Methanol to Olefins Conversion over Silicoaluminophosphates with AEI Structure: Effect of the Active Site Type

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Abstract—Effect of the type of active site on the catalytic properties of microporous crystalline silicoaluminophosphates with AEI structure synthesized at 150, 170, and 190°C has been investigated. The state of the active site was changed by varying the catalyst synthesis conditions. It has been established that during the synthesis of silicoaluminophosphates with the AEI structure from the reaction mixture of the same composition, an increase in the temperature and crystallization time leads to an increase of the silicon content and crystal size growth. The observed changes in the physicochemical properties are accompanied by the change of the silicon state in the structure of silicoaluminophosphates with the predominant formation of silicoal "islands" via the SM3 mechanism. According to ²⁹Si NMR data, the formation of active sites of silicoaluminophosphates via the SM2 mechanism in the form of isolated silicon atoms in the structure is also observed for these materials. The presence of such sites, along with the morphological features of the crystals, determines the unusual catalytic properties of silicoaluminophosphate with AEI structure in MTO process, which are a high ethylene yield up to 41 wt % at an ethylene : propylene molar ratio of 1 : 6.

Keywords: silicoaluminophosphates, morphological features, acid properties, type of active site, conversion of methanol into olefins

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Like crystalline silicoaluminophosphate with the CHA structure (SAPO-34), silicoaluminophosphate with the AEI structure (SAPO-18) is a well known catalyst for the production of lower olefins from methanol (MTO process) [1]. This material was prepared for the first time in 1993 [2] and characterized later [3]. The similarity of the catalytic properties of SAPO-34 and SAPO-18 is determined by the features of the crystal structure of these materials, which are microporous molecular sieves with a window size of 0.38 nm. The structure of silicoaluminophosphates is formed by alternating layers of hexagonal prisms. The differences in their structure are associated with translation symmetry (parallel layer packing) in SAPO-34 and translation-reflection symmetry in SAPO-18 (layers are arranged in reflection symmetry to each other) [3]. As a result of these differences, the CHA unit cell has a prismatic shape with dimensions of 0.94×1.27 nm and the AEI unit cell has a pear-like shape with a size of 1.16 × 1.27 nm [4].

Chen et al. [5] found that the differences in the acid properties of CHA and AEI are due to the absence of strong acid sites in AEI. According to ¹H NMR data [6], the concentration of bridging hydroxyl groups in AEI is threefold lower than that in CHA. These differences are attributed to the state of silicon atoms in the structure of silicoaluminophosphates, which determines the acidic properties of these materials. Known mechanisms of isomorphous substitution in the structure of silicoaluminophosphates, which are discussed in detail in [7], show that there are only two likely variants of incorporation of silicon into the structure for these materials due to the impossibility of the formation of the Si-O-P bond (Fig. 1). The first variant (SM2 mechanism) involves the incorporation of silicon in the form of isolated tetrahedra by the $P^{+5} \rightarrow Si^{+4} + H^+$ substitution resulting in the formation of a bridging OH group and generation of According an acid site. to the second variant, silicon forms the so-called silicon islands in the silicoaluminophosphate structure via the substitution $P^{+5} + Al^{+3} \rightarrow 2Si^{+4}$ (SM3 mechanism), with acid sites being formed only at the islet boundaries and, hence, the concentration of these sites being noticeably lower. According to the existing concepts, both of the mechanisms exist for the CHA and AEI structures, but the SM3 mechanism is considered to be predominant for AEI.

The above-specified features of the structure, active site types and acid properties of silicoaluminophosphates determine the differences in their catalytic properties in MTO reaction. According to Marcus



Fig. 1. Types of isomorphous substitution in the silicoaluminophosphates structure.

et al. [8], the pearlike shape of the AEI unit cell and possible forms of orientation of coke deposits in it contributes to stable catalytic activity of this silicoaluminophosphate, whereas CHA fast deactivated. The low acidity of AEI leads to the predominant formation of propylene: according to published data [9], the ethylene : propylene ratio in the reaction products does not exceed 0.54. This fact has caused that the interest of researchers in the AEI structure silicoaluminophosphate has decreased.

