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# Microporous and Mesoporous Materials

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# Effect of coating with silica on acidic and catalytic properties of SAPO-18 in MTO conversion



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Keywords: Silicoaluminophosphates SAPO-18 Polydimethylsiloxane and tetraethoxysilane Coating with silica MTO conversion	Silicoaluminophosphate with AEI structure has been modified by silica coating using polydimethylsiloxane (PDMS) and tetraethoxysilane (TEOS) as silica sources. The single step procedure including deposition of 0.5, 1.0, 1.5 and 2.0 wt% of silicon in one step and the multistep procedure including stepwise deposition of silica source by small portions corresponding to 0.5 wt% of silicon with intermediate calcination steps have been applied. The modified materials have been characterized by X-ray fluorescence spectroscopy, X-ray diffraction analysis, low temperature nitrogen adsorption, <sup>29</sup> Si MAS NMR, thermoprogrammed desorption of ammonia and FTIR spectroscopy of adsorbed 2,6-ditertbutylpyridine (2,6-DTBPy). The results show that multistep procedure leads to the gradual increase of silicon content and results in the deposition of 2 wt% of Si in 4 steps, whereas single step procedure does not lead to the desired result. Coating with silicon leads to poisoning of Brønsted acid sites located on the external surface of SAPO-18 crystal. This effect is more pronounced in the case of PDMS due to more uniform silica deposition in this case. Coated materials show higher stability of catalytic activity with time on stream in methanol to olefins conversion (MTO) and higher stelectivity to light olefins. The mechanism of

silica coating with PDMS and TEOS is discussed.

# 1. Introduction

Methanol and/or dimethyl ether conversion to light olefins, primarily to ethylene and propylene, over silicoaluminophosphates nowadays is among the most perspective technology for natural gas upgrading [1–3]. Silicoaluminophosphates with CHA and AEI structures are considered as the most efficient catalysts for this process due to their unique structure allowing to achieve high selectivity to light olefins [2-4]. The main problem of methanol conversion to light olefins over these catalysts is their fast deactivation [2]. In many cases, this deactivation is due to secondary reactions on the external surface acid sites leading to formation of heavy polyaromatic carbonaceous deposits on the catalyst crystals surface [5,6].

To protect the external surface of the crystals from coke deposition, postsynthetic treatments with different silicon-containing compounds are widely used in the case of zeolites (ZSM-5, MOR etc.) [7-13]. This approach is based on the modification of zeolites external surface with silica leading to poisoning of acid sites responsible for the formation of large carbonaceous deposits on the external surface of the crystal. Besides that, silica deposition results in pore mouths narrowing followed by the increase of the selectivity towards the products with the smallest size. Tetraethoxysilane (TEOS) is commonly used for zeolites external surface modification due to its rather large size restricting its diffusion into zeolites intracrystalline space [7–13]. Valtchev with coauthors [12] have demonstrated that in the case of methanol to hydrocarbons conversion the passivation of external surface acid sites of MFI-type zeolite catalyst leads to lower selectivity to  $C_4^+$  hydrocarbons.

Although many reports have been published on the influence of zeolites modification with silica [7-13] on their catalytic performance in different reactions, there is a lack of information on the effect of silica coating in the case of silicoaluminophosphates. Moreover, this information is rather controversial. Thus, Park et al. [14] pointed that there is no effect of chemical vapor deposition of TEOS over SAPO-34 on its catalytic performance in methanol conversion. On the contrary, in our previous study [6] we observed enhanced catalyst stability in methanol conversion in a slurry reactor after polydimethylsiloxane (PDMS) deposition over SAPO-34. These observations call for the systematic study of the influence of silica deposition over silicoaluminophosphates on their textural, acidic and catalytic properties.

In this study, we aimed to clarify the effect of the reagent type, the

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deposition procedure and the content of silica deposited on the physicochemical and catalytic properties of SAPO-18 in methanol conversion into olefins. For this purpose, single step and multistep deposition of 0.5–2 wt% of silica using TEOS and PDMS as reactants were performed over SAPO-18. The mechanism of silica deposition was studied by <sup>29</sup>Si MAS NMR, Fourier transform infrared (FTIR) spectroscopy of adsorbed 2,6-ditertbutylpyridine (2,6-DTBPy) and temperature-programmed desorption of ammonia (TPD NH<sub>3</sub>). The catalytic properties in methanol conversion were evaluated in fixed bed reactor. The results show that the catalyst lifetime and its selectivity to ethylene and propylene ( $\overline{C_2}$ ,  $\overline{C_3}$ ) can be improved by tuning the reagent type, the deposition procedure and the content of silica deposited.

