# Synthesis of ZSM-22 and Testing Its Catalytic Properties in the Ethylene Oxide Isomerization Reaction

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**Abstract**—The influence of the key parameters of the synthesis of a TON-type zeolite (ZSM-22) with or without an organic structure-directing agent on its phase composition has been established. The optimal composition of the reaction mixture and the crystallization time of ZSM-22 in the presence of 1,6-diaminohexane under static conditions have been determined. The dynamics of the formation of an impurity ZSM-5 by cocrystallization during the synthesis with stirring has been revealed. For zeolite ZSM-22 synthesized using the template-free procedure, the most important factors affecting the crystallinity and the crystallization time are the synthesis temperature, the amount of seed, and agitation of the reaction mixture. The zeolites synthesized according to the both procedures have been examined in the reaction of isomerization of ethylene oxide to acetaldehyde. Zeolite ZSM-22 obtained without adding the template is not inferior in activity to the zeolite of the same structure prepared in the presence of 1,6-diaminohexane. Moreover, it exhibits higher selectivity of ethylene oxide conversion to acetaldehyde. The complete conversion of ethylene oxide has been observed on ZSM-22 zeolites of both types at a reaction temperature of 400°C, the selectivity of its conversion to acetaldehyde being at least 93%.

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Zeolites that have the porous space formed by 10membered rings and possess a one-dimensional channel system are of great interest for catalysis, since they exhibit high configurational selectivity for products in a number of the most important petrochemical and petroleum refining reactions [1, 2]. This class of zeolites includes materials with the TON framework structure: ZSM-22, Theta-1, Nu-10, etc. It is known that they exhibit sufficient catalytic activity and high selectivity for the desired products in important reactions, such as hydroisomerization [3, 4], isomerization of butenes [5] and xylenes [6], alkylation and disproportionation of toluene [7], and methanol reforming to hydrocarbons [8].

As other high-silica zeolites, ZSM-22 is synthesized by hydrothermal synthesis in the presence of a number of organic structure-directing agents (templates), such as 1,6-diaminohexane, 1,8-diaminooctane, and 1-ethylpyridinium bromide [9-11]. In the literature on the synthesis of these zeolites, it is noted that the use of the most available templates 1,6-diaminohexane and 1,8-diaminooctane usually leads to the formation of impurities ZSM-5 and cristobalite in the resulting zeolite material along with the main phase ZSM-22 [12]. Researchers propose various approaches to the synthesis of ZSM-22 zeolites, but basically they boil down to the optimal organization of the agitation of the reaction mixture during the synthesis (speed, horizontal or vertical stirring, periodicity) [13]. All of these options lead in varying degrees to a reduction in the number of foreign phases and amorphous impurities.

At the same time, synthesis methods for any zeolite, including ZSM-22, using organic structuredirecting agents have common drawbacks: the formation of impurity phases, the presence of defects in the zeolite structure due to the removal of the template during high-temperature calcination, the high cost and toxicity of the templates, and the formation of harmful emissions and effluents during the synthesis process. Therefore, studies devoted to the development of template-free synthesis methods based on the use of seed or seed solutions [14, 15] are of particular interest.

This paper is devoted to a comparative study of the features of two different procedures for the synthesis of zeolite ZSM-22: with the use of 1,6-diaminohexane and without a template. The main objective of the study was to identify the key synthesis parameters that affect the phase composition, morphology, texture, and acidity of zeolites and their catalytic properties in a test reaction.

As a test, the reaction of ethylene oxide isomerization to acetaldehyde was chosen [16]. It has already been shown that ZSM-23 zeolites, which, like ZSM-22, have a one-dimensional system of channels of similar diameter, exhibit high selectivity for the desired product in this reaction [17]. This gives grounds to hope that ZSM-22 will also be of interest as an isomerization catalyst.

