

Comparative Study of Catalysts Based on Zeolites BEA and MWW in Benzene Alkylation with Propylene

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Abstract—The physicochemical properties of catalysts synthesized from zeolites of the BEA and MWW framework types using pseudoboehmite as a binder and their catalytic activity in benzene alkylation with propylene in the gas-phase and liquid-phase modes have been studied. It has been found that the MWW-based catalyst is characterized by stronger acidity in terms of both amount and strength of acid sites; however, the catalytic activity of this sample is inferior to that of zeolite BEA. The observed effect is attributed to the higher accessibility of acid sites in the three-dimensional system of zeolite BEA. With respect to some parameters, such as cumene selectivity and on-stream stability, zeolite MWW is superior to zeolite BEA; the difference is attributed to the structural features of these zeolites.

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Benzene alkylation with propylene is the main method for the production of cumene, which is an important intermediate in the synthesis of phenol and acetone. In the domestic industry, this process is catalyzed by mineral acids (e.g., H₃PO₄ supported on kieselguhr, zeolite, or AlCl₃). However, environmental, economic, and technical factors (corrosion of equipment) have given an impetus to the development of new catalysts based on zeolites. These catalysts are environmentally friendly; they do not cause corrosion of equipment; this feature favorably affects the process economics [1–3].

Benzene alkylation with lower olefins is most commonly catalyzed by zeolites BEA, Y, MOR, and MWW (MCM-22) [1, 4–9]. In the presence of an MCM-22 catalyst, propylene polymerization is significantly lower than that over BEA, Y, and MOR; therefore, the cumene selectivity in the presence of MCM-22 is higher.

Comparison of the catalytic properties of BEA and MCM-22 is described in [1, 4, 5, 8, 9]. It was found that, at relatively high degrees of dilution of propylene with benzene (benzene : propylene ratio of 6–8 : 1), zeolite BEA was the most active of these catalysts [4]. Zeolite MWW was slightly less active; however, at a benzene : propylene molar ratio of about 3–4 : 1, it exhibited a more stable on-stream behavior and a higher cumene selectivity [1]; therefore, the energy

costs for benzene recycling and the target product isolation can be significantly reduced.

The BEA structure is a three-dimensional system of intersecting channels with a size of 6.4 × 7.6 and 5.5 × 5.5 Å. The MWW structure is composed of two nonintersecting pore systems. One of the pore systems comprises sinusoidal channels accessible through 10-membered ring windows with a size of 4.1 × 5.1 Å. The other pore system is represented by large supercages with a diameter of 7.1 Å and a height of 18.2 Å, which are linked by 10-membered ring windows. The outer surface of the crystal is formed by bowl-shaped half-pockets, each of which is a half of a large supercage [10]. In liquid-phase benzene alkylation with propylene, all BEA sites are accessible, whereas in MWW only the outer surface and active sites located in the vicinity of the crystal surface are accessible [2].

Catalysts used in industry are synthesized by molding a zeolite component with a binder to impart strength and a desired shape to the catalyst pellets. Silica, alumina, their mixtures, or clays are most commonly used as the binders. The interaction of a zeolite with a binder leads to a change in the physicochemical and catalytic properties of the zeolite [11, 12]. Therefore, it is important to compare the catalytic properties of the samples synthesized with a binder. There are no published data on comparison of the catalytic proper-

ties of different catalysts with a binder in benzene alkylation with propylene. In this study, the physico-chemical properties of catalysts synthesized from zeolites BEA and MWW with a binder and their catalytic properties in benzene alkylation with propylene are compared.

EXPERIMENTAL

Zeolite BEA was synthesized as described in [13] using silica gel as a silicon source. Zeolite MWW was synthesized as described in [14] using hexamethylenimine (HMI) as a template from the reaction mixture of the following composition: $0.09\text{Na}_2\text{O} \cdot 0.033\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 0.5\text{HMI} \cdot 45\text{H}_2\text{O}$. 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 with distilled water on a Buchner funnel and dried at 95°C .