# 2. Experimental section

The initial silicoaluminophosphate with the AEI structure (SAPO-18) was synthesized by hydrothermal crystallization from the reaction mixture with the following composition:  $Al_2O_3 \cdot 2P_2O_5 \cdot 0.6SiO_2 \cdot 4$  ( $C_2H_5$ )<sub>4</sub>NOH · 140H<sub>2</sub>O. The reactants were aluminum isopropoxide, aqueous silicasol (40 wt %), orthophosphoric acid (85 wt %), and aqueous tetraethylammonium hydroxide solution (35 wt %). After mixing of the initial components, the reaction mixture was homogenized for 1 h, brought to pH 7 by adding concentrated HCl and homogenized additionally for 1 h. The crystallization time was 12 h at 170 °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 a flow of air (heating rate, 2 °C/min).

Coating of SAPO-18 with silica was carried out by incipient wetness impregnation with PDMS or TEOS in hexane followed by calcination in a flow of air at 500 °C for 3 h and washing with water to remove silica species, which are not attached to the catalyst surface. Single step and multistep procedures were applied. Single step procedure included deposition of 0.5, 1, 1.5 and 2 wt% of silicon in one step. Whereas multistep procedure involved gradual stepwise deposition of precursor by small portions corresponding to 0.5 wt% of silicon with intermediate calcinations steps. The amount of silica deposited was varied from 0.5 to 2 wt%. The samples obtained were denoted as X/NS/reagent used for deposition in wt.% and NS corresponds to the number of steps applied. The initial silicoaluminophosphate with AEI structure was denoted as SAPO-18. The full list of samples and their designations are given in Table 1.

The chemical composition was determined by the X-ray fluorescence analysis on a Thermo Scientific ARL PERFORM'X WDXRF spectrometer operating at 2.5 kW and using a Rh-tube. The phase composition was

### Table 1 List of the samples.

Sample	$Si_P$ , wt. % <sup>a</sup>	Si, wt. % <sup>b</sup>	Modification agent
S	0.0	0.0	_
0.5/1S/PDMS	0.5	0.5	PDMS
1/2S/PDMS	1.0	0.9	PDMS
1.5/3S/PDMS	1.5	1.4	PDMS
2/4S/PDMS	2.0	1.9	PDMS
0.5/1S/PDMS	0.5	0.5	PDMS
1/1S/PDMS	1.0	0.8	PDMS
1.5/1S/PDMS	1.5	0.7	PDMS
2/1S/PDMS	2.0	0.8	PDMS
0.5/1S/TEOS	0.5	0.5	TEOS
1/2S/TEOS	1.0	0.9	TEOS
1.5/3S/TEOS	1.5	1.4	TEOS
2/4S/TEOS	2.0	2.0	TEOS
0.5/1S/TEOS	0.5	0.5	TEOS
1/1S/TEOS	1.0	0.7	TEOS
1.5/1S/TEOS	1.5	0.8	TEOS
2/1S/TEOS	2.0	0.8	TEOS

<sup>a</sup> calculated content of additional silicon.

<sup>b</sup> content of additional silicon according to X-ray fluorescence data.

analyzed by XRD on the D2 PHASER (Bruker) diffractometer. The measurements were carried out at 30 kV and 10 mA with X-ray tube containing a copper anode (Cu K $\alpha$ 1 = 1,5418 Å).

Nitrogen adsorption-desorption isotherms were recorded at  $-196\ ^\circ C$  using a volumetric adsorption porosimeter (Micromeritics, ASAP 2010).

The morphology and size of the SAPO-18 crystals were determined by scanning electron microscopy (SEM) on Hitachi TM3030 apparatus.

 $^{29}\text{Si}$  CP MAS NMR spectra of initial and modified samples were collected on a Bruker AVANCE-II 400 spectrometer ( $\nu^{29}\text{Si}=79.5$  MHz,  $\nu^{1}\text{H}=400.1$  MHz). The MAS spinning rate was 8000 Hz.

