of the binder. The MWW-HZ powder was mixed with a binder; the resulting mixture was molded into 5×4 mm cylindrical granules, which were dried at a temperature of 90°C and calcined at 550°C for 6 h. To determine the characteristics of the pore structure of the binders, granules from the precursors were prepared.

The binder content in the catalyst was controlled by X-ray fluorescence analysis on a Thermo Scientific ARL Perform^X instrument with a 3.5-kW rhodium tube at the Center for shared use of the Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences.

The mechanical crushing strength of the samples with binder was determined using the ASTM D6175-03 international regulatory document.

Acid site concentration in the zeolites was determined by temperature-programmed desorption of ammonia (NH_3 TPD). A weighed portion of 150–200 mg was calcined in a helium stream at 500°C; after that, the sample was cooled to 60°C and saturated with ammonia in a stream of an NH_3/N_2 (1/9) gas mixture for 30 min. Next, the sample was heated to 100°C to

blow off physically adsorbed ammonia in a helium stream for 60 min. Analysis was conducted in a temperature range of 100–800°C at a heating rate of 8°C/mi; desorbed ammonia was recorded using a thermal conductivity detector.

Low-temperature nitrogen adsorption isotherms were recorded on an ASAP2000 automatic porosimeter (Micromeritics, United States). Micropore volume was determined by the t-plot method.

The morphology of the synthesized samples was studied by scanning electron microscopy (SEM) on a Hitachi 4 Tabletop Microscope TM3030Plus electron microscope. The accelerating electrode voltage was 15 kV.

Tests on the catalytic properties of the catalysts were conducted on a laboratory flow system [7] with a steel reactor. The catalyst load was 1.5 cm^3 .

Before each test, the catalyst was dehydrated in an argon stream (flow rate of 15 mL/min per cubic centimeter of catalyst) with a stepwise rise in temperature and holding as follows: 120°C for 1 h, 300°C for 1.5 h, 400°C for 1 h, and 500°C for 1 h. The tests were conducted under standard conditions: a temperature of 205°C; atmospheric pressure; a benzene : propylene molar ratio of 8 : 1; and a flow rate of benzene and propylene of 13.2 and 0.9 g/(g h), respectively. The test duration was 240 min; samples were collected every 40 min.

Reaction products were analyzed on a Shimadzu GC2030 gas chromatograph equipped with a flame ionization detector and a capillary column (DB-1, 100 m \times 0.25 mm \times 0.50 μm).

RESULTS AND DISCUSSION

The SEM photographs (Fig. 1) show that the MWW has the form of disks with a diameter of about 1 μm and a height of 100 nm. Recrystallization has little effect on the morphology of the MWW crystals.

Characteristics of the pore structure and acidic properties of the MWW-HZ and the binders used to synthesize the zeolite-containing samples are given in Table 1. The table shows that the textural properties of the used binders differ, in particular, by the presence of micropores (Al_2O_3 /boehmite and Al_2O_3 /hydroxide samples) and the mesopore diameters. In addition, the Al_2O_3 binders prepared from the different precursors have an intrinsic acidity; for these binders, the AS concentration is 350 and 560 μmol of NH_3 /g. Unlike Al_2O_3 , silica prepared from silica sol is characterized by extremely low acidity (Table 1).

The synthesis conditions and physicochemical properties of the samples with the binder are given in Table 2; the low-temperature nitrogen adsorption isotherms are shown in Fig. 3.

Test sample no. 1 was synthesized using boehmite as a binder. The characteristics of this sample listed in

