

Lanthanum Hierarchical SAPO-34: Synthesis, Characterization, and Catalysis Evaluation in Methanol to Propylene Process

Ghalbi Ahangary, Masoumeh

College of Alborze, University of Tehran, Tehran, I.R. IRAN

Rashidi Ranjbar, Parviz*⁺

School of Chemistry, University of Tehran, Tehran, I.R. IRAN

ABSTRACT: Hierarchical SAPO-34 molecular sieve has been synthesized with *n*-propylamine as a mesoscale template and used to prepare La-Hierarchical SAPO-34 by impregnation by Lanthanum nitrate and has been used in Methanol-to-Propylene (MTP) conversion process. La-H-SAPO-34 demonstrated higher activity and selectivity for propylene (48.9%) compared to a conventional SAPO-34 catalyst (28.7%) in a fixed-bed reactor under atmospheric pressure at 450 °C and WHSV of 1.0 h⁻¹. High selectivity and longer catalytic lifetime (7 hours) of methanol to propylene conversion have been attributed to the reduction in the acidic character of active sites and the increasing mesopore volume. The catalyst has been characterized by XRD, FE-SEM, BET, NH₃-TPD, and TGA techniques and compared with SAPO-34.

KEYWORDS: Hierarchical SAPO-34; Methanol to propylene; Metal impregnated SAPO-34; Lanthanum oxide.

INTRODUCTION

According to increasing demand for propylene, Methanol-to-Propylene (MTP) process is an important route in the petrochemical industry. Among all the factors in MTP process, the catalyst properties have the most important role[1, 2].

The SAPO-34 catalyst is well known as the best catalyst for the MTO process. It has molecular sieve structure with 8-membered ring cage-type and cage entrance diameter of 0.38 nm. SAPO-34 catalyst has high selectivity to light olefins[3]. However, rapid deactivation by coke deposition and diffusion limitation are obstacles of SAPO-34 catalyst that leading to a serious decrease in activity and selectivity of catalyst. One of the strategists

to overcome obstacles is the development of hierarchical zeolites with a bimodal pore system with different length scales from micropores to mesopores[4, 5].

On the other hand, modification of SAPO-34 with different metals improves the acid properties and catalytic performance of SAPO-34. Mesoporous structure in hierarchical zeolites provides a proper situation for deposition and metals by impregnation method[6].

In the present study, A hierarchical SAPO-34 synthesized by hydrothermal method and *n*-propyl amine (NPA) was employed as the mesoporous generating agent. Lanthanide nitrate was added to hierarchical SAPO-34 to enhance the catalyst selectivity to propylene.

* To whom correspondence should be addressed.

+ E-mail: Ranjbar@khayam.ut.ac.ir

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The synthesized catalysts were characterized by XRD, FE-SEM, BET, NH₃-TPD and TG techniques. The effect of La modification and mesopores structure on physicochemical properties and catalytic performance of La-H-SAPO-34 samples were investigated and compared with the unmodified sample.

EXPERIMENTAL SECTION

Materials

Tetraethyl ammonium hydroxide (TEAOH, 20wt.% aqueous solution), methanol (MeOH,) and ortho-phosphoric acid (H₃PO₄), were purchased from Merck. Aluminum hydroxide hydrate (Al(OH)₃, XH₂O), Tetraethyl ortho-silicate (TEOS) and n-propylamine (NPA) purchased from Aldrich and lanthanide nitrate was purchased from Sigma Aldrich. All chemical reagents were of analytical grade and used as received without further purification.

Synthesis of catalysts

Literature methods[7-9] with slight modifications were used in the preparation of SAPO-34 samples.

Synthesis of H- SAPO-34

Hierarchical SAPO-34 was synthesized with molar compositions of: (Al₂O₃:0.4 SiO₂:1 P₂O₅:1 NPA:2 TEAOH: 50 H₂O (H-SAPO-34)).

To prepare SAPO-34, a certain amount of Al(OH)₃ dissolved in deionized water, ortho-phosphoric acid (H₃PO₄, 85 wt%) was added to the solution dropwise while stirring the reaction mixture for additional 30 minutes; then TEOS was added to the solution and stirred vigorously until a homogeneous solution formed. The certain amounts of tetraethyl ammonium hydroxide (TEAOH, 20 % aqueous solution) and n-propylamine (NPA) were added drop wise to the mixture. The resultant gel was allowed to age and hydrolyze at room temperature for 24 h.