# **EXPERIMENTAL**

#### Zeolite Synthesis

The following chemicals were used to synthesize ZSM-22 zeolites: 1,6-diaminohexane  $(NH_2(CH_2)_6NH_2, 98\%)$ , aluminum sulfate  $(Al_2(SO_4)_3 \cdot 18H_2O, \ge 97\%)$ , and ammonium nitrate  $(NH_4NO_3, \ge 99\%)$  from Sigma-Aldrich; silica sol (30% SiO<sub>2</sub>, Ludox AS30, DuPont); and potassium hydroxide (KOH, 85%) and tetraethoxysilane  $(C_2H_5O)_4$ Si, 99+%) of Alfa Aesar.

In the presence of 1,6-diaminohexane (DAH), the zeolite was synthesized according to the procedure described in [9] with minor changes. The reaction mixture with a molar ratio of components 27.5DAH : xKOH : Al<sub>2</sub>O<sub>3</sub> : 90SiO<sub>2</sub> : 3650H<sub>2</sub>O (x = 20.1, 22.8, or24.7) was held under hydrothermal conditions at a temperature of 160°C for 48 h in the static mode (autoclave volume, V = 100 mL) and up to 26 h in an autoclave with stirring ( $V_{\text{autoclave}} = 600 \text{ mL}$ , the stirrer rotation speed of 100 rpm). After that, the solid phase was separated from the mother liquor by filtration, washed with distilled water, and dried for 18 h at room temperature and 8 h at 110°C. To be converted into the H<sup>+</sup> form, zeolites were calcined at 650°C for 3 h to remove the template. Next, the zeolite was subjected to ion exchange in a 1 M NH<sub>4</sub>NO<sub>3</sub> solution, followed by filtration, washing with water, and drying at room temperature for 18 h and at 110°C for 8 h. Samples in the  $NH_4^+$  form were calcined at 480°C for 2 h. Zeolite samples synthesized by this method are designated by symbol "T": ZSM-22-T.

The synthesis of ZSM-22 without the use of an organic template was based on the procedure described in [18]. The reaction mixture with the component ratio of *x*KOH :  $Al_2O_3$  :  $100SiO_2$  :  $4450H_2O$  (x = 19 or 21) and a seed (ZSM-22 in H<sup>+</sup>-form) content or 2.3 to 10% was held under hydrothermal conditions at temperatures of 140 and 150°C within 92 h in the static mode (autoclave V = 100 mL) and at a temperature of 160°C for up to 24 h in an autoclave with agitation ( $V_{autoclave} = 600$  mL, 100 rpm). After hydrothermal treatment, the synthesized samples were separated from the mother liquor by filtration and further treated similar to the ZSM-22-T samples. Zeolites synthesized by this method are denoted by symbol "TF": ZSM-22-TF.

A sample of zeolite ZSM-23 (MTT structure) used in this work for comparison was synthesized and characterized previously [17].

## Characterization of Synthesized Zeolites

The concentration of aluminum, iron, and potassium in all samples was determined by inductively-coupled-plasma atomic emission spectroscopy (AES-ICP) using a PerkinElmer OPTIMA 4300 DV ICP spectrometer.

X-ray phase analysis (XRD) was performed using a HZG-4C high-resolution diffractometer in the angular range of  $2\theta = 4^{\circ}-40^{\circ}$  (CuK $\alpha$  radiation).

The textural characteristics of zeolites were determined by low-temperature nitrogen adsorption at 77 K on a Micromeritics ASAP 2010 instrument. Before nitrogen adsorption, the samples were outgassed by vacuum pumping at  $250^{\circ}$ C for 10 h.

The morphology of zeolites was studied using a Jeol JSM 6460LV scanning electron microscope at an accelerating voltage of 20 kV.

Examination by high-resolution transmission electron microscopy (HR-TEM) was performed on a Jeol JEM-2010 electron microscope (accelerating voltage 200 kV, resolution 1.4 Å (lattice)). The samples to be studied were applied using an ultrasonic disperser on standard carbon-coated copper grids, which were placed in special holders.

The acidic properties of the TON and MTT zeolites were characterized using the technique of thermally programmed desorption of ammonia (TPD NH<sub>3</sub>) in an adsorption unit, equipped with a mass spectrometer, in a semiautomatic mode. A 1-g portion of zeolite was poured into the reactor zone with controlled temperature. The sample was preliminarily calcined in a helium stream at a flow rate of 1 cm<sup>3</sup>/s in the temperature-programmed mode from room temperature to 550°C. After calcination, the sample was cooled to 100°C in a helium stream and ammonia was adsorbed for 5 min. The TPD of ammonia was measured upon linear heating (10°C/min) of the sample layer at a constant helium flow rate of 1 cm<sup>3</sup>/s.

