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HIGH MODULUS MOR-TYPE ZEOLITE CATALYSTS

КАТАЛИЗАТОРЫ НА ОСНОВЕ ВЫСОКОМОДУЛЬНОГО ЦЕОЛИТА ТИПА MOR

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Abstract. This paper is dedicated to synthesis of MOR-type zeolite specimens in Na- and H-form of high phase purity and having crystallinity degree of nearly 100% with molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3 = 15-24$ in deep-decationated form, and investigation of their properties.

To obtain chemically homogeneous silica-alumina hydrogel, mixing of crystal-forming components was implemented with reaction mass being continuously stirred. The stirring was still continuing during the process of crystallization. Crystallization was conducted at a temperature of 150-160 °C.

The compositions of oligomers were quantified by high-performance liquid chromatography.

The conversion of the initial olefin, its composition and amount of its isomers, the amount of low molecular weight oligomers (with a molecular weight less than the dimers) as well as the number of dimer were measured by gas-liquid chromatography.

The dimer fraction was extracted by reaction mixture distillation under reduced pressure and analyzed by nuclear magnetic resonance (NMR) ^1H , ^{13}C , IR- and mass spectrometry methods.

By method of temperature-programmed ammonia desorption it was found that with zeolite module increasing there was an increase in strength of zeolite acid sites.

For evaluation of catalytic properties of the derived H-form of MOR-type zeolite specimens with various modules, model reaction of α -methylstyrene dimerization was used.

It was found that with zeolite module increasing there was an increase in cyclic dimers formation selectivity from 20 to 52%. The α -methylstyrene conversions on MOR-type zeolite specimens were investigated at a temperature of 80 °C with a 10% catalyst in nitrogen atmosphere. The catalyst was calcinated prior to the reaction at a temperature of 300 °C during 2-3 hours with rare gas current in the reaction flask.

Implementation of the method developed makes it possible to expand the raw materials base, simplify the synthesis and reduce the cost of powdery mordenite type zeolite.

Аннотация. Синтезированы образцы цеолита типа MOR в Na- и H-форме высокой фазовой чистоты и степени кристалличности близкой к 100% с молярным отношением $\text{SiO}_2/\text{Al}_2\text{O}_3 = 15-24$ в глубокодекатинированной форме и исследованы их свойства.

Для получения однородного по химическому составу силикаалюмогидрогеля смешение кристаллообразующих компонентов осуществлено при непрерывном перемешивании реакционной массы, которое не прекращали

и при кристаллизации. Кристаллизацию проводили при 150-160 °С.

Составы олигомеров определены с помощью высокоэффективной жидкостной хроматографии.

Степень превращения исходного олефина, состав и количество его изомеров, количество низкомолекулярных олигомеров (с молекулярной массой меньше, чем димеры), а также количество димеров определены методом газожидкостной хроматографии.

Фракции димеров выделены перегонкой реакционной массы при пониженном давлении и анализированы методами ЯМР ^1H , ^{13}C , ИК- и масс-спектрометрии.

Методом термопрограммированной десорбции аммиака установлено, что с увеличением модуля цеолита наблюдается увеличение силы кислотных центров.

Для оценки каталитических свойств полученных H-форм образцов цеолита типа MOR с различным модулем использована модельная реакция димеризации α -метилстирола.

Обнаружено, что с увеличением модуля цеолита увеличивается селективность образования циклических димеров с 20 до 52%. Превращения α -метилстирола на образцах цеолита типа MOR изучены при 80 °С в присутствии 10% катализатора в атмосфере азота. Катализатор перед реакцией прокален при 300 °С в течение 2-3 ч в реакционной колбе в токе инертного газа.

Внедрение разработанного способа позволяет расширить сырьевую базу, упростить синтез и снизить себестоимость порошкообразного цеолита типа морденит.

Key words: zeolite, synthesis, ion-exchange forms, zeolite module, mordenite, crystallization, sodium silicate.

