



Ultrasonic and Microwave Pretreatment for Hydrothermal Synthesis of Nanosized SAPO-34s and their Catalytic Performance in MTO Reaction

H. Sharifi Pajaie, M. Taghizadeh*

Chemical Engineering Department, Babol University of Technology, Babol, Iran.

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ABSTRACT

In order to enhance the catalytic performance of SAPO-34 catalyst for the reaction of methanol to olefins (MTO), ultrasonic and microwave-assisted aging method was employed in static hydrothermal method to synthesize nano-sized SAPO-34. The effects of the application of this method on the chemical composition, morphology, surface area and total acidity of SAPO-34 were investigated by XRD, FE-SEM, nitrogen adsorption-desorption and NH_3 -TPD techniques. The catalytic performance of synthesized SAPO-34 was investigated for MTO reaction in a fixed-bed reactor under the same operating conditions ($T = 450\text{ }^\circ\text{C}$, $P = 1\text{ atm}$, and $\text{WHSV} = 4\text{ h}^{-1}$). Comparing with the SAPO-34 synthesized with conventional hydrothermal method, the sample synthesized with simultaneous use of US and MW-assisted aging methods possessed larger surface area and small crystal size and exhibited higher selectivity to light olefins ($C_2^= - C_4^=$) and longer lifetime.

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1. INTRODUCTION

In order to introduce raw materials appropriate for poly olefins, ethylene and propylene known as light olefins are good candidates. In the petrochemical industry they can be usually supposed as the starting materials for various chemicals [1]. It is thoroughly believed that the shortage of petroleum resources is anticipated for future life. Also the demand for light olefins is continuously growing. Taking into consideration these two facts, the methanol-to-olefin (MTO) technology is recognized as an alternative process for the light olefins production from nonpetroleum sources using low amount of energy and has received significant academic and industrial attention these years.

Characteristics like having small pore, moderate acidity, exceptional selectivity for lower olefins and excellent thermal/hydrothermal stability has made SAPO-34 (Silicoaluminophosphate) a desired catalyst for the MTO reaction [2-4]. The major disability which

makes the lifetime of these catalysts short is the rapid deactivation which is caused by coke formation during MTO reaction. Focusing on the catalysts which are more resistant to coke formation is mandatory. Because even in regeneration by hot-air blowing, loss of carbon cannot be avoided [5-8].

Till now, researches have mainly focused on the MTO reaction mechanism and the effect of different synthesis parameters on the properties of SAPO-34 [9-11]. All these investigations suggest that control of SAPO nanocrystals size is a fundamental factor in improving the catalysts lifetime and their catalytic activity. However, to obtain desirable morphology and mesoporosity with narrow size distribution some problems associated with crystals synthesis will arise. Recently application of nonconventional methods for SAPO-34 nanocrystal formation has gained attention [12, 13]. This has led to the improvement of different techniques for the formation process.

Few problems such as difficult control of nucleation, uncontrollable nucleation because of slow rate of mixing and long crystallization time can be appointed to

*Corresponding Author's Email: m_taghizadehf@yahoo.com (M. Taghizadeh)

crystallization of zeolites by the conventional static hydrothermal method [14].

Recently, microwave (MW) heating assisted ultrasound (US) agitation has been considered as a fruitful method in hydrothermal synthesis of various nanoporous material types (porous materials with pore diameters less than 100 nm) including zeolites. Compared with conventional hydrothermal synthesis techniques, ultrasound and microwave-assisted techniques are rapid in preparing more homogeneous and stable materials [14-16].

The use of MW radiation in the synthesis of zeolites suggests some advantages over conventional methods, including a higher heating rate in a shorter time, which can be associated to its volumetric heating [17-19]. Not only to reduce preparation time but also to prepare unique materials, microwave irradiation can be a good choice [16]. The utilization of ultrasound to improve chemical reactivity has been represented to affect the yield, the rate and properties of the product in several processes. In order to improve and modify the process of dissolution, chemical reactions, nucleation and growth of precipitates, use of ultrasound is preferred [19-21].

The aim of this work was to investigate the effect of simultaneous utilization of MW and US methods during the aging time on properties and performance of nanosized SAPO-34 in MTO reaction. Physicochemical properties of prepared catalysts were characterized by XRD, FE-SEM, BET and NH₃-TPD methods and performance of selected catalysts was tested in MTO reaction using a fixed-bed flow reactor under the same operating conditions.