# Catalytic Tests

Catalytic experiments were performed in an automated flow-through unit with on-line chromatographic analysis of the gas phase. A gaseous mixture of ethylene oxide and helium (10% ethylene oxide by volume, the rest is helium) was passed at a flow rate of 50 cm<sup>3</sup>/min through a stainless steel reactor of a 0.5 cm diameter, into which 0.2 g of the test zeolite in the form of granules of 0.25–0.5 mm in diameter was preloaded. . Before feeding the reaction mixture, the zeolites were calcined in a stream of dry air at 500°C for 2 h; then, the reactor was cooled in a stream of He to the required temperature of the experiment and held under these conditions for 10 min. The temperature in the reactor was varied from 300 to 400°C. The contact time was about 0.5 s. Chromatographic analysis was performed in a temperature-programming

Sample	Agitation	Molar ratio of reaction mixture components	Crystallization condition	
		vnthesis in the presence of 1.6-diaminohexane		
ZSM-22-T-1	No	$ 27.5\text{DAH} : 24.3\text{KOH} : \text{Al}_2\text{O}_3 : 90\text{SiO}_2 : 3650\text{H}_2\text{O}_2$	160°C, 48 hours	
ZSM-22-T-2	No	27.5DAH : 22.5KOH : Al <sub>2</sub> O <sub>3</sub> : 90SiO <sub>2</sub> : 3650H <sub>2</sub> O	160°C, 48 hours	
ZSM-22-T-3	No	27.5DAH : 19.8KOH : Al <sub>2</sub> O <sub>3</sub> : 90SiO <sub>2</sub> : 3650H <sub>2</sub> O	160°C, 48 hours	
ZSM-22-T-4	No	27.5DAH : x19.8KOH : Al <sub>2</sub> O <sub>3</sub> : 90SiO <sub>2</sub> : 3650H <sub>2</sub> O	160°C, 26 hours	
ZSM-22-T-5	Yes	27.5DAH : 22.5KOH : Al <sub>2</sub> O <sub>3</sub> : 90SiO <sub>2</sub> : 3650H <sub>2</sub> O	160°C, 20 hours	
ZSM-22-T-6	Yes	27.5DAH : 19.8KOH : Al <sub>2</sub> O <sub>3</sub> : 90SiO <sub>2</sub> : 3650H <sub>2</sub> O	160°C, 6 hours	
ZSM-22-T-7	Yes	27.5DAH : 19.8KOH : Al <sub>2</sub> O <sub>3</sub> : 90SiO <sub>2</sub> : 3650H <sub>2</sub> O	160°C, 12 hours	
ZSM-22-T-8	Yes	27.5DAH : 19.8KOH : Al <sub>2</sub> O <sub>3</sub> : 90SiO <sub>2</sub> : 3650H <sub>2</sub> O	160°C, 20 hours	
ZSM-22-T-9	Yes	27.5DAH : 19.8KOH : Al <sub>2</sub> O <sub>3</sub> : 90SiO <sub>2</sub> : 3650H <sub>2</sub> O	160°C, 26 hours	
	I	Template-free synthesis	I	
ZSM-22-TF-1	No	19KOH : Al <sub>2</sub> O <sub>3</sub> : 100SiO <sub>2</sub> : 4450H <sub>2</sub> O	140°C, 92 hours	
		2.3% seed		
ZSM-22-TF-2	No	19KOH : Al <sub>2</sub> O <sub>3</sub> : 100SiO <sub>2</sub> : 4450H <sub>2</sub> O	150°C, 48 hours	
		2.3% seed		
ZSM-22-TF-3	No	$19KOH : Al_2O_3 : 100SiO_2 : 4450H_2O$	150°C, 92 hours	
		2.3% seed		
ZSM-22-TF-4	No	$19KOH : Al_2O_3 : 100SiO_2 : 4450H_2O$	150°C, 92 hours	
		5% seed		
ZSM-22-TF-5	No	$19$ KOH : $Al_2O_3$ : $100$ SiO <sub>2</sub> : $4450$ H <sub>2</sub> O	150°C, 92 hours	
		10% seed		
ZSM-22-TF-6	Yes	$21$ KOH : $Al_2O_3$ : $100$ SiO <sub>2</sub> : $4450$ H <sub>2</sub> O	140°C, 48 hours	
		5% seed		
ZSM-22-TF-7	Yes	21KOH : $Al_2O_3$ : 100SiO <sub>2</sub> : 4450H <sub>2</sub> O	160°C, 16 hours	
		10% seed		
ZSM-22-TF-8	Yes	21KOH : Al <sub>2</sub> O <sub>2</sub> : 100SiO <sub>2</sub> : 4450H <sub>2</sub> O	160°C, 24 hours	

