Microporous Crystalline Silicoaluminophosphates: Effect of Synthesis Conditions on the Physicochemical and Catalytic Properties in the Reaction of Methanol to C_2-C_4 Olefins Conversion

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Abstract—Effect of the synthesis parameters (reaction mixture composition, crystallization temperature and duration) on the physicochemical and catalytic properties of microporous crystalline silicoaluminophosphates (SAPOs) has been studied. Methods for the directional control of phase composition, degree of crystallinity, morphology and size of SAPO crystals crystallized from colloidal silicoaluminophosphate sols stabilized in tetraethylammoniun hydroxide solution as a template have been developed. It has been determined that the use of more severe synthesis conditions (increase in temperature and duration of crystallization) leads to the formation of larger crystals and a growth in the concentration of medium strength sites in the samples, which causes a rapid deactivation of the samples in the reaction of methanol conversion to C_2-C_4 olefins. Crystallization under milder conditions (a decrease in pH and temperature) promotes the acid formation of CHA/AEI intergrowth crystals exhibited a high and steady performance in the methanol conversion for more than 8 h at a total yield of olefins of 95 wt %.

Keywords: silicoaluminophosphates, methanol-to-olefins conversion reaction **DOI**: 10.1134/S0965544114040069

Over the past twenty years, fundamental and applied aspects of the production of lower olefins from alternative feedstock have been intensively developed in view of the enormous practical importance of ethylene and propylene as petrochemical intermediates [1]. Oxygenates (methanol or dimethyl ether, DME), which are prepared from the products of either methane or coal processing, are used as a feedstock for the production of lower olefins [2]. Possibility to control ethylene/propylene ratio in the products of the conversion of oxygenates primarily involves the use of various crystalline molecular sieve catalysts. When using a zeolite with MFI structure, propylene predominates in the reaction products; in the presence of SAPO-34 silicoaluminophosphate of the chabazite (CHA) structure ethylene and propylene are formed in an equimolar ratio [1]. The main problem when using SAPO-34 in the MTO (methanol to olefins) process is its rapid deactivation during the course of the reaction. As shown in [3, 4], the most important factors influencing the rate of SAPO-34 deactivation are the size of its crystals and its acidic properties. A decrease in the crystal size leads to an increase in the time of steady performance of the catalyst. According to [4, 6, 7], the size of SAPO-34 crystals is determined by the synthesis conditions, including type of starting reagents and structure-forming template, ratio of the reaction mixture components, degree of condensation (sol or gel) of the reaction mixture, temperature and duration of crystallization. The acidic properties of silicoaluminophosphate depend on the method of the silicon-oxygen tetrahedra incorporation into the crystal lattice of the material during crystallization—in the form of isolated tetrahedra (SM1 mechanism) or silicon—oxygen islets (SM2 or SM3 mechanisms) [3, 5]. In the case of SM1 mechanism the acidic properties of silicoaluminophosphates are due to isolated Brönsted centers that form the basis of SAPO-34 acidity [3].

Analysis of a significant number of publications on SAPO-34 shows that synthesis of silicoaluminophosphates may be performed from the reaction mixtures obtained by varied combination of precursors for Al₂O₃ (aluminum isopropoxide [6, 8–10], pseudoboehmite [3–5, 7, 11]), P₂O₅ (concentrated phosphoric acid [3–11]), SiO₂ (silica sol [3–5, 7–11], Aerosil [7], silicic acid [10]), and templates (triethylamine [3, 5, 11], diethylamine [9, 11], tetraethylammonium hydroxide [6–8, 11], morpholine [7] or their mixtures). The influence of synthesis conditions on the physicochemical properties of SAPO-34 as reported in [3, 5, 8] was analyzed without relation to the catalytic properties, and in the published data [4, 6, 7,

9–11] on the SAPO-34 catalytic activity in the reaction of methanol conversion to lower olefins do not make it possible to correctly assess the effect of synthesis conditions on the properties of the samples, since the catalysts were prepared in various conditions from different groups of precursors.

In this work, we comprehensively studied the influence of synthesis conditions on the physicochemical and catalytic properties of microporous crystalline silicoaluminophosphates prepared from silicoaluminophosphate sols stabilized in solution by tetraethylammonium hydroxide as a template. The choice of the reaction mixture type is caused by the possibility to produce silicoaluminophosphates with a crystal size of less than 500 nm from colloidal systems [8]. The ratio of the reaction mixture components (P_2O_5/Al_2O_3 , SiO₂/Al₂O₃, template/Al₂O₃, H₂O/Al₂O₃), the pH of the mixture, and the temperature and duration of crystallization were considered as factors influencing the physicochemical and catalytic properties of the catalysts.