The synthesized zeolites were calcined at 550°C in an air stream for 8 h; after that, a fivefold ion exchange was run in a $0.1\text{ M NH}_4\text{NO}_3$ solution at 80°C ; it was followed by calcining at 550°C to convert the zeolite to the protonated form.

To synthesize samples with a binder, pseudoboehmite purchased from SASSOL was used as an alumina source. Zeolite-based catalysts were synthesized taking 70 wt % of a zeolite and 30 wt % of a binder. To pelletize a zeolite with a binder, a suspension of the zeolite in water was prepared; a calculated amount of pseudoboehmite was added to the suspension. The resulting mixture was mechanically stirred to obtain a homogeneous mass, which was then molded on a perforated fluoroplastic plate to form cylindrical pellets with a size of $5 \times 4\text{ mm}$. To improve the strength characteristics of the catalysts, nitric acid in an amount of 5–10 wt % of the weight of Al_2O_3 was added to the mixture during pelletizing. The molded pellets were dried at room temperature for 12 h and then at a temperature of 100°C for 24 h; after that, they were calcined in an air stream at a temperature of 500°C for 6 h.

The chemical composition of the samples was monitored by X-ray fluorescence analysis on a Thermo Scientific ARL Perform'X instrument equipped with a 3.5-kW rhodium tube.

The phase analysis of the samples was conducted using diffraction patterns recorded on a Bruker D2PHASER X-ray diffractometer using CuK_α radiation. The diffraction patterns were recorded in a 2θ angular range of 4° – 80° in increments of 0.09° at a slit width of 1 mm and an acquisition time of 5 s per point.

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

Acid site (AS) 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. After that, 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 $8^\circ\text{C}/\text{min}$; desorbed ammonia was recorded using a thermal conductivity detector.

The catalytic properties of the catalysts were studied on a laboratory flow catalytic system with a steel reactor in two modes: a liquid-phase mode (3 MPa, 170°C , a benzene/propylene molar ratio of 10, a feed space velocity of 1300 h^{-1}) and a gas-phase mode (0.1 MPa, 200°C , a benzene/propylene molar ratio of 5, a feed space velocity of 300 h^{-1}). Reaction products were analyzed on a Kristall 2000M gas–liquid chromatograph equipped with a flame ionization detector using nitrogen as a carrier gas and a 50-m-long quartz capillary column coated with the SE-30 nonpolar liquid phase. Methane was used as an internal standard to analyze the gas samples.

RESULTS AND DISCUSSION

To compare the catalysts in benzene alkylation with propylene, samples of zeolites BEA and MCM-22 with close $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 26 and 30, respectively, were synthesized.

Figure 1 shows diffraction patterns of the synthesized zeolites; all diffraction reflections in the patterns correspond to the BEA and MWW framework types [15]. The crystal structure of the BEA and MWW zeolites is preserved after binding them with pseudoboehmite; the diffraction patterns of the samples with the binder exhibit additional reflections at $2\theta = 46^\circ$ and 67° corresponding to the $\gamma\text{-Al}_2\text{O}_3$ phase [16]. Similar relationships were observed by the authors in [11], where the diffraction pattern of a sample, synthesized by binding BEA with pseudoboehmite and subsequent calcining, exhibited reflections attributed to $\gamma\text{-Al}_2\text{O}_3$.

Scanning electron microscopy micrographs show that the synthesized BEA zeolite has the form of irregularly shaped crystals with a size of 200–400 nm, while the MWW zeolite has the form of individual elliptical dish-shaped crystals with a size of 1.0–1.5 μm and a thickness of about 100 nm (Fig. 2).

During binding, the binder and the zeolite crystals undergo a tight interaction, while the crystal morphology remains unchanged.

Figure 3 shows adsorption isotherms of the synthesized zeolites and the samples synthesized with the binder; Table 1 lists their pore structure characteristics.