Table 1. Synthesis conditions of zeolites ZSM-22

mode from 50 to 170°C on a DB-1701 capillary column (J&W Scientific) using FID.

10% seed

The conversion was calculated from the data on ethylene oxide (EO) concentration at the reactor outlet. The selectivity for a particular product was determined as the ratio of the analyte concentration to the total concentration of all the products.

#### **RESULTS AND DISCUSSION**

In the zeolite syntheses in the presence of 1,6diaminohexane, three parameters affecting the formation of ZSM-5 and cristobalite impurity phases were varied: the  $OH^{-}/SiO_{2}$  ratio in the reaction mixture, the agitation of the reaction mixture, and the crystallization time (Table 1). Under static conditions, the zeolites were synthesized from the reaction mixture with  $OH^{-}/SiO_{2}$  ratios of 0.22, 0.25, and 0.27.

Figures 1a and 1b show powder diffraction patterns of zeolite samples of the ZSM-22-T series synthesized under static conditions with different OH<sup>-</sup>/SiO<sub>2</sub> ratios and in an autoclave with agitation at a constant OH<sup>-</sup>/SiO<sub>2</sub> value, but over different crystallization times, respectively. As OH<sup>-</sup>/SiO<sub>2</sub> decreases (Fig. 1a, diffractograms 2-4), the intensity of the peaks due to the ZSM-5 phase decreases. All samples synthesized within 48 h are characterized by the presence of a cristobalite impurity. By reducing the crystallization time to 26 h, a sample had been obtained in which the ZSM-5 phase was present in trace amounts and the cristobalite phase was absent altogether (Fig. 1a, diffractogram 5). From the reaction mixture with a composition similar to that of the sample having diffraction pattern 3, but in an autoclave with stirring, a sample with a higher ZSM-5 content was obtained after 20 h (Fig. 1a, diffractogram 1). Thus, agitation of the



**Fig. 1.** Powder X-ray diffraction patterns of zeolites of the ZSM-22-T series synthesized (a) under static conditions: (*1*) ZSM-22-T-5 (for reference), (*2*) ZSM-22-T-1, (*3*) ZSM-22-T-2, (*4*) ZSM-22-T-3, and (*5*) ZSM-22-T-4 or (b) in an autoclave with stirring: (*1*) ZSM-22-T-6, (*2*) ZSM-22-T-7, (*3*) ZSM-22-T-8, and (*4*) ZSM-22-T-9.

synthesis gel during the crystallization process accelerates the formation of the impurity phase.

To clarify the ZSM-5 formation route, the synthesis was carried out in an autoclave with stirring at the optimum composition of the reaction mixture, as determined by synthesis under static conditions (see Fig. 1a, the sample with diffraction pattern 5 and Table 1). In Fig. 1b, it can be seen that the peaks characteristic of the ZSM-5 phase begin to appear on the diffraction pattern of the sample synthesized for 6 h and their intensity increases with increasing crystallization time. This means that ZSM-5 is formed almost simultaneously with the desired ZSM-22 phase as a result of cocrystallization. It should be noted that during the synthesis with stirring, a decrease in the OH<sup>-</sup>/SiO<sub>2</sub> ratio leads to a decrease in the amount of ZSM-5 in the sample (Fig. 1a, diffractogram 1 and Fig. 1b, diffractograms 3, 4). The samples synthesized with stirring contained a small amount of the cristobalite phase.