Ключевые слова: цеолит, синтез, ионообменные формы, модуль цеолита, морденит, кристаллизация, силикат натрия.

Among the zeolites used in adsorption and catalysis, a MOR-type zeolite has a special place due to its acid-resistance, thermostability and acidic properties.

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio increase in zeolite leads to enhancement of its thermostability and stability in acid medium [1]. To obtain high modulus mordenites ($\text{SiO}_2/\text{Al}_2\text{O}_3 > 13$) it is suggested to conduct dealumination of low-modulus ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 8-10$) mordenites [1] or high-temperature synthesis in the presence of organic additives used as templates [2]. Quaternary alkyl ammonium compounds are usually used for these purposes. Information on synthesis conditions for high-modulus mordenites in the presence of tetraalkylammonium bromide is given in points [3-5], whereas the data on physicochemical and catalytic properties of the zeolites being synthesized are very limited.

This paper is dedicated to synthesis of MOR-type zeolite of high phase purity and crystallinity degree of nearly 100% with molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3 = 15-24$ in deep-decanted form, and investigation of its properties.

Experimental Part

The powdered MOR-type zeolite is synthesized at temperatures above 100 °C and under superatmospheric pressures.

In this paper crystallization of zeolite specimens was conducted in a 5-litre crystallizer tank equipped with a gate agitator rotating at 60 revolutions per minute, electrical heating and a sampling instrument. The sampling instrument available allowed taking samples without disturbance of crystallization behavior.

Powdered zeolites were obtained by mixing the initial reagents: sodium silicate and sodium aluminate solutions, industrial carbon white (BS-100) containing not less than 98 % of silicon (SiO_2), and an organic structure-forming agent. As a result, silica-alumina hydrogel was obtained with chemical composition being changed in the following way, depending on the experiment purpose: $(4,6-9,0)\text{R}_2\text{O} \cdot (2,2-3,2)\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot (15-30) \text{SiO}_2 \cdot (400-540)\text{H}_2\text{O}$, where R is an organic cation.

In order to obtain chemically homogeneous silica-alumina hydrogel, mixing of crystal-forming components was carried out with reaction mass being constantly stirred. The stirring was still continuing during the process of crystallization. The crystallization was conducted at a temperature of 150-160 °C.

After the crystallization was finished, the suspension underwent the vacuum filtration. The powdered zeolite was cleaned up to pH = 9,0-10,0. After the synthesis and cleaning from the excess of sodium cations, the MOR-type zeolite specimens were exposed to heat treatment at a temperature of 500-550 °C during 4 hours (temperature increase rate was 150 °C per hour) in air. At the same time the template was being removed from the zeolite void structure.

Deep-decationated forms of zeolite were synthesized by ionic replacement of Na⁺ cations by NH₄⁺ cations and the further heat treatment at a temperature of 600 °C during 4 hours in air.

Chemical compositions of liquid and solid phases were analyzed by methods of flame photometry and chelatometry [6-9]. To quantify phase composition of the specimens, X-ray powder diffraction phase analysis was applied using a PHILIPS PW 1800 X-ray diffractometer in monochromated Cu-k α radiation with a voltage of 40 kV and a current intensity of 40 mA. Diffractograms were obtained during shooting with a step in $2\theta = 0,02^\circ$ and an integral time of 5 seconds per point. To measure the relative crystallinity (RC), the internal standard method was used. According to ASTM D 3906-03, the relative crystallinity was measured as a ratio of the sums of the specimen peak areas to the sum of the peak areas of the "standard" model [2].

Measuring equilibrium adsorption capacities of zeolites (mg / g) by water, benzene and heptane vapors (A_{H_2O} , $A_{C_6H_6}$, $A_{C_7H_{16}}$, respectively) was conducted under static conditions by an "exsiccator method" [10] at a temperature of 20 °C and $P / P_s = 0,7 - 0.8$.

Catalytic properties of powdered mordenites were studied during dimerization of α -olefins. The dimerization of α -olefins was carried out in glass ampoules where olefin and a catalyst agent were put. The ampoules were placed in

a metal autoclave after sealing. Heating of autoclaves was carried out in a thermostatic oven where they continuously rotated at a predetermined temperature during the required period of time. When the reaction was finished, the autoclaves were condensed; the ampoules were removed from the autoclaves and opened. The reaction mixture was filtered and analyzed.

The composition of oligomers was determined by high-performance liquid chromatography (HP-1090 chromatograph was used, the analysis conditions being as follows: Plgel-50Å polystyrene leg, toluene conveying speed of 0.8 ml / min, tape speed of 1.5 cm⁻¹, refractive index detector). The initial olefin conversion, its composition, the amount of its isomers, low molecular weight oligomers (with a molecular weight being less than the dimers) and the amount of dimers were measured by gas-liquid chromatography (HRGS 5300 Mega Series "Carlo Erba" chromatograph with a flame ionization detector was used, the analysis conditions being as follows: 25 m glass capillary column, 50-280 °C temperature with preset heating of 8 °C / min, the detector temperature of 250°C, the evaporimeter temperature of 300°C, gas carrier (helium) with a conveying speed of 30ml/min).

The dimer fraction was extracted by distillation of the reaction mixture under reduced pressure and analyzed by nuclear magnetic resonance, ¹H, ¹³C, IR and mass spectrometry methods.

NMR spectra were recorded on a "Bruker AVANCE - 400" spectrometer, 400.13 (1H) and 100.62 MHz (13C) in CDCl₃. The high resolution mass spectra were recorded with the help of Fisons Trio 1000 instrument having a chromatograph equipped with DB 560 silica capillary column of 50 m; temperature programming was from 50 °C to 320 °C at a speed of 4 °C /min, with an electron impact of 70 eV.

Discussion of the results

It is known that with enhancement of the modulus the zeolite crystal structure thermal stability increases. For obtaining mordenite type high-modulus zeo-

lites the secondary treatment (by dealumination method) of low-modulus ($M = 8.10$) zeolites or direct high temperature synthesis with quaternary alkylammonium salts were previously used.

In this paper research was carried out using the following reaction mixtures: $(4,6-9,0)R_2O \cdot (2,2-3,2)Na_2O \cdot Al_2O_3 \cdot (15-30) SiO_2 \cdot (400-540)H_2O$, containing organic template - tetraethyl ammonium bromide (TEABr).

It is known that crystallization results depend on the nature of raw material components, reaction mixture composition, temperature and duration of crystallization. Initially we studied the effect of the reaction mixture composition on properties of crystallization products.

Table 1 shows properties of the zeolite specimens obtained by crystallization of the reaction mixture compositions given above at a temperature of 150-160 °C.

Table 1. Effect of reaction mixture composition on crystallization products properties at a temperature of 150-160 °C

The reaction mixture composition	Equilibrium adsorption capacities (sm^3/g) for:			The X-ray fluorescence analysis data	SiO ₂ /Al ₂ O ₃ modulus
	water	heptane	benzene		
$4,6R_2O \cdot 2,2 Na_2O \cdot Al_2O_3 \cdot 15 SiO_2 \cdot 444H_2O$	0,14	0,16	0,15	MOR	15
$4,6R_2O \cdot 2,2 Na_2O \cdot Al_2O_3 \cdot 20 SiO_2 \cdot 444H_2O$	0,14	0,16	0,15	MOR	17
$4,6R_2O \cdot 2,2 Na_2O \cdot Al_2O_3 \cdot 25 SiO_2 \cdot 444H_2O$	0,14	0,16	0,15	MOR	21
$4,6R_2O \cdot 3,2 Na_2O \cdot Al_2O_3 \cdot 25 SiO_2 \cdot 444H_2O$	0,14	0,16	0,15	MOR	21
$9,0R_2O \cdot 2,2 Na_2O \cdot Al_2O_3 \cdot 25 SiO_2 \cdot 444H_2O$	0,14	0,16	0,15	MOR	24
$9,0R_2O \cdot 3,2 Na_2O \cdot Al_2O_3 \cdot 25 SiO_2 \cdot 444H_2O$	0,14	0,16	0,15	MOR	24

duration – 48 h, template – tetraethylammonium bromide.

It follows from the table data that during crystallization of all types of the above-mentioned reaction mixture compositions high modulus MOR-type zeolite with high phase purity and crystallinity degree of nearly 100% can be obtained. Figure 1 shows XRD patterns of MOR-type zeolite specimens after 18

hours of crystallization of the reaction mixture compositions differing in R_2O / Al_2O_3 and Na_2O / Al_2O_3 ratios.

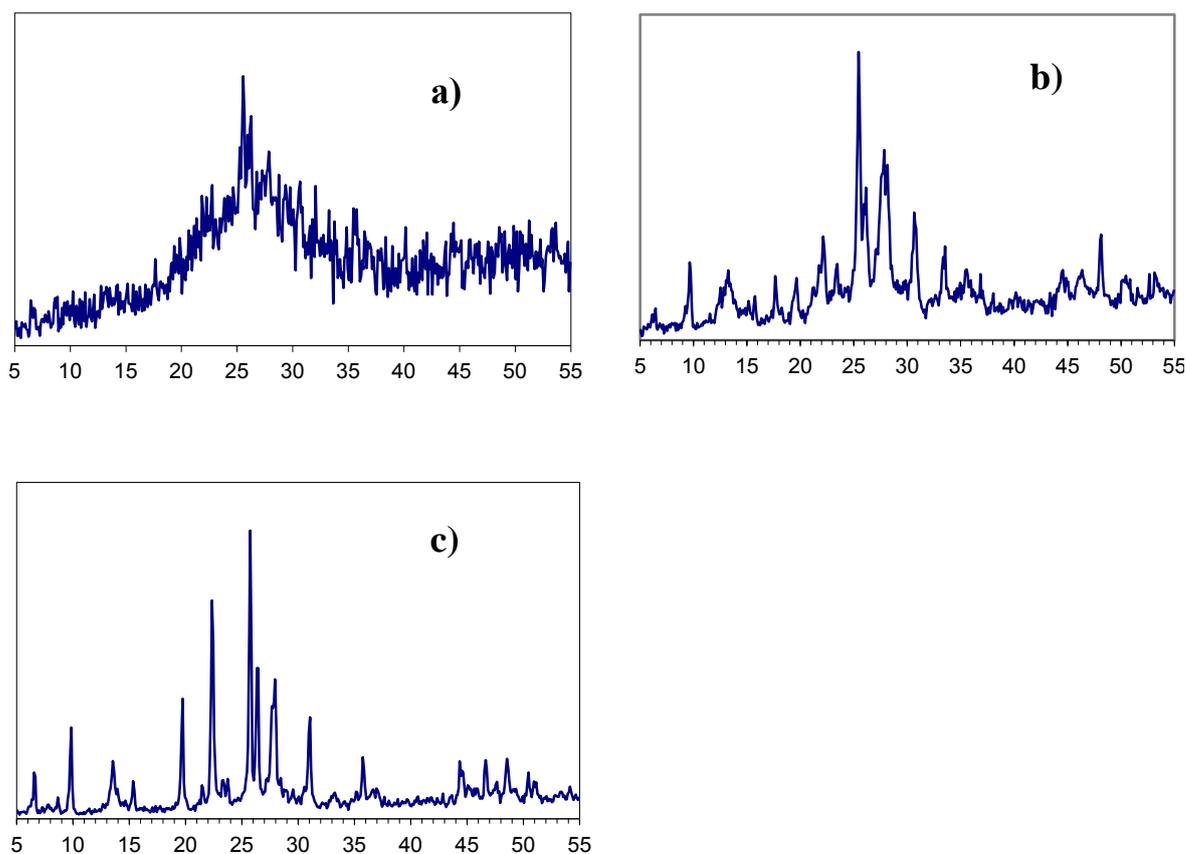


Figure 1. X-ray diffraction patterns of the MOR-type zeolite samples after 18 hours of crystallization of the following reaction mixture compositions: a) $4,6R_2O \cdot 2,2 Na_2O \cdot Al_2O_3 \cdot 25 SiO_2 \cdot 444H_2O$; b) $4,6R_2O \cdot 3,2 Na_2O \cdot Al_2O_3 \cdot 25 SiO_2 \cdot 444H_2O$; c) $9,0R_2O \cdot 3,2 Na_2O \cdot Al_2O_3 \cdot 25 SiO_2 \cdot 444H_2O$

Figure 1a shows that with the reaction mixture composition of $4,6R_2O \cdot 2,2 Na_2O \cdot Al_2O_3 \cdot 25 SiO_2 \cdot 444H_2O$ after 18 hours of crystallization the product becomes amorphous. Increase in the medium alkalinity and the amount of organic structure-forming agent leads to a faster crystallization process, as the main apexes (Figure 1b,c) at 51° , $9,70^\circ$, $13,45^\circ$, $19,61^\circ$, $22,20^\circ$, $26,25^\circ$, $27,67^\circ$, $30,89^\circ$ and $35,61^\circ$ diffraction angles show. These peaks are typical for MOR-type zeolite [11] only. Therefore, the resulting product is MOR type zeolite of high phase purity. Thus, it is established that an increase in R_2O / Al_2O_3 и Na_2O / Al_2O_3 ratio causes an increase in crystallization rate, consequently, reducing the synthesis process duration from 48 to 18 hours.

During the synthesis of zeolites using organic templates, some of the cationic sites are occupied by cations of tetraethylammonium which remain in zeolite channels after removal of mother liquor components. To remove these cations, it is suggested [2] to use heat treatment at a temperature of 540 -600 °C for several hours in the air flow before or after exchange treatments. In this study MOR-type zeolite heat treatment was conducted before ion exchange.

The results of the obtained material study by X-ray fluorescence analysis before and after burning out the template are shown in Figure 2.

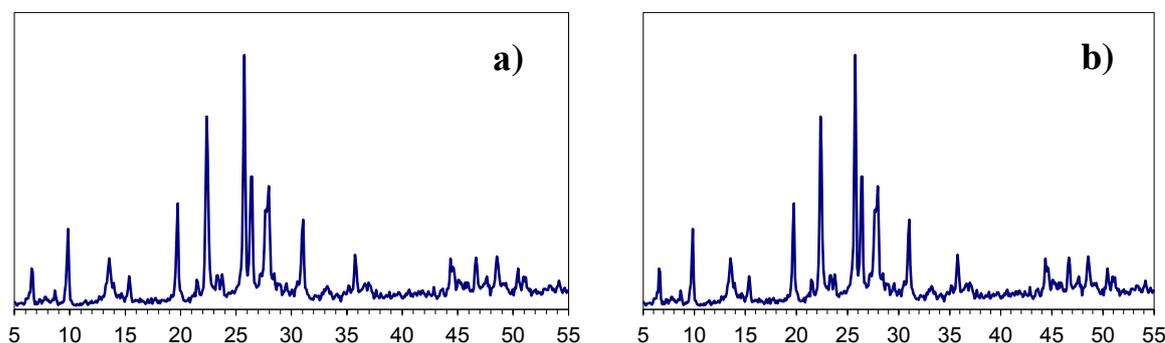


Figure 2. X-ray diffraction patterns of MOR-type zeolite samples ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 21$): a) Na- MOR before burning out a template; b) HNa- MOR after burning out a template

It is obvious, that the main apexes which are typical for MOR-type zeolite only, are preserved after heat-treating operation. Therefore, removal of template from zeolite structure does not lead to its destruction.

For preparation of a deep-decanted form of MOR-type zeolite the following conditions were selected: temperature = 80-90 °C; duration - 1 hour; NH_4^+ gram equivalent proportion in the solution to Na^+ gram equivalent in zeolite (GNH_4) = 1,5. H form of MOR-type zeolite was prepared using heat treatment at a temperature of 600 °C.

As MOR-type zeolite has a canal structure providing that there are no Na^+ cations crystallographic positions which would be problematic for double decomposition, there was no transitory heat treatment between ionic replacements. X-ray diffraction patterns of the prepared specimens are shown in Figure 3.

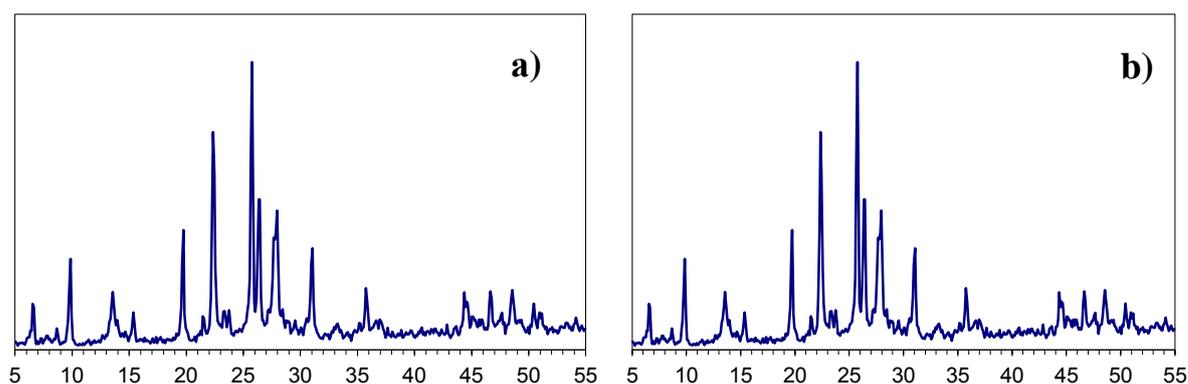


Figure 3. X-ray patterns of MOR zeolite specimens ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 21$):
a) NH_4^+ -MOR; b) H-MOR

As a result of ion-exchange treatments, MOR-type zeolite specimens were prepared with various modules in H-form having Na^+ degree of double decomposition in H^+ equal to 0,95. Equilibrium adsorption capacities of these specimens for water ($A_{\text{H}_2\text{O}}$), benzol ($A_{\text{C}_6\text{H}_6}$), n-heptane ($A_{\text{C}_7\text{H}_{16}}$) are given in Table 2.

It is obvious that with substitution of Na^+ cations to H^+ cations there is an increase in $A_{\text{H}_2\text{O}}$, $A_{\text{C}_6\text{H}_6}$, $A_{\text{C}_7\text{H}_{16}}$ values. It is connected with intracrystalline volume availability increase.

Table 2. Equilibrium adsorption capacities (cm^3/g) of MOR-type zeolite specimens with various modules before and after ionic replacement

(SiO ₂ / Al ₂ O ₃) module of MOR-type zeolite	Before ionic replacement			after ionic replacement		
	A _{H₂O}	A _{C₇H₁₆}	A _{C₆H₆}	A _{H₂O}	A _{C₇H₁₆}	A _{C₆H₆}
15	0,14	0,16	0,15	0,18	0,22	0,20
17	0,14	0,16	0,15	0,18	0,22	0,20
21	0,14	0,16	0,15	0,18	0,22	0,20
24	0,14	0,16	0,15	0,18	0,22	0,20

* - 20 °C , P/P_s= 0.8

Acid site concentrations of these specimens were measured by transfer desorption of ammonia preliminary adsorbed. In Table 3 the amounts of high modulus specimens of acid sites in comparison with H-form low-modulus MOR zeolite are given.

