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CHARACTERISTIC PROPERTIES OF SYNTHESIS PROCESS OF OLEFINS FROM METHANOL OVER MICROPOROUS SILICOALUMINOPHOSPHATE CATALYSTS

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Silicoaluminophosphate catalysts (SAPO-34) were synthesized using hydrothermal method. It was investigated the influence of structure directing agents (tetraethylammonium hydroxide, morpholine, triethylamine, diethylamine), which were used during synthesis process, to the structure and also to the activity and stability of obtained patterns in the process of conversion of methanol to light C₂-C₄ olefins. It was defined that using of tetraethylammonium hydroxide/morpholine mixed agents lead to the formation of catalyst with stable structure, yield of light olefins over this catalyst is higher in compare to other patterns and consist of 78%.

Keywords: zeolite, methanol, light olefins, hydrothermal, tetraethylammoniumhydroxide, morpholine, diethylamine, triethylamine

Methanol conversion to light olefins (MTO), starting from natural gas or coal with methanol as intermediates is now well established as the most successful process. For the MTO process, SAPO - 34 is the best catalyst known among silicoaluminophosphates because of its remarkable pore structure and hydrothermal stability, it shows an exceptional selectivity for light olefins and the complete conversion of methanol in MTO process. Silicoaluminophosphate molecular sieves (SAPOs) have considerable potential as acidic catalysts which can play different key roles such as membrane or adsorbent in sorption reactions and catalyst in petrochemical reactions. This molecular sieves may possess Bronsted acidic sites with the substitution of Si into the neutral framework of AlPO₄-n. Aluminophosphate (AlPO₄) molecular sieves framework is electrically neutral without ion exchange capability. Introduction of silicon atoms into their structure causes a negative imbalance in the framework's charge. Hydroxyl groups as Bronsted acidic sites are formed by neutralization of the negatively charged centers with the proton left after decomposition of organic template in the calcination process [3].

It is well known that organic templates play important roles in the synthesis of molecular sieves, such as structure-directing, space-filling and charge-compensating roles. One template may produce molecular sieves with different structures by varying the synthetic conditions; and one type

of molecular sieve could also be synthesized in the presence of different organic templates. The elemental composition, local microscopic structure and morphology of one specific molecular sieve may change with the use of different templates. Therefore, the catalytic performance and adsorption properties of the obtained materials may be different [4,5]. Many organic templates, such as, tetraethylammonium hydroxide (TEAOH), morpholine, triethylamine (TEA), diethylamine (DEA), isopropylamine, piperidine and so on, have been used as the template to synthesize SAPO-34 [6]. Our main aim was to synthesize SAPO-34 silicoaluminophosphate via hydrothermal method with using of different structure directing agents and to investigate influence of these templates to the activity and stability of catalyst.

In order to synthesize stable SAPO-34 catalyst, different single and mixed templates such as DEA, TEA, TEAOH/TEA, TEAOH/morpholine (further abbreviated as S1, S2, S3 and S4) were used from us as structure directing agents. Required components for synthesizing of zeolite were mixed for 25 h, then transferred into stainless-steel autoclaves and heated at 200°C. Crystallization time for these samples are 24 h. After heating catalysts washed with distilled water several times, then dried at 120°C and at the end calcined at 550°C [6]. Figure 1 describes XRD analysis of obtained patterns.