Finally, the precursor gels were transferred into Teflon-lined stainless steel autoclaves for hydrothermal treatment at 200°C for 12 h under autogenously pressure. The solid product was washed, dried, calcined and then shaped in order to be employed in MTP process.

Synthesis of La-H-SAPO-34

La-H-SAPO-34 catalyst was prepared using sequential impregnation by lanthanide nitrate to achieve a

Hierarchical SAPO-34 having 0.5 % lanthanide oxide. For this purpose, certain amount of lanthanide nitrate hexahydrate was dissolved in deionized water and added to the suspension of H-SAPO-34 while stirring. The resulting product was dried at 120°C and calcined to produce La-H-SAPO-34.

Catalysts Characterization

The crystallinity and phase purity of the samples identified by powder X-Ray Diffraction (XRD) using PHILIPS- PW1840 diffractometer with Nickel filtered Cu K α radiation at 40 kV and 25 mA. (an angular range 2 θ , from 1° to 50°).

Crystal size and shape of catalysts were observed by using Field emission scanning electron microscopy (Philips XL30 scanning electron microscope).

The total surface areas of crystals were measured by nitrogen gas adsorption at the liquid nitrogen temperature in gas of nitrogen flow as the carrier gas using BET analyzer (Micromeritics 3020) in the P/P₀ range 0.05-0.25, and the total pore volume was estimated from the amount of nitrogen adsorbed at a relative N₂ pressure (P/P₀) of 0.99. The mesopore size distributions and the average diameter of mesopores were estimated by using Barrette-Joynere-Halenda (BJH) method from the desorption branch of the isotherms.

The surface acidities of the catalysts were measured by temperature programmed desorption of ammonia (NH₃-TPD) using a chemisorptions analyzer (Micromeritics TPD/TPR 2900). NH₃-TPD profiles were obtained from 100 to 650 °C with a temperature ramping rate of 20°C /min for about 60 min.

Coke amounts of all samples were analyzed by thermogravimetric analyses (TGA, STA 1640). It is performed in the temperature of ambient to 800°C under flowing air (100 mL/min) at a constant rate of 10°C /min.

Catalytic activity measurements

The conversion of methanol to propylene of the prepared samples was carried out in a fixed bed flow reactor at atmospheric pressure and in the temperature 450°C. 1.0 g catalyst powder of calcined catalyst was packed in the center of a Pyrex (i.d.1 cm, length 50 cm) reactor and heated by a tubular furnace. The weight hourly space velocity (WHSV) was 1.0 h⁻¹. Water-methanol mixture (3:1) was used as the feed. Water was mixed up methanol,

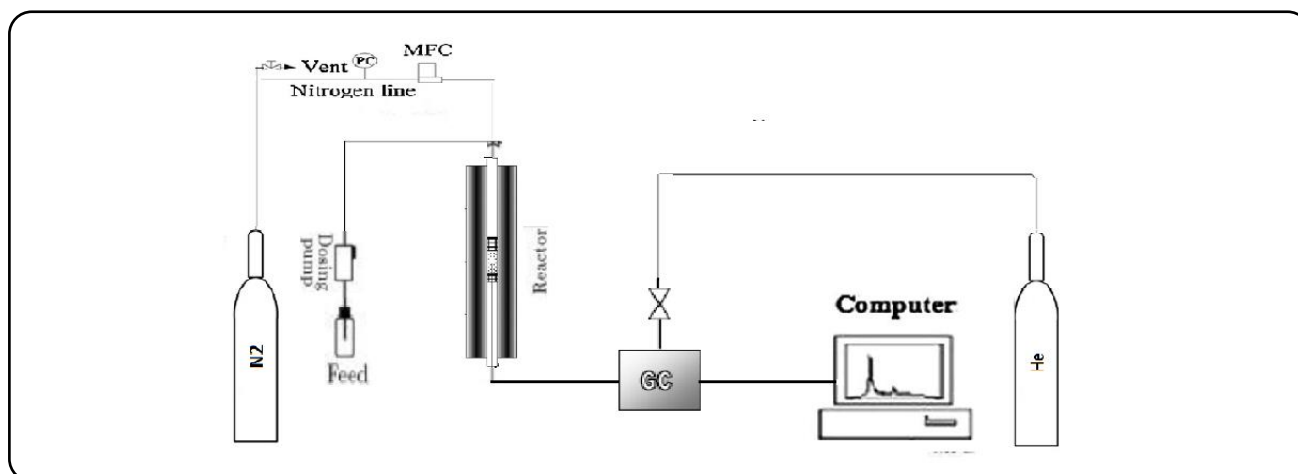


Fig. 1: A schematic MTP of the catalytic setup.

due to decreases the catalyst deactivation rate. Nitrogen gas was fed, as inert diluents at a flow rate of 60 mL/min.