In the case of template-free synthesis of zeolites, the key parameters are agitation, synthesis temperature (T, °C), and seeding. The data on the templatefree synthesis conditions of zeolite samples are also presented in Table 1. In contrast to the published data [18], we have shown that the crystallization temperature of 140°C is insufficient for the synthesis of ZSM-22 over a time appropriate for the fabrication

 Table 2. Textural characteristics of synthesized zeolites

Sample	$S_{\rm BET}$ , m <sup>2</sup> /g	$V_{\rm micro},$ cm <sup>3</sup> /g	$V_{\rm meso},$ cm <sup>3</sup> /g	$V_{\rm tot},$ cm <sup>3</sup> /g	$S_{\rm micro},$ m <sup>2</sup> /g
ZSM-22-T-4	239	0.08	0.17	0.25	186.4
ZSM-22-TF-7	151	0.034	0.18	0.22	92

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process both under static conditions (Fig 2a, diffractogram 1) and in the stirring-assisted synthesis (Fig. 2b, diffractogram 1). The above diffraction patterns show the presence of a large amount of the amorphous phase (halo in the region of  $19^{\circ}-25^{\circ}$ ). An increase in the process temperature to 150°C for the process carried out for 92 h with the same amount of seed (2.3%)led to an increase in the intensity of the peaks characteristic of ZSM-22 (Fig. 2a, diffractogram 3). From the results of the further experiments with increasing the amount of seed in the reactant mixture to 10%, it was concluded at with the given gel composition  $(OH^{-}/SiO_{2} = 0.19)$ , the process temperature of 150°C, and the amount of seed of 5-10% in the static mode, the resulting ZSM-22 had an admixture of amorphous material. Synthesis in the autoclave with stirring was carried out using a reaction mixture of the same composition, but with a ratio of  $OH^{-}/SiO_{2} = 0.21$ , at a temperature of 160°C. The conditions found made it possible to reduce the ZSM-22 synthesis time to 16 h (Fig. 2b, diffractogram 2).

According to the SEM and TEM data (Fig. 3), the ZSM-22 samples synthesized with 1,6-diaminohexane are bundled needle crystals of a 30–50 nm width. The size of the bundles is 2 to 3  $\mu$ m. There was no noticeable impurity of amorphous material. The ZSM-22 samples prepared by the template-free synthesis also represent a mixture of bundled needleshaped crystals of about 100–200 nm in width and 4– 6  $\mu$ m in length and a certain amount of amorphous material. The morphology of the samples of both types complies with the morphology of TON zeolites described in the literature [9, 18].

Table 2 presents the textural characteristics of the zeolites synthesized with 1,6-diaminohexane and according to the template-free procedure. The volume of micropores of the zeolite synthesized using the tem-



**Fig. 2.** Powder X-ray diffraction patterns of zeolites of the ZSM-22-TF series synthesized (a) under static conditions: (1) ZSM-22-TF-1, (2) ZSM-22-TF-2, (3) ZSM-22-TF-3, (4) ZSM-22-TF-4, and (5) ZSM-22-TF-5 or (b) in an autoclave with stirring: (1) ZSM-22-Tf-6, (2) ZSM-22-TF-7, and (3) ZSM-22-TF-8.



Fig. 3. SEM image of ZSM-22-T-4 synthesized with the template (left) and TEM image of ZSM-22-TF-7 prepared by template-free synthesis (right).

plate agrees with the data available in the literature for the pure phase [19], thereby indirectly confirming the absence of impurities of cristobalite and amorphous material. The zeolite synthesized without a template has a smaller micropore volume, which is natural for an insufficiently crystallized sample containing a noticeable amount of amorphous material.