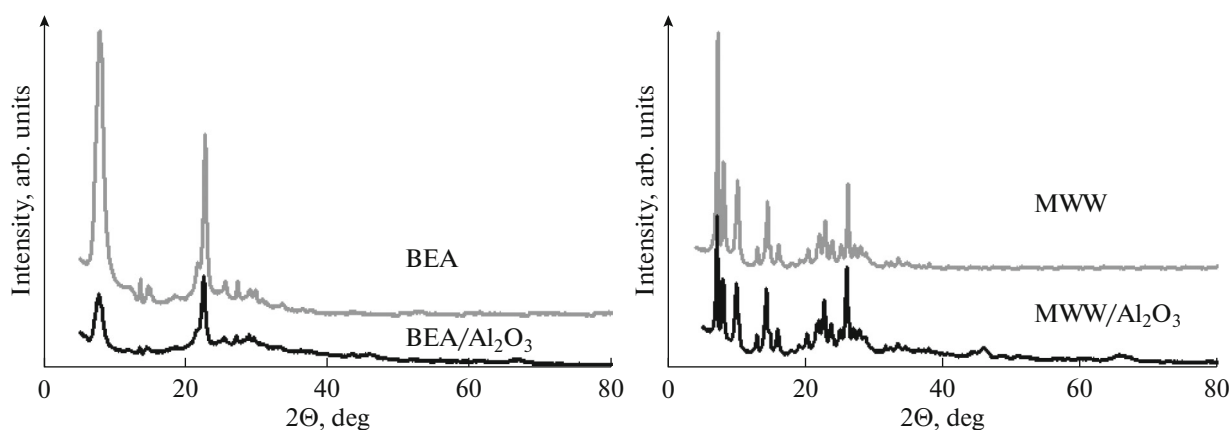


Fig. 1. Diffraction patterns of BEA, MWW, BEA/Al₂O₃, and MWW/Al₂O₃.

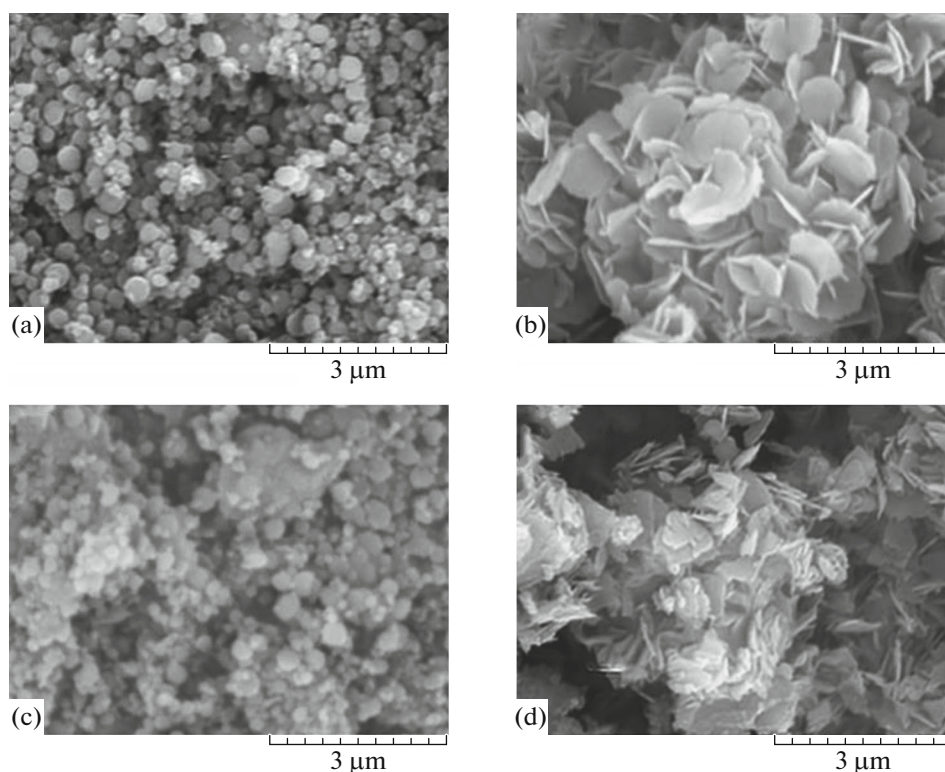


Fig. 2. Scanning electron microscopy images of (a) BEA, (b) MWW, (c) BEA/Al₂O₃, and (d) MWW/Al₂O₃.