The analysis products were performed using a gas chromatograph (Agilent 6890 GC, PONA and Al₂O₃ capillary columns, TCD and FID detectors). Gas chromatography was performed every 1 h for gaseous products. Fig. 1 shows the catalytic set up used in this research.

RESULTS AND DISCUSSION

Characterization

The X-ray patterns of conventional (SAPO-34), hierarchical (H-SAPO-34) and hierarchical SAPO-34 modified by Lanthanum (La-H-SAPO-34) are displayed in Fig. 2 in the range 5-50°. All peaks cohere with the chabazite pattern and samples are phase pure. The extra peaks could just be impurities or might come from a different SAPO phase.

This technique is not able to provide additional information on the pore system and others technique are required. There is some difference in peaks height in samples, which can generally be attributed to the actual degree of crystallinity. H-SAPO-34 sample has lost more crystallinity than conventional SAPO-34, while La-H-SAPO-34 has higher crystallinity. Since there is not any reflections corresponding to La in La-H-SAPO-34 sample, It could be related to the low content of La[10].

The SEM images of (SAPO-34), (H-SAPO-34) and (La-H-SAPO-34) are presented in Fig. 3.

As shown, all samples have cubic morphology, considering particle size of conventional SAPO-34 crystals is larger. The surface of H-SAPO-34 and La-H-

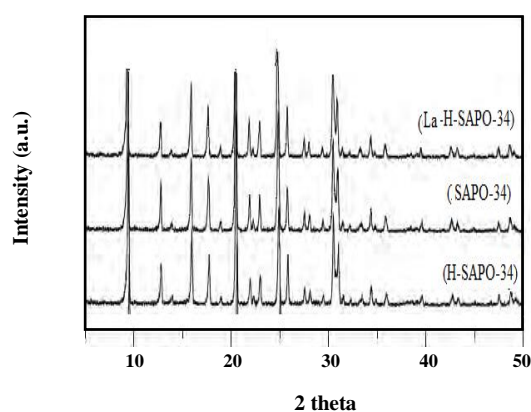


Fig. 2: The X-ray patterns of synthesis catalysts.

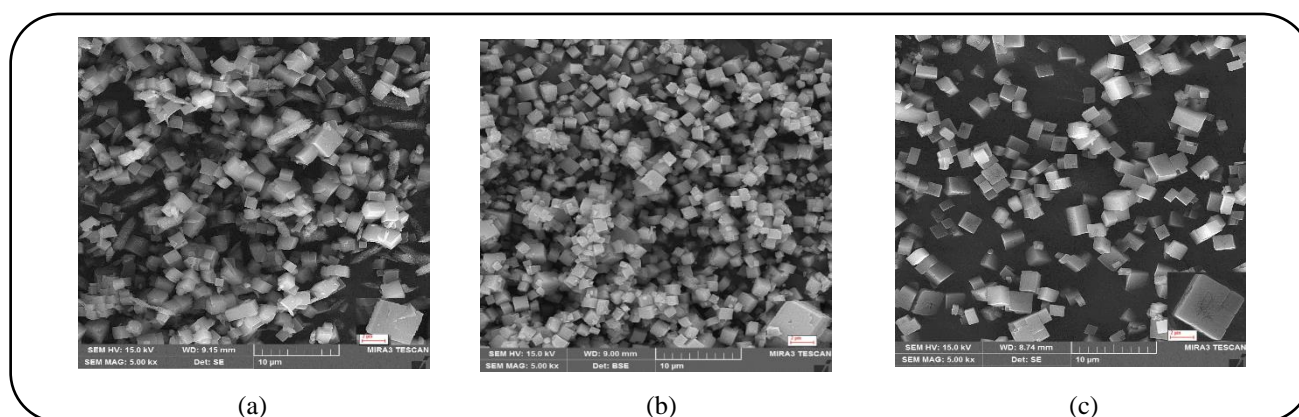
SAPO-34 samples is coarse. In dead, mesogens agent (NPA) affected the crystallization process. Presence of La ions does not affect morphology but increase the nucleation rate[11].

