



Synthesis of SAPO-34 catalysts via sonochemically prepared method and its catalytic performance in methanol conversion to light olefins

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Abstract

Methanol-to-olefin (MTO) reaction was investigated over sonochemically (SAPO-34-U40, SAPO-34-U70, SAPO-34-U100) and hydrothermally (SAPO-34-HT) prepared nanocatalysts. The catalytic performance of prepared samples was investigated over all samples at 450 °C and over SAPO-34-U40 at 350–450 °C temperature range. The higher yield ~ 97 wt% (31.4 wt% C₂₌, 49.4 wt% C₃₌ and 16.1 wt% sumC₄₌) of light olefins was obtained at 375 °C on SAPO-34-U40. Physico-chemical properties of catalysts were characterized by XRD, SEM, BET, ICP techniques. XRD analysis showed suitable crystalline structure and SEM images confirmed perfect crystallinity of sonochemically prepared samples. BET analysis indicated remarkable surface area of SAPO-34-U40. The amount of carbon deposits and character of coke was determined by TPO analysis. The higher amount of coke was determined over SAPO-34-HT in comparison to another's at 450 °C. The character of coke deposited over SAPO-34-U40 was similar for 375–425 °C temperatures.

Keywords SAPO-34 · Ultrasound · Hydrothermal · Nanocatalyst · Catalytic performance · MTO

Introduction

Light olefins such as ethylene and propylene are widely used as raw materials for large-scale production of various polymers, fibers, resins and solvents. Owing to the rapid development of the world economy, there is increased demand for ethylene and particularly for propylene. Methanol-to-olefin (MTO) process has attracted attention as a potential indirect route for the production of light olefins, because methanol is commercially produced from synthesis gas generated from natural gas and/or coal [1].

Silicoaluminophosphate molecular sieve, especially SAPO-34 catalyst is one of the best candidates for the process of obtaining light olefins from methanol. Because of

its CHA framework and small particle sizes, SAPO-34 enhances the accessibility of methanol into its cages and leads to better catalytic performance [2, 3]. The main inability which makes the lifetime of SAPO-34 catalysts short is a fast deactivation because of accumulation of large aromatic species inside the cages of these catalysts. In this case, preparing of catalysts which are more resistance to coke formation is one of the main problems [4–6].

Until now, many researches have mainly focused on the different synthesis methods which are effect on the various properties of SAPO-34, such as catalyst acidity, pore size and shape, particle size, etc. [7–9]. Last few years, great attention has been paid to the use of ultrasound energy. The main advantages of SAPO-34 synthesized by this method are: to obtain higher surface area with narrow size distribution and enhanced catalytic performance. It was proved by many researches that ultrasonic treatment prevents the further growth of the particles and their agglomeration. Furthermore, achieving smaller particles decline the secondary reactions in MTO process [10–14]. Therefore, in this work the effect of ultrasound wave's frequency on physicochemical properties and catalytic activity of synthesized SAPO-34 have been studied and are compared with SAPO-34 catalyst, synthesized using conventional hydrothermal method. To this end, synthesized via ultrasound treatment SAPO-34

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catalyst's catalytic performance was investigated at different temperatures in MTO reaction. The catalysts were characterized by XRD, SEM, ICP, BET and TPO analysis.

Materials and methods

Materials

Boehmite (CAPATAL B, 70.5% Al_2O_3), tetraethylorthosilicate (TEOS, Merck, $\geq 98\%$) and ortho-phosphoric acid (Aldrich, 85%) were used as sources of aluminum, silicon and phosphorus, respectively. The tetraethyl ammonium hydroxide (TEAOH, ALDRIX, 35 wt% aqueous solution) was applied as template for SAPO-34 synthesis. All materials were used as received without any further treatments. The catalysts, synthesized by hydrothermal method (HT) and by ultrasound waves with 40, 70 and 100% powers (8, 14 and 20 kHz), were further abbreviated as SAPO-34-HT, SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100, respectively.

Catalyst preparation and procedures

To synthesize active catalysts with desirable properties, adding and mixing are main clauses. So, for the preparation of SAPO-34 catalysts using ultrasound waves, for avoiding of creating of lumps, 6.5 g boehmite was gradually (approximately 2 h) added to 32.3 g TEAOH and during adding the power for stirring was increased. Mixture was stirred for 90 min; then 2.4 g TEOS was added drop-wise and solution stirred additional for 60 min. Afterwards, 8.9 g of phosphoric acid diluted in 12.7 g of distilled water was added drop-wise; at the end, remaining water was added to the mixture. The final gel was sonicated in argon flow for 30 min, by an Ultrasonic Homogenizer *SONOPLUS HD 2070* (Bandelin) with a frequency of 20 kHz and input power of 70 W. The pH of gel was 7. For preparation of SAPO-34 catalyst via hydrothermal method, the same components were mixed without using ultrasound frequency. In both synthesis methods, final mixture was transferred into stainless steel autoclaves and heated at 200 °C for 48 h. Temperature of crystallization was controlled by temperature controller. After crystallization, samples were centrifuged and washed twice with distilled water. Then, the synthesized samples were dried at 110 °C for 12 h, at the end calcined at 550 °C in the air for 12 h to remove the organic template molecules. Prior to the catalytic tests, the catalysts were pelleted, crushed and sieved into 250–600 μm fraction.