EXPERIMENTAL

The silicoaluminophosphates were synthesized by hydrothermal crystallization from the reaction mixture with a composition of $Al_2O_3 \cdot (2-3)P_2O_5 \cdot (0.3-$ 1.8)SiO₂ · (4–6) (C₂H₅)₄NOH · (80–140)H₂O at temperatures of 170-190°C for 20-60 h. Aluminum isopropoxide, pseudoboehmite, silica sol (40 wt %), phosphoric acid (85 wt %), tetraethylammonium hydroxide (aqueous solution, 35 wt %), and morpholine were used as reactants. The pH value of the reaction mixture was adjusted by titration with concentrated HCl to a predetermined value. Crystallization was conducted at 170-190°C for 20-60 h in autoclaves with stirring at a speed of 300 rpm. The solid products were separated from the liquid phase by filtration or centrifugation, washed, dried at 100°C for 12 h and calcined at 500°C for 2 h in an air stream (heating rate, 2°C/min.)

Phase analysis of silicoaluminophosphates was performed using diffraction patterns obtained on a STOE STADI P θ/θ -diffractometer X-ray diffractometer, Cu K_{α} radiation. The diffraction patterns were recorded by rotating the sample in a horizontal plane at 2 θ angles of 5°-40° with a step of 0.05 deg, a slit width of 1 mm, and a dwell time per point of 3 s.

IR spectra of the samples were recorded using a Nicolet Protégé 408 IR spectrometer at frequencies of 400–1400 cm⁻¹. Before recording the spectrum, 1 mg of the sample was mixed with 150 mg of KBr and compressed into a tablet. The IR spectra obtained were processed using the OMNIC E.S.P. software package (Nicolet).

Thermogravimetric (TGA) and differential thermal (DTA) analyzes were performed on a SDT Q600 instrument (TA Instruments production). TG-DTA curves were recorded using linear temperature rise mode at a rate of 10° C/min in the temperature range $20-800^{\circ}$ C in air flow (100 mL/min).

Details of the porous structure of silicoaluminophosphates were determined using low-temperature nitrogen adsorption—desorption method. Registration of the isotherms was performed by standard method on an ASAP 2010 porosimeter (Micromeritics, USA).

Electron microscopic images of the samples were obtained on a CAMSCAN electron microscope. Before shooting, the surface of the samples was covered with a gold—iridium alloy layer by vacuum sputtering.

The acid properties of the samples were studied by the ammonia thermal-programmed desorption (TPD) technique. Experiments were conducted on an USGA-101 chemisorption analyzer produced by UNISIT (Russia). A sample (0.15–0.20 g) was placed in a quartz tubular reactor; standard automatic preprocessing involved sequential calcination of the sample at 500°C for 1 h in a helium flow, saturation with ammonia at 60°C for 15 min, removal of physically adsorbed ammonia in a helium flow at 100°C. The experiment on NH₃ TPD was carried out in a helium flow (30 mL/min) at a rate of temperature rise of 8°/min, the evolved ammonia was registered by a thermal conductivity detector.

The catalytic activity of the samples in the methanol-to-olefins process was studied on a flow catalytic reactor. Pretreatment of the catalyst (0.5-1 mm frac-)tion) included calcination at a temperature of 500°C for 1.5 h and cooling down to an operating temperature of 400°C under nitrogen flow. The mass flow rate of methanol supply was 2 h⁻¹. The sampling was performed every 35-40 min. Chromatographic analysis of the reaction products was carried out on two chromatographs. The reaction products were analyzed using gas chromatography method on a Kristall 2000 M instrument of Chromatec Analytic Company with a flame-ionization detector and a capillary column with SE-30 applied phase. Analysis of C_1-C_4 alkanes and alkenes was conducted on a Chrom-5 chromatograph with a flame-ionization detector and H₂ carrier gas using a capillary column with the KCl/Al₂O₃ applied phase.

RESULTS AND DISCUSSION

Phase Composition

A reaction mixture with a basic composition of $Al_2O_3 \cdot 2P_2O_5 \cdot 0.6SiO_2 \cdot 4(C_2H_5)_4NOH \cdot 80H_2O$ was crystallized to form silicoaluminophosphate with the chabazite (CHA) structure at 180°C for 20 h (sample SAPO-1, Table 1, Fig. 1). The data in Table 1 shows that the CHA phase was formed as a single crystalline product in SAPO-1, 2, 4–9 and SAPO-13 samples.