2. EXPERIMENTAL PROCEDURE

2. 1. Catalyst Preparation The SAPO-34 crystals were synthesized using hydrothermal treatment from a gel with the molar composition of 1 Al₂O₃:1 P₂O₅:0.4 SiO₂:2 TEAOH: 70 H₂O. The sources of the framework elements were aluminum isopropoxide Al(OPri)₃ (AIP, 98 wt.%, Merck), ortho phosphoric acid (85 wt.% aqueous solution, Merck), tetra ethyl orthosilicate (TEOS, 98 wt.%, Merck) and distilled water. Tetraethyl ammonium hydroxide (TEAOH, 20 wt. % in water, Merck) was used as a structure-directing agent. AIP was firstly mixed with TEAOH solution and deionized water at room temperature until it was dissolved completely. The hydrolysis was completed in 1.5 h with vigorous

stirring, yielded to a homogeneous white gel. TEOS was then added as the silica source and stirred for 2 h. Finally, phosphoric acid was dispersed slowly into the above solution. The reaction mixture was further stirred for 3 h just in conventional method. On the other hand, in MW aging process the synthetic mixture was heated by a household microwave oven at 2.45 GHz (SAMSUNG-CS/4550, maximum power of 900 W), with a Teflon reaction vessel equipped with a condenser to prevent evaporation of vapor of the reaction mixture. The aging treatment was performed at the preset power for a predetermined time. The microwave power was 200 W throughout the whole aging steps.

A 50 W US irradiation at frequency of 40 kHz (BANDELIN-SONOREX DIGITEC, Germany) was also used for sonication treatment. In case of US treatment, the synthetic mixture was carried out with the ultrasonic bath. The sonication temperature was controlled through a water bath at a temperature of 25 °C. The sonication was continued until the solution had nucleated and became slurry.

The final gel mixture was in the pH = 8 condition. The crystal's nuclei were then allowed to grow by placing the initial gel in a 100 mL Teflon-lined stainless steel autoclave and then heating statically in a conventional oven at 200 °C under autogenous pressure without stirring. Finally, after the HT treatment, the autoclave was quickly cooled down to room temperature and then the white crystalline product was centrifuged at a speed of 15,000 rpm and washed several times with double distilled water. The obtained product was dried at 110 °C for 12 h, and calcined in air at 550 °C for 6 h at a heating rate of 2 °C/min to remove the template molecules. Table 1 indicates a summary of synthesis conditions for different SAPO-34 samples.

2. 2. Characterization Techniques Powder X-ray diffraction (XRD) patterns of the calcined samples were recorded on a Philips PW3050X-ray diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The diffractometer was operated at 40 kV, 30 mA at as can rate of 0.04° min⁻¹. XRD patterns were recorded in the range of 5–40° (2 θ). Relative crystallinities of samples were calculated by intensity summation method (Equation (1)) based on the five characteristic peaks at Bragg angles of 9.58, 13.8, 16.18, 20.5 and 30.78 [22]. Among all obtained samples, the one with the strongest intensity was assigned as the reference with 100% crystallinity.

TABLE 1. Preparation conditions for SAPO-34 samples

Samples	Aging methods	Aging time (h)	Crystallization temperature (°C)	Crystallization time (h)
S34-1	Stirring aging	3	200	18
S34-2	US aging	0.5	200	18
S34-3	MW aging	0.5	200	18
S34-4	MW & US aging	0.5 & 0.5	200	18

$$\text{Crystallinity}\% = \frac{\sum_{i=1}^5 I_{i,\text{sample}}}{\sum_{i=1}^5 I_{i,\text{reference}}} \times 100 \quad (1)$$

The surface area, pore size distribution, and pore volume of the prepared samples were determined using a BELSORP-max instrument (BEL, JAPAN) by nitrogen adsorption-desorption isotherm at a liquid-nitrogen temperature ($-196\text{ }^{\circ}\text{C}$). Prior to the adsorption-desorption measurements, samples were degassed at $120\text{ }^{\circ}\text{C}$ in a N_2 flow for 3 h to remove moisture and other impurities. The external surface area of the samples was calculated by the t-plot method.

The acidic properties of the samples were measured via temperature-programmed desorption of ammonia (NH_3 -TPD), using a PulseChemiSorb 2705 instrument (Micromeritics, Norcross, GA) with a conventional flow device, which was equipped with an online thermal conductivity detector (TCD). In a typical analysis, 0.3 g of the sample was degassed at $500\text{ }^{\circ}\text{C}$ under a helium flow rate of 50 mL/min at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ for 120 min.