The corresponding amount of desorbed ammonia along with the temperature of desorption peaks are given in Table 1.

The conventional SAPO-34 shows two desorption peaks around 200 °C and 400 °C, which correspond to weak and strong acid sites, respectively. In H-SAPO-34 the ammonium desorption temperature at 400 °C is slightly lower, indicating that the acidity of the H-SAPO-34 is weaker than that of the conventional SAPO-34, due to the existence of meso/macropores structures[12, 13]. The ammonium desorption peaks are strongly reduced in (La-H-SAPO-34) in both temperatures. This means that La ions have improved acidity of SAPO-34.

Table 1: NH₃-TPD data and acid amount of (SAPO-34), (H-SAPO-34) and (La-H-SAPO-34).

Sample	Acid amount (mmol/g)		Peak temperature (°C)	
	Weak acidity	Strong acidity	TP1 ^a	TP2 ^b
SAPO-34	1.48	1.77	198	398
H-SAPO-34	1.07	1.36	185	395
La-H-SAPO-34	0.99	1.25	179	387

**Fig. 3: FE-SEM images of (a) conventional SAPO-34, (b) H-SAPO-34 and (c) La-H-SAPO-34.**

The N₂ adsorption-desorption isotherms of the calcined samples of SAPO-34, (H-SAPO-34) and (La-H-SAPO-34) are shown in Fig. 4.

The adsorption/desorption isotherm of the conventional SAPO-34 exhibits the type I and isotherm of the hierarchical SAPO-34 exhibits the representative characteristics of type IV isotherm according to the IUPAC classification. One sharp percept is observed at the very initial stage of the isotherm, which shows micropores are presented in the H-SAPO-34. The presence of mesopores of the hierarchical SAPO-34 is also reflected hysteresis loops in the region $0.5 < P/P_0 < 1$ at relative pressures 0.8[14].

The parameters of the isotherms and their textural properties of the calcined samples of (SAPO-34), (H-SAPO-34) and (La-H-SAPO-34) are presented in Table 2.

The pore size distribution of samples as calculated from the BJH method. Porosity value of (La-H-SAPO-34) is more than the (H-SAPO-34). It could be noted that the hierarchical SAPO-34 has a bimodal micropore/mesopore pore size distribution. Hence, the position of the metals particles is important[15].

The total surface area was calculated according to the BET equation. The SAPO-34 catalyst has the largest

surface area (605 m²/g). It could be related to high crystallinity and purity of this sample. The surface area of H-SAPO-34 is less than of the SAPO-34(501.4), due to the existence of mesopores that partially losses its crystallinity. By La impregnation, the surface area strongly reduced. Reduction of surface area with La impregnation can be attributed to the filling of the pores during the impregnation process.

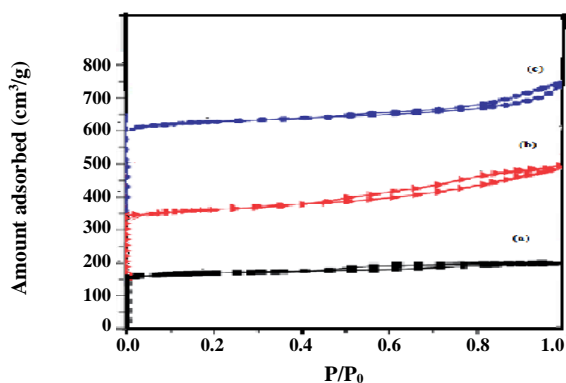
Catalyst performance

The catalytic performance of (SAPO-34), (H-SAPO-34) and (La-H-SAPO-34) for MTP reaction are shown in Fig 5. In the primary stage, all catalysts show a conversion 90 %, with the increasing time on, decreasing the conversion rate for all samples, which can be attributed to blockage of the pore and coverage of acid sites by carbon deposit[16, 17]. While reducing conversion for (La-H-SAPO-34) slower than (SAPO-34) and (H-SAPO-34). This indicates that the loading of (La) in the synthesis of (La-H-SAPO-34) is useful to improve the catalytic stability and activity in the conversion of methanol to propylene. This improvement results from the less acidity[18].

Fig. 6 shows Propylene selectivity on the methanol reaction over samples. The considerable selectivity toward

Table 2: BET specific surface area and average pore size of SAPO-34, H-SAPO-34, and La-H-SAPO-34.