The acidic properties were studied by TPD NH<sub>3</sub> and FTIR of adsorbed 2,6-DTBP. The TPD NH<sub>3</sub> experiment was performed on an USGA-101 universal gas sorption analyzer (Unisit). Before the NH<sub>3</sub> adsorption the samples were activated at 500 °C in a flow of He. Saturation with ammonia was conducted in a flow of dry NH<sub>3</sub>/N<sub>2</sub> mixture (1:9) for 15 min. Physically adsorbed ammonia was removed at 373 K in a flow of helium for 1 h. Afterwards the sample was cooled down to 70 °C and the temperature was increased to 800 °C in a flow of He with the rate of 8 °C·min<sup>-1</sup>.

FTIR spectra were recorded on a Nicolet Protégé 460 FTIR spectrometer with 4 cm<sup>-1</sup> optical resolution. Prior to the measurements, the catalysts were pressed into self-supporting disks and activated in the infrared (IR) cell attached to a vacuum line at 400 °C for 2 h. The adsorption of 2,6-ditertbutylpyridine (2,6-DTBP) was performed at 150 °C for 30 min. The excess of probe molecules was evacuated at 150 °C for 15 min. The number of Brønsted acid sites on external surface of the catalyst was deduced from the intensity of the band at ca. 1615 cm<sup>-1</sup> of adsorbed 2,6-DTBP.

The catalytic properties of the samples were evaluated in methanol conversion in a fixed-bed reactor. A 1 g portion of the catalyst (0.5–1 mm fraction) was placed in a quartz reactor. The catalyst pretreatment involved calcination at 500 °C for 1 h in a flow of nitrogen (50 mL/min). The experiment was conducted under atmospheric pressure, at 400 °C, weight hourly space velocity (WHSV) of 2 h<sup>-1</sup> and a molar ratio of N<sub>2</sub>: 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, respectively.

# 3. Results and discussion

#### 3.1. Characterization of parent silicoaluminophosphate

The parent SAPO-18 sample obtained by hydrothermal synthesis shows XRD pattern of silicoaluminophosphate with AEI structure [15] as depicted in Fig. S1a of Supporting Information. No impurities corresponding to other crystalline or amorphous phases are detected. SEM image (Fig. S1b) reveals plate-shaped crystals typical for SAPO-18 [16] with a diameter of 300–500 nm and thickness of about 100 nm. Nitrogen adsorption isotherm (Fig. S1c) corresponds to type I adsorption isotherm according to IUPAC classification [17], micropore volume being typical for SAPO-18 (Table 2) [16].

According to X-ray fluorescence data, the content of Si in the parent sample is ~4.8 wt%. <sup>29</sup>Si MAS NMR spectra (Fig. 1a) indicate that the silicon atoms incorporated during synthesis represent both isolated sites isomorphically substituting phosphorus in the framework (Si(4Al), -89 ppm) and "island-like" sites (Si(0-3Al), -95 to -115 ppm), which is in line with literature data [18]. The "island-like" sites are enriched with silanol groups as confirmed by the appearance of the line at ca. – 99 ppm in <sup>29</sup>Si CP MAS NMR spectra (Fig. 1b).

# 3.2. Effect of silica deposition on structural, textural and acidic properties of SAPO-18

Silica deposition on the surface of parent SAPO-18 sample was carried out by single step and multistep procedures both in the case of TEOS

#### Table 2

Physical chemical characteristics of initial and modified silicoaluminaphosphates.

Sample	Porous struct	a <sub>0</sub> <sup>e</sup> , µmol/g		
	$S_{BET}^{b}$ , m <sup>2</sup> /g	V tot <sup>c</sup> , cm <sup>3</sup> /g	V micro <sup>d</sup> , cm <sup>3</sup> /g	
S	434	0.270	0.179	939
0.5/1S/PDMS	408	0.253	0.166	995
1/2S/PDMS	406	0.238	0.167	804
1.5/3S/PDMS	393	0.242	0.160	761
2/4S/PDMS	387	0.244	0.156	666
0.5/1S/TEOS	427	0.263	0.178	973
1/2S/TEOS	410	0.257	0.169	884
1.5/3S/TEOS	399	0.248	0.169	815
2/4S/TEOS	395	0.245	0.167	805

<sup>a</sup> according to low temperature adsorption-desorption of nitrogen (by using BET, t-Plot, BJH methods).

<sup>b</sup> surface area.

<sup>c</sup> total pores volume.