Catalyst characterization

The crystallographic properties of calcined samples were analyzed by X-ray diffraction (XRD) using a PANanalytical

X'Pert Pro powder with Cu $K\alpha$ radiation X-ray (wavelength $\lambda = 0.15 \text{ nm}$). XRD patterns were recorded in the range of 0°–40° (2θ). The crystal morphology and crystal size were analyzed by scanning electron microscopy (SEM, Bruker). The metal content of the calcined catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian 715-ES). The specific surface areas of synthesized catalysts were calculated from N_2 adsorption–desorption isotherms collected at 77 K on a BELSORP-mini II (BEL Japan). The Brunauer, Emmett and Teller (BET) equation was applied for an N_2 relative pressure range of $P/P_0 = 0.05\text{--}0.3$. The amount of carbon deposits formed over catalysts during MTO process was determined from TPO analysis using a quadrupole mass spectrometer (Pfeiffer Vacuum OmniStar 200).

Continuous flow catalytic tests

MTO tests over SAPO-34 catalysts were performed in a multi-channel set-up consisting of 15 plug flow fixed-bed quartz tube reactor (i.d. = 3.8 mm), at 350–450 °C temperature, and 1.2 bar, for 7 h on stream using $\text{CH}_3\text{OH}/\text{N}_2 = 60/40$ feed with a modified contact time of 2.05 $\text{g}_{\text{cat}} \text{min ml}^{-1}$ with respect to methanol. Each reactor was filled with 200 mg of fresh catalyst. Before reaction catalysts were heated to request temperature of process (different temperatures, from 350 to 450 °C) in air (13 ml min^{-1} per channel) held in air flow for 2 h and then flushed with N_2 for 30 min. Hereafter, a mixture of 60 vol% CH_3OH in N_2 was fed into the catalyst bed at a rate of 10 ml min^{-1} per reactor. After, experiment reactors were cooled to room temperature in N_2 .

The feed components and the reaction products were analyzed using an on-line gas chromatograph (Agilent 6890) equipped with PLOT/Q (for CO_2), HP-PLOT Al_2O_3 “KCl” (for hydrocarbons) and Molsieve 5 (for H_2 , O_2 , N_2 , and CO) columns and flame ionization and thermal conductivity detectors. The GC analysis was carried out reactor by reactor.

Calculation of carbon deposits

The amount of carbon of discharged catalysts after MTO reaction was determined from the amounts of CO and CO_2 evolved during temperature-programmed oxidation (TPO). The TPO measurements were performed in a set-up equipped with eight individually heated plug-flow fixed-bed quartz tube reactors (i.d. = 6.9 mm). The used catalysts were heated to 900 °C in a flow (10 ml min^{-1}) of 10 vol% O_2 in Ar. The measurements were performed successively, i.e., during heating (TPO) of the analyzed sample; all other samples were kept at 25 °C under Ar. Oxygen consumption and formation of the reaction products were monitored using a quadrupole mass spectrometer

(Pfeiffer Vacuum OmniStar 200). The following atomic mass units (AMUs) were obtained: 44 (CO_2), 40 (Ar), 32 (O_2), 28 (CO, CO_2), and 18 (H_2O). The concentrations of O_2 , CO and CO_2 were determined from the respective AMUs using standard fragmentation patterns and sensitivity factors determined by analyzing calibration gas mixtures.