Under the chosen synthesis conditions, the phase purity of the crystalline product was not affected by the P_2O_5 and SiO_2 concentration in the reaction mixture,

Sample	Reaction mixture composition, mol/mol Al ₂ O ₃			reaction	$T_{\rm cr}, ^{\circ}{\rm C}$	τ _{cr} , h	Phase	Content $(C_2H_5)_4^+$,
	P_2O_5	SiO ₂	SiO ₂ R ^a mixture pH are composition	µmol/g				
SAPO-1	2	0.6	4 ^b	8	180	20	CHA	930
SAPO-2	3	0.6	6 ^b	8	180	20	CHA	800
SAPO-3	2	0.3	4 ^b	8	180	20	amorphous phase	—
SAPO-4	2	1.2	4 ^b	8	180	20	CHA	850
SAPO-5	2	1.8	4 ^b	8	180	20	CHA	890
SAPO-6	2	0.6	$2^{b} + 2^{c}$	8	180	20	CHA	970
SAPO-7	1	1	2 ^c	8	180	20	CHA	800
SAPO-8	2	0.6	4 ^b	8	180	40	CHA	900
SAPO-9	2	0.6	4 ^b	8	180	60	CHA + amorphous phase	670
SAPO-10	2	0.6	4 ^b	7.4	180	20	CHA + AEI	1100
SAPO-11	2	0.6	4 ^b	7 ^d	180	20	AEI	1200
SAPO-12	2	0.6	4 ^b	8	170	20	CHA + AEI	1200
SAPO-13	2	0.6	4 ^b	8	190	20	CHA	900

 Table 1. Synthesis conditions and phase composition of silicoaluminophosphate samples

^a, template; ^b, tetraethyl ammonium hydroxide; ^c, morpholine; ^d, pH was adjusted by adding conc. HCl.

the template type, the crystallization time, and other factors. In the case of varying the P_2O_5 concentration in the reaction mixture, it was taken into account that P_2O_5 : template molar ratio of 2 : 4 ensures the maintenance of the pH of reaction mixture at 8.0. Therefore, an increase in the phosphorus content was inevitably accompanied by an increase in the template/Al₂O₃ and H₂O/Al₂O₃ ratios (sample SAPO-2, Table 1).

An increase in the SiO₂/Al₂O₃ ratio in a wide range from 0.3 to 1.8 did not affect crystallization selectivity, but determined the crystallinity of the product. Moreover, from the reaction mixture with the lowest SiO₂ content the CHA phase could not be obtained (SAPO-3 sample, Table 1.) The IR spectrum of the sample (Fig. 2a) contained absorption bands (ABs) indicating the presence of an amorphous phosphate material (ABs at 1108 and 1004 cm⁻¹), an amorphous silicate material (AB at 787 cm⁻¹), as well as a structured aluminosilicate material (AB at 533 cm⁻¹ corresponding to vibrations of the T–O bands in the (Si,Al)O₄ tetrahedra) containing six-membered rings (AB at 640 cm⁻¹) [3, 8].

An increase in the silicon content in the samples SAPO-4—SAPO-6 (Table 1) resulted in the formation of highly crystalline products containing in their structure aluminum, phosphorus and silicon in a tetrahedral oxygen environment. The presence of phosphorus–oxygen tetrahedra in the crystalline framework of the samples is manifested by absorption bands at ~570 cm⁻¹ (T–O bonds in the PO₄ tetrahedron), ~730 cm⁻¹ (P–O bond symmetric vibrations) and

~1212 cm⁻¹ (asymmetric vibrations of the P–O–Al bonds) (Fig. 2b–d) [3, 8].

According to Table 1, the CHA phase is formed when compounds of different properties—tetraethylammonium hydroxide, morpholine and their equimolar mixtures are used as a template (SAPO-1, SAPO-6, and SAPO-7 samples). However, it should be noted that morpholine turned out inactive as an individual template when aluminum isopropoxide was used as an Al_2O_3 precursor, and the synthesis of SAPO-7 sample was possible only by using pseudoboehmite.

An increase of crystallization time from 20 to 60 h (samples SAPO-1, SAPO-8, and SAPO-9) did not result in a change in the phase purity of the product. At the same time, the annealing of the reaction mixture at 180° C for 60 h was accompanied by partial amorphization of the SAPO-9 sample.