<sup>d</sup> micropores volume.

e according to TPD NH3 data.

and PDMS reagents. The analysis of XRD patterns of modified samples (Fig. S2) show that the catalyst structure is affected neither by the type of the procedure nor by the type of the reagent. However, the type of the procedure has significant influence on the degree of silica deposition as shown in Table 1. Thus, multistep procedure leads to gradual increase of silicon in the samples up to 2 wt% and the amount of deposited Si corresponds to the amount taken for deposition. On the contrary, single step procedure does not lead to the desired result. In this case, the amount of deposited Si increases with the amount of Si taken for deposition only at low Si contents and then does not change. The highest amount of Si deposited reaches only 0.8 wt%. This observation is due to washing out of silica, which is not bonded to the surface.

Thus, silica deposition requires direct contact of the reagent with the surface active sites, which according to Ref. [10] could be represented by acidic sites or surface defects. The adsorption of the first layer of reagent does not hinder this interaction, but the molecules from the second layer are prevented to access the vicinal sites. However, these sites become accessible only after sample calcination and elimination of bulky ethoxy and methyl groups.

To conclude, stepwise coating leads to higher silica content and more

complete silicon deposition on the catalyst surface. Therefore, further studies were carried out only for the samples obtained by multistep deposition procedure.

The porous structure of modified silicoaluminophosphates has been studied by low temperature nitrogen adsorption. The results show that modification of parent silicoaluminophosphate by silica does not affect the type of nitrogen adsorption isotherms indicating that inner porous structure remains unaffected during modification procedure (Fig. S3). However, the total pore volume and the micropore volume is found to decrease with the amount of silica deposited on the surface, which is most probably due to partial pore blocking by silica (Table 2). This effect is more pronounced in the case of modification with PDMS.

The changes in acidity with silica deposition were followed by TPD-NH<sub>3</sub> (Fig. 2, Table 2) and FTIR of adsorbed 2,6-DTBPy (Fig. 3). TPD-NH<sub>3</sub> data provided information on the total amount of sites and their strength, whereas FTIR results gave insight into the external surface acidity. TPD-NH<sub>3</sub> profiles of all the samples show two desorption peaks with the maxima at ca. 200 and 400 °C, corresponding to weaker and stronger acid sites of SAPO-18. Deposition of silica does not influence the amount and the strength of the stronger acid sites indicating that the bulky reagents are deposited only on the outer surface the crystals. Meanwhile the amount of weaker acid sites is gradually decreasing due to covering the external surface acid sites and the sites located in the pore mouths. At high coverages with silica, the decrease of acid sites could be also due to partial pore blocking. The interesting result is observed at low coverages with silica in the case samples 0.5/1S/PDMS and 0.5/1S/TEOS showing the increase of weak acid sites content with respect to parent sample (Fig. 2, Table 2). This observation is most probably due to the creation of new acid sites as a result of interaction of PDMS or TEOS with the catalyst surface. At high silica coverages, these sites are covered with the next silica layers along with intrinsic SAPO-18 sites.

To characterize the acid sites on the outer surface of the crystals 2,6ditertbutylpyridine was selected as a probe molecule. This probe molecule cannot enter the porous system of SAPO-18. Besides that, it is not adsorbed on Lewis sites due to steric hindrance caused by the presence of the tertbutyl groups [19]. Thus, it gives information on the amount of Brønsted sites on the external surface of the crystal. For the measurement of Brønsted sites concentration at the outer surface the band at 1615 cm<sup>-1</sup> was used [20]. The results depicted in Fig. 3 show that the increase of silica content leads to the gradual decrease of



Fig. 1. <sup>29</sup>Si one pulse (a) and CP (b) NMR MAS spectra of initial and modified silicoaluminophosphates.



Fig. 2. TPD NH<sub>3</sub> profiles for initial and modified by PDMS (a) and TEOS (b) SAPO-18 samples.



**Fig. 3.** The share of Bronsted acid sites accessible for 2,6-DTBPy molecules for initial and modified silicoaluminophosphates. 100% corresponds to the share of acid sites of initial silicoaluminophosphate.

Brønsted acid sites accessible for 2,6-DTBPy in both series. In the case of PDMS this effect is more pronounced. Deposition of 4 layers of PDMS (sample 2/4S/PDMS) leads to poisoning of more than 50% of external sites. Whereas in the case of TEOS (sample 2/4S/TEOS) this value does not exceed 25%.

It should be noted that FTIR of adsorbed 2,6-DTBPy technique does not detect the formation of new acid sites revealed by TPD-NH<sub>3</sub> for samples 0.5/1S/TEOS and 0.5/1S/TEOS. These sites are most probably not accessible or sterically hindered for bulky 2,6-DTBPy.