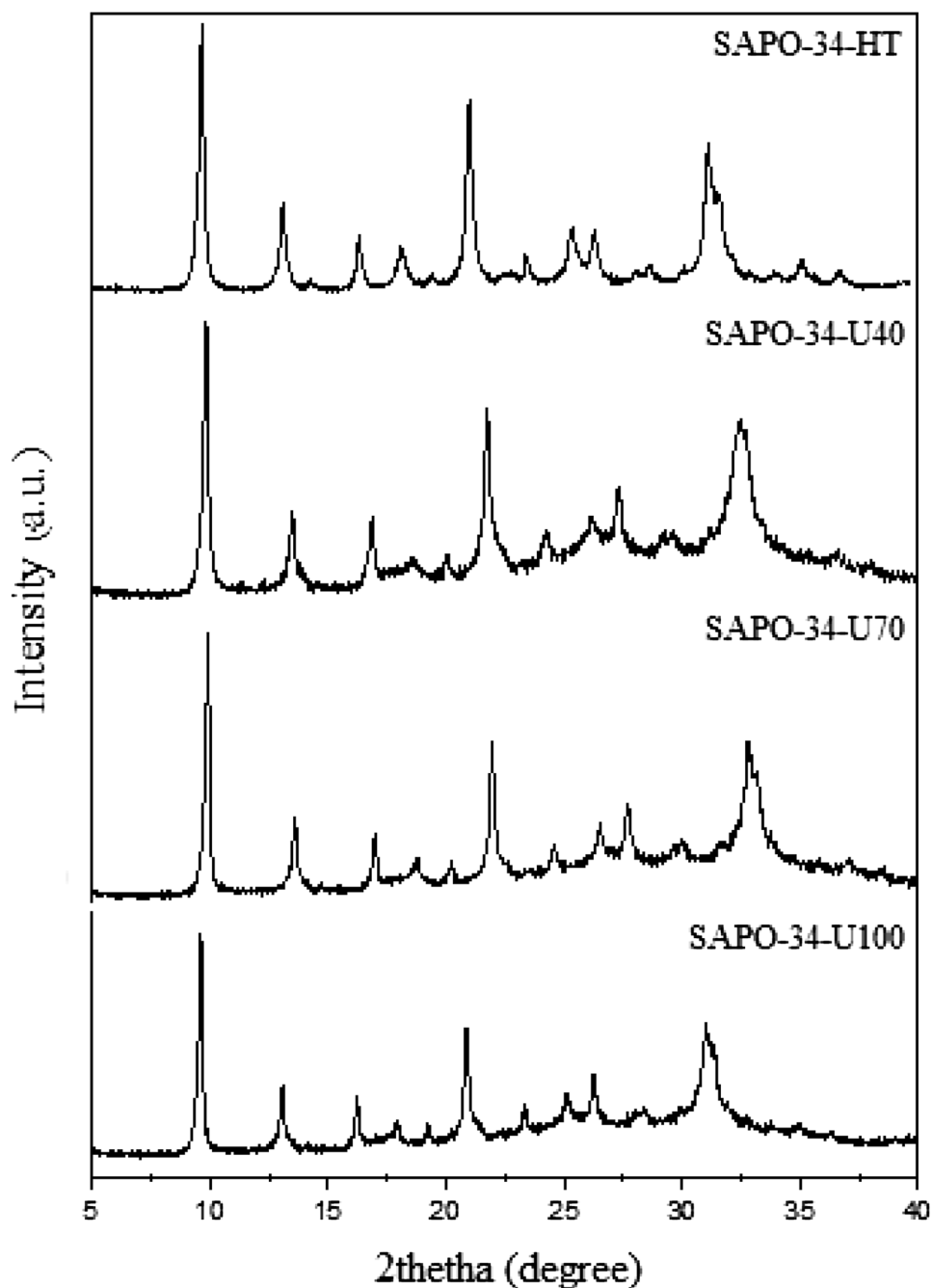
Results and discussion

Catalyst characterizations

XRD analysis

The XRD patterns of synthesized SAPO-34-HT, SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100 catalysts are shown in Fig. 1.

Fig. 1 XRD patterns of the nanostructured SAPO-34-HT, SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100 catalysts



All synthesized samples demonstrate typical powder diffraction patterns corresponding to CHA structure of SAPO-34, without any presence of impurity phase. The XRD peak intensity for all SAPO-34 samples was determined at $2\theta = 9.58^\circ, 12.9^\circ, 16.25^\circ, 20.87^\circ, 23.3^\circ, 25.1^\circ, 26.2^\circ$ and 31° [10]. The crystallinity of SAPO-34-HT, SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100 was found to be 60, 70, 68 and 65%, respectively. The average crystallite sizes (nm) were calculated using the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos\theta}, \quad (1)$$

where k is a constant, λ is the wavelength of the X-ray, β is the full width of diffraction peak at half maximum intensity, θ is the diffracting angle [15]. Table 1 presents some properties, also the XRD results of synthesized SAPO-34 samples. All catalysts are in cubic form, and average crystallite size calculated for SAPO-34-HT, SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100 are 45, 27, 27.9 and 28.2 nm, respectively. It can be concluded that in comparison to hydrothermal method, ultrasound irradiation of gel leads to obtaining of lower average crystallite size. Also, different frequency of used ultrasound waves has a slightly influence to crystallinity and crystal size of synthesized samples.

SEM analysis

The SEM analysis of synthesized samples is shown in Fig. 2. Synthesized catalysts are in cubic structure and this structure is similar to chabazite [8, 16–19].