It is to be noted that unlike SAPO-34, SAPO-18 is characterized by a minimal number of synthesis variations. It is prepared according to two main procedures using N, N-diisopropylethylamine [3] and tetraethylammonium hydroxide [10] as a structure-directing agent (template). The procedure involving N, N-diisopropylethylamine does not provide high selectivity of crystallization, and the crystallization products contain an admixture of SAPO-5 [3]. In the presence of tetraethylammonium hydroxide, phase-pure SAPO-18 crystallizes with a high yield in the form of flat ellipsoid crystals. However, the procedure suggests hard hvdrothermal treatment of the reaction mixture at 215°C for 5 days, whereas SAPO-34 crystallizes at a lower temperature during shorter period of time. To date, neither the synthesis of SAPO-18 under milder conditions nor the properties of materials of this type have been studied.

In this work, we comprehensively studied the physicochemical and catalytic properties of silicoaluminophosphates with the AEI structure and different states of active sites. The change of an active-site state in the samples synthesized from the reaction mixture of the same composition was achieved by varying the catalyst synthesis conditions, such as crystallization temperature (150, 170, and 190°C) and hydrothermal treatment time (6–72 h).

EXPERIMENTAL

Silicoaluminophosphates with the AEI structure were synthesized by hydrothermal crystallization from a reaction mixture with the composition $Al_2O_3 \cdot 2P_2O_5 \cdot 0.6SiO_2 \cdot 4(C_2H_5)_4NOH \cdot 140H_2O$. The reactants were aluminum isopropoxide, aqueous silica sol (40 wt %), orthophosphoric acid (85 wt %), and aqueous tetraethylammonium hydroxide solution (35 wt %). After mixing the initial components, the reaction mixture was homogenized for 1 h, brought to pH 7 by adding concentrated HCl, and homogenized for 1 h again. The crystallization times were 24 and 72 h at 150°C, 12 and 18 h at 170°C, and 6 and 12 h at 190°C. After completion of crystallization, the solid products were separated from the liquid phase by centrifugation, washed, dried at 100°C for 12 h, and calcined at 500° C for 2 h in an air flow (heating rate, 2° C/min). Six catalyst samples denoted as T-N, where T is the synthesis temperature (°C) and N is the duration of synthesis (h).

The phase analysis of silicoaluminophosphates was performed using diffraction patterns obtained on a Bruker D2PHASER X-ray diffractometer (CuK α radiation). The diffraction patterns were recorded within the angular range of 5–40°20 with a step size of



Fig. 2. (a) X-ray diffraction pattern of sample 170-18 and (b) SEM image of sample 190-12.

 0.05° , a slit width of 1 mm, and a count time per step of 3 s.

Thermogravimetric (TGA) and differential thermal (DTA) analyses were performed on an SDT Q600 instrument (TA Instruments). The TG–DTA curves were recorded in the linear temperature programming mode at a heating rate of 10° C/min in the temperature range of 20–800°C in an air flow (100 mL/min).

The characteristics of the porous structure of silicoaluminophosphates were determined using the lowtemperature nitrogen adsorption—desorption method. The isotherms were recorded according to the standard procedure on a Micromeritics ASAP 2010 porosimeter.

Electron microscope images of the samples were obtained on a CAMSCAN electron microscope. Before examination, the surface of the samples was decorated with a gold—iridium alloy applied by vacuum sputter deposition.

The acid properties of the samples were studied using temperature-programmed desorption of ammonia (TPD NH₃). The experiments were conducted on a USGA-101 chemisorption analyzer (Unisit, Russia). A quartz tube reactor was charged with 0.15-0.20 g of the sample; standard automatic pretreatment included sequential operations of sample calcining at 500° C for 1 h in a helium flow, saturation with ammonia at 60° C for 15 min, and removal of physisorbed ammonia in a helium flow at 100° C. The TPD NH₃ experiment was conducted in a helium flow (30 mL/min) at a heating rate of 8° C/min; the ammonia released was measured with a thermal conductivity detector.