Sample	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore volume (cm ³ /g)
SAPO-34	605.1	0.14	0.02
H-SAPO-34	501.4	0.25	0.16
La-H-SAPO-34	404.4	0.26	0.17

**Fig. 4: Nitrogen adsorption-desorption isotherms of (a) conventional SAPO-34, (b) H-SAPO-34 and (c) La-H-SAPO-34**

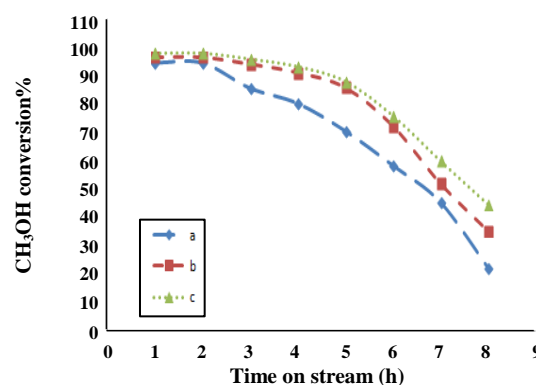
propylene is observed for (La-H-SAPO-34). Prolonging the reaction time, the selectivity of propylene is slightly low. Prolonging the reaction time, the carbon deposit blocked the cages and caused to the diffusion resistance for bulky products. Considering the methanol conversion more than 60 %, lifetime for (La-H-SAPO-34) is 7 hours, for (H-SAPO-34) is 6 hours and for (SAPO-34) is 5 hours. The differences in the catalytic lifetime could be related to suitable acidity and the increasing mesoporosity for hierarchical SAPO-34 samples enhance the diffusion efficiency which promoted the stability [19].

Table 3 provides the main products distribution on the MTP reaction for (SAPO-34), (H-SAPO-34) and (La-H-SAPO-34).

Coke Formation

Coke amounts of all used synthesis samples were analyzed by thermogravimetric analyses. Fig. 7 shows the TG curves of all used samples.

There are two weight-loss steps in temperature range of defined, the first one at temperature below 200 °C is from desorption of adsorbed water. The second weight loss at temperatures higher than 200 °C is attributed to the

**Fig. 5: Methanol conversion variation with time-on-stream of (a) conventional SAPO-34, (b) H-SAPO-34 and (c) La-H-SAPO-34 (T = 450 °C, WHSV = 1.0 h⁻¹)**

decomposition of carbon deposit during methanol conversion. The weight losses from coke combustion for all used synthesis samples are in the order SAPO-34 > H-SAPO-34 > La-H-SAPO-34.

The lower weight loss in (La-H-SAPO-34) sample could be due to better diffusion and lower retention time of products formed on catalyst pores. Also the lower acidity of catalytic sites in (La-H-SAPO-34), preventing the polymerization of olefins which reduced coke formation [20, 21]. The weight loss data and average rates of coke formation are listed in Table 4.

The presence of strong acidic sites of the SAPO-34 samples plays an important role in the secondary reactions of MTP reaction such as oligomerization and polymerization, as a result increased the rate of coke formation. The less total acid amount for (La-H-SAPO-34) sample decreased the formation rate of carbon deposit. Therefore, (La-H-SAPO-34) has the less carbon deposit amounts.

CONCLUSIONS

SAPO-34 and H-SAPO-34 were prepared by the effective method, then H-SAPO-34 modified with La, and studied for their performances in methanol to propylene.

Table 3: Product distribution of MTP reaction over (SAPO-34), (H-SAPO-34) and (La-H-SAPO-34). (T = 450 °C, WHSV = 1.0 h⁻¹).

	SAPO-34	H-SAPO-34	La-H-SAPO-34
Methanol conversion (%)	94.8	96.9	98.2
Selectivity (C%)			
^a C ₁₋₄	19.5	6.5	5.3
C ₂ H ₄	17.6	12.3	11.5
C ₃ H ₆	28.7	44.5	48.9
C ₄ H ₈	18.6	20.3	21.2
C ₂ ⁻ -C ₄ ⁼	64.9	77.1	81.6
P/E ratio	1.6	3.6	4.6
^b C ₅ ⁺	15.6	16.4	13.1

a: saturated hydrocarbons

b: C₅ and higher hydrocarbons and aromatics

Table 4: The weight loss data and average rates of coke formation samples.