Figure 4 depicts ammonia TPD spectra on the ZSM-22-T-4 and ZSM-22-TF-7 samples, and Table 3 shows the temperatures of ammonia desorption maxima, determined by the Gaussian deconvolution of the curves, and the concentrations of  $NH_3$  desorption sites. As can be seen from Fig. 4 and Table 3, zeolites have two types of acid sites which are close in strength (although the temperature of the maximum due to desorption from strong acid sites in ZSM-22-T-4 is



**Fig. 4.** TPD NH<sub>3</sub> spectra for zeolites (1) ZSM-22-T-4 and (2) ZSM-22-TF-7.

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Zaolita	Peak 1		Р	eak 2	Peak 3		ΣC,	
Zeonie	$T_{\rm max}$ , °C	C, µmol∕g	$T_{\max}$ , °C*	C, µmol∕g	$T_{\rm max}$ , °C	C, µmol/g	µmol/g	
ZSM-22-T-4	_	_	220	190	452	178	368	
ZSM-22-TF-7	158	42	221	123	441	112	235	

**Table 3.** TPD NH<sub>3</sub> data for zeolites ZSM-22-T-4 and ZSM-22-TF-7

\*Accuracy of determination  $\pm 2^{\circ}$ C.

higher by 11°C than that in ZSM-22-TF-7), but significantly differ in concentration.

The catalytic properties of the ZSM-22 samples obtained in this work were investigated in the gasphase isomerization reaction of ethylene oxide (EO) to acetaldehyde (AA). This reaction proceeds at 250–400°C on various acid catalysts; thermodynamic equilibrium at these temperatures is shifted toward the formation of AA [20, 17].

Earlier, we showed that the reaction of EO isomerization to AA barely proceeds in this temperature range in the absence of a catalyst. The EO conversion does not exceed 1% at a temperature of  $300^{\circ}$ C and is

**Table 4.** Catalytic properties in the reaction of ethylene oxide isomerization to acetaldehyde (10 vol % EO, the rest is He, contact time 0.5 s). MD stands for 2-methyl-1,3-dioxolane; DO, for 1,4 dioxane; CA, for crotonaldehyde; and LHC, for light hydrocarbons

	EO	Selectivity. %						
Time, h	EO							
	conversion, 70	AA	MD	DO	CA	LHC + CO		
ZSM-22-T-4, 300°C								
0.3	95	90	6.2	1.8	1.4	0.08		
1.1	95	88	6.6	2.0	1.0	0.07		
10	75	90	7.2	2.2	0.6	0.04		
16	66	90	6.3	2.5	0.5	0.05		
ZSM-22-TF-7, 300°C								
0.4	100	91	3.3	3.6	1.4	0.4		
1.1	100	92	3.3	3.7	0.3	0.3		
10	96	95	1.9	3.3	0.15	0.15		
16	90	95	1.3	2.9	0.1	0.1		
ZSM-22-T-4, 400°C								
0.4	100	90	0.2	1.1	2.7	6.2		
1.1	100	94	0.3	0.3	2.6	3.1		
10	100	97	0.2	0.3	1.8	0.8		
16	100	99	0.3	0.2	0.4	0.6		
ZSM-22-TF-7, 400°C								
0.4	100	93	0.1	0.4	4.8	2.3		
1.1	100	94	0.05	0.5	4.2	1.6		
10	100	97	0.2	0.3	2.3	0.6		
16	100	97	0.3	0.4	1.7	0.4		
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about 15% at 400°C. On ZSM-23 zeolites, in addition to the main product, acetaldehyde, crotonaldehyde, 1,4-dioxane, 2-methyl-1,3-dioxolane, and degradation products (light hydrocarbons and carbon oxides) are formed during the reaction [21]. Figure 5 illustrates the change in the EO conversion and the AA selectivity during the isomerization of ethylene oxide at temperatures of (a) 300 and (b) 400°C. The selectivity values for the other products in the initial period of the process and for catalyst on-stream times of 10 and 16 h are presented in Table 4. At 300°C, the EO conversion on ZSM-22-TF-7 is 100% within the first 6 hours of the reaction and then decreases to 90% for the on-stream time of 10 h. The EO conversion on ZSM-22-T-7 decreases much faster: within the catalyst on-steam time of 12 h, the value decreases from 97 to 72%. Since zeolite deactivation is due to the formation of coke precursors on acid sites of the zeolite and coke deposition on the catalyst surface, these differences can be explained in terms of different levels of acidity in the samples. In the sample ZSM-22-T-4, the concentration of both strong and medium-strength acid sites exceeds that in ZSM-22-TF-7 by more than a factor of 1.5. At 400°C, the EO conversion on both types of zeolites is maintained at 100% for 16 h on stream. The selectivity for AA at the beginning of the reaction does not exceed 93% due to side reactions, as can be seen from the selectivity for light hydrocarbons (Table 4), which are the products of degradation of larger molecules. However, contribution of side reactions decreases with the progress of the reaction and the AA selectivity reaches a stationary value of more than 97%.

