Characterization and optimization of SAPO-34 catalysts synthesized by mixed templates in MTO reaction

Sh. Masoumi, J. Towfighi*

Faculty of Chemical Engineering, Tarbiat Modares University, Tehran, Iran

Abstract

The effects of templating on the catalytic performance of SAPO-34 catalyst have been investigated in conversion of methanol to olefins. SAPO-34 catalysts were synthesized using a different combination of morphine, tetraethyl ammonium hydroxide (TEAOH) and triethylamine (TEA) as structure-directing agents during synthesis of gel with nominal composition as $1Al_2O_3:1P_2O_5:0.4SiO_2:2yTEAOH:2xTEA:2(1-(x+y))morpholine:70H_2O$. The different SAPO-34 samples were characterized by XRD, SEM, FTIR, BET, EDX and TPD techniques. Increasing TEAOH in synthesis gel led to decreasing mean crystal size. The catalytic performance of the synthesized catalysts was tested in MTO reaction at 410 ℃ and a feed WHSV of 6.5 1/h. The catalyst synthesized by combination of tri-templates exhibited highest light olefins yield in 100% methanol conversion. The optimum values (X=0.17, Y=0.34) were obtained by central composite design and response surface contour plots.

Keywords: *MTO Reaction, Light Olefin, SAPO-34, Template*

1. Introduction

Crystalline microporous aluminophosphates (named $AlPO_4$ –n) formed by AlO_4 and PO_4 tetrahedra are connected by their vertices, which are electrically neutral [1]. The introduction of silicon atoms in ALPO frameworks (SAPO) leads to the appearance of bronsted acidity relevant for catalyzed reactions such as methanol-to-olefins (MTO), n-alkane cracking and hydrocracking and so on. Increased public attention has been focused on MTO process because of the increasing price of crude oil [2]. SAPO-34, with relatively mild acidity, chabazite structure (CHA), good thermal/ hydrothermal stability, high selectivity to light olefins is recognized as the best candidate for MTO process [3,4]. It is well

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* Corresponding author: towfighi@modares.ac.ir

known that templates play important roles in the synthesis of SAPO molecular sieves such as structure-directing, space-filling, and charge-compensating roles [5,6]. Two kinds of Si substitution mechanisms are accepted in the crystallization of SAPO molecular sieves. In the first one, called SM2, a phosphorous atom is replaced by a silicon atom resulting in a negatively charged framework. The other is the double substitution of adjacent P and Al by two Si atoms (SM3) [1,7]. Alvaro-Munoz *et al*. [8] used different templates such as tetraethyl ammonium hydroxide (TEAOH), triethylamine (TEA) and morpholine (MOR) in SAPO-34 synthesis. Wang *et al*. [9] used triethyl amine (TEA) and TEAOH as mixture templates to synthesize SAPO-34. The results showed that the chemical composition, morphology, crystal size, and Si incorporation of SAPO-34 were affected greatly by the molar ratio of TEAOH/TEA. Although three kinds of amines, namely TEAOH, TEA, MOR and a mixture of two of these templates have been used as the most common SDA in the synthesis gel, the effect of different combinations of a new tri-templating agent TEAOH/TEA/MOR has not been investigated. Research interest has been focused on the effect of mixed templates on characterization of SAPO-34 and its catalytic performance, however,three kinds of amines, namely tetraethyl ammonium hydroxide (TEAOH), morpholine (MOR) and triethylamine (TEA) have been used as the most common structure directing agents in the reaction gel. In this regard, the aim of this paper is to investigate the effect of mixed templates and also new combination of tri-templateing on the physico-chemical

properties of SAPO-34 catalyst and its performance in MTO reaction.

2. Experimental
2-1. Sample preparation
Three SAPO-34 samples with different templates molar ratio were synthesized based on the hydrothermal method from a gel composition of $1Al_2O_3:1P_2O_5:0.4SiO_2:2y$ TEAOH:2xTEA:2(1-(x+y))morpholine: $70H_2O$ which is presented in Table 1. The source of Al, P and Si were Aluminum isopropoxide (AIP, Merck), phosphoric acid (85 wt% H_3PO_4, Merck), Silica gel (SiO_2, Merck) respectively. Tetraethyl ammonium hydroxide (20 wