Ultrasonic-assisted hydrothermal synthesis and catalytic behavior of a novel SAPO-34/Clinoptilolite nanocomposite catalyst for high propylene demand in MTO process

Eshagh Moradiyan¹, Rouein Halladj^{*1}, Sima Askari² and Parisa Moghimpour Bijani³

¹ Faculty of Chemical Engineering, Amirkabir University of Technology, Tehran Polytechnic, P.O. Box 15875-4413, Hafez Ave., Tehran, Iran. Fax: +98 2166405847; Tel: +98 2164543151

² Department of Chemical Engineering, Science and research branch, Islamic azad university, Tehran, Iran.

³ Catalyst Research Group, Petrochemical Research and Technology Company, National Petrochemical Company, P.O. Box 1435884711, Tehran, Iran

Corresponding author:

* Rouein Halladj

Professor,

Faculty of Chemical Engineering

Amirkabir University of Technology

e-mail: halladj@aut.ac.ir

Phone: +98 2164543151

Fax: +98 2166405847

Abstract: SAPO-34 as a catalyst has high selectivity and hydrothermal stability, but it is rapidly deactivated by the formation of coke in its micropores. Evaluating the natural Clinoptilolite capability as a binder in nanocomposite catalysts is of interest because of its low cost, and accelerating the reaction. The SAPO-34/Clinoptilolite (S/C) nanocomposite catalysts were synthesized via ultrasonic-assisted hydrothermal method using Clinoptilolite as a binder. Subsequent performance of the catalyst was investigated in the methanol to olefins (MTO) reaction. The structures of synthesized nanocomposite were characterized with several methods such as XRD, XRF, FESEM, TEM, NH₃-TPD, FT-IR, and nitrogen adsorption techniques. The modified Clinoptilolite was attained using nitric acid treatment. Although the physicochemical analysis indicated that HNO₃-treatment decreases the crystallinity of the Clinoptilolite, the specific surface area of natural zeolite enhances considerably from 20.07 to 187.8 m²/g. The nanocomposite catalysts showed high selectivity toward light olefins with 100% conversion and 90% selectivity to light olefins as desired products at 450°C. Nanocomposite with the additional diffusion paths for mass transfer provided by binder-filled space ascend to higher catalytic lifetimes in compare with free SAPO-34 catalyst.

Key-words: SAPO-34/Clinoptilolite, nanocomposite catalysts, MTO process, ultrasonic-assisted hydrothermal method

1. Introduction

Besides the rising of the global crude oil price, there is an increasing demand for ethylene and propylene as an essential raw materials for polyolefin production which consequently drawn the attention of researchers to catalytic conversion of methanol to light olefins (MTO) process [1, 2]. Since, Zeolitic molecular sieves based on uniform three dimensional nano-channels have different strength of acid sites and portions, they become indispensable members for separation and catalytic processes [3, 4]. Natural Zeolite nanocomposites catalyst can be used for more investigation due to their structural and functional similarities such as large surface area, valuable ion exchange capability and their eco-friendly nature compared with other vastly used catalysts [5]. Accordingly, unique features such as micropores, and proper acidic strength make SAPO-34 the most common catalyst manipulated in the MTO process [6-8]. Thus, SAPO-34 has high selectivity, and high hydrothermal stability; however, it is rapidly deactivated by the formation of coke in its micropores [9-11].

Until the present time, considerable efforts have been made to ameliorate the selectivity and activity of the SAPO-34 catalysts in light olefins production including changes in initial components, structure directing agent, and synthesis conditions [12, 13]. In some studies, SAPO-34 has been used as a composite with a second component, e.g. ZrO_2 [14], graphite [15] and ceramic [16]. Many researches have investigated the effect of particle size, and dispersion of nanocatalysts in different methods and it was found that sonochemical technique provides better performance with more affordable cost [13, 17-20].

Among inorganic materials, Clinoptilolite is a natural zeolite aluminum silicate with a Si/Al ratio of 4-6.5 which is widely used in various environmental and industrial applications due to its abundant and low-cost sources [21]. Clinoptilolite zeolites have been previously exposed to

modification by acid or base treatments. For example, through acid treatment, the framework dealumination leads to soar sorption and form mesopore [20, 22-24]. Using additional component as a substrate or filler for the phase growth has recently received considerable attentions in preparation of the nanocomposite materials [25]. This strategy is based on modifying the surface of nanocatalysts, and applies hierarchy to the pores [26]. The coexistence of individual components with different functionalities and pore structures causes synergistic behavior in most cases. It is worth being mentioned that the most important function of the matrix is to enhance the intraparticle transportation of both reactants and products [27, 28].

The catalysts based on Clinoptilolite have been studied in methanol conversion [29], propane dehydrogenation process [30], direct synthesis of dimethyl ether [5], catalyst for the selective catalytic reduction of NO_x by ammonia (NH₃-SCR) [31] and adsorbents [32-35]. Moreover, the nanocomposites based on SAPO-34 have been studied in propane dehydrogenation process (ZSM-5/SAPO-34 and SAPO-34/ZSM-5) [36], dimethyl ether conversion to light olefins (SAPO-34/ZrO₂) [14], ethanol conversion to propylene (HZSM-5/SAPO-34) [37, 38], and methanol conversion to olefins (ZSM-5/SAPO-34) [9].

In this research, a novel a novel nanocomposite catalysts including silicoaluminophosphate (SAPO) and modified Clinoptilolite have been presented. The major aim is to use sonochemical technique in order to disperse nanoparticles in Clinoptilolite as a catalytic binder in synthesis of SAPO-34/Clinoptilolite (S/C) nanocomposite. Combining SAPO-34 with CHA and Clinoptilolite with HEU structure, leads to the prepared hierarchical composite ascertains useful physicochemical properties of the mentioned types of zeolites alongside with the improvement in surface properties and modified distribution of active centers.