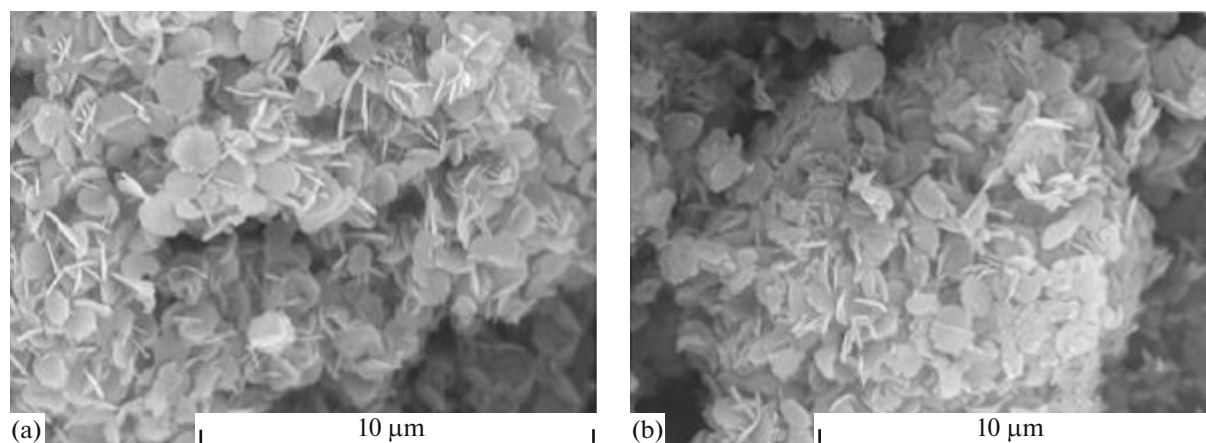


Fig. 1. Scanning electron microscopy micrographs of (a) microporous MWW and (b) MWW-HZ.

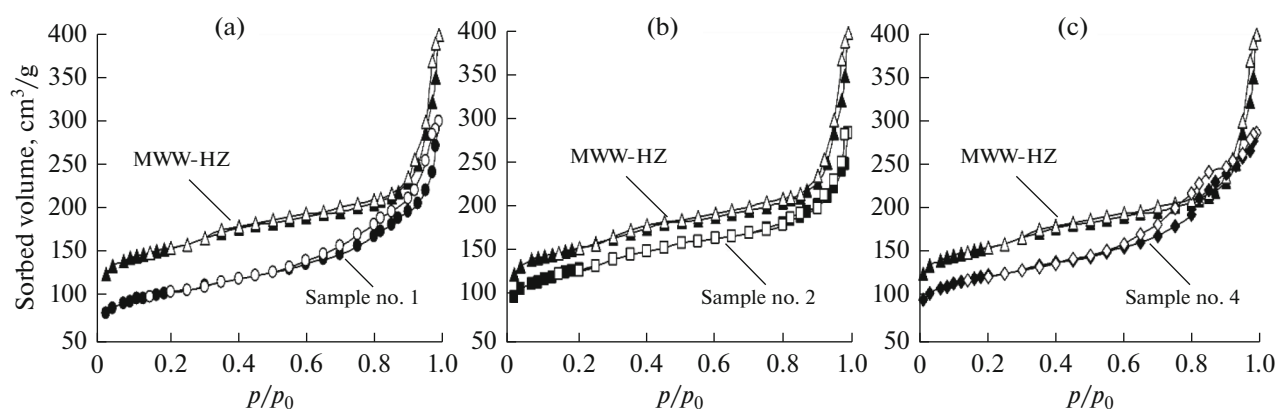


Fig. 2. Low-temperature nitrogen adsorption–desorption isotherms on the active phase of the MWW-HZ catalyst and samples synthesized with different binders.

Table 2 show that the use of this binder provided the crushing strength of the granules of 2.8 kg/mm². However, during the synthesis of sample no. 1, the micropores of the active zeolite phase were partially blocked, as evidenced by the shift of the nitrogen adsorption isotherm down the ordinate axis (Fig. 1a) and a lower micropore volume calculated in accordance with this

isotherm (Table 2). This effect can be attributed to the specific features of the binder, the particle size of which does not exceed 300 nm. At the same time, the pore diameter distribution curves for the MWW-HZ, Al₂O₃ (boehmite), and sample no. 1 (Fig. 3) show the following: the presence of two peaks in the distribution curve for sample no. 1 confirms the preservation of the

Table 1. Physicochemical properties of the MWW-HZ and the binding components

Zeolite component	Binder		Pore structure characteristics				a_0 , $\mu\text{mol NH}_3/\text{g}$
	substance	precursor	S_{BET} , m ² /g	V_{pore} , cm ³ /g	$V_{\text{micropore}}$, cm ³ /g	mesopore diameter, nm	
MWW-HZ	—	—	530	0.565	0.142	3	880
—	Al ₂ O ₃	Boehmite	300	0.420	0	7	350
—	Al ₂ O ₃	Al(OH) ₃	260	0.154	0.083	3	560
—	SiO ₂	Silica sol	180	0.174	0	4	120
—	Kaolin	Kaolin	18	0.040	0	—	—