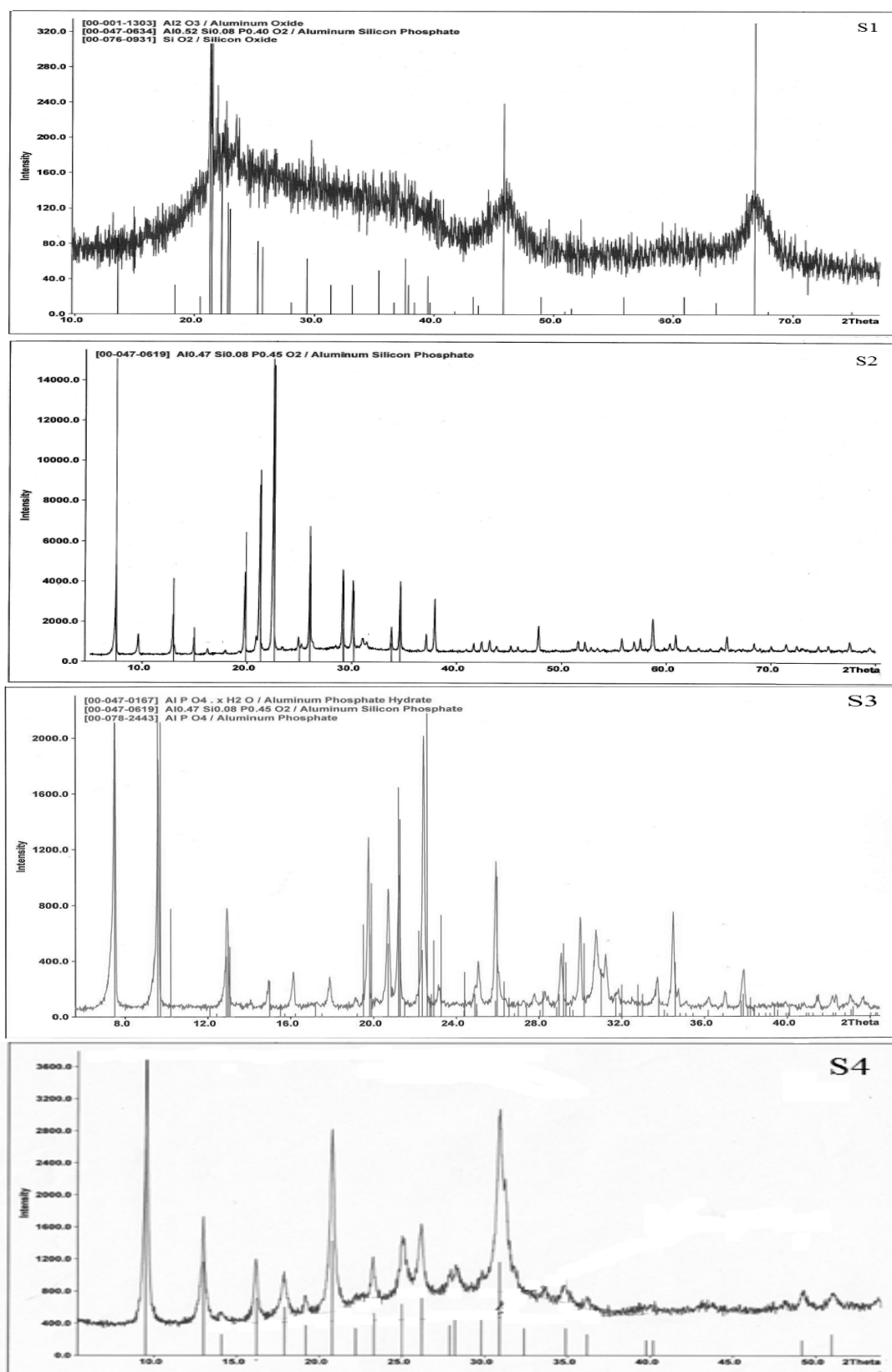


Fig. 1. XRD patterns of the synthesized samples using different templates. S1:DEA, S2: TEA, S3:TEAOH/TEA, S4:TEAOH/morpholine

As it seems from figure 1, when only DEA was used as organic template, obtained material was in amorphous phase. When only TEA and mixed TEOH/TEA templates were used some diffraction peaks of SAPO-5 ($2\theta=7.5^\circ$, $2\theta=14.9^\circ$, $2\theta=19.8^\circ$) were observed, too. In the case of TEOH/morpholine according peaks ($2\theta=9.4^\circ$, $2\theta=20.9^\circ$) of pure SAPO-34 phase were detected. So, using of morpholine and TEOH mixture lead mainly to SAPO-34.

The crystal size and elemental composition of prepared samples were described in table 1.

Compared to single template, mixed template leads to the particle size reduction. Besides, the catalytic stability of SAPO-34 was found to be affected by the preparation parameters

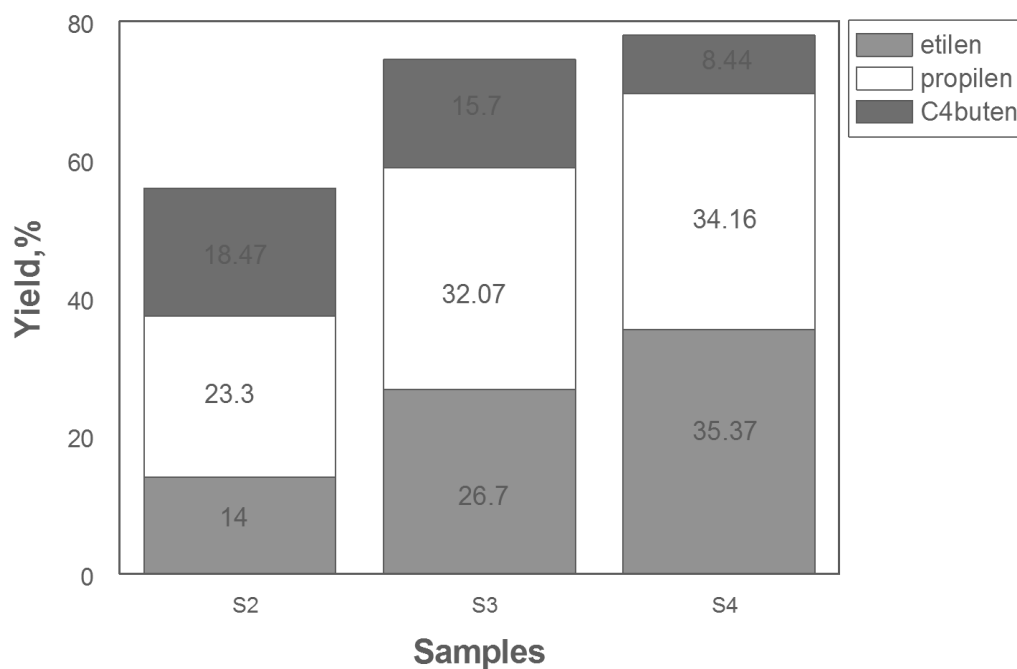
during synthesis which are closely related with crystal size and the silicon contents during synthesis. The reduction of silicon content during synthesis of gel led to the formation of only pure SAPO-34 phase. Thus, S4 sample because of its small crystal size (33 nm) and a low amount of silicon content (6 wt.%) shows best behaviour in MTO reaction and deactivates a little bit slowly in compare to samples S2 and S3.