The analysis of the influence of the type of reagent used for coating on the textural and acidic properties of SAPO-18 points that in the case of PDMS the influence of silica deposition is more pronounced than in the case of TEOS. It should be mentioned that quite an opposite result was observed previously for zeolite catalysts. TEOS was more efficient for modification of MFI zeolite with respect to PDMS [13]. This difference can be accounted for by different nature of the active sites on the surface of zeolites and SAPOs and therefore different mechanisms of interaction of PDMS and TEOS with the surface of these materials.

The interaction of TEOS with zeolites has been widely studied and presented in the literature [7–13]. The mechanism proposed [10] involves two stages: (i) interaction of TEOS ethoxy group with surface Brønsted or Lewis acid sites accompanied by elimination of ethanol molecule and formation of Si–O–Al bonds between TEOS molecules and

the surface aluminum atom; (2) oxidation of residual ethoxy groups of TEOS into hydroxyl groups, which partially condense with vicinal silanol groups of the surface and with each other to form Si–O–Si bonds. As a result, zeolites modification is accompanied by the decrease of the concentration of Bronsted sites, Lewis sites and terminal silanol groups. The reactivity of these sites was found to change in the following order: Lewis sites > Brønsted sites > silanol groups [10].

Different situation is observed in the case of SAPO materials due to different type of sites facing the external surface over these catalysts. FTIR spectrum of the parent SAPO-18 sample shows 4 bands in the hydroxyl region (Fig. 4): a band at 3743 cm<sup>-1</sup> corresponding to silanol groups, a band at 3678 cm<sup>-1</sup> originating from framework P–OH defects and two bands at 3600 and 3626 cm<sup>-1</sup> attributed to bridging hydroxyl groups [21–23]. These OH-groups can be located partially at the outer surface of the crystal and partially in the intracrystalline space. The main difference of SAPO with respect to zeolites is the absence of large amount of terminal silanol groups homogeneously distributed all over the crystal surface. The silanol groups observed in the FTIR spectrum of SAPO-18 are due to the presence of silica islands over this material. As a result, these groups are not homogeneously distributed over the surface of the crystal, but appear rather randomly, in the places where silica islands are facing the crystal surface (Fig. 5).

This feature is most probably responsible for "island-like" deposition





of TEOS on SAPO-18. Indeed, instead of condensing with terminal SiOH, as it was proposed for zeolites [10], TEOS molecules are condensing mostly with each other and form silica reach islands on the isolated and island-like sites, facing the external surface of SAPO-18 crystal as shown in Fig. 5. The deposition process is accompanied by the consumption of bridging hydroxyls and formation of silanol groups originating from the oxidation of TEOS (Fig. 4). This is confirmed by  $^{29}$ Si MAS NMR and  $^{29}$ Si MAS NMR spectra (Fig. 1), which show the growing resonance at ca. -107 ppm corresponding to amorphous silica reach in silanol groups [24] and weakly interacting with catalyst surface.

In the case of PDMS, the absence of homogeneous coverage of the surface of SAPO crystals with silanol groups has an opposite effect. The deposition of polymeric reagent might be more flat than in the case of zeolites, due to the absence of terminal silanol groups. As a result, the surface coverage is more uniform and the interaction with the surface is more efficient (Fig. 5). This is confirmed by the appearance of a broader feature in the range of -95 to -115 ppm in <sup>29</sup>Si MAS NMR spectrum (Fig. 1a) and more pronounced decrease of the intensity of the bands corresponding to bridging hydroxyls in the FTIR spectrum for the sample modified by PDMS (Fig. 4).

#### 3.3. Catalysts evaluation in MTO conversion

The influence of silica deposition on the catalytic properties of SAPO-18 was evaluated in methanol conversion into light olefins. The main reaction products observed over the parent and modified catalysts involved ethylene ( $C_2^{-}$ ), propylene ( $C_3^{-}$ ) and butylenes (Table S1). Besides that, small amounts of methane, ethane, propane,  $C_4^+$  products are detected.

The results depicted in Figs. 6 and 7 point to the significant improvement of catalyst performance due to coating with silica. Coated materials show higher stability of catalytic activity with time on stream (Fig. 6) and better selectivity to  $C_2^{=}$  on the expense of  $C_4^{+}$  products (Fig. 7). The higher stability is due to poisoning of the external acid sites responsible for building up of bulky carbonaceous deposits on the outer surface of the catalyst. Whereas the increase of the yield of  $C_2^{=}$  is due to two factors: (i) pore mouths narrowing, which favors the diffusion of smaller molecules and (ii) reduction of the contribution of secondary reactions proceeding on the catalyst external sites and leading to the formation of  $C_4^+$  products.