Table 3. The amount of weak and strong acid sites (microkilomol per gramme) in MOR zeolite specimens with various modules

SiO ₂ / Al ₂ O ₃) module of MOR-type zeolite	Weak acid sites*		strong acid sites**	
	before ionic replacement	after ionic replacement	before ionic replacement	after ionic replacement
10	405	536	225	342
15	455	565	274	374
17	475	570	279	380
21	577	643	294	457
24	581	647	302	477

* stripped NH₃ amount (microkilomol per gramme) in temperature interval from 100 to 350 °C.

** stripped NH₃ amount (microkilomol per gramme) in temperature interval from 350 to 550 °C.

Based on the results obtained, it is possible to conclude that with Na⁺ cations being substituted for H⁺ cations, acid site concentration of all MOR zeolite specimens increases. Besides, with the acid sites being increased, zeolite module enhancement is observed.

In order to evaluate catalytic properties of the derived H-forms of MOR-type zeolite specimens with various modules, α -methylstyrene dimerization model reaction was used. Its dimers are valuable petro-chemicals. The in-line not-saturated dimers of α -methylstyrene are used as molecular weight regulators in the process of production of high-impact polystyrene, acrylonitrile butadiene styrene phenolics, lacquer solvent, dielectric liquids, plasticizers of polymers and rubber masterbatches, circuit-breaker oil. Closed-chain dimers of vinylarenes with indan structure are used as lubricating and insulating material; they can be also applied in atomic industry as scintillometer elements for radiation detection and high-temperature heat transfer agents, the basic for preparation of chromane compounds, anthraquinone derivatives, pesticides and colouring agents.

α -methylstyrene conversions on MOR-type zeolite specimens were studied at a temperature of 80 °C with a 10% catalyst in nitrogen atmosphere, the experi-

ment duration being 3 hours. The catalyst was calcinated before the reaction at a temperature of 300 °C during 2-3 hours with rare gas current in a reaction flask.

The results of α -methylstyrene dimerization in the presence of the MOR-type zeolite specimens in H-forms are given in Table 4.

Table 4. α -methylstyrene dimerization in the presence of initial and decationated MOR-type zeolite specimens

(SiO ₂ / Al ₂ O ₃) module of MOR-type zeolite	Change ratio %	Selectivity, %		
		CCD	LD	Tr.
10	98,8	21,5	68,1	10,4
15	98,0	32,2	62,8	5,0
17	98,0	35,6	58,9	5,5
21	98,2	50,1	45,9	4,0
24	98,5	52,3	42,9	4,8

CCD- closed-chain dimer; LD- linear dimers; Tr. – trimers

It is obvious that all the specimens demonstrate high catalytic activity – α -methylstyrene change ratio is 98,0-98,8%.

The main products of the reaction (90-96%) are α -methylstyrene dimers, with trimer amount being 4-10%. The study of oligomers shows that with zeolite module enhancement selectivity of formation of cyclic dimers increases from 20 to 52%. With enhancement of selectivity of formation of cyclic dimers, the proportion of linear dimers in oligomers decreases.

Conclusions

1. Synthesis of high phase purity mordenite was developed, with mordenite having a molecular ratio of SiO₂/Al₂O₃ = 15-24 and crystallinity degree of nearly 100 % based on crystallization at a temperature of 150-170 °C of silica alumina hydrogel with the following composition:



2. It is shown that in the process of transition from MOR-type zeolite NNa form to H-form concentration of acid sites in all the specimens increases. Fur-

thermore, with zeolite module increasing, the increase of acid site strength is observed.

3. It was found that with zeolite module increasing, there is an enhancement of selectivity of formation of cyclic dimers from 20 to 52%. As selectivity of formation of cyclic dimers in oligomers increases, the proportion of linear dimers decreases.

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