Sample	TG weight loss (%)	Average rates of coke formation
SAPO-34	16.3	3.26
H-SAPO-34	12.5	2.08
La-H-SAPO-34	9.9	1.42

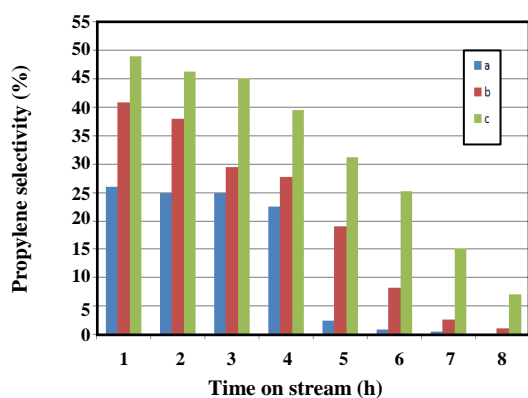


Fig. 6: Propylene selectivity variation with time-on-stream of (a) conventional SAPO-34, (b) H-SAPO-34 and (c) La-H-SAPO-34 (T = 450 °C, WHSV = 1.0 h⁻¹).

La-H-SAPO-34 catalyst is prepared using impregnation method and improved acid properties. Compared with H-SAPO-34, the La-H-SAPO-34 sample exhibited the slight reduction in the strong acid sites from NH₃-TPD results. Lower acidity and less rate of coke formation could be employed to explain the longer lifetime (7h) and favored

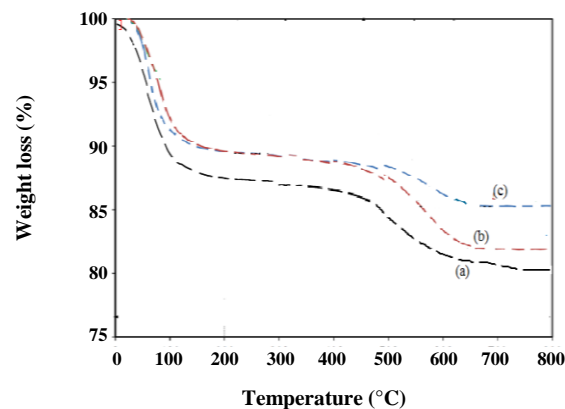


Fig. 7: The weight loss and thermal events from TGA measurements (a) conventional SAPO-34, (b) H-SAPO-34 and (c) La-H-SAPO-34.

propylene selectivity (48.9%) over modified catalysts.