The comparison of the results obtained over the samples modified

with different reagents, PDMS and TEOS, shows that the source of silica has significant effect on the catalyst lifetime (Fig. 6a and b) and the yields of  $C_2^{=}$  and  $C_4^{+}$  products (Fig. 7a and b). In both cases, the effect of modification is more pronounced for PDMS series, which is fully in line with textural and acidic properties of the samples. According to FTIR (Fig. 4), <sup>29</sup>Si MAS NMR (Fig. 1) and nitrogen adsorption data (Fig. S3, Table 2), modification with PDMS results in more homogeneous silica deposition on the catalyst surface (Fig. 5) and more efficient reduction of the external acid sites content (Fig. 3). As a result, only one step deposition of 0.5 wt % of silicon leads to significant improvement of catalyst lifetime and  $C_2^{-}$  yield. Further deposition of higher amounts of silica is not required, since it results in pore mouths narrowing, which causes diffusion limitations for reaction products and decreases the catalyst stability with time on stream.

On the contrary, in the case of TEOS "island-like" silica deposition takes place, leading to less homogeneous silica distribution on the catalyst surface (Fig. 5) and less pronounced reduction of acid sites content on the external surface (Fig. 3). As a result, deposition of small amounts of silica corresponding to 0.5 wt% of Si does not have any effect on the catalyst lifetime and selectivity to light olefins (Figs. 6 and 7). The noticeable effect is observed only after deposition of 1.5–2 wt% Si. However, even in this case the effect is less important in comparison with 0.5/1S/PDMS.

Thus, the catalytic performance in terms of stability of the catalytic activity, selectivity and yield of light olefins is achieved over 0.5/1S/PDMS sample. Over this sample the catalyst life time increases by a factor of 2.8 and the yield of  $C_2^=$  and  $C_3^=$  increases from 80 to 82% (Fig. 8).

#### 4. Conclusions

The single step and multistep procedures for silicoaluminophosphates coating with TEOS and PDMS as silica sources are applied for SAPO-18 catalyst. The results show that the multistep procedure leads to the gradual increase of silicon content on the external surface of the catalyst and results in deposition of 2 wt% in 4 steps. On the contrary, single step procedure does not lead to the desired result. The highest amount of silicon deposited reaches only 0.8 wt%.

It is demonstrated that the gradual increase of silicon content leads to the gradual poisoning of Brønsted acid sites located on the external surface of SAPO-18 crystal as confirmed by FTIR of adsorbed 2,6-DTBPy.



Fig. 5. Mechanism of silicoaluminophosphate external surface modification.



Fig. 6. Methanol conversion with TOS for initial and modified by PDMS (a) and TEOS (b) silicoaluminophosphates. 400  $^{\circ}$ C, 1 atm, 2 h<sup>-1</sup>, methanol/N<sub>2</sub> = 5/1.



Fig. 7. Yield of  $C_2^=$  and  $C_4^+$  with TOS for initial and modified by PDMS (a) and TEOS (b) silicoaluminophosphates. 400 °C, 1 atm, 2 h<sup>-1</sup>, methanol/N<sub>2</sub> = 5/1.



Fig. 8. Maximal yield of  $C_2^-$  and  $C_3^-$  with TOS for initial and modified silicoaluminophosphates. 400 °C, 1 atm, 2 h<sup>-1</sup>, methanol/N<sub>2</sub> = 5/1.

 $^{29}$ Si MAS NMR, FTIR and the adsorption data suggest that in the case of PDMS reagent, silica deposition on the external surface is more uniform and the effect of surface coating is more pronounced. Whereas in the case of TEOS, the external acid sites are reduced only by 25%, coating with PDMS leads to 50% sites reduction.

The catalytic properties of SAPO-18 studied in methanol conversion into light olefins are shown to be significantly improved by coating with silica. Coated materials provide for higher stability of catalytic activity with time on stream and higher selectivity to light olefins on the expense of  $C_4^+$  products. The best catalyst performance is achieved over SAPO-18 coated with 0.5 wt% Si using PDMS as a source of silica.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRediT authorship contribution statement

**Stanislav V. Konnov:** Conceptualization, Methodology, Writing - original draft, Investigation. **Vladimir S. Pavlov:** Investigation, Visualization. **Irina I. Ivanova:** Supervision, Project administration, Writing - review & editing.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.micromeso.2020.110158.

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