A change in the crystallization selectivity was achieved by variation of such parameters as pH of the reaction mixture and crystallization temperature. Together with the CHA phase or instead of it the AEI phase was crystallized differing in the orientation mode of the layers of hexagonal prisms forming the SAPO crystal lattice [5]. Crystallization under milder conditions, namely, a decrease in the reaction mixture pH value (sample SAPO-10, Fig. 1b) and a decrease in the crystallization temperature to 170°C (sample SAPO-12, Fig. 1c) promoted the AEI phase formation.

According to published data [12], changes in the diffraction patterns of samples SAPO-10 and SAPO-12 in the 2θ range of 15° - 19° , namely, the disappear-



Fig. 1. Diffractograms of silicoaluminophosphates: (*a*) SAPO-1, (*b*) SAPO-10, (*c*) SAPO-12, (*d*) SAPO-11, and (*e*) SAPO-13.

ance of the reflection at 20 18.8 20 (Fig. 1a, *) and the appearance of a reflection at 20 17.1° (Fig. 1b, \mathbf{V}) prove the formation of the CHA/AEI intergrowths. Differences in the intensity ratios for the reflections at 20 16.0° and 17.1° make it possible to suggest that samples SAPO-10 and SAPO-12 are formed by intergrowths having different CHA/AEI ratios. Thus, variation in the synthesis conditions makes it possible to adjust the composition of SAPO CHA/AEI intergrowths.

An increase in the crystallization temperature to 190° C resulted in the formation of a material, the diffraction pattern of which contains reflections characteristic of the CHA phase, namely, at 20 9.5°, 12.9°, 16.1°, 17.9°, and 20.6° (Fig. 1e). At the same time, changes in the reflection intensities ratio compared with the SAPO-1 sample indicate that the silicoaluminophosphate crystal phase formed at an elevated temperature has some structural features, the determination of which requires further investigation. At a decrease in the pH of the reaction mixture to 7



Fig. 2. IR spectra of silicoaluminophosphates: (*a*) SAPO-3, (*b*) SAPO-1, (*c*) SAPO-4, and (*d*) SAPO-5.

(SAPO-11 sample) the AEI phase is formed as a single crystalline product (Fig. 1d).

In addition to X-ray diffraction and infrared spectroscopy, the quality of the molecular sieve material obtained using the template synthesis can be characterized by the quantitative content and the state of the structure-forming template. The first property can be determined from the TG curve by the mass loss value in the temperature range corresponding to the decomposition of the template by heating. The second parameter can be evaluated by the type of the thermal effect and its position on the DTA curve. According to [8, 11], highly crystalline samples with the CHA structure contain in their composition from 11 to 15 wt % of a template $(840-1150 \mu mol/g)$, the decomposition of which upon heating of the samples is accompanied by an exothermic effect with a maximum at 450°C. The study of the SAPO samples using TG-DTA analvsis (Table 1, Fig. 3) showed both quantitative and qualitative differences between the samples with the CHA structure and the samples containing the AEI phase.

The content of a template, $(C_2H_5)_4N^+$ cation, in the SAPO-10, SAPO-11, and SAPO-12 samples is 1100–1200 µmol/g, which is higher than in the samples with the CHA structure (800–970 µmol/g) (Table 1). In addition, the decomposition of the template by heating of the SAPO-1 and SAPO-11 samples



Fig. 3. DTA curves of silicoaluminophosphates: (*a*) SAPO-1, (*b*) SAPO-10, and (c) SAPO-11.

(DTA curves in Fig. 3) is accompanied by exothermic effects, the positions of the maxima for which differ by 115°C. Probably, this fact is related to the peculiarities of the template removal from a more open AEI structure, which is confirmed by the DTA curve for the CHA/AEI intergrown crystalline sample (SAPO-10, Fig. 3), on which there are three exothermic effects—at 330°C (similar to the AEI structure), 455°C (similar to the CHA structure), and an intermediate effect at 360°C.

As the study of the silicoaluminophosphate porous structure showed, they all had an extended surface $(480-580 \text{ m}^2/\text{g})$, the micropore volume in the samples was $0.23-0.27 \text{ cm}^3/\text{g}$.

Crystal Morphology

The results of the scanning electron microscopy show that the reference sample SAPO-1 consists of cubic crystals $0.3-0.5 \ \mu m$ in size (Fig. 4, Table 2). Changes in the synthesis parameters such as the ratio of the reaction mixture components, template type, crystallization temperature and duration did not change the morphology, but resulted in an increase in the crystal size.