SEM images show that using conventional hydrothermal method, cubic crystals with size of < 300 nm are obtained for SAPO-34-HT, but applying ultrasound waves to the synthesis of catalysts gives small cubic crystals with size of < 100 nm for SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100. In addition, it is obvious that (Fig. 2a–c), relatively uniform particles were obtained for SAPO-34 catalysts, synthesized using ultrasound treatment. So, ultrasound irradiation of gel improves uniformity of the synthesized samples, and also gives possibility to obtain small cubic crystals.

BET analysis

Specific surface areas of synthesized SAPO-34 catalysts are given in Table 1. Because of synthesized samples are microporous materials, specific surface areas were determined by “ t -plot” method. According to this analysis, the surface of internal micropores of SAPO-34-HT, SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100 were obtained $358.58, 887.8, 713.8$ and $704.77 \text{ m}^2 \text{ g}^{-1}$, external surface of samples $75.42, 100.1, 97.44$ and 98.92 , respectively. Thus, SAPO-34-HT has lower ($434 \text{ m}^2 \text{ g}^{-1}$) specific surface area; SAPO-34-U40 possesses a higher specific surface area ($987.9 \text{ m}^2 \text{ g}^{-1}$) in comparison to SAPO-34-U70 and

Table 1 Element content (wt%) and structural properties of nanostructured SAPO-34-HT, SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100 catalysts

Samples	Element content (wt%)				Surface area ($\text{m}^2 \text{ g}^{-1}$)			Average crystallite size (nm)	Relative crystallinity (%)	Product phase SAPO-34
	Al	Si	P	O	S_{BET}	$S_{\text{micropore}}$	S_{external}			
SAPO-34-HT	21	7	16	56	434	358.58	75.42	45	60	Cubic
SAPO-34-U40	17.5	5.9	15.8	60.8	987.9	887.78	100.12	27	70	Cubic
SAPO-34-U70	18.0	6.4	16	59.6	811.2	713.76	97.44	27.9	68	Cubic
SAPO-34-U100	18.5	6.2	16.6	58.7	804.7	704.77	98.92	28.2	65	Cubic

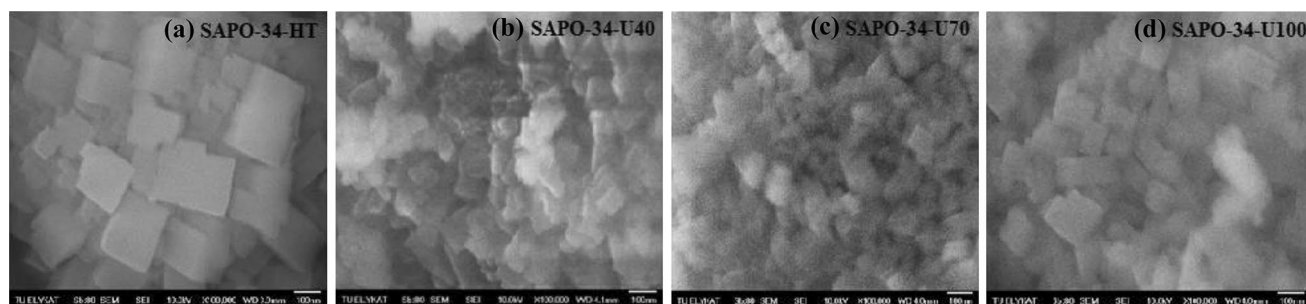


Fig. 2 SEM images of nanostructured catalysts: **a** SAPO-34-HT, **b** SAPO-34-U40, **c** SAPO-34-U70 and **d** SAPO-34-U100

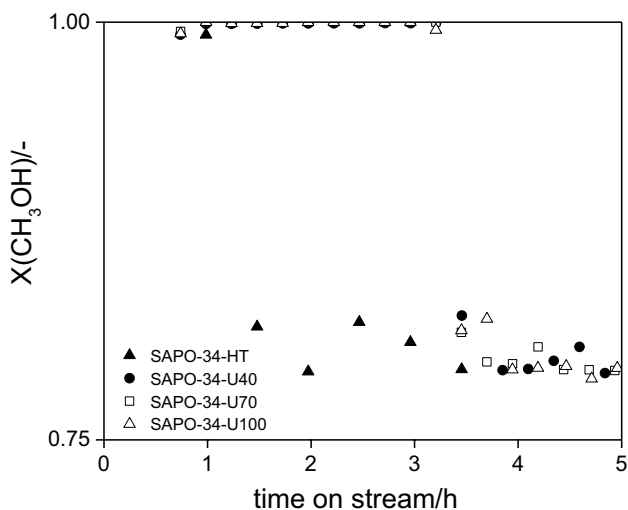


Fig. 3 Conversion of methanol over nanostructured SAPO-34-HT (filled triangle), SAPO-34-U40 (filled circle), SAPO-34-U70 (open square) and SAPO-34-U100 (open triangle) catalysts. Reaction conditions: 450 °C, CH₃OH/N₂ = 60/40, contact time = 2.05 g_{cat} min ml⁻¹ with respect to methanol, catalyst = 0.2 g

SAPO-34-U100 (811.2 and 804.7 m² g⁻¹). The surface area analysis showed that ultrasound treatment of gel increases specific surface area of catalysts.