Although there are several reports on the fabrication of SAPO-34 composite catalyst applied to MTO reaction, but there is no report on fabrication of S/C composite and the impact of ultrasonic assisted hydrothermal procedure. Physiochemical properties of the composite catalysts and physical mixture of SAPO-34 and Clinoptilolite were identified by XRD, FESEM, EDX, BET and FTIR techniques. In addition, their catalytic performance in the MTO reaction were evaluated. S/C composite prepared by ultrasonic assisted hydrothermal synthesis showed high selectivity toward light olefins and good catalytic stability due to its special properties.

2. Materials and methods

2.1. Catalyst preparation

Natural Iranian zeolites from Semnan province was used as a binder. Preparing the Silicoaluminophosphate/Clinoptilolite nanocomposite catalysts through three main steps schematically illustrated in Fig. 1. In the first step (a), in order to obtain H^+ -zeolite with a high degree of H^+ -exchange, Clinoptilolite powder acid is treated with HNO_3 solution. In the second step (b), precursor SAPO-34 gel with molar ratio of $1Al_2O_3$: $1 P_2O_5$: $0.8SiO_2$: $8.0 DEA$: $20H_2O$ was prepared. The sources of the framework elements for P and Al were H_3PO_4 [85 wt% aqueous solution, Merck], and Aluminum isopropoxide [$98\% Al (OPri)_3$, Merck] respectively. Diethylamin [DEA, 99 wt%, Merck] was used as the structure directing agents. For the primary gels, Tetraethyl orthosilicate [TEOS, Merck] was selected as a silica source. Finally, at the third step (c), modified Clinoptilolite was mixed with SAPO-34 gel, stirred for an hour, and then the resulting gel was irradiated with ultrasound at a frequency of 24 kHz. The primary gel was placed into a 40 ml Teflon-lined stainless steel autoclave, and heated in an oven at $190^\circ C$ for 24 h. The final solid product was recovered, and washed three times by centrifuging with distilled

water, and then it dried at 120 °C for 12 h. Suitable experimental conditions to calcinate the synthesized crystals were found to be 500 °C in the air for 4 h.

Figure 1. Schematic flow chart for (a) treatment of Clinoptilolite using HNO₃, (b) preparation of SAP-34 gel and (c) design of composite catalyst system.

2.2. Catalyst characterization

The phase and crystallinity of the samples were analyzed by X-ray diffractometer (Equinox 3000) operated at 30 mA and 40 kV with a Cu K α X-ray source ($\lambda=1.54056$ °A) at ambient temperature. The particle morphology was identified using a Zeiss Sigma VP field-emission electron microscope (FESEM). The chemical composition of calcinated samples was determined by X-ray florescence technique (XRF; Philips PW 1480). Transmission electron microscopy

(TEM) was performed with a Philips CM200 at 200 KV electron microscope. Ammonia temperature programmed desorption (NH₃-TPD) carried out in the temperature range of 50–800 °C using a 0.2 g of catalyst under 2% NH₃/He gas mixture stream (60 N ml/min) from ambient temperature up to 800 °C at a heating rate of 10 °C/min. Moreover, catalyst samples in all samples were treated in a He flow rate of 60 N ml/min for 1 h and during this period the temperature was raised from ambient temperature up to 800 °C at a heating rate of 10 °C/min.

Textural properties of calcinated samples counting total surface area, total pore volume, micropore volume, and average pore diameter were calculated via BET (Brunauer, Emmett and Teller), t-plot, and BJH (Barrett–Joyner–Halenda) methods. Isotherm data of nitrogen adsorption in the relative pressure (P/P₀) ranges from 0.05 to 0.30 obtained at 77.35 K using Quantachrome Autosorb-1 analyzer. FT-IR spectrum was measured using KBr-diluted pellet on an IR spectrophotometer (PerkinElmer).

3. Results and discussions

3.1. HNO₃-modified Clinoptilolite

The treatment of the natural zeolitic with HNO₃ led to the dealumination (hydrolysis of Al–O–Si bonds) and exchange of the cations by hydronium ions (H₃O⁺). Table 1 shows the elemental composition of the non-treated and treated Clinoptilolite according to the XRF analysis. The Si/Al ratio of natural Clinoptilolite is 3.2 (wt. %), which is a common value for this natural zeolite. Although different Si/Al ratios have been reported for Clinoptilolite, all of them are within the range of 4–6.5 (wt. %). In this research, the HNO₃ treatment increased the Si/Al ratio in Clinoptilolite from 3.2 to 8.8 (wt. %).

Table 1. Characterization data of the samples.

Sample name	Product composition (wt. %)									
	Si	Al	Fe	Na	K	Ca	P	Ti	Mn	Mg
Natural Clinoptilolite	62.2	19.3	1.8	6.07	6.7	3.2	0.03	0.17	0.03	0.5
Modified Clinoptilolite	85.5	9.7	0.1	0.4	3.9	0.1	0.02	0.2	0.02	0.06
S/ C	76.04	15.5	1.02	0.37	4.2	0.08	2.6	0.17	0.01	0.01