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REFERENCES

- [1] Kulbo K., Lida H., Igarashi A., Comparison of Steaming Stability of Cu-ZSM-5 with Those of Ag-ZSM-5, P/H-ZSM-5, and H-ZSM-5 Zeolites as Naphtha Cracking Catalysts to Produce Light Olefin at High Temperatures, *Applied Catalysis A: General*, **489**: 272-279 (2015).
- [2] Sedran U., Mahay A., De Lasa H., Modelling Methanol Conversion to Hydrocarbons: Revision and Testing of a Simple Kinetic Model, *Chemical Engineering Science*, **45**(5): 1161-1165 (1990)
- [3] Fougerit J., Gnep, N., Guisnet M., Selective Transformation of Methanol Into Light Olefins over a Mordenite Catalyst: Reaction Scheme and Mechanism, *Microporous and Mesoporous Materials*, **29**(1-2): 79-89 (1999).
- [4] Wilson S., Barger P., The Characteristics of SAPO-34 Which Influence the Conversion of Methanol to Light Olefins, *Microporous and Mesoporous Materials*, **29**(1-2): 117-126 (1999).
- [5] Wragg D.S., O'Brien M.G., Bleken F.L., Michiel M.D., Olsbye U., Fjellvåg H., Watching the Methanol-to-Olefin Process with Time-and Space-Resolved High-Energy Operando X-Ray Diffraction, *Angewandte Chemie International Edition*, **51**(32): 7956-7959 (2012).
- [6] Dubois D.R., Obrzut D.L., Liu J., Thundimadathil J., Adekkanattu P.M., Guin J.A., Punnoose A., Seehra M.S., Conversion of Methanol to Olefins over Cobalt-, Manganese- and Nickel-Incorporated SAPO-34 Molecular Sieves - Sciencedirect, *Fuel Processing Technology*, **83**(1): 203-218 (2003).
- [7] Hajfarajollah H., Askari S., Halladj R., 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**(2): 723-736 (2014).
- [8] Wu L., Liu Z., Qiu M., Yang Ch., Xia L., Liu X., Sun Y., Morphology Control of SAPO-34 by Microwave Synthesis and Their Performance in the Methanol to Olefins Reaction, *Reaction Kinetics, Mechanisms And Catalysis*, **111**(1): 319-334 (2014).
- [9] G.Ahangari M., R.Ranjbar P., Rashidi A.M., Teymuri M., The High Selectivity of Ce-Hierarchical SAPO-34 Nanocatalyst for the Methanol to Propylene Conversion Process, *Reaction Kinetics, Mechanisms and Catalysis*, **122**(2): 1265-1279 (2017).
- [10] Yoon J.W., Jung S.H., Kim Y.H., Park S.E., Chang J.S., Selective Crystallization of SAPO-5 and SAPO-34 Molecular Sieves in Alkaline Condition: Effect of Heating Method, *Bulletin of the Korean Chemical Society*, **26**(4): 558-562 (2005).
- [11] Patel A., "Understanding The Kinetics, "Understanding The Kinetics, Stereoselectivity, and Catalysis of Pericyclic Reactions In Chemistry and Biology Through Quantum Mechanical Computations", University of California, Los Angeles (2015).
- [12] Yang S.T., Yekim J.I., Chae H.J., Kim M., Jeong S.Y., Ahn W.S., Microwave Synthesis of Mesoporous SAPO-34 with a Hierarchical Pore Structure - Sciencedirect, *Materials Research Bulletin*, **47**(11): 3888-3892 (2012).
- [13] Cui Y., Zhang Q., He J., Wang Y., Wei F., Pore-Structure-Mediated Hierarchical SAPO-34: Facile Synthesis, Tunable Nanostructure, and Catalysis Applications for the Conversion of Dimethyl Ether into Olefins, *Particuology*, **11**(4): 468-474 (2013).
- [14] Janssen A., Schmidt I., Jacobsen C.J.H., Koster A.G., Jong K.P., Exploratory Study of Mesopore Templating with Carbon During Zeolite Synthesis, *Microporous and Mesoporous Materials*, **65**(1): 59-75 (2003).
- [15] Emrani P., Fatemi S., A.Talesh S., Effect of Synthesis Parameters on Phase Purity, Crystallinity and Particle Size of SAPO-34, *Iran. J. Chem. Chem. Eng.(IJCCE)*, **30**(4): 29-36 (2011).
- [16] Nawaz Z., Chu Y., Yang W., Tang X., Wang Y., Wei F., Study of Propane Dehydrogenation to Propylene in an Integrated Fluidized Bed Reactor Using Pt-Sn/Al-SAPO-34 Novel Catalyst, *Industrial & Engineering Chemistry Research*, **49**(10): 619-614 (2010).
- [17] Zhou S., Wu Z., Rong J., Wang S., Yang G., Zhu X., Zhang L., Highly Efficient Hydrophosphonylation of Aldehydes and Unactivated Ketones Catalyzed by Methylene-Linked Pyrrolyl Rare Earth Metal Amido Complexes. - Pubmed - NCBI, *Chemistry-A European Journal*, **18**(9): 2653-2659 (2012).
- [18] Hajjashrafi T., Nemat Kharat A., Dauth A., R.Lewis A., Preparation And Characterization of Lanthanide Modified SAPO-34 Nano Catalysts and Measurement of Their Activity for Methanol to Olefin Conversion | Springerlink, *Reaction Kinetics, Mechanisms And Catalysis*, **113**(2): 585-603(2014).

- [19] Song W., M. Marcus D., Fu H., O. Ehresmann J., F. Haw J., [An Oft-Studied Reaction That May Never Have Been: Direct Catalytic Conversion of Methanol or Dimethyl Ether To Hydrocarbons on the Solid Acids HZSM-5 Or HSAPO-34](#), *Journal of the American Chemical Society*, **124(15)**: 3844-3845 (2002).
- [20] Song W., F Haw, J., B. Nicholas J., S. Heneghan C., [Methylbenzenes Are the Organic Reaction Centers For Methanol-To-Olefin Catalysis on HSAPO-34](#), *Journal of the American Chemical Society*, **122(43)**: 10726-10727 (2000).
- [21] Dai W., Wu G., Li L., Guan N., Hunger M., [Mechanisms of the Deactivation of SAPO-34 Materials with Different Crystal Sizes Applied as MTO Catalysts](#), *American Chemical Society Catalysis*, **3(4)**: 588-596 (2013).