Catalytic performance

Methanol conversion (Fig. 3) over all samples synthesized using ultrasound waves reaches 100% during 3-h of reaction time, then decreases to 79% with deactivation of catalysts. All catalysts (SAPO-34-U40, SAPO-34-U70, SAPO-34-U100) show approximately similar results. On the contrary, SAPO-34-HT is active only 1 h and after 1.4 h methanol conversion decreases to 80%. Comparison between SAPO-34-HT and SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100 performances on methanol conversion approves better activity of SAPO-34 catalysts, synthesized via ultrasound treatment, for MTO reaction.

Figure 4 illustrates synthesized catalysts performance toward light olefins, CH₄, DME and sumC₆₊ production. Over all synthesized catalysts C₂=–C₄= olefins were main reaction products; DME and sumC₆₊ major by-products

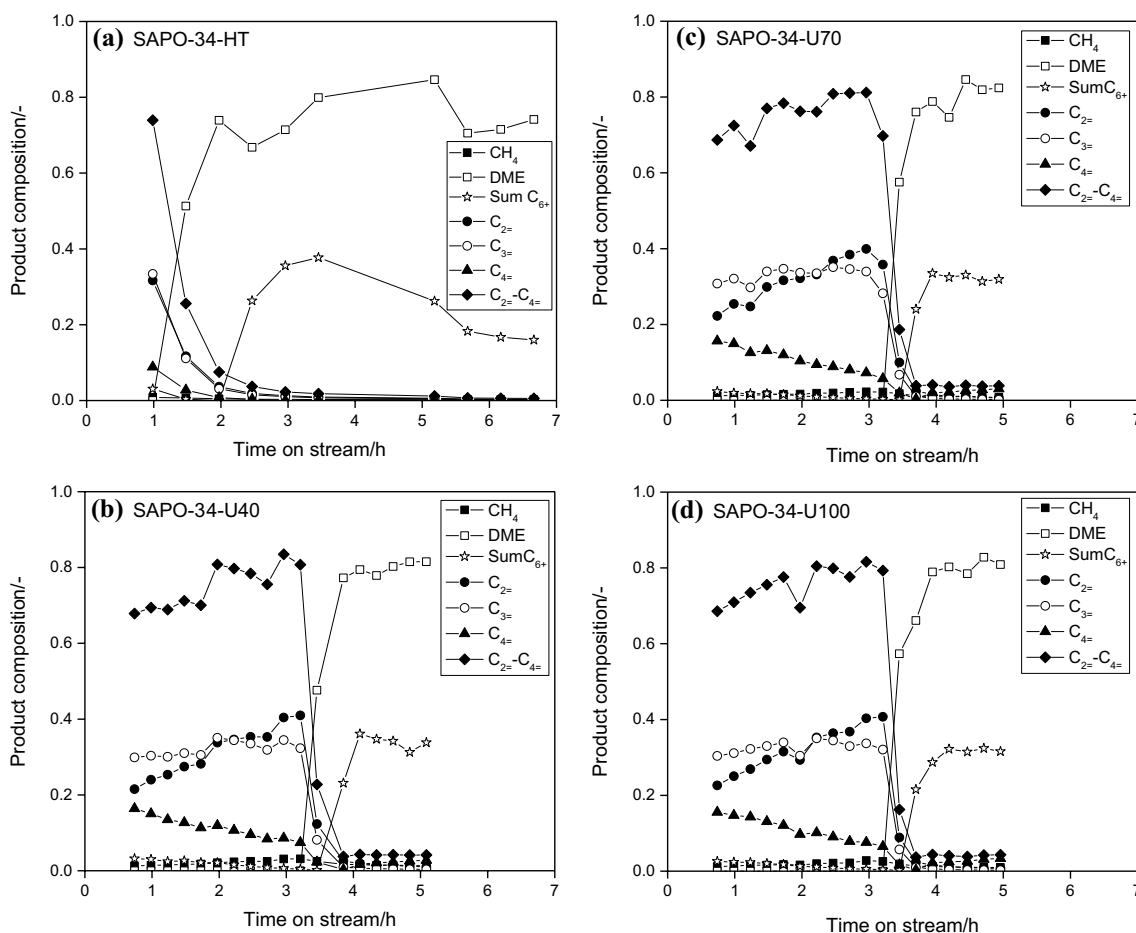


Fig. 4 Product distribution in the MTO reaction over nanostructured **a** SAPO-34-HT, **b** SAPO-34-U40, **c** SAPO-34-U70 and **d** SAPO-34-U100 catalysts. Reaction conditions: 450 °C, CH₃OH/N₂ = 60/40, contact time = 2.05 g_{cat} min ml⁻¹ with respect to methanol, catalyst = 0.2 g

were detected with deactivation of catalysts, while CH_4 was formed in low amounts.