The BEA sample has a more developed outer surface and a higher pore volume than the respective parameters of MWW. The same is true of the samples with the binder. During the synthesis of the samples with the binder, the micropores of the active zeolite phase are partially blocked, as evidenced by a shift of the nitrogen adsorption isotherm down the ordinate axis (Fig. 3) and a decrease in the micropore volume (Table 1). In terms of the pure zeolite component, the micropore volume in BEA/Al₂O₃ and MWW/Al₂O₃ is

0.157 and 0.142 cm³/g, respectively, which corresponds to a decrease in the micropore volume in the zeolite phase by 15 and 7%, respectively. This finding can be attributed to the high degree of dispersion of the pseudoboehmite particles.

The occurrence of a hysteresis in the region of $p/p_0 > 0.5$ indicates the formation of a secondary pore structure, which is attributed to the presence of the binder, and suggests that the sample synthesized with the binder is of high quality.

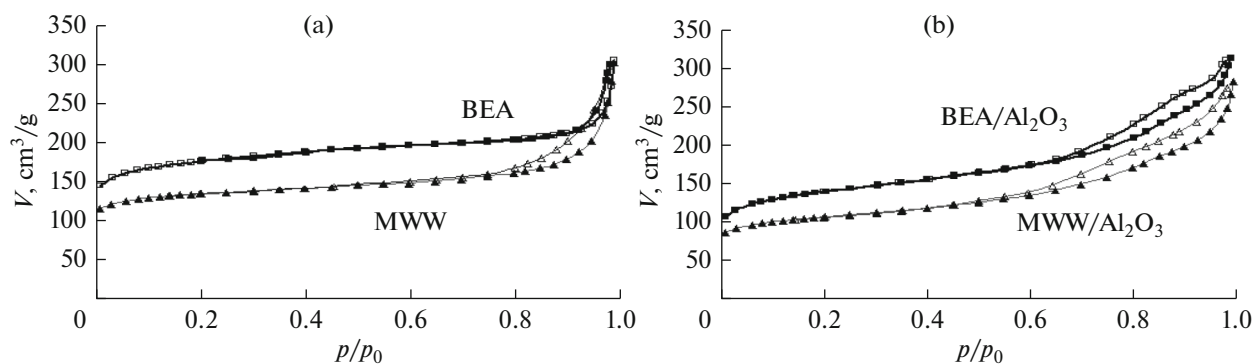


Fig. 3. Low-temperature nitrogen adsorption isotherms for (a) BEA and MWW and (b) BEA/Al₂O₃ and MWW/Al₂O₃.

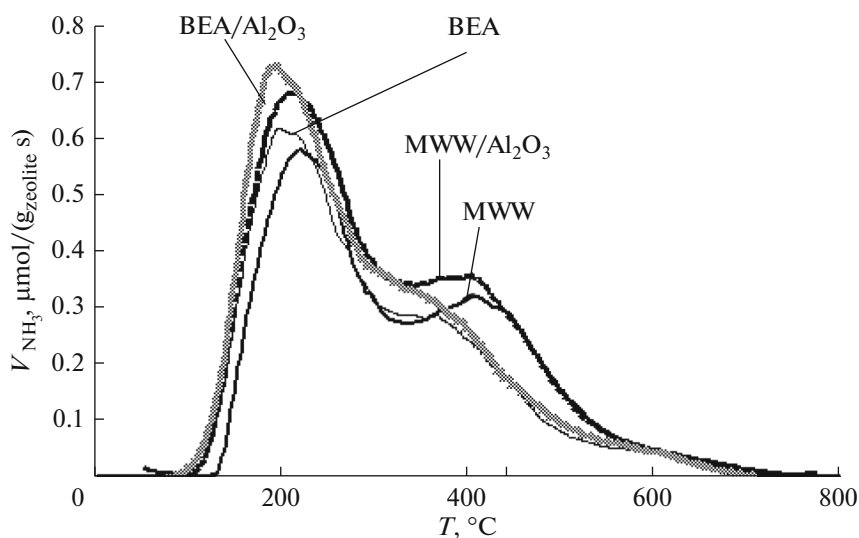


Fig. 4. Ammonia TPD curves for BEA, MWW, BEA/Al₂O₃, and MWW/Al₂O₃.