Figure 5 also presents the results of testing zeolite ZSM-23 with the MTT structure having a onedimensional channel system with similar pore sizes. It can be seen that the catalytic properties of the ZSM-22 zeolites prepared by both methods are close to those of the MTT-type ZSM-23 zeolite tested under the same conditions.

Thus, the study of the influence of the key parameters of the synthesis of TON-type zeolites (ZSM-22) using the organic template 1,6-diaminohexane or the template-free procedure on the phase composition of the synthesized samples has led the following conclusions. The alkalinity (OH<sup>-</sup>/SiO<sub>2</sub> molar ratio) of the initial reaction mixture and the time of the hydrothermal process are the main factors that allow fine con-



**Fig. 5.** Dependence of the ethylene oxide conversion and the selectivity for acetaldehyde on the on-stream time of zeolite samples (1) ZSM-22-T-4 and (2) ZSM-22-TF-7 and (3) reference zeolite ZSM-23 at (a) 300 and (b) 400°C. 10 vol % OE in He, contact time, 0.5 s.

trol of the amount of the ZSM-5 phase in the zeolite product, both under static crystallization conditions and in an autoclave with stirring. For example, a decrease in the OH<sup>-</sup>/SiO<sub>2</sub> ratio in the reaction mixture from 0.27 to 0.19 and the process time to 12 h in the case of crystallization in the static mode makes it possible to obtain ZSM-22 zeolite that does not contain ZSM-5. Dynamic synthesis conditions (stirring the reaction mixture during crystallization) facilitate the formation of ZSM-5. Nonetheless, by reducing the  $OH^{-}/SiO_{2}$  ratio, it is possible to obtain the desired ZSM-22 phase and minimize the amount of the byproduct ZSM-5 phase. However, it should be noted that the formation of ZSM-5 cannot be completely avoided under these conditions; thus, it can be concluded that the ZSM-22 and ZSM-5 phases are formed simultaneously, not consecutively. As regards the condensed cristobalite phase, its formation is accelerated by stirring under the same synthesis parameters, although the presence of this impurity in the case of synthesis in the static mode is determined by the process time.

As in the template-free synthesis of other zeolites, the most important factor in the synthesis of TON zeolites in the absence of an organic template is the use of seeding. The optimal amount of seed is about 5 wt % ZSM-22 relative to the amount of SiO<sub>2</sub> contained in the starting reaction gel. Increasing the temperature to 160°C and stirring the reaction gel during the crystallization process significantly increase the rate of formation of the target phase, thereby reducing the synthesis time from 92 to 16 h.

The catalytic experiments have shown that ZSM-22 zeolites with a ratio of Si/Al = 40-50, obtained by both methods, exhibit a high activity in the gas-phase reaction of isomerization ethylene oxide to acetaldehyde. At a process temperature of  $400^{\circ}$ C, the complete EO conversion is observed. The selectivity for AA is 93–94% within the first hours of the reaction, and it gradually increases to reach a value of 97–99%, remaining unchanged within 16 hours of the process. Using the example of EO isomerization reaction to give AA, we have shown that the zeolite ZSM-22 synthesized in the absence of a template

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can serve as a cheaper and more environmentally friendly alternative to the classical "templatedirected" ZSM-22. In particular, it exhibits catalytic properties close to those of a zeolite synthesized in the presence of an organic template. Undoubtedly, syntheses in the absence of a template are distinguished by high adaptability, environmental friendliness, and low cost. Subject to further optimization or the development of new methods for template-free synthesis of ZSM-22 zeolites, these zeolites can be key components of a variety of catalysts for various processes.

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