Comparison between SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100 performances on $\text{C}_2\text{--C}_4\text{=}$ production approves same activity of samples for MTO reaction. The yield of low olefins increases with time on stream and at 3 h it reaches 83.5, 81.2 and 81.6 wt% for SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100, respectively. Over SAPO-34-HT, yield of light olefins is 73.9 wt% during 1 h, after 1.4 h with rapid deactivation of catalyst it decreases to 25 wt%. Thus, the lowest activity of SAPO-34-HT catalyst corresponds to its lower crystallinity and lower surface area which are important factors affecting deactivation of the catalyst [20].

The decrease in light olefins formation for all samples corresponds to an increase in the formation of DME and higher hydrocarbons. All catalysts present a high content of dimethyl ether after 3.4 h (for SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100) and after 1.4 h (for SAPO-34-HT) of TOS as shown in Fig. 4. The high yield of DME can be attributed to the deactivation of the stronger acid centers of the catalysts, which are able to produce the dehydration of DME to the light olefins [12]. With deactivation of catalysts, the role of secondary reactions take place and this factor leads to formation of higher hydrocarbons (C_{6+}).

As the results of MTO process over sonochemically synthesized samples are similar, we decided to use SAPO-34-U40 (which possesses higher surface area and smaller crystallite size) for further investigations. So, this sample was undergone to methanol-to-olefin tests at different temperatures. Figures 5 and 6 show the methanol conversion and

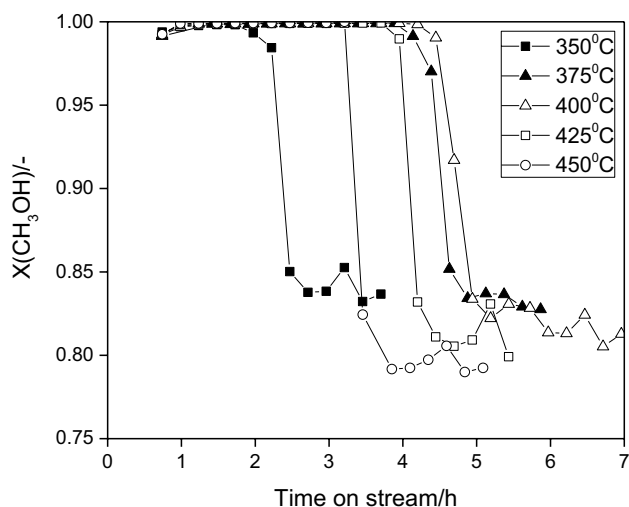


Fig. 5 Methanol conversion vs. temperature over nanostructured SAPO-34-U40 catalyst. Reaction conditions: $\text{CH}_3\text{OH}/\text{N}_2 = 60/40$, contact time = $2.05 \text{ g}_{\text{cat}} \text{ min ml}^{-1}$ with respect to methanol, catalyst = 0.2 g