Next, the sample was cooled to $100\text{ }^{\circ}\text{C}$ and then saturated with pure ammonia for 120 min. The sample was then purged with a helium flow for 60 min to remove weakly and physically adsorbed ammonia on the surface of the catalyst. Afterward, the sample was cooled to room temperature and then heated again under a flow of helium carrier gas (50 mL/min) at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$, from 35 to $800\text{ }^{\circ}\text{C}$. Finally, the amount of NH_3 in the effluent was measured using TCD and recorded as a function of the temperature.

The morphology and particle size of the samples were characterized using a Mira 3-XMU (TESCAN, Czech Republic) field emission scanning electron microscope (FE-SEM).

2. 3. Catalytic Activity Test The MTO reaction over SAPO-34 catalysts was performed in a fixed bed stainless reactor (i.d. = 4 mm) under atmospheric pressure. Figure 1 presents a simplified flow diagram of the setup. One g of calcined SAPO-34 catalyst was pelletized, crushed and sieved into 0.2–0.4 mm particle size and then packed in the center of the reactor. The top and bottom sections of the bed were filled with 5 and 3 g quartz, respectively. By doing this, the pressure drop over the catalyst bed was minimized, gas flow and mass transport conditions were reproducible, and the formation of hot-spots was prevented. The catalysts were pretreated with 30 mL/min flow of N_2 at $550\text{ }^{\circ}\text{C}$ for 1 h and then the temperature was adjusted to a reaction temperature of $450\text{ }^{\circ}\text{C}$ in the presence of nitrogen flow before switching to feeding methanol (Merck, 99%). The methanol aqueous solution (50 wt%) with a weight hourly space velocity (WHSV) of 4 h^{-1} ,

was fed by syringe pump into a preheater kept at $150\text{ }^{\circ}\text{C}$. The products were analyzed by on-line gas chromatograph (Varian GC3800) equipped with a FID linked with a CP Volamine capillary column and a TCD detector linked with a Porapak Q packed column.

Methanol conversion and selectivity of the desired products (ethylene and propylene) are defined by Equations (2)–(4), respectively:

$$\text{MeOH conversion} = \frac{(\text{mole of MeOH})_i - (\text{mole of MeOH})_o - 2(\text{mole of DME})_o}{(\text{mole of MeOH})_i} \quad (2)$$

$$\text{Selectivity of ethylene} = \frac{2[(\text{mole of ethylene})_o - (\text{mole of ethylene})_i]}{(\text{mole of MeOH})_i - (\text{mole of MeOH})_o - 2(\text{mole of DME})_o} \quad (3)$$

$$\text{Selectivity of propylene} = \frac{3[(\text{mole of propylene})_o - (\text{mole of propylene})_i]}{(\text{mole of MeOH})_i - (\text{mole of MeOH})_o - 2(\text{mole of DME})_o} \quad (4)$$

3. RESULTS AND DISCUSSIONS

3. 1. Catalyst Characterization

3. 1. 1. Phase Analysis Figure 2 depicts XRD patterns of as-synthesized SAPO-34 samples prepared by different methods of assisted aging processes. Accordingly, all the synthesized patterns exhibited typical repetitive powder diffraction patterns corresponding to CHA-structure of SAPO-34, where intensity and peak position of each peak match well with that of reported for SAPO-34 material without any presence of impurity phases [22]. However, with applied assisted aging method, an increase in peak intensity and line broadening is observed as can be seen in Figure 2. Based on XRD peak intensity of the peaks appearing at $2\theta = 9.58^{\circ}, 13.8^{\circ}, 16.18^{\circ}, 20.78^{\circ}$ and 31° , the crystallinity of SAPO-34 phase was calculated by Equation 1 and found to be 54, 67, 92 and 100% respectively.