The catalytic properties of the samples in the MTO process were studied in a flow catalytic unit. A 1-g portion of the catalyst (0.5-1 mm fraction) was placed in a quartz reactor. The catalyst pretreatment involved calcining at 500°C for 1 h in nitrogen at a flow rate of 50 mL/min. The experiment was conducted at 400°C,

atmospheric pressure, a feedstock WHSV of 2 h^{-1} , and a molar ratio of N₂ : methanol = 5 : 1. Chromatographic analysis of the products was conducted on a Chromatec Analytic Kristall 5000 chromatographs equipped with flame ionization (FID) and thermal conductivity (TCD) detectors and a PoraBond Q and Porapak Q column.

RESULTS AND DISCUSSION

The synthesized samples of silicoaluminophosphates were characterized using a set of instrumental methods. By XRD data, it was established that the synthesis conditions chosen ensure the preparation of highly crystalline samples as a phase-pure material with the AEI structure. The set of lines in the diffraction patterns of the samples (e.g., see Fig. 2a) corresponds to published data. The crystallinity of the samples was high (90-100%). The yield of the crystalline phase determined by the ratio of the weight of the resulting sample to the total weight of the frameworkforming elements in the reaction mixture depended on the temperature and reached a maximum of 80% in sample 170-18 (Table 1). It is noticeably higher than that in SAPO-34, for which the yields in similar syntheses did not exceed 25%.

Crystal morphology of the obtained samples also corresponds to published data: the crystals had a shape of flat ellipses (Fig. 2b). The data presented in Table 1 shown that the dimensions of axes *a* and *b* of the ellipse and crystal thickness *c* increased with an increase in the crystallization time and temperature. The maximum crystal size was achieved in the samples obtained at 190°C. The crystal thickness in sample 190-12 was 0.3 μ m, which is two and one and half times that of samples 150-72 and 170-18, respectively.

The data presented in Table 1 also show that all the synthesized samples have a developed porous structure, as indicated by high values of pore volume and

	Samples							
	150-24	150-72	170-12	170-18	190-6	190-12		
Yield of crystalline product, %	73	78	62	80	50	57		
Crystal size, µm								
a	1.0	1.0	1.0	1.1	1.3	1.4		
b	0.50	0.60	0.55	0.65	0.70	0.80		
С	0.15	0.17	0.18	0.20	0.20	0.30		
Pore volume, cm ³ /g	0.358	0.360	0.362	0.350	0.235	0.240		
Micropore volume, cm ³ /g	0.237	0.248	0.252	0.261	0.155	0.168		
Chemical composition, mol/mol Al ₂ O ₃ :								
P_2O_5	0.97	0.95	0.94	0.95	0.94	0.95		
SiO ₂	0.07	0.16	0.10	0.17	0.18	0.20		
Amount of $(C_2H_5)_4N^+$, μ mol/g	1080	1115	1070	1100	1070	1120		
Concentration of acid sites, $a_0(NH_3)$, $\mu mol/g$	850	910	970	1050	1040	790		

Table 1. Physicochemical properties of silicoaluminophosphates with the AEI structure

micropore volumes. At the same time, it should be noted that samples 190-6 and 190-12 are noticeably inferior to their analogues in pore volume values. Obviously, crystal formation at elevated temperature has its unique features. It may be assumed that the observed decrease in the micropore volume is due to the presence in the crystal of zones with non-through porosity, which are formed under fast crystal growth conditions.

Analysis of the chemical constitution of the samples (Table 1) shows that an increase in the synthesis temperature and the crystallization time has almost no effect on the concentration of P_2O_5 and leads to an increase in the SiO₂ content of the samples. The maximal SiO₂/Al₂O₃ ratios of 0.18 and 0.20 was achieved in samples 190-6 and 190-12, respectively.