Table 2. Physicochemical properties of the zeolite catalysts

Sample	Sample composition		MCS*, kg/mm ²	Characteristics of the pore structure of samples with a binder				a_0 , μmol NH ₃ /g
	zeolite component	binder		S_{BET} , m ² /g	V_{pore} , cm ³ /g	$V_{\text{micropore}}$, cm ³ /g	$V_{\text{micropore}}^{**}$, cm ³ /g	
No. 1	70% MWW-HZ	30% Al ₂ O ₃ (boehmite)	2.8	350	0.340	0.075	0.107	730
No. 2	70% MWW-HZ	30% Al ₂ O ₃ (Al(OH) ₃)	0.6	440	0.343	0.087	0.124	800
No. 3	70% MWW-HZ	24% Al ₂ O ₃ + 6% kaolin	0.6	410	0.318	0.087	0.124	740
No. 4	70% MWW-HZ	30% SiO ₂	1.1	410	0.383	0.098	0.140	580
No. 5	70% MWW-HZ	24% SiO ₂ + 6% kaolin	0.7	370	0.330	0.095	0.135	620

* Mechanical crushing strength.

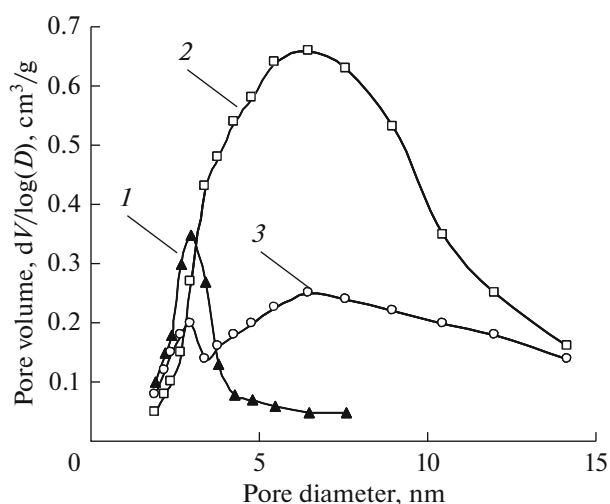
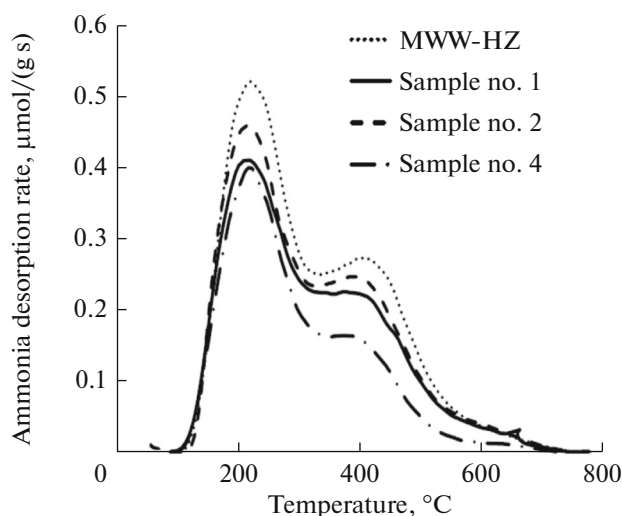
** Micropore volume in terms of the pure zeolite component.

mesopores from the MWW-HZ (3-nm pores) and Al₂O₃ (boehmite) (7-nm pores). However, a decrease in the intensity of the peaks in the distribution curves of the pure materials and the catalyst suggests that the zeolite component and the binder can have a mutual effect on each other, which leads to the blocking of not only the micropores of the MWW-HZ, but also the mesopores.

It is evident from Table 2 that the replacement of boehmite led to a deterioration in the strength characteristics of the catalysts: the mechanical strength of the granules of catalyst samples nos. 2–5 decreased to 0.6–1.1 kg/mm². The addition of kaolin in an amount of 20% of the amount of the binder into the catalyst did not have a positive effect. The decrease in the strength of the granules is apparently attributed to the morphological features of the MWW-HZ having the form of flat disks with a diameter of about 1 μm and a thickness of about 100 nm. The obtained data suggest

that there is an optimum particle size of the binder that can provide the relative orientation of the particles of the active phase of the catalyst and the particles of the binder to achieve a high strength of the granules. According to Table 2, test catalyst samples nos. 2–5 with a low strength of the granules are characterized by high micropore volumes. In this case, the reduced micropore volume values, i.e., the values recalculated with allowance for the active phase content in the catalyst of 70%, are close to the micropore volume in the original MWW-HZ sample (Table 1). These data suggest that the MWW-HZ and the binder in the catalyst undergo a weak interaction, which can be responsible for the low strength of the samples.