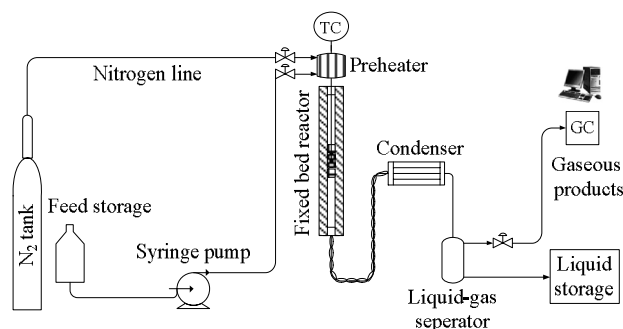


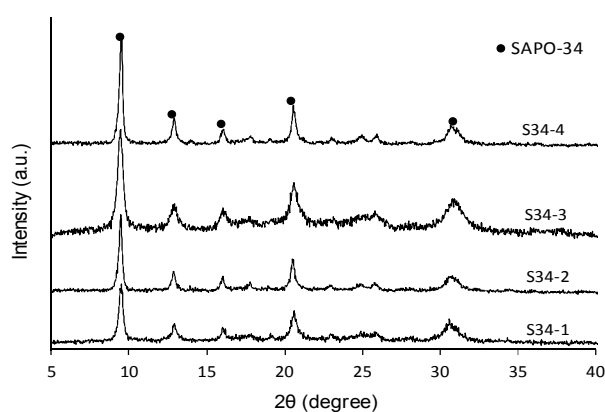
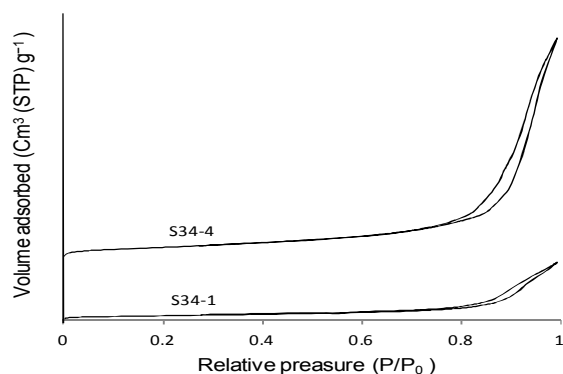
Figure 1. A schematic view of the experimental setup

TABLE 2. XRD results of SAPO-34 samples prepared by different methods

Samples	Mean crystallite size (nm) ^a	Relative crystallinity (%)	Phase of product
S34-1	531.22	54	SAPO-34
S34-2	52.44	67	SAPO-34
S34-3	45.18	92	SAPO-34
S34-4	38.50	100	SAPO-34

^a Determined by XRD**TABLE 3.** Physical properties of selected catalysts

Samples	specific surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cm ³ /g)	Total acidity (mmol/g _{drv sample}) ^b
S34-1	215.7	4.68	0.26	0.52
S34-4	578	3.07	0.48	0.71

^b Analyzed by NH₃-TPD.**Figure 2.** XRD patterns of selected SAPO-34 catalysts**Figure 3.** N₂ adsorption/desorption isotherms of selected SAPO-34 catalysts

The mean crystallite sizes (nm) were calculated using the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (5)$$

where k is a constant of ~ 1.0607 for cubic crystals, λ is the wavelength of the X-ray, β is the full width of diffraction peak at half maximum intensity (FWHM),

and θ is the diffracting angle [23]. Table 2 presents the XRD results of SAPO-34 samples prepared by different methods. The use of US and MW assisted aging had a positive effect on the crystallite size of catalysts and led to the decrease of SAPO-34 crystallite sizes. Among the considered aging methods, MW had the highest effect. According to the results in Table 2, it can be concluded that, in comparison to the catalyst synthesized by the conventional static hydrothermal technology, applying MW and US methods effectively decreased the crystallite size of SAPO-34. The simultaneous utilization of these methods caused more reduction in the SAPO-34 crystallite sizes as compared to the case when only MW or US was employed. This demonstrates the synergetic effect of MW and US aging method.

3. 1. 2. BET and Pore Size Distribution Analysis

The physical properties (specific surface area, total pore volume, and average pore diameter) of selected SAPO-34 samples were analyzed by low-temperature N₂ adsorption–desorption and the results are collected in Table 3. The results, as compared with a catalyst which is synthesized by the conventional static hydrothermal method, demonstrate that the simultaneous use of MW and US assisted aging methods enhanced the total surface area and decreased the pore diameter. This proves the synergetic effect of US and MW assisted aging on the synthesis of nanosized SAPO-34 molecular sieves.

The nitrogen adsorption–desorption isotherms of the selected samples are presented in Figure 3, which can be classified as a type IV isotherm, typical of mesoporous materials [24, 25].