3.2. Characterization of SAPO-34/Clinoptilolite

3.2.1. XRD analysis

XRD spectrograms of the natural Clinoptilolite, modified Clinoptilolite with HNO₃, SAPO-34 and S/C nanocomposite are represented in Fig. 2. The structure of natural zeolite sample complies well with the literature [32, 39]. The structure of Clinoptilolite changed and crystallinity of the Clinoptilolite decreased during the ion exchange process. The characteristic peaks of natural Clinoptilolite were observed at $2\theta = 9.82^\circ, 22.37^\circ, 24^\circ, 27.8^\circ, 29.58^\circ$ and 30.5° . For the modified Clinoptilolite, the peaks were at $2\theta = 21.41^\circ, 22.49^\circ, 27.02^\circ, 28.8^\circ, 30.5^\circ$ and 31.5° . The simultaneous existence of SAPO-34 and Clinoptilolite peaks in the XRD pattern of composite samples demonstrates the presence of both phases in the nanocomposite structure. Furthermore, as observed in XRD spectra of nanocomposites, ultrasonication in the synthesis process via sonochemical led to the formation of fully crystalline product. This is due to the fact that ultrasonication can effectively contribute to the improvement of nucleation stage, generation of a large number of nuclei in a lower level of supersaturation as it has been indicated by other researchers [40, 41]. The subsequent heat treatment allows growth of nuclei to reach a fully crystalline state.

Figure 2. XRD patterns of (a) non-treated Clinoptilolite, (b) HNO_3 -treated Clinoptilolite, (c) SAPO-34, (d) S/C(50 wt. %), (e) S/C(70 wt. %) and (f) S/C(90 wt. %).

3.2.2. FESEM analysis

Field Emission Scanning Electron Microscopy (FESEM) was used to reveal structure of the synthesized samples and the targeted core-shell structure in S/C nanocomposite. According to Fig. 3 (a) and (b) natural Clinoptilolite has rough and leaf-like surface with a dense structure while Fig. 3 (c) and (d) shows surface of Modified Clinoptilolite treated with HNO_3 which has more smooth and sheet like surface. It is believe that as result of ion exchange and evacuation of

extra ions on the structure of natural Clinoptilolite, modified Clinoptilolite structure is being smoother. Also, Fig. 4 (a) indicates morphology of SAPO-34 with a smooth and regular polyhedral morphology with approximately 2 μm in size. FESEM results indicate formation of core-shell structure of nanocomposite due to grow of SAPO-34 crystal on the modified Clinoptilolite as support for active phase. Ultrasonic assisted hydrothermal procedure leads to the small size of the SAPO-34 because of better nucleation sites and controlled crystal growth [41-43]. However, Fig. 4 (b), (c) and (e) shows synthesized S/C nanocomposite structure with hydrothermal method, thus S/C nanocomposite crystals has about 2 μm diameter while Fig. 4 (d) and (f) indicates S/C that prepared with ultrasound assisted hydrothermal method has lower grain size with about 80 nm. Accordingly, assisted hydrothermal method is an effective method for fairly homogeneous dispersion of Clinoptilolite in nanocomposite while hydrothermal method results into agglomeration of Clinoptilolite in nanocomposite. Also, as discussed above, ultrasound assisted method has impact in controlling the size of SAPO-34 too.

Figure 3. FESEM images of (a) and (b) natural Clinoptilolite, (b) and (c) modified Clinoptilolite.

Figure 4. FESEM images of (a) SAPO-34, (b) H-S/C(50 wt. %), (c) H-S/C(50 wt. %) and (d) U-S/C(50 wt. %), (e) H-S/C(70 wt. %) and (f) U-S/C(70 wt. %). (H: Hydrothermal, U: ultrasonic).

3.2.3. TEM analysis

Figure 5 illustrates the TEM micrographs of S/C nanocomposite catalyst at different magnifications. The Clinoptilolite acts as a suitable surrounding material in which the SAPO-34 can easily grow. As seen in this Fig. 5 (a), the resultant leads to fabrication of the S/C core/shell

nanocomposite catalyst with hierarchical structure containing in-plane and inter-layer micro-, meso-, and macropores, which is in good accordance with SEM and BET results. Furthermore, the lattice fringes interconnected between core and shell are obviously shown in magnified image (Figs. 5 (c) and (d)).

Figure 5. TEM images of S/C nanocomposite at different magnifications.

As schematically shown in Fig. 6, Clinoptilolite particles interconnected to the SAPO-34 catalyst surface and as a role of matrix, they provide the suitable substrates for the growth of nano crystals. These particles lead to decomposition of nanocatalysts from each other and enhancement of their surface area. Furthermore, they cause interconnection of micropores, mesopores and macropores due to formation of hierarchical structure. This specific structure increases the mass transfer during chemical reactions. This could be related to cavitation bubbles acting as nuclei for crystal growth and disruption for the nuclei present within the medium thus increasing the number of nuclei in the medium. However, collapsing of bubbles in acoustic cavitation take place in less than a nanosecond and so, subsequent high rate of temperature decreases (1011 K/s) preventing the organization and agglomeration of particles [41].

Figure 6. Schematic illustration of the nanocomposite catalyst of S/C.

3.2.4. FTIR analysis

FTIR spectroscopy was performed to identify any changes in the structure of S/C nanocomposites compared to their primary structure. Figure 7 shows FTIR spectra of natural zeolite, modified Clinoptilolite and SAPO-34/Clinoptilolite. The main characteristic bands of natural Clinoptilolite are at the wavelengths of 470 cm^{-1} , 607 cm^{-1} , 796 cm^{-1} , 1070 cm^{-1} , 1434 cm^{-1} , 1632 cm^{-1} , 3436 cm^{-1} and 3617 cm^{-1} . The appearance of a peak centered at 470 cm^{-1} in composite spectrum is attributed to stretching vibration of Al-O. Moreover, the peak at 670 cm^{-1} is ascribed to vibration of the external linkage of the tetrahedral. The bands at 796 cm^{-1} and 1070 cm^{-1} are assigned to Si-O-Si bonds, while the intense band at 3436 cm^{-1} is attributed to the stretching vibration of O-H and N-H bonds. The Si-O(Si) and Si-O(Al) stretching bands (T-O-T bond) shift from 1070 cm^{-1} to higher wavenumbers 1093 cm^{-1} due to the loosening of Al^{3+} cations (dealumination of zeolite framework) during HNO_3 modification and the change in the bond strength and Si-O-Si angle [44, 45]. The bands at 1630 cm^{-1} and 3620 cm^{-1} are related to deformation vibration of absorbed water and acidic hydroxyls Si-O(H)-A respectively.