Catalytic tests in the presence of these samples were conducted at 450°C -, and 0.125 MPa-, for 5 h on stream using $\text{CH}_3\text{OH}:\text{N}_2=60:40$ feed with a contact time of $2.05 \text{ mg}_{\text{cat}} \cdot \text{min} \cdot \text{ml}^{-1}$ with respect to methanol. Figure 2 exemplifies the initial yield to $\text{C}_2\text{-C}_4$ olefins over silicoaluminophosphate catalysts.

Table

Crystal size and elemental composition of prepared samples

Sample №	Elemental composition (wt.%)				Crystallite size, nm	Phase
	Si	Al	P	O		
S1	-	-	-	-	-	Amorphous
S2	8.6	20.5	21.6	49.3	>100	SAPO-34+SAPO-5
S3	7	21	16	56	45	SAPO-34+SAPO-5
S4	6	15	16	63	33	SAPO-34

Fig. 2. Initial yield to $\text{C}_2\text{-C}_4$ olefins over silicoaluminophosphate catalysts

C₂-C₄ low olefins were main products of reaction and the yield of light olefins over S2, S3 and S4 was 55.8%, 75% and 78% respectively. It was revealed that using a single structure directing agent in SAPO-34 synthesis, results in rapid coke formation and the coke cover acidic sites and block the pores of SAPO-34 which finally leads to catalyst deactivation. That's why S2 and S3 deactivate fast and it prevents obtaining of lower olefins. Also compared with using a single template, a mixed template leads to the particle size reduction.

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MIKROMƏSAMƏLİ SİLİKOALÜMOFOSFAT KATALİZATORUNUN İŞTİRAKI İLƏ METANOLDAN OLEFİNLƏRİN SİNTEZİ PROSESİNİN XÜSUSİYYƏTLƏRİ

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Hidrotermal üsuldən istifadə etməklə silikoalümofofosfat (SAPO-34) katalizatorları sintez edilmişdir. Sintez prosesində istifadə olunan strukturlaşdırıcı agentlərin (tetraetilammonium hidroksid, dietil amin, trietil amin, morfolin) alınan nümunələrin strukturuna, eyni zamanda metanoldan aşağı molekullu C₂-C₄ olefinlərinin alınması prosesində aktivlik və sabitliyinə təsiri öyrənilmişdir. Məlum olmuşdur ki, tetraetilammonium hidroksid/morfolin tərkibli qarışıq agentlərin istifadəsi daha stabil quruluşlu katalizatorun alınmasına səbəb olur və bu katalizator üzərində aşağı molekullu olefinlərin çıxımı digər nümunələrdən fərqli olaraq yüksək olub, 78% təşkil edir.

Açar sözlər: seolit, metanol, aşağı molekullu olefinlər, hidrotermiki, tetraetilammonium hidroksid, morfolin, dietilamin, trietilamin

ОСОБЕННОСТИ ПРОЦЕССА СИНТЕЗА ОЛЕФИНОВ ИЗ МЕТАНОЛА НА МИКРОПОРИСТЫХ СИЛИКОАЛЮМОФОСФАТНЫХ КАТАЛИЗАТОРАХ

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Гидротермическим методом были синтезированы силикоалюмофосфатные (SAPO-34) катализаторы. Изучено влияние использованных структурированных агентов (тетраэтиламмоний гидроксид, диэтиламин, триэтиламин, морфолин) на структуру полученных образцов, а также на активность и стабильность катализаторов в процессе получения низших C₂-C₄ олефинов из метанола. Выявлено, что при использовании смеси агентов тетраэтиламмоний гидроксид/морфолин ведет к получению более стабильных катализаторов, выход низших олефинов на этом катализаторе по сравнению с другими образцами выше и составляет 78%.

Ключевые слова: цеолит, метанол, легкие олефины, гидротермический, тетраэтиламмоний гидроксид, морфолин, диэтиламин, триэтиламин