3. 1. 3. Morphology Figure 4 depicts the FE-SEM images of selected SAPO-34 catalysts. According to Figure 4(b), the catalyst prepared by simultaneous use of US and MW assisted aging methods is characterized by a good dispersion and the morphology of the particles is almost regular and uniform.

TABLE 4. Product distribution and catalyst lifetime on SAPO-34 catalysts in methanol conversion reaction

Samples	Catalyst lifetime (min)	MeOH conversion (%)	Light olefins selectivity (%)		
			Ethylene	Propylene	$C_2^- - C_4^-$
S34-1	180	100	30	23.5	59.7
S34-2	240	100	33.4	28.2	68.05
S34-3	255	100	33	29.1	69.9
S34-4	300	100	41.2	31.2	80.8

Reaction conditions: catalyst = 1 g, WHSV = 4 h⁻¹, MeOH:H₂O = 1:1 (wt./wt.), reaction temperature = 450 °C.

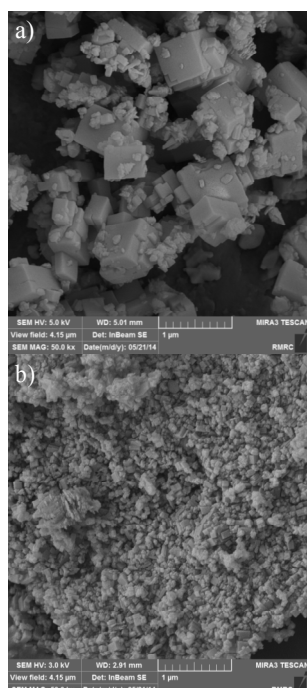


Figure 4. SEM images of selected calcined SAPO-34 catalysts: (a) S34-1 and (b) S34-4

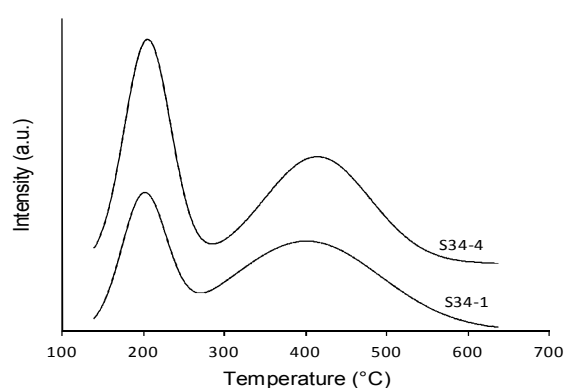


Figure 5. NH₃-TPD profiles of selected SAPO-34 catalysts

Also, simultaneous use of these methods of aging decreased the particle size. This proves the synergistic effect of US and MW assisted aging on the synthesis of nano-sized SAPO-34 molecular sieves. Also, these results confirm the crystalline sizes of particles obtained

by XRD analysis. Furthermore, the SEM image indicates that samples are slightly sintered after calcination.

3. 1. 4. Surface Acidic Properties of SAPO-34 Catalysts

The acid sites concentration and strength of the calcined samples were characterized by temperature programmed desorption of ammonia (NH₃-TPD) technique (Figure 5). There are two peaks in each curve: low temperature desorption (LTD) around 150–250 °C and high temperature desorption (HTD) around 300–500 °C. According to the literature [26, 27], only the HTD peak is indicative of strong acidity related to the structural acid site and sample S34-4 shows stronger HTD peak intensity than other samples. The selectivity of $C_2^- - C_4^-$ olefins of S34-4 sample (80.8%) is the highest among these four samples. It is known that there is great relationship between strong acid sites and selectivity [10], so we can assume that the highest selectivity for S34-4 sample is due to the strongest acids corresponding to the strongest peak around 300–500 °C in NH₃-TPD analysis. Furthermore, the inactivation point time for sample S34-4 is the longest, this might be attributed to the increased accessibility to the activate sites introduced by the mesopores in S34-4 sample. The results of ammonia TPD-titration that contain the amount of desorbed ammonia and acidity content of the synthesized catalysts are summarized in Table 3.