Figure 7. FT-IR spectra of (a) natural Clinoptilolite, (b) modified Clinoptilolite and (c) S/C.

3.2.5. Textural properties

The BET area and pore volume of the calcined nanocatalysts are listed in Table 2. The sample of natural Clinoptilolite does not possess microporous structure, which was observed in acid treated of Clinoptilolite. However, the results highlight that the natural Clinoptilolite and protonated Clinoptilolite agglomerates are mesoporous. During HNO_3 treatment surface area of natural Clinoptilolite increases from 20.07 to 187.8 m^2/g .

As a result of protonation, mesopore volume increases from 0.067 to 0.116 ml/g due to thermal treatment of zeolite particles. Reduction of diffusion resistance due to increase of mesoporosity is highly desired for synthesized catalysts during reaction. According to Table 2 SAPO-34 catalyst that synthesized with ultrasound method has more mesoporosity compared to conventional hydrothermal method. Furthermore, S/C shows higher mesoporosity due to composite which has 0.22 ml/g Mesopore volume while SAPO-34 has 0.27 ml/g Mesopore volume. However, results suggest that ultrasound method is an effective method to increase the mesoporosity of synthesized catalysts.

Table 2. Textual properties of SAPO-34, Clinoptilolite, S/C.

Nomenclature	Synthesis Method	Surface area (m^2/g)		Pore volume(ml/g)		Acid amount (mmol/g)	
		S_{micro}	S_{total}	V_{micro}	V_{total}	Weak acidity	Strong acidity
CL (n)	Natural	0	20.07	0	0.067	1.3	0
C (m)	Modified (HNO_3 -treated)	17	187.8	0.019	0.135	1.08	0.35
S	Hydrothermal	286.3	377.8	0.19	0.29	0.88	0.91
S	Hydrothermal/Ultrasound	173.28	453.7	0.13	0.35	0.78	1.01
S/C (m)	Hydrothermal/Ultrasound	203.5	490	0.15	0.42	0.175	0.101

C: Clinoptilolite, S: SAPO-34

3.2.6. NH₃-TPD characterization

NH₃-TPD results are displayed in Fig. 8 which indicate the nature and distribution of the acid sites on the as-synthesized catalysts. Obviously, there are two acid sites for all of synthesized catalysts, desorption of ammonia at low and high temperature attributed to weak and strong acidity respectively.

Thus, NH₃-TPD for SAPO-34 indicate two acid sites at 200 and 480 °C with 0.8 and 1.09 mmol NH₃/gr. On the other hand, natural Clinoptilolite and modified Clinoptilolite have a weak and strong acid site but with different intensity and concentration. Natural Clinoptilolite catalyst has only a weak acid site at 210 °C, in contrast to modified Clinoptilolite catalyst that has two acid sites at 207 and 620 °C. Furthermore, S/C catalyst has the strongest acid site compared to the other samples due to the modification of its structure and according to NH₃-TPD has most strong acid site in comparison to the other samples while strong acid site of S/C nanocomposite catalyst shifted to 725 °C with the same weak acid site as other samples. The summarized information of the acidity of catalysts is given in Table 2.

Suitable acidity is key properties for MTO process. Weak acid sites can shift methanol to dimethyl ether (DME) only and completing reaction occur on strong acid sites where on this sites DME change to light olefins such as ethylene or propylene. Thus, all of catalyst has similar manner at weak acid sites with the acid site around 200 °C for all samples but Fig. 8 shows change in strong acid site where shifted around 480 to 725 °C for SAPO-34 to S/C nanocomposite samples.

Figure 8. NH_3 -TPD patterns of different samples: natural Clinoptilolite, modified Clinoptilolite, H-SAPO-34. U-SAPO-34 and S/C.

3.3. Catalyst performance

The catalytic activity of prepared samples was studied at 723 K with a feed WHSV of 4.5 h^{-1} . Catalytic performance analyses of all prepared samples were carried out in a differential -reactor for methanol conversion to olefins and the results were compared with those of individual SAPO-34, Clinoptilolite and physical mixture-derived catalysts (Figs. 9 and 10). All binary structures performed better than Clinoptilolite and SAPO-34 single structure catalyst. Nanocomposite catalyst showed higher conversion and propylene selectivity than physical mixture.

Figure 9. Methanol conversion over the SAPO-34, Clinoptilolite, physical mixture and nanocomposite S/C catalysts. Reaction conditions: Catalyst = 0.5 g, 450 °C, WHSV = 4.5 h⁻¹, Feed: methanol in water (20 vol. %).