According to the AS concentrations determined by the ammonia TPD method (Table 2) and from the ammonia TPD curves (Fig. 4), regardless of the binder type, the AS concentration in the test samples

**Fig. 3.** Pore diameter distribution curves: (1) the MWW-HZ, (2) the Al₂O₃ (boehmite) binder, and (3) sample no. 1.**Fig. 4.** Ammonia TPD curves for the MWW-HZ and the catalysts based on it.

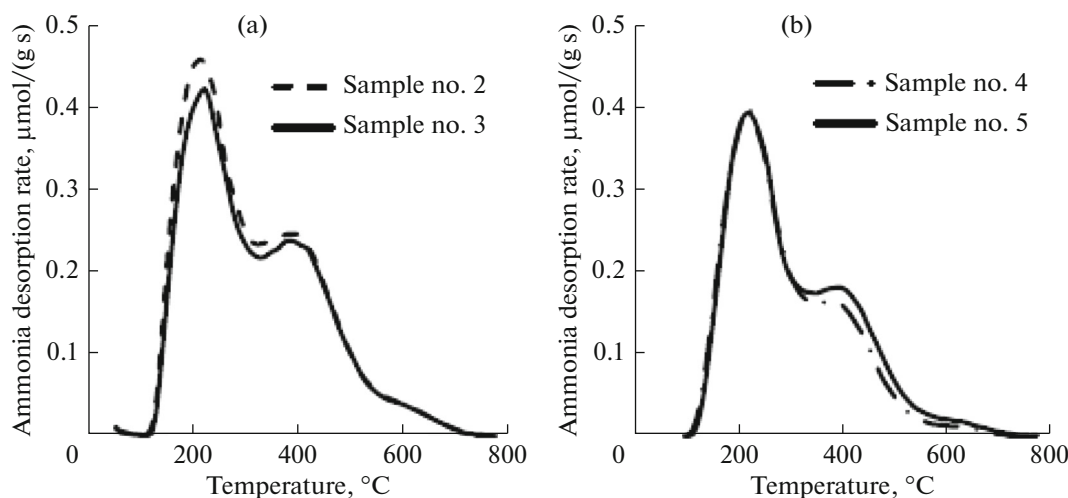


Fig. 5. Ammonia TPD curves for the zeolite-containing samples: (a) nos. 2 and 3 and (b) nos. 4 and 5.

is always lower than that in the MWW-HZ zeolite phase. Analysis of the ammonia TPD curves in Fig. 4 shows that the interaction of the zeolite component and the binder is accompanied by quantitative and qualitative changes in the acidic properties of the test samples. The quantitative changes associated with a decrease in the concentration of both strong and weak ASs occur in the following order: MWW-HZ > sample no. 1 > sample no. 2 > sample no. 4. The qualitative changes are evident from the position of the high-temperature peak in the TPD curve, which is shifted to low temperatures in the following order: MWW-HZ > sample no. 2 > sample no. 1 > sample no. 4. This finding suggests that the strength of the ASs in the test samples decreases in the above order.

Kaolin has an interesting effect on the acidic properties of the test samples. According to Table 2, the

addition of kaolin to $\text{Al}(\text{OH})_3$ leads to a decrease in the AS concentration in samples nos. 2 and 3, while the addition of kaolin to silica sol leads to an increase in the AS concentration in samples nos. 4 and 5. Comparison of the TPD profiles of the test samples (Fig. 5) shows that, in the case of $\text{Al}(\text{OH})_3$, the acidity decreases owing to a decrease in the number of weak ASs, as evidenced by a decrease in the intensity of the low-temperature peak (Fig. 5a). In the case of SiO_2 , the AS concentration increases owing to an increase in the number of strong sites, as evidenced by an increase in the intensity of the high-temperature peak (Fig. 5b).

Thus, the use of the different binders makes it possible to control the strength, textural, and acidic characteristics of the test samples over a wide range.