As it has been shown in [11], the amount of the template in the silicoaluminophosphate structure after synthesis can serve as a quantitative characteristic of high crystallinity of these materials. The data presented in Table 1 indicate that, independently of the temperature and duration of the synthesis, the amounts of the template in the samples are very close and differ by no more than 4%. The concentration of the template cation $(C_2H_5)_4N^+$ in the samples is 1070–1120 µmol/g. This value confirms, together with the XRD data, the high crystallinity of the obtained samples.

The concentration of acid sites $a_0(NH_3)$ (Table 1) were determined using TPD of ammonia. Comparison of the values of $a_0(NH_3)$ shows that an increase in the crystallization time led to an increase in a_0 for samples 150-24, 150-72, 170-12, and 170-18. In the case of the samples synthesized at 190°C, $a_0(NH_3)$ decreased with an increase in the duration of synthesis. Regardless of

the synthesis temperature, a general tendency toward growth in the number of strong acid sites in the samples with increasing of the crystallization time was observed. This fact was recorded by the appearance of a shoulder (for sample 150-72, Fig. 3?) or a maximum (for samples 170-18 and 190-12, Figs. 3b and 3c) at a temperature of about 400°C in the TPD NH₃ curves (Fig. 2). Obviously, the increase in the time of synthesis of silicoaluminophosphates led not only to the change in the SiO₂ concentration in the samples, but also to qualitative changes of their acidic properties.

To identify the nature of forming sites, the local environment of silicon was studied using ²⁹Si NMR spectroscopy. As follows from the NMR spectra (Fig. 4) silicon in samples 150-24 and 170-12 is mostly present in the form of isolated tetrahedra. This is registrated by a single maximum at -91.8 ppm (Figs. 4a, 4b). Probably the SM2 mechanism implementes under these conditions of silicoaluminophosphate synthesis. An increase of the reaction time leads to the formation of the so-called silicon islands, which is recorded by signals at -95.5 and -109.7 ppm in the ²⁹Si NMR spectra of samples 150-72 and 170-18. The observed changes of spectra indicates that under longterm synthesis, the incorporation of silicon into the silicoaluminophosphate structure proceeds according to both the SM2 and the SM3 mechanism. The formation of silicon islands proceeding to a smaller extent in the case of sample 170-18 when compared to sample 150-72, probably due to the shorter time of its crystallization. Under more hard conditions (synthesis temperature of 190°C), in the structure of silicoaluminophosphates 190-6 and 190-12 (Fig. 4c). Obviously, the observed differences in the state of silicon are due to the peculiarities of the synthesis of silicoaluminophos-



Fig. 3. Curves of TPD ammonia of silicoaluminophosphates with AEI structure.



Fig. 4. ²⁹Si NMR spectra of silicoaluminophosphates with AEI structure.

phates at different temperatures, but this fact requires special investigation.

The study of the catalytic properties of silicoaluminophosphates with AEI structure in MTO process showed the following. All the samples had a high initial conversion of 97–100%. As shown from data, presented in Fig.5, the deactivation of the samples proceeded at different rates. The fastest decrease of activity was for samples 150-24 and 170-12, which had time-on-stream of 100 and 130 min, respectively (Figs. 5a, 5b). The identical patterns of the TPD NH₃ curves and ²⁹Si NMR spectra for these samples suggest that the cause of deactivation is associated with the type of acid sites in these samples. For sample 190-6, the deactivation occurred at a lower rate, and timeon-stream of this sample was 230 min (Fig. 5c).

Samples 150-72, 170-18, and 190-12, for which the time-on-stream decreased in the order 150-24 > 170-18 > 190-12 and was 430, 330, and 270 min, respectively (Fig. 5), were chosen for further comparison. Analysis of the composition of reaction products

showed that gaseous C_2-C_4 olefins, liquid C_{5+} and methane were the main products of methanol conversion. Gaseous C_2-C_4 alkanes were formed in insignificant quantities, and their yield did not exceed 0.2 wt %. The amount of CO_x and hydrogen in the products did not exceed 1%.