As presented in Fig. 9, the conversion profiles of the samples in the MTO reaction vary considerably according to their structure in terms of deactivation behavior. In all of them, the methanol conversion increases with time on stream, and after about 60 min the methanol conversion remains at almost 100%. Induction period in the early time on stream (TOS) leads to incomplete conversion of methanol [41, 46, 47] that can be explained through hydrocarbon pool (HP) mechanism. Haw and Kolboe reported that cyclic organic species such as hexamethylbenzene (HMB) play the role of the reaction centers for light olefins production as MTO reaction proceeds by a HP mechanism [18, 48]. Accordingly, the time for the formation of these cyclic organic species causes the induction period, i.e. an increase in activity before maximum conversion. However, the small cage size of the SAPO-34 molecular sieve causes the formation of HMB in the cages works which serve as a diffusion barrier for methanol and lower olefins. Thus, it is expected that the growth of the active intermediates and enhancement of HMB

concentration increase the methanol conversion [48]. Aforementioned common feature of the MTO reaction is related to the buildup of the HP, which is essential for catalytic activity [41, 46]. Although methanol conversion of SAPO-34 from 60 min to 260 min is high, it is rapidly deactivated due to coke formation. Modified Clinoptilolite shows good performance at the beginning of the reaction but it is rapidly deactivated as SAPO-34. This is because Clinoptilolite contains meso and macro pores that produces heavy hydrocarbons and consequently produced light olefins which diminishes as time elapses.

Methanol conversion of physical mixture is similar to that of SAPO-34 from 60 min to 300 min. However, it is deactivated very slowly in contrast to the SAPO-34 and modified Clinoptilolite. Nanocomposite of S/C shows better performance than other samples and maintains this performance for a longer time. Moreover, high deactivation rate observed in Clinoptilolite and SAPO-34 does not happen when nanocomposite S/C is used as catalyst. Accordingly, it guaranties better performance of nanocomposite for a longer time. High performance of nanocomposite S/C can be related to high surface area in nano-scale and better distribution of particles because of ultrasound waves leading to separation of the particles and uniform distribution of SAPO-34 among particles. Also, this high performance is because of contribution of Clinoptilolite phase itself in the MTO reaction.

Since methanol molecules finally adsorbed and converted on the acidic sites with respect to time on stream, the molecules product formed diffuse out of the pore structure [49]. The S/C nanocomposite catalyst converted rapidly and its activity (for example methanol conversion) lasts for over 420min, at a later time, its conversion rapidly reduces at the end of 280 min. Figure 10 shows the product distribution with time on stream for the four catalysts samples. A high content of light olefins was obtained over the S/C nanocomposite catalyst. At the beginning of

the reaction, SAPO-34 produces a considerable amount of light olefins but after 150 min amount of olefins decreases whereas S/C nanocomposite high olefins production lasts for 420 min and thereafter the production gradually reduces. Note that more propylene is produce and this higher production continues for a longer time.

At the beginning of the time on stream, the propylene/ethylene ratio is the same for all the catalysts, thereafter it decreases when the reaction is terminated. Propylene content decreases more rapidly than ethylene which can be related to the coking effect that reduces the pore size of SAPO-34. It prevents high production of hydrocarbons such as propylene [50-52] However, using nanocomposite causes high production of propylene in contrast to SAPO-34 [18]. Clinoptilolite as a binder separates SAPO-34 particles from each other and increases the surface area. Moreover, Clinoptilolite itself contributes in the reaction which produces more propylene. In the other hand, interconnection between micro, meso and macro pores probably causes higher production of propylene. As expected, modified Clinoptilolite exhibits activity and selectivity to light olefins due to its structure. However, its performance is inferior to those of the other samples. Physical mixture shows good performance in comparison to S/C nanocomposite, nevertheless high olefin productions more rapidly diminishes. Accordingly, the composite synthesized in this study might be a promising catalyst to meet a change of market demand for light olefin such as ethylene and propylene.

Figure 10. Product composition with time on stream over the SAPO-34, Clinoptilolite, physical mixture and S/C nanocomposite catalysts. Reaction conditions: Catalyst = 0.5 g, 450 °C, WHSV = 4.5 h⁻¹, Feed: methanol in water (20 vol. %).

3.4. Performance Comparison

The catalytic efficiency of the prepared catalyst was compared with those of some nanocomposites of SAPO-34 catalysts in the MTO reaction. The data in Table 3 shows that the nanocomposite of S/C catalyst gives a higher selectivity, and yields light olefins compared with other nanocomposite of SAPO-34 catalysts. Good performance of this catalyst could be related to acceleration of the reaction rate in the presence of Clinoptilolite as a binder, homogeneous

disperse of particle due to ultrasonic wave, micro-meso- macroporous structure and the connected channels between SAPO-34 and Clinoptilolite.

Table 3. Comparison of performance of prepared nanocomposite catalyst and various reported nanocomposite of SAPO-34 catalysts.

Nanocomposite catalyst	MeOH conv. (%)	Product selectivity and yield (%)				Reaction conditions	Ref.
		$C_2^=$		$C_3^=$			
ZSM-5/SAPO-34	97	40.5	—	38	—	MTO reaction, 1.2 g catalyst, WHSV=2.4 h ⁻¹ , T=400 °C	[1]
ZSM-5/SAPO-34	100	26.6	—	29	—	MTO reaction, 0.2 g catalyst, WHSV=1.6 h ⁻¹ , T=400 °C	[9]
SAPO-34/ZrO ₂	100	40.2	—	36.1	—	DTO reaction, , 0.2 g catalyst, WHSV=3.54 h ⁻¹ , T=400 °C	[14]
SAPO-34/ α -Al ₂ O ₃	99.5	39.2	—	41.5	—	DTO reaction, , 0.2 g catalyst, WHSV=3.54 h ⁻¹ , T=400 °C	[14]
ZSM-5/SAPO-34	100	10	4	80	31	MTO reaction, 0.5 g catalyst, WHSV=4 h ⁻¹ , T=600 °C	[36]
HZSM-5/SAPO-34	100	—	26.6	—	32.3	ethanol to propylene reaction, 0.5 g catalyst, T=500 °C	[38]
S/C	100	42	—	47.5	—	MTO reaction, 0.5 g catalyst, WHSV=4.5 h ⁻¹ , T=450 °C	This work