With an increase in the phosphorus and silicon content in the reaction mixture the crystal size either increased 1.5–2 times (SAPO-2, SAPO-4 samples) or crystals with a more wide size distribution were formed (SAPO-5) (Table 2). A partial or complete substitution of tetraethylammonium hydroxide template for morpholine (SAPO-6 and SAPO-7 samples, Table 2, Fig. 4) and running the crystallization for 40 h (SAPO-8 sample, Table 2) exert the greatest influence on the size of the crystals. The crystal size increased by an order of magnitude for SAPO-6 and SAPO-8 samples compared with the SAPO-1 sample and by more than thirty times for the SAPO-7 sample.

A similar effect of complete or partial substitution of templates in the reaction mixture based on pseudoboehmite was described by in [2] for SAPO-34 synthesized at 200°C. A crystallization time longer than 40 h for SAPO-9 sample, as shown above, was accompanied by its amorphization; as a result, the impact on the crystal size was leveled.

The presence of the AEI phase in the crystallization products changed the crystal morphology from cubic to a plate-like one. In the samples of CHA/AEI intergrowths (SAPO-10, SAPO-12, Table 2) crystal plates were squares with a side of 0.3–0.5 μ m and a thickness of 0.1 μ m. Crystals of SAPO-11 sample with the AEI structure had the shape of a flat ellipse with transverse dimensions 0.5 × 0.8 μ m and 0.1 μ m thick.



Fig. 4. Electron microscopic images of silicoaluminophosphates: (a) SAPO-1, (b) SAPO-6, and (c) SAPO-7.

Sample	Crystal morphology	Crystal size, µm	Concentration of acid centers a_0 , µmol/g	Part of medium strength sites in the TPD pattern
SAPO-1	Cubic	0.3-0.5	1520	0.35
SAPO-2	Cubic	0.5-1	1550	0.38
SAPO-4	Cubic	0.5-1	1920	0.40
SAPO-5	Cubic	0.2-0.8	2040	0.47
SAPO-6	Cubic	2-4	1350	0.60
SAPO-7	Cubic, crystalline aggregates	10-20	1450	0.70
SAPO-8	Cubic	4–6	800	0.60
SAPO-9	Cubic	0.5-0.8	900	0.33
SAPO-10	Square plates	0.4–0.5, thickness 0.1	1140	0.15
SAPO-11	Square plates	0.5×0.8 , thickness 0.1	1300	0.05
SAPO-12	Square plates	0.3–0.4, thickness 0.1	1660	0.16
SAPO-13	Cubic	0.5-1	1500	0.46

 Table 2. Physicochemical properties of silicoaluminophosphates

Acid Properties

The acid properties of the synthesized silicoaluminophosphates were evaluated by the TPD-NH₃ method. The values presented in Table 2 for the concentration of acid sites a_0 , measured as the area under the ammonia thermal desorption curve, show that compared with the reference sample SAPO-1, an increase in the silicon content in the reaction mixture resulted in a noticeable increase in a_0 (samples SAPO-4, SAPO-5) and an increase in the crystallization time led to a marked decrease in a_0 (samples SAPO-8, SAPO-9). In addition to the observed quantitative differences, qualitative changes in the acid properties of the silicoaluminophosphates occurred as well. On the TPD-NH₃ patterns of the samples shown in Fig. 5, there are two distinct peaks with thermal desorption maxima around 200°C and 400°C corresponding to the acid sites of low and medium strength. Analysis of the TPD-NH₃ patterns (Table 2, Fig. 5) shows that for samples with the CHA structure change in the synthesis parameters such as the ratio of the reaction mixture components, type of templating agent used and pH of the reaction mixture led to an increase in the proportion of medium-strength sites in the TPD pattern. The greatest increase in the concentration of these sites (up to 0.6-0.7) was reached in the samples SAPO-6-SAPO-8 that stand out because of their large crystals (Table 2). The effect of silicon concentration in the reaction mixture is less pronounced—the a₀ value increased to 0.4 and 0.47 for SAPO-4 and SAPO-5 samples, respectively; in this case, SiO_2/Al_2O_3 ratio in the reaction mixture correlated with the proportion of medium-strength sites in the samples (Tables 1, 2).