3. 2. MTO Reactions over SAPO-34

The catalytic performances of SAPO-34 catalysts for the MTO reaction were tested at 450 °C with WHSV of 4 h⁻¹. The selectivity of methane, ethylene, propylene, butylene and DME over the SAPO-34 catalysts after 120 min on stream is presented in Figure 6. As can be seen light alkanes (C₁–C₃ alkanes) selectivity was relatively low. Table 4 shows the distribution of major products after 120 min on stream for the catalyst synthesized with different methods. It can be seen that over all SAPO catalysts, almost 100% conversion of methanol can be obtained. The selectivities of products vary significantly. Actually the reaction time sustaining catalyst activity until intermediate product DME exists in the products is considered as the catalysts lifetime. S34-2 and S34-3 which are synthesized through US and MW assisted aging methods respectively, exhibit longer

lifetime and selectivity toward light olefins in comparison with the sample synthesized under hydrothermal conditions (S34-1). Being synthesized with simultaneous use of US and MW assisted aging methods, S34-4 revealed relative longer lifetime (300 min) and selectivity toward light olefins (80.8%) compared to the other SAPO-34 samples. The significant difference in lifetime can be explained as follows: MTO is a typically acid-dominating and shape-selectivity reaction. The non-framework species decrease the number of active sites and block partial micropores, thereby decreasing the effectiveness of SAPO-34 due to the existence of inactive amorphous species.

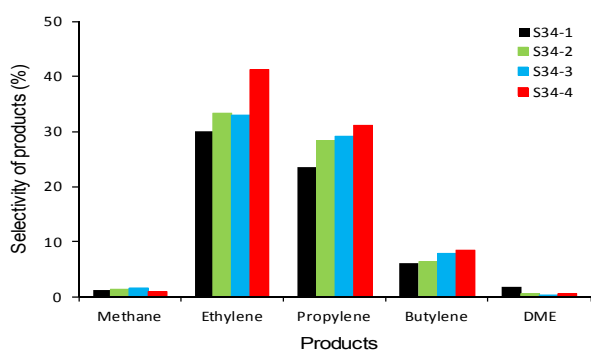


Figure 6. Selectivity of products over SAPO-34 catalysts

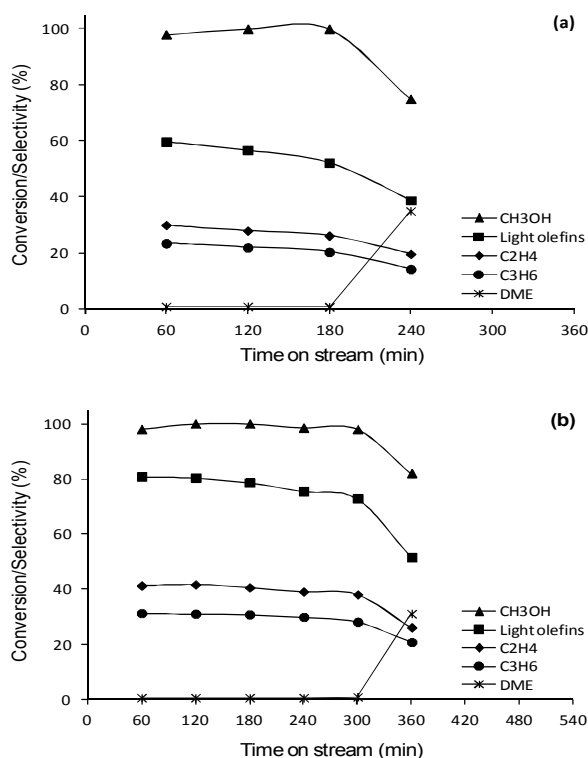


Figure 7. Stability test of selected SAPO-34 catalysts: (a) S34-1 and (b) S34-4

S34-4 possesses a developed mesopore system and sufficient strong acid sites to convert methanol to olefins. The particle size and relative crystallinity of S34-4 catalyst were smaller and higher than the others, respectively. By decreasing the particle size, diffusion resistance will be decreased and, therefore, the reactants can easily reach the center of the catalyst.

As a result, the available surface, methanol conversion and selectivity of light olefins will be increased. On the other hand, for large catalysts, the residence time in a crystal for the hydrocarbons is long because of the longer diffusion length. Aromatic compounds cannot escape from the pores of SAPO-34, and successive polymerizations readily occur because of the long reaction time and the catalyst will deactivate rapidly [4, 28].

S34-1 possesses a lower amount of weak acid sites (Figure 4), which can only convert methanol to DME but the further conversion to olefins is restrained for the lack of sufficient strong acid sites. Thus the DME yield on S34-1 is higher than the other three samples.

3. 3. Stability Test

The time-dependant conversion of CH₃OH and products selectivity at constant temperature, feed composition and WHSV of selected SAPO-34 catalysts are plotted in Figure 7.