The data presented in Table 2 show that the total yield of C_2-C_4 olefins changed from 83.0 to 90.7 wt %; highest yield of olefins obtained over sample 170-18. Figure 6 demonstrates the yields of individual MTO products as a function of the reaction time. As follows from these relationships for the yields of individual olefins, the samples form the following series:

ethylene 170-18 > 150-24 > 190-12; propylene 190-12 > 170-18 > 150-24; and buttlenes 100, 12 > 150, 24 > 170, 18

butylenes 190-12 > 150-24 > 170-18.

For sample 190-12, there is a tendency toward the formation of heavier products: this sample is superior to the others in the yield of $C_{4=}$ and C_{5+} hydrocarbons (Fig. 6c). It can be assumed that both this feature of the sample and its fast deactivation relative to that of



Fig. 5. Change in the catalytic activity of silicoaluminophosphates with AEI structure in MTO process as a function of the synthesis conditions.

the formation of heavy products and fast deactivation of this sample relate to samples 150-72 and 170-18 is due to a long transport pathway of the molecules participating in the reaction throughout the volume of the crystal. The values of the crystal volume is 0.26, 0.11 and 0.26 μ m³ for samples 190-12, 170-16 and 150-72, respectively.

The data on the catalytic activity and composition of MTO products on sample 170-18 shows that this sample has an optimal combination of morphological features, acid properties, and the active site structure, which makes it possible to achieve catalytic properties unusual for silicoaluminophosphate with the AEI structure. The catalytic properties of sample 170-18 noticeably differ from those of samples 150-72 and 190-12: it surpasses the analogues in the yield of ethylene (Fig. 6b), the value of which reaches 40.6–41.2 wt %. As a consequence, the total ethylene + propylene yield and the yield of total lower olefins are also the highest among the test samples. The data presented in Table 2 show that there is a very high ethylene : propylene molar ratio of 1.56–1.68 in the products obtained on this sample. Note that, ethylene : propylene molar ratios for samples 150-72 and 190-12, are also higher than those described in literature.

In summary, conducting the synthesis of silicoaluminophosphates with the AEI structure under mild conditions $(150-190^{\circ}C, 6-72 \text{ h})$ has allow to adjust the physicochemical properties of the materials, including the crystal size, silicon content, varying of structure of active site and acidity. The catalytic properties of silicoaluminophosphates prepared under mild conditions are determined by the combination of morphological features, the active-site state, and the acid properties. The catalytic properties of the materials synthesized in this study differ from those reported in literature by high values of the ethylene : propylene molar ratio in MTO products. It has been found that silicoaluminophosphate with AEI structure synthesized at $170^{\circ}C$ for 18 h, on which the yield of total



Fig. 6. Yields of the products of methanol conversion in the presence of silicoaluminophosphate with AEI structure (a) 150-72, (b) 170-18, and (c) 190-12. Notations: (\bullet) ethylene, (\blacktriangle) propylene, (\blacksquare) butylenes, (*) liquid C₅₊ hydrocarbons, and (\bullet) methane.

METHANOL TO OLEFINS CONVERSION

Parameter of process	Sample	Reaction time, min					
		80	180	280	380	480	
Total yield of olefins C_2-C_4	150-72	85.9	87.4	88.2	87.7	84.5	
	170-18	89.0	90.7	89.5	83.0		
	190-12	85.8	88.8	83.8			
Ethylene : propylene molar ratio	150-72	1.22	1.34	1.39	1.40	1.40	
	170-18	1.56	1.62	1.68	1.57		
	190-12	1.05	1.10	1.12			

Table 2. Catalytic properties of silicoaluminophosphates with AEI structure in MTO process

lower olefins reaches 90.7 wt %, ethylene yield of up to 41.2 wt %, ethylene : propylene molar ratio up to 1.68 is the most promising.

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