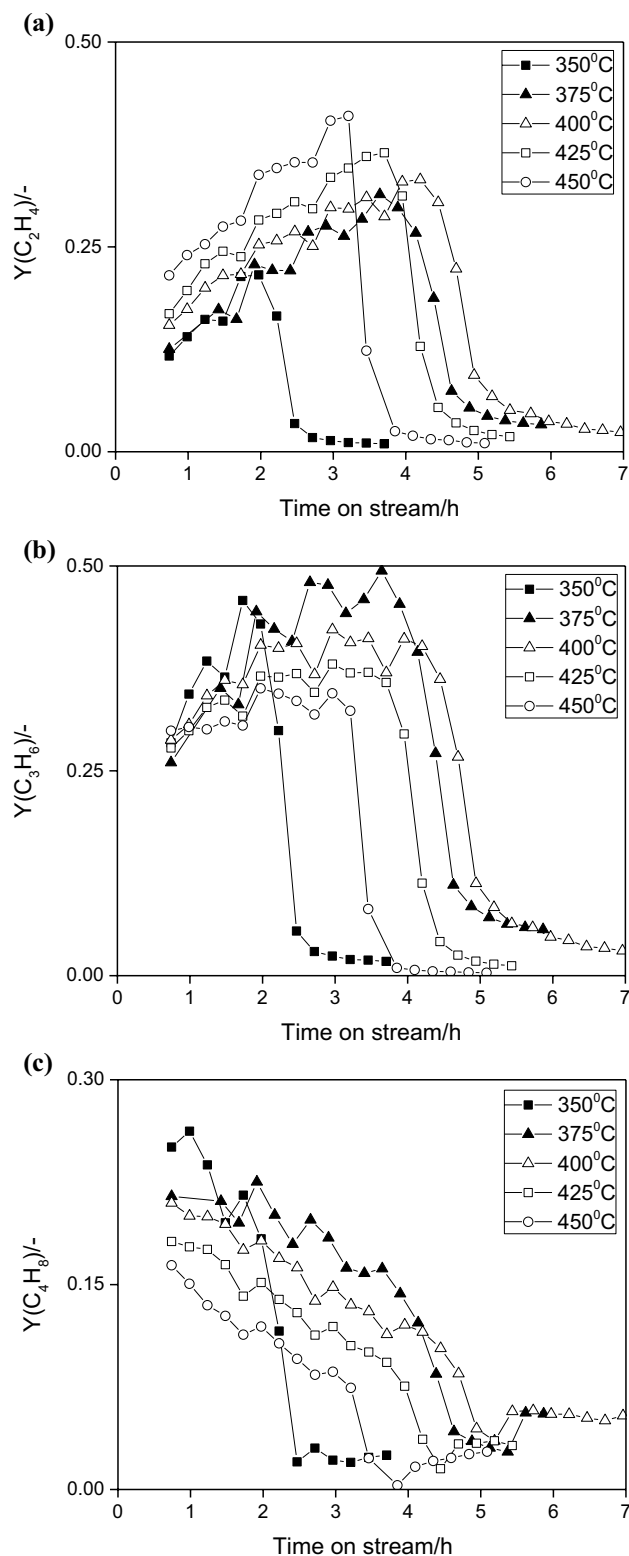


Fig. 6 Ethylene (a), propylene (b) and butylene's (c) yield vs. temperature over nanostructured SAPO-34-U40 catalyst. Reaction conditions: $\text{CH}_3\text{OH}/\text{N}_2 = 60/40$, contact time = $2.05 \text{ g}_{\text{cat}} \text{ min ml}^{-1}$ with respect to methanol, catalyst = 0.2 g

product ($C_{2=}$, $C_{3=}$ and $C_{4=}$) yield as a function of time on stream on SAPO-34-U40 catalyst at different temperatures.

At lower (350 °C) and higher (450 °C) temperatures, methanol conversion and general yield of light olefins decrease faster than at medium temperatures, showing that catalyst deactivates faster at lower and higher temperatures. The yield of DME increases with decreasing yield of light olefins. It can be explained with two conclusions for this study. First, secondary reactions (hydrogen transfer, alkylation and others), which take place at higher temperatures, lead to coke formation resulting in deactivation of catalyst. With blocking of small pores inside the catalyst, DME formation occurs over external surface of SAPO-34 on the weak acidic sites. Second, lower temperature is not enough for cracking of bulky oligomers and they are remaining in inside channels of catalyst, causing deactivation. Therefore, the conversion reaction of methanol to DME takes place at the external surface of catalyst. Also, it was observed that at higher temperature (450 °C) yield of ethylene decreases, which is explained with cracking of propylene and butenes at this temperature. Oligomerization and cracking reactions in some ways are balanced at medium temperatures and are not enough to generate too much coke [12, 21]. Because of this reason catalyst deactivates slowly. Medium temperatures are working temperatures. From Figs. 5 and 6 it is clear that synthesized SAPO-34-U40 is more active and stable at 375 °C temperature. The yield of olefins reach approximately 97 wt% (31.4 wt% $C_{2=}$, 49.4 wt% $C_{3=}$ and 16.1 wt% sum $C_{4=}$) at 3.6 h reaction time. For our MTO tests over SAPO-34-U40 catalyst, which were conducted at several temperatures, 375 °C was found to be an optimal temperature.

Coke formation

The amount of carbon deposits formed during the MTO reaction was analyzed by TPO of spent catalysts after the 7-h experiment. The amount of carbon formed in MTO tests over SAPO-34-HT, SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100 (at 450 °C) and SAPO-34-U40 (from 350 to 450 °C) was determined by integrating the CO and CO₂ profiles recorded in the TPO tests and the results are shown in Fig. 7.

The results (Fig. 7a) show that over SAPO-34-HT, SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100, the amount of carbon deposition per gram of the catalyst is 0.3, 0.24, 0.24 and 0.22, respectively. Carbon deposition over SAPO-34-HT is higher in comparison to another samples, which is a reason of its low surface area, hence its fast deactivation. So, high surface area of the catalyst is helpful for the prolongation of its lifetime [22]. The amount of carbon deposition over samples synthesized using ultrasound waves is similar.