The presence of the AEI phase in the crystallization products has resulted in a drastic change in the TPD patterns (Fig. 5). For CHA/AEI intergrowths (samples SAPO-10 and SAPO-12) the proportion of

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medium strength centers decreased to 0.15-0.16, for SAPO-11 sample with the AEI structure, to 0.05. In these samples the range of acidity is almost completely represented by weak acid sites.

Thus, changes in the synthesis conditions made it possible to control the acidic properties of silicoaluminophosphates in a wide range.

Catalytic Properties

Based on the results of the study of the physicochemical properties of silicoaluminophosphates, we selected for catalytic testing a set of six samples, SAPO-1, 4, 6, 7, 10, and 11, differing in the crystal structure, crystal size, and the proportion of mediumstrength acid sites (Figs. 6, 7; Table 2).



Fig. 5. Ammonia *TPD* curves for silicoaluminophosphates: (*a*) SAPO-1, (*b*) SAPO-4, (*c*) SAPO-7, (*d*) SAPO-10, and (*e*) SAPO-11.



Fig. 6. Change in the catalytic activity of silicoaluminophosphates over time in the methanol-to-olefins reaction.

As shown by the curves of change in the activity of the samples over time (Fig. 6), the catalysts were clearly divided into two groups according to their steady operation time—the samples deactivated in a short time (SAPO-4, 6, and 7), and ones working steadily (SAPO-1, 10, and 11). In the first group, the deactivation rate for the samples (SAPO-7 > SAPO-6 > SAPO-4) correlated with both the crystal size (10– $20 \ \mu\text{m} > 2-4 \ \mu\text{m} > 0.5-1.0 \ \mu\text{m}$) and the proportion of medium-strength sites in the samples (0.7 > 0.6 > 0.4). The results are consistent with the relationships revealed in [4, 7, 10, 11] for the influence of the crystal size and the acidity spectrum on the catalytic proper-

ties of SAPO-34 synthesized under conditions other than those in the present study. In this case, the SAPO-7 sample was completely deactivated after 100 min of the catalytic experiment. The differences in the selectivity in ethylene formation for the SAPO-4 and SAPO-6 samples (54 and 48 wt %, respectively; Fig. 7) are related obviously to a decrease in the diffusion restrictions in crystals of a smaller size.

In the second group characterized by the lowest values of crystal sizes and concentrations of medium strength sites among the studied samples (Table 2) the rate of deactivation in the SAPO-1 > SAPO-11 > SAPO-10 series did not correlate with the physicochemical properties of the samples. For individual CHA (SAPO-1 sample) and AEI (SAPO-11 sample) phases 100% methanol conversion was maintained for 4 and 5 h, respectively. In this case, the SAPO-1 sample showed a higher selectivity for ethylene (Fig. 7), apparently due to strong stereoselective effect resulting from parallel packing of the layers of hexagonal prisms in the crystal lattice of the CHA structure [5]. The SAPO-11 sample that has a more open AEI structure exhibited higher selectivities in the formation of propylene and butenes than the SAPO-1 sample (Fig. 7).

The on-stream time of the SAPO-10 sample without loss of activity was more than 8 h. It was intermediate in the selectivity of the formation of lower individual olefins after 100 min of the reaction between the SAPO-1 and SAPO-11 samples (Fig. 7), but surpassed them in the selectivity in the formation of C_2-C_4 olefins, the total value of which for the sample was 95 wt %. Thus, as a result of the variation in silicoaluminophosphate synthesis conditions the preparation of



Fig. 7. Selectivity of the formation of methanol conversion products (wt %) after 100 min of the reaction.

AEI/CHA intergrowths made it possible to control the composition of the products of the methanol to olefins conversion process and time of steady catalyst performance.

Thus, the effect of the synthesis conditions of microporous crystalline SAPOs on their physicochemical and catalytic properties in the process of methanol conversion to lower olefins was studied. The variation in the composition of the reaction mixture, temperature and duration of the crystallization of colloidal silicoaluminophosphate sols stabilized in a solution of tetraethylammonium hydroxide as a template made it possible to develop the ways to the directional control of the degree of crystallinity, morphology and size of the crystals, as well as the acidic properties of silicoaluminophosphates. An increase in the temperature and duration of the synthesis resulted in the formation of larger crystals and in an increase in the proportion of medium strength sites in the acidity spectra of the samples. Crystallization under milder conditions (a decrease in the pH value and temperature of the synthesis) led to the formation of CHA/AEI intergrowths exhibited a high and steady performance in the methanol to C_2-C_4 olefins conversion process for more than 8 h.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 12-03-00624a.

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Translated by V. Makhaev