Figure 7(a) shows the distribution of major products with time on stream (TOS) for the synthesized catalyst with conventional hydrothermal method (S34-1). According to defined statement for lifetime, catalyst S34-1 shows shorter lifetime (180 min) compared to sample S34-4 (300 min). The selectivity of light olefins was maintained over 50% until catalytic activity abruptly decreased by deactivation of catalyst. Meanwhile, in the case of S34-1, DME with a selectivity of 35% is detected after 240 min and then increases rapidly.

Figure 7(b) shows the distribution of major products with TOS for the catalyst prepared with simultaneous use of MW and US methods of aging (S34-4). Methanol conversion is relatively stable at 100% for the first 300 min of TOS. S34-4 exhibits relative longer lifetime (300 min) compared to that of SAPO-34s reported in literature [10, 29, 30].

This is mainly due to its smaller crystal size and higher amount of strong acid sites. After 300 min of TOS, catalyst deactivates and the conversion decreases to 82% after 360 min of reaction time. The primary reason for the deactivation of the catalyst is ascribed to coke formation which blocks pores and poisons acid sites. After deactivation when most strong and moderate acid sites were blocked by coke formation, the selectivity of light olefins decreased rapidly from 80.8 to 51.82% after 360 min of reaction time, with simultaneously increasing of DME in the product stream.

4. CONCLUSIONS

In this paper, ultrasonic and microwave assisted aging processes in static hydrothermal method were employed to synthesize the SAPO-34 catalysts with higher catalytic performance and stability for the MTO reaction. The method of aging in nanocatalysts synthesis can noticeably affect the chemical composition, morphology, acidity and crystal sizes and the catalytic activity and lifetime of SAPO catalysts for the MTO reaction.

Here, all prepared catalysts showed similar methanol conversion for MTO reaction (100%). The sample resulted from simultaneous use of US and MW assisted aging method in synthesis (S34-4), exhibited 100% methanol conversion for 300 min, an ethylene selectivity of 41.2% and light olefins ($C_2^- - C_4^-$) selectivity of 80.8%. Comparing these results with that of the sample with a rather big cubic morphology synthesized under hydrothermal conditions, in which 100% methanol conversion could only be kept for 180 min, it is comprehended that the results were better. This was also conceivable with an ethylene selectivity of 30% and a $C_2^- - C_4^-$ selectivity of 59.7%. Features like unique crystal morphology, large surface area, small crystal size and the appropriate amount of strong acid sites which results in a slower coke formation rate can justify the superior MTO performance on the S34-4.

5. ACKNOWLEDGEMENTS

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Ultrasonic and Microwave Pretreatment for Hydrothermal Synthesis of Nanosized SAPO-34s and their Catalytic Performance in MTO Reaction

RESEARCH NOTE

H. Sharifi Pajaie, M. Taghizadeh

Chemical Engineering Department, Babol University of Technology, Babol, Iran

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بمنظور افزایش عملکرد کاتالیستی SAPO-34 برای واکنش تبدیل متانول به اولفین (MTO)، از روش‌های پیرسازی به کمک اولتراسونیک و مایکروویو برای سنتز SAPO-34 در ابعاد نانو بروش هیدروترمال استفاده گردید. تاثیر بکارگیری این روش‌ها بر روی ترکیب شیمیایی، مورفولوژی، سطح‌ویژه و اسیدیته کل کاتالیست SAPO-34 بوسیله روش‌های FE-SEM, XRD, جذب و واجذب نیتروژن و NH_3 -TPD مورد بررسی قرار گرفت. عملکرد کاتالیستی کاتالیست های SAPO-34 سنتز شده برای فرآیند MTO در یک راکتور بستر ثابت و در شرایط عملیاتی یکسان ($T = 450 \text{ }^\circ\text{C}$, $\text{WHSV} = 4 \text{ h}^{-1}$ و در فشار اتمسفریک) مورد ارزیابی قرار گرفت. در مقایسه با کاتالیست SAPO-34 سنتز شده بروش هیدروترمال معمولی، نمونه‌ی سنتز شده با بکارگیری همزمان روش‌های اولتراسونیک و مایکروویو سطح‌ویژه بزرگتر و اندازه کریستال کوچکتر و بهره‌ی بالاتر نسبت به اولفین‌های سبک ($C_2^= - C_4^=$) و طول عمر بیشتری را دارا می‌باشد.

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