4. Conclusions

S/C nanocomposites were synthesized through hydrothermal assistance ultrasonic methods and used in MTO reaction. Due to easy accessibility and low price of Clinoptilolite natural zeolite, it was blended with expensive synthesized SAPO-34 catalyst to make a nanocomposite with high economical margin. In fact, adding Clinoptilolite decreases the amount of SAPO-34 in nanocomposite and in turn reduces the total cost and Clinoptilolite presence accelerates MTO reaction (by producing DME from Methanol). XRD, XRF, FT-IR, FESEM, TEM, NH₃-TPD and

N₂ isotherm analysis results highlighted that synthesized composites are superior to their initial state. Notably, it was shown that the synthesized nanocomposite has the morphology with Clinoptilolite as the binder and SAPO-34 as the active component. Using HNO₃-treatment, the specific surface area of natural zeolite increased obviously, whereas the crystallinity of the Clinoptilolite decreased. Furthermore, the FESEM analysis indicated that morphology of the Clinoptilolite changes with the modification of zeolite. The nanocomposite catalyst synthesized in this study is highly efficient in olefins production especially propylene by 45%. The Catalytic lifetimes were also improved in compare with the free SAPO-34 in MTO process. S/C composite catalyst could be regarded as a promising MTO catalyst to meet a market demand for light olefin.

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References

- [1] F. Liu, X. Wang, F. Xu, Q. Lin, H. Pan, H. Wu, J. Cao, Fabrication and characterization of composites comprising (CHA) SAPO-34 with (MFI) ZSM-5 topologies and their catalytic performances on MTO reaction, *Microporous and Mesoporous Materials* (2016).
- [2] S. Askari, R. Halladj, M. Sohrabi, Methanol conversion to light olefins over sonochemically prepared SAPO-34 nanocatalyst, *Microporous and Mesoporous Materials* 163 (2012) 334-342.
- [3] A. Corma, From microporous to mesoporous molecular sieve materials and their use in catalysis, *Chemical reviews* 97 (1997) 2373-2420.
- [4] R.M. Behbahani, A.S. Mehr, Studying activity, product distribution and lifetime of Sr promoted alkali modified low Si ZSM-5 catalyst in MTO process, *Journal of Natural Gas Science and Engineering* 18 (2014) 433-438.
- [5] R. Khoshbin, M. Haghighi, N. Asgari, Direct synthesis of dimethyl ether on the admixed nanocatalysts of CuO-ZnO-Al₂O₃ and HNO₃-modified clinoptilolite at high pressures: Surface properties and catalytic performance, *Materials Research Bulletin* 48 (2013) 767-777.
- [6] S. Askari, R. Halladj, M. Nazari, Statistical analysis of sonochemical synthesis of SAPO-34 nanocrystals using Taguchi experimental design, *Materials Research Bulletin* 48 (2013) 1851-1856.
- [7] N. Najafi, S. Askari, R. Halladj, Hydrothermal synthesis of nanosized SAPO-34 molecular sieves by different combinations of multi templates, *Powder Technology* 254 (2014) 324-330.
- [8] F.M. Shalmani, S. Askari, R. Halladj, Microwave synthesis of SAPO molecular sieves, *Reviews in Chemical Engineering* 29 (2013) 99-122.
- [9] H.-J. Chae, Y.-H. Song, K.-E. Jeong, C.-U. Kim, S.-Y. Jeong, Physicochemical characteristics of ZSM-5/SAPO-34 composite catalyst for MTO reaction, *Journal of Physics and Chemistry of Solids* 71 (2010) 600-603.
- [10] W. Dai, C.-M. Wang, M. Dybala, G. Wu, N. Guan, L. Li, Z. Xie, M. Hunger, Understanding the early stages of the methanol-to-olefin conversion on H-SAPO-34, *ACS Catalysis* (2015).
- [11] M. Nazari, G. Moradi, R.M. Behbahani, M. Ghavipour, Dry gel conversion as a suitable method for increasing the lifetime of SAPO-18 in MTO process, *Journal of Natural Gas Science and Engineering* 29 (2016) 337-344.
- [12] P. Wang, A. Lv, J. Hu, J.a. Xu, G. Lu, The synthesis of SAPO-34 with mixed template and its catalytic performance for methanol to olefins reaction, *Microporous and Mesoporous Materials* 152 (2012) 178-184.
- [13] F.M. Shalmani, R. Halladj, S. Askari, Effect of contributing factors on microwave-assisted hydrothermal synthesis of nanosized SAPO-34 molecular sieves, *Powder technology* 221 (2012) 395-402.
- [14] S.-G. Lee, H.-S. Kim, Y.-H. Kim, E.-J. Kang, D.-H. Lee, C.-S. Park, Dimethyl ether conversion to light olefins over the SAPO-34/ZrO₂ composite catalysts with high lifetime, *Journal of Industrial and Engineering Chemistry* 20 (2014) 61-67.
- [15] L. Bonaccorsi, L. Calabrese, E. Proverbio, A. Frazzica, A. Freni, G. Restuccia, E. Piperopoulos, C. Milone, Synthesis of SAPO-34/graphite composites for low temperature heat adsorption pumps, *Journal of Energy Chemistry* 22 (2013) 245-250.
- [16] Z. Lixiong, J. Mengdong, M. Enze, Synthesis of SAPO-34/ceramic composite membranes, *Studies in Surface Science and Catalysis* 105 (1997) 2211-2216.
- [17] S. Askari, Z. Sedighi, R. Halladj, Rapid synthesis of SAPO-34 nanocatalyst by dry gel conversion method templated with morpholine: Investigating the effects of experimental parameters, *Microporous and Mesoporous Materials* 197 (2014) 229-236.