The acidic properties of the samples were studied by the NH₃-TPD method (Fig. 4). The NH₃-TPD curves exhibit two peaks with maximum temperatures of 200–230 and 370–410°C, which correspond to weak ASs and physically adsorbed ammonia and strong ASs, respectively. The number of strong ASs in the MWW zeolite is larger than that in BEA; in addition, the maximum temperature of the high-tempera-

ture peak for MWW is shifted to higher temperatures; this fact suggests that the ASs of MWW are stronger. The introduction of the binder leads to an increase in the number of ASs in the samples, while the strength of the ASs remains unchanged (Fig. 4, Table 1).

The authors of [10] assumed that, during calcining, the zeolite and the binder undergo interaction, which leads to the incorporation of aluminum into the tetra-

Table 1. Physicochemical properties of the samples

Sample	SiO ₂ /Al ₂ O ₃ , mol/mol	Binder content, %	Pore structure characteristics				Acid site concentration, μmol/g	
			S _{BET} , m ² /g	S _{micro} , m ² /g	V _{pore} , cm ³ /g	V _{micro} , cm ³ /g		
BEA	26	—	599	403	0.345	0.186	804	804*
MWW	30	—	451	330	0.312	0.153	886	886*
BEA/Al ₂ O ₃		30	483	240	0.410	0.110	676	966*
MWW/Al ₂ O ₃		30	365	215	0.337	0.099	746	1066*

* In terms of the zeolite component.

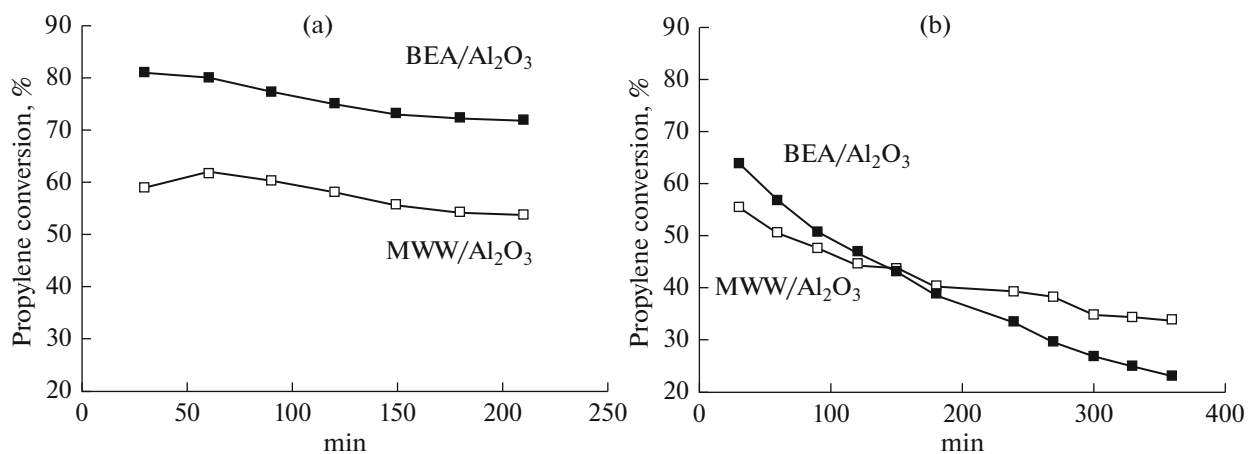


Fig. 5. Dependence of propylene conversion on the test time in (a) the liquid-phase mode, 3 MPa, 170°C, 1300 g/(g h), benzene/propylene = 10 and (b) the gas-phase mode, 0.1 MPa, 200°C, 300 g/(g h), benzene/propylene = 5.