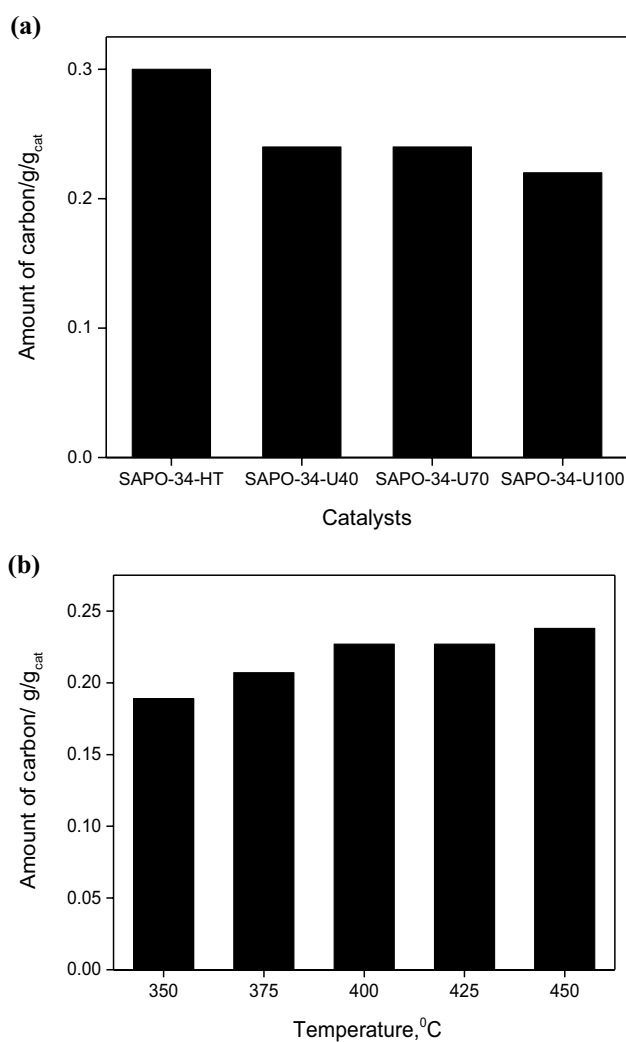


Fig. 7 The amount of carbon deposited per gram of the catalyst: **a** SAPO-34-HT, SAPO-34-U40, SAPO-34-U70, SAPO-34-U100 (at 450 °C) and **b** SAPO-34-U40 (from 350 to 450 °C). Reaction conditions: CH₃OH/N₂ = 60/40, contact time = 2.05 g_{cat} min ml⁻¹ with respect to methanol, catalyst = 0.2 g

According to the results in Fig. 7b, it can be concluded that the amount of carbon deposition increases with increasing temperature. At 450 °C, the amount of carbon deposition is higher (0.24). Generally, a high operating temperature enhances the reactions involved in coke formation such as oligomerization, cyclization, hydrogen transfer and alkylation to yield larger hydrocarbon species. At 350 °C catalyst deactivates rapidly and the amount of carbon deposition is lower (0.189) in this temperature. Ethylene and propylene, which are first hydrocarbons formed during MTO reaction, are not likely to produce aromatic hydrocarbons at low temperature. At temperature range of 375–425 °C, the amount of formed coke is equally (0.2), it means that the character of coke is similar at these temperatures [12]. The reason of

low coke amount at these temperatures was explained in previous text.

Conclusions

Methanol-to-olefin reaction was investigated over SAPO-34-HT (prepared hydrothermally), SAPO-34-U40, SAPO-34-U70, SAPO-34-U100 (synthesized sonochemically) catalysts. Catalysts, synthesized sonochemically, were used to elucidate the effect of frequency of ultrasound waves on their catalytic performance, especially in terms of lifetime and selectivity toward light olefins and are compared with results obtaining over SAPO-34 catalyst, synthesized using conventional hydrothermal method. The product distribution in MTO process and coke deposition over catalysts synthesized hydrothermally and sonochemically were different, but over SAPO-34-U40, SAPO-34-U70 and SAPO-34-U100 were almost similar. According to physico-chemical analysis, SAPO-34-HT has lower surface area, lower crystallinity and it deactivates rapidly. Physico-chemical properties of catalysts prepared sonochemically are almost the same, except surface area, which is higher in SAPO-34-U40 in comparison to others. This catalyst was tested in MTO reaction at 350–450 °C temperature range. The higher yield ~ 97 wt% (31.4 wt% C₂₌, 49.4 wt% C₃₌ and 16.1 wt% sumC₄₌) of light olefins was obtained at 375 °C and this temperature was found as an optimal temperature for MTO reaction over SAPO-34-U40 catalyst.

The lower amount of coke was determined at 350 °C, the higher at 450 °C. The character of coke deposited over SAPO-34-U40 was similar for 375–425 °C temperatures.

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