- [18] S. Askari, R. Halladj, Effects of ultrasound-related variables on sonochemically synthesized SAPO-34 nanoparticles, *Journal of Solid State Chemistry* 201 (2013) 85-92.
- [19] Z. Yinghuai, Application of ultrasound technique in the synthesis of methanofullerene derivatives, *Journal of Physics and Chemistry of Solids* 65 (2004) 349-353.
- [20] M. Barzegar, A. Habibi-Yangjeh, M. Behboudnia, Ultrasonic-assisted preparation and characterization of CdS nanoparticles in the presence of a halide-free and low-cost ionic liquid and photocatalytic activity, *Journal of Physics and Chemistry of Solids* 71 (2010) 1393-1397.
- [21] G.T. Kokotailo, C.A. Fyfe, Perspective: Zeolites; Unique materials for research and industry, *Journal of Physics and Chemistry of Solids* 50 (1989) 441-447.
- [22] J. Kim, Y. Kim, J. Yoon, D. Park, H. Woo, Catalytic degradation of polypropylene: effect of dealumination of clinoptilolite catalyst, *Polymer degradation and stability* 75 (2002) 287-294.
- [23] D. Verboekend, T.C. Keller, M. Milina, R. Hauert, J. Pérez-Ramírez, Hierarchy Brings Function: Mesoporous Clinoptilolite and L Zeolite Catalysts Synthesized by Tandem Acid–Base Treatments, *Chemistry of Materials* 25 (2013) 1947-1959.
- [24] M. Sprynskyy, R. Golembiewski, G. Trykowski, B. Buszewski, Heterogeneity and hierarchy of clinoptilolite porosity, *Journal of Physics and Chemistry of Solids* 71 (2010) 1269-1277.
- [25] J. Zheng, G. Wang, M. Pan, D. Guo, Q. Zhao, B. Li, R. Li, Hierarchical core–shell zeolite composite ZSM-5@ SAPO-34 fabricated by using ZSM-5 as the nutrients for the growth of SAPO-34, *Microporous and Mesoporous Materials* 206 (2015) 114-120.
- [26] R. Miao, J. Yang, Y. Wu, J. Wang, Y. Nuli, W. Lu, Nanoporous silicon from low-cost natural clinoptilolite for lithium storage, *RSC Advances* 5 (2015) 56772-56779.
- [27] R. Parton, L. Uytterhoeven, J. Martens, P. Jacobs, G. Froment, Synergism of ZSM-22 and Y zeolites in the bifunctional conversion of n-alkanes, *Applied catalysis* 76 (1991) 131-142.
- [28] P.G. Smirniotis, L. Davydov, E. Ruckenstein, Composite zeolite-based catalysts and sorbents, *Catalysis Reviews* 41 (1999) 43-113.
- [29] S.-C. Baek, Y.-J. Lee, K.-W. Jun, S.B. Hong, Influence of Catalytic Functionalities of Zeolites on Product Selectivities in Methanol Conversion, *Energy & Fuels* 23 (2009) 593-598.
- [30] T.K. Katranas, A.G. Vlessidis, V.A. Tsiatouras, K.S. Triantafyllidis, N.P. Evmiridis, Dehydrogenation of propane over natural clinoptilolite zeolites, *Microporous and mesoporous materials* 61 (2003) 189-198.
- [31] R. Moreno-Tost, J. Santamaría-González, E. Rodríguez-Castellón, A. Jiménez-López, M.A. Autié, E. González, M.C. Glacial, C.D.I. Pozas, Selective catalytic reduction of nitric oxide by ammonia over Cu-exchanged Cuban natural zeolites, *Applied Catalysis B: Environmental* 50 (2004) 279-288.
- [32] Y. Zeng, H. Woo, G. Lee, J. Park, Removal of chromate from water using surfactant modified Pohang clinoptilolite and Haruna chabazite, *Desalination* 257 (2010) 102-109.
- [33] M. Doula, A. Dimirkou, Use of an iron-overexchanged clinoptilolite for the removal of Cu²⁺ ions from heavily contaminated drinking water samples, *Journal of hazardous materials* 151 (2008) 738-745.
- [34] E. Ivanova, B. Koumanova, Adsorption of sulfur dioxide on natural clinoptilolite chemically modified with salt solutions, *Journal of hazardous materials* 167 (2009) 306-312.
- [35] M. Sprynskyy, T. Ligor, M. Lebedynets, B. Buszewski, Kinetic and equilibrium studies of phenol adsorption by natural and modified forms of the clinoptilolite, *Journal of hazardous materials* 169 (2009) 847-854.
- [36] M. Razavian, S. Fatemi, Synthesis and application of ZSM-5/SAPO-34 and SAPO-34/ZSM-5 composite systems for propylene yield enhancement in propane dehydrogenation process, *Microporous and Mesoporous Materials* 201 (2015) 176-189.
- [37] C. Duan, X. Zhang, R. Zhou, Y. Hua, J. Chen, L. Zhang, Hydrothermally synthesized HZSM-5/SAPO-34 composite zeolite catalyst for ethanol conversion to propylene, *Catalysis letters* 141 (2011) 1821-1827.