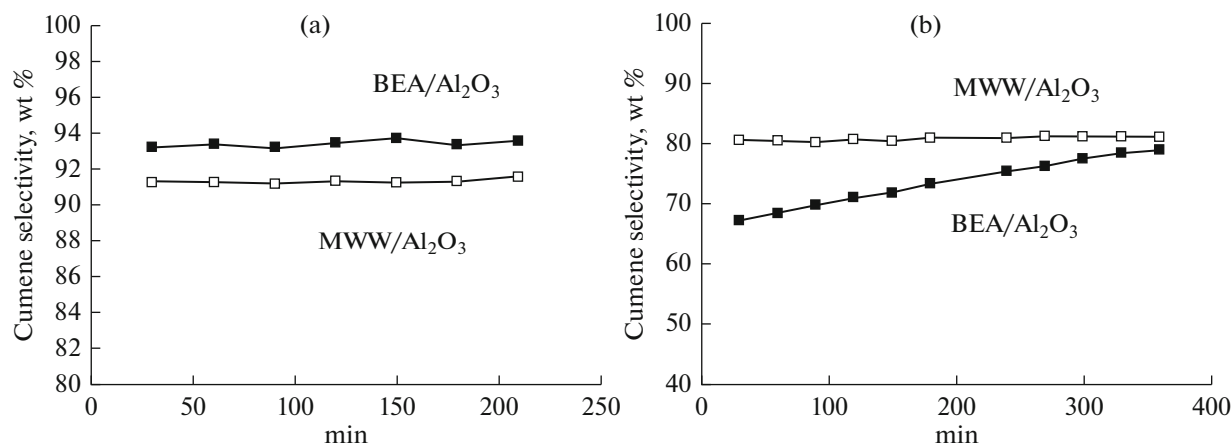


Fig. 6. Dependence of the cumene selectivity on the test time in (a) the liquid-phase mode, 3 MPa, 170°C, 1300 g/(g h), benzene/propylene = 10 and (b) the gas-phase mode, 0.1 MPa, 200°C, 300 g/(g h), benzene/propylene = 5.

hedral positions of the zeolite framework and the formation of new ASs.

In industry, benzene alkylation with propylene is run at a temperature of 125–220°C, a pressure of 0.1–30 MPa, a reactant feed space velocity of 2–4 h⁻¹, and a benzene : propylene molar ratio in the feedstock of 3 : 1 to 9 : 1. Under these conditions, the propylene conversion is close to 100%, while the product selectivity and the on-stream stability of the catalysts do not change for more than 2 years [1, 4, 17, 18]. Therefore, in this study, to compare the catalysts in activity and selectivity, the tests were conducted in special modes: under conditions of liquid-phase alkylation at a high reactant feed space velocity and under conditions of gas-phase alkylation at a high propylene content in the reaction mixture.

Results of the catalytic tests on the liquid-phase and gas-phase alkylation of benzene with propylene in the presence of BEA/Al₂O₃ and MWW/Al₂O₃

are shown in Figs. 5 and 6 and in Table 2. Diisopropylbenzenes (DIPBs), triisopropylbenzenes (TIPBs), and *n*-propylbenzene, along with the main alkylation product (cumene), were observed in the reaction products. In addition, the catalyzate contained small amounts of oligomers of propylene and alkyl aromatic hydrocarbons, which were formed in benzene alkylation with oligomers and their fragmentation products; in Table 2, they are designated as “other.” Diisopropylbenzenes and TIPBs can also be considered target products, because they can be converted to cumene via transalkylation with benzene. Under conditions of liquid-phase alkylation at a benzene/propylene ratio of 10, as under conditions of gas-phase alkylation at a benzene/propylene molar ratio of 5, BEA/Al₂O₃ is more active than MWW/Al₂O₃.