According to the results of the catalytic tests on benzene alkylation with propylene (Figs. 6–8), the studied samples can conventionally be divided into

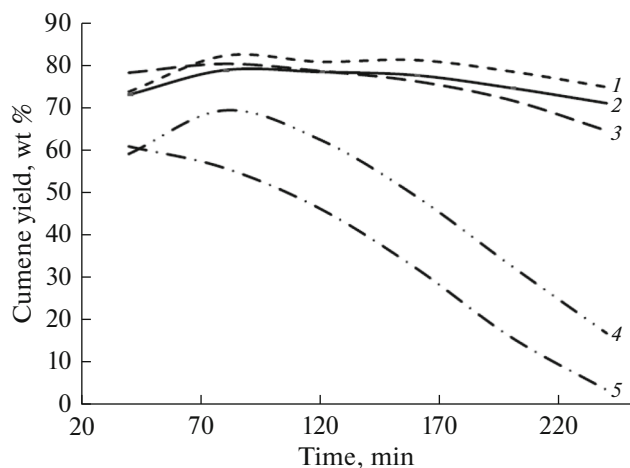


Fig. 6. Dependence of the cumene yield on the test duration: (1) sample no. 2, (2) sample no. 1, (3) sample no. 3, (4) sample no. 5, and (5) sample no. 4.

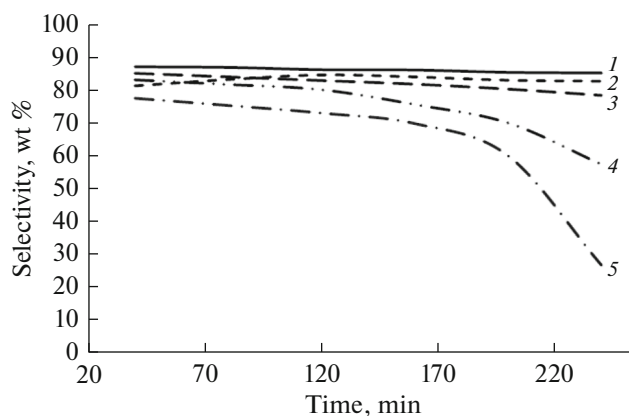


Fig. 7. Dependence of the cumene selectivity on the test duration: (1) sample no. 2, (2) sample no. 1, (3) sample no. 3, (4) sample no. 5, and (5) sample no. 4.

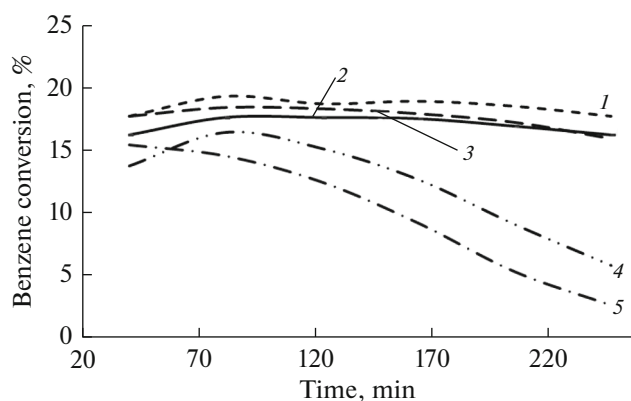


Fig. 8. Dependence of the benzene conversion on the test duration: (1) sample no. 2, (2) sample no. 1, (3) sample no. 3, (4) sample no. 5, and (5) sample no. 4.

three groups, which have significantly different parameters. The first group consists of one sample—no. 2—exhibiting high stability over time with respect to all main parameters (cumene yield, benzene conversion, and cumene selectivity). The second group includes samples nos. 1 and 3; compared with sample no. 2, their parameters are less stable over time; however, the loss of stability is fairly smooth. The third group consists of two samples—nos. 4 and 5; their parameters abruptly decrease over time. These relationships suggest that benzene conversion is determined by the AS concentration in the samples.

The results of the tests conducted on a laboratory flow system suggest that, of all the tested catalysts, the highest activity and stability in benzene alkylation with propylene is exhibited by sample no. 2, which has the following average parameters: a cumene yield of 78.8%, a cumene selectivity of 83.3%, and a benzene conversion of 18.7%.

CONCLUSIONS

According to the described results, it can be concluded that there is a fairly clear correlation between the catalytic test data and the acidity of the test samples. The use of domestic $\text{Al}(\text{OH})_3$ as a precursor for Al_2O_3 does not have an adverse effect on the acidic properties of the catalyst; therefore, the yield of the target reaction product is maintained at a high level. The addition of kaolin to this catalyst does not affect the strength characteristics; however, it leads to a decrease in the acidity and, as a consequence, in the cumene yield.

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