- [38] C. Duan, X. Zhang, R. Zhou, Y. Hua, L. Zhang, J. Chen, Comparative studies of ethanol to propylene over HZSM-5/SAPO-34 catalysts prepared by hydrothermal synthesis and physical mixture, *Fuel processing technology* 108 (2013) 31-40.
- [39] A. Olad, B. Naseri, Preparation, characterization and anticorrosive properties of a novel polyaniline/clinoptilolite nanocomposite, *Progress in Organic Coatings* 67 (2010) 233-238.
- [40] J. Talebi, R. Halladj, S. Askari, Sonochemical synthesis of silver nanoparticles in Y-zeolite substrate, *Journal of materials science* 45 (2010) 3318-3324.
- [41] S. Askari, R. Halladj, Ultrasonic pretreatment for hydrothermal synthesis of SAPO-34 nanocrystals, *Ultrasonics sonochemistry* 19 (2012) 554-559.
- [42] M. Sayyah, E. Abbasi, Y. Lu, J. Abbasian, K.S. Suslick, Composite CaO-Based CO₂ Sorbents Synthesized by Ultrasonic Spray Pyrolysis: Experimental Results and Modeling, *Energy & Fuels* 29 (2015) 4447-4452.
- [43] L. Yosefi, M. Haghighi, S. Allahyari, S. Ashkriz, The beneficial use of HCl-activated natural zeolite in ultrasound assisted synthesis of Cu/clinoptilolite–CeO₂ nanocatalyst used for catalytic oxidation of diluted toluene in air at low temperature, *Journal of Chemical Technology and Biotechnology* 90 (2015) 765-774.
- [44] W. Mozgawa, The influence of some heavy metals cations on the FTIR spectra of zeolites, *Journal of Molecular Structure* 555 (2000) 299-304.
- [45] A. De Man, S. Ueda, M. Annen, M. Davis, R. Van Santen, The stability and vibrational spectra of three-ring containing zeolitic silica polymorphs, *Zeolites* 12 (1992) 789-800.
- [46] H. Hajfarajollah, S. Askari, R. Halladj, Effects of micro and nano-sized SAPO-34 and SAPO-5 catalysts on the conversion of methanol to light olefins, *Reaction Kinetics, Mechanisms and Catalysis* 111 (2014) 723-736.
- [47] B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gajek, T.R. Cannan, E.M. Flanigen, Silicoaluminophosphate molecular sieves: another new class of microporous crystalline inorganic solids, *Journal of the American Chemical Society* 106 (1984) 6092-6093.
- [48] U. Lohse, R. Bertram, K. Jancke, I. Kurzawski, B. Parlitz, E. Löffler, E. Schreier, Acidity of aluminophosphate structures. Part 2.—Incorporation of cobalt into CHA and AFI by microwave synthesis, *Journal of the Chemical Society, Faraday Transactions* 91 (1995) 1163-1172.
- [49] A. Izadbakhsh, F. Farhadi, F. Khorasheh, S. Sahebdehfar, M. Asadi, Y.Z. Feng, Effect of SAPO-34's composition on its physico-chemical properties and deactivation in MTO process, *Applied Catalysis A: General* 364 (2009) 48-56.
- [50] W. Song, H. Fu, J.F. Haw, Supramolecular origins of product selectivity for methanol-to-olefin catalysis on HSAPO-34, *Journal of the American Chemical Society* 123 (2001) 4749-4754.
- [51] W. Song, H. Fu, J.F. Haw, Selective synthesis of methylnaphthalenes in HSAPO-34 cages and their function as reaction centers in methanol-to-olefin catalysis, *The Journal of Physical Chemistry B* 105 (2001) 12839-12843.
- [52] B. Arstad, J.B. Nicholas, J.F. Haw, Theoretical study of the methylbenzene side-chain hydrocarbon pool mechanism in methanol to olefin catalysis, *Journal of the American Chemical Society* 126 (2004) 2991-3001.

Table captions:

Table 1. Characterization data of the samples.

Table 3. Textual properties of SAPO-34, Clinoptilolite, SAPO-34/Clinoptilolite.

Table 3. Comparison of performance of prepared nanocomposite catalyst and various reported nanocomposite of SAPO-34 catalysts.

Figure captions:

Figure 1. Schematic flow chart for (a) treatment of Clinoptilolite using HNO_3 , (b) preparation of SAP-34 gel and (c) design of composite catalyst system.

Figure 2. XRD patterns of (a) non-treated Clinoptilolite, (b) HNO_3 -treated Clinoptilolite, (c) SAPO-34, (d) S/C(50 wt. %), (e) S/C(70 wt. %) and (f) S/C(90 wt. %).

Figure 3. FESEM images of (a) and (b) natural Clinoptilolite, (b) and (c) modified Clinoptilolite.

Figure 4. FESEM images of (a) SAPO-34, (b) H-S/C(50 wt. %), (c) H-S/C(50 wt. %) and (d) U-S/C(50 wt. %), (e) H-S/C(70 wt. %) and (f) U-S/C(70 wt. %). (H: Hydrothermal, U: ultrasonic).

Figure 5. TEM images of S/C nanocomposite at different magnifications.

Figure 6. Schematic illustration of the nanocomposite catalyst of S/C.

Figure 7. FT-IR spectra of (a) natural Clinoptilolite, (b) modified Clinoptilolite and (c) S/C.

Figure 8. NH_3 -TPD patterns of different samples: natural Clinoptilolite, modified Clinoptilolite, H-SAPO-34. U-SAPO-34 and S/C.

Figure 9. Methanol conversion over the SAPO-34, Clinoptilolite, physical mixture and nanocomposite S/C catalysts. Reaction conditions: Catalyst = 0.5 g, 450 °C, WHSV = 4.5 h^{-1} , Feed: methanol in water (20 vol. %).

Figure 10. Product composition with time on stream over the SAPO-34, Clinoptilolite, physical mixture and S/C nanocomposite catalysts. Reaction conditions: Catalyst = 0.5 g, 450 °C, WHSV = 4.5 h^{-1} , Feed: methanol in water (20 vol. %).

Schematic illustration of the nanocomposite catalyst of SAPO-34/Clinoptilolite