The fact that MWW/Al₂O₃ is less active than BEA/Al₂O₃, although it has a larger number of stronger ASs, is attributed to the presence of a three-dimen-

Table 2. Parameters of benzene alkylation with propylene on BEA/Al₂O₃ and MWW/Al₂O₃

Process parameters	Catalyst			
	BEA/Al ₂ O ₃ *	MWW/Al ₂ O ₃ *	BEA/Al ₂ O ₃ **	MWW/Al ₂ O ₃ **
Propylene conversion, %	81.1	59.1	64.0	55.5
Selectivity, wt %				
Cumene	93.1	91.2	67.5	80.6
<i>n</i> -propylbenzene	0.03	0.03	0.1	0.1
DIPBs	6.5	7.9	29.2	15.6
TIPBs	0.02	0.6	1.8	3.2
Σ “other”	0.3	0.2	1.0	0.3

* Liquid-phase mode, 3 MPa, 170°C, 1300 g/(g h), benzene/propylene = 10.

** Gas-phase mode, 0.1 MPa, 200°C, 300 g/(g h), benzene/propylene = 5.

sional pore system in BEA and the accessibility of all ASs of BEA to the reactant molecules. In MCM-22, the reaction occurs on ASs located in the “cups” on the outer surface of the crystals, while the remaining ASs are not accessible to benzene molecules [2, 4, 8]. Comparison of the results with the published data on zeolites BEA and MWW without a binder showed that the introduction of a binder does not lead to significant changes. Some discrepancies with the data of [1, 8] are apparently associated with differences in the process conditions.

Comparison of the selectivity for the desired product cumene in the presence of the catalysts based on BEA and MWW showed that, in the liquid-phase mode, the differences are not significant and the cumene selectivity is slightly higher in the case of BEA. Conversely, in the gas-phase mode, the initial cumene selectivity of BEA/Al₂O₃ is lower than that of MWW/Al₂O₃; however, the cumene selectivity of BEA/Al₂O₃ increases over time; after 6 h of reaction, it approaches the cumene selectivity of MWW/Al₂O₃. This finding is attributed to the fact that, in the gas-phase mode, at the beginning of the test, the DIPB and TIPB selectivity is higher in the presence of the BEA-based catalyst; during reaction, the DIPB and TIPB selectivity decreases. The selectivity for the sum of alkylated products (cumene, DIPBs, TIPBs) in the presence of the studied catalysts is similar in the two modes (Table 2). In the presence of MWW/Al₂O₃, in the liquid-phase mode, larger amounts of DIPBs and TIPBs are formed, because the reaction occurs on the outer surface of this catalyst and there are no steric hindrances to the formation of polyalkylated products. The formation of a larger amount of polyalkylated products over BEA/Al₂O₃ in the gas-phase mode is apparently attributed to the fact that, in the gas phase, the diffusion of large DIPB and TIPB molecules from the catalyst pores occurs more readily than in the liquid-phase mode; however, during coking, the BEA pores become narrower; this factor hinders both the formation of large molecules and their diffusion from

the zeolite channels. According to the results that were obtained in the liquid-phase mode [1, 4, 8, 9], the cumene selectivity is higher in the presence of MWW than in the case of BEA. These results were attributed in [4, 8] to the fact that the amount of Brønsted acid sites responsible for the formation of cumene in BEA is smaller than that in MWW, whereas Degnan et al. [1] attributed the results to the lower propylene oligomer selectivity in the presence of MWW. A decrease in the benzene/propylene ratio naturally leads to an increase in the amount of polyalkylated products (Table 2).

Studies of the catalyst deactivation showed that, in the liquid-phase mode, the two catalysts lost their activity only slightly: within the entire test, the propylene conversion decreased by less than 10%. In the gas-phase mode test (atmospheric pressure, benzene/propylene molar ratio of 5), the on-stream behavior of MWW/Al₂O₃ was more stable than that of BEA/Al₂O₃ throughout the entire test. These data are consistent with the results of [4]. In the presence of BEA, at a high propylene content in the reaction mixture, on ASs located inside the zeolite channels, propylene undergoes oligomerization to form condensation products, whereas in the presence of MWW, the formation of cumene occurs on the outer surface of the crystals; therefore, the propylene oligomerization inside the MWW channels does not have a significant effect on the on-stream stability of the catalyst. Another factor contributing to the stable on-stream behavior of MWW/Al₂O₃ is that large molecules—coke precursors—diffuse on the outer surface of MWW crystals more readily and rapidly than they do inside the BEA channels [4, 8]; this finding is consistent with the fact that, in the presence of BEA, the DIPB and TIPB yield is almost two times higher than the yield in the presence of MWW (Table 2).

Comparison of the published data and the results obtained in this study suggests that the introduction of a binder does not have a significant effect on the catalytic properties of the samples.

Thus, it has been found that the shaping of zeolites BEA and MWW with pseudoboehmite as a binder does not affect the morphology of the zeolite component; however, it has an effect on the textural and acidic characteristics of the catalysts with the binder. The introduction of the binder leads to a partial blocking of the micropores of the active zeolite phase, the formation of a secondary pore structure, which is attributed to the presence of the binder, and an increase in the number of ASs in the samples, while the strength of the ASs remains unchanged. Slight changes in textural and acidic properties do not have a significant effect on the catalytic properties of the zeolites in benzene alkylation process with propylene. The BEA/Al₂O₃ catalyst is more active in alkylation than MWW/Al₂O₃ in both the liquid-phase and gas-phase modes. However, with respect to some parameters, such as cumene selectivity and time-on-stream stability, the MWW/Al₂O₃ catalyst is superior to BEA/Al₂O₃. The observed differences are attributed to the structural features of the BEA and MWW zeolites.

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REFERENCES

1. T. F. Degan, Jr., C. M. Smith, and Ch. R. Venkat, *Appl. Catal.*, A **221**, 283 (2001).
2. G. Sastre, C. R. A. Catlow, and A. Corma, *J. Phys. Chem. B* **103**, 5187 (1999).
3. C. Perego and P. Ingallina, *Catal. Today* **73**, 3 (2002).
4. A. Corma, V. Martinez-Soria, and E. Schnoefeld, *J. Catal.* **192**, 163 (2000).
5. S. Gomm, R. Glaser, and J. Weitkamp, *Stud. Surf. Sci. Catal.* **154**, 760 (2004).
6. G. C. Laredo, R. Quintana-Solorzano, J. J. Castillo, et al., *Appl. Catal.*, A **454**, 37 (2013).
7. G. Bellussi, G. Pazzuconi, C. Perego, et al., *J. Catal.* **157**, 227 (1995).
8. G. C. Laredo, J. J. Castillo, J. Nawarrete-Bolanos, et al., *Appl. Catal.*, A **413–414**, 140 (2012).
9. G. Buelna, M. Ulutagay-Kartin, and T. M. Menoff, *Chem. Eng. Commun.* **193**, 606 (2006).
10. S. L. Lawton, M. E. Leonowicz, R. D. Partridge, et al., *Microporous Mesoporous Mater.* **23**, 109 (1998).
11. T. O. Bok, E. P. Andriako, E. E. Knyazeva, et al., *Pet. Chem.* **58**, 833 (2018).
12. U. J. Etim, P. Bai, Y. Wang, et al., *Appl. Catal.*, A **571**, 137 (2019).
13. T. O. Bok, E. D. Onuchin, A. V. Zabil'skaya, et al., *Pet. Chem.* **56**, 1160 (2016).
14. V. Fornes and A. Corma, *Microporous Mesoporous Mater.* **90**, 73 (2006).
15. *Verified Syntheses of Zeolitic Materials*, Ed. by S. Mintova and N. Barrier (XRD Patterns), 3rd Ed. (International Zeolite Association, 2016).
16. E. M. Moroz, K. I. Shefer, D. A. Zyuzin, and A. N. Shmakov, *J. Struct. Chem.* **52**, 326 (2011).
17. F. Zhao, Y. Zhang, S. Geng, et al., *Adv. Mater. Res.* **549**, 283 (2012).
18. O. A. Ponomareva, E. E. Knyazeva, A. V. Shkuropatov, et al., *Pet. Chem.* **57**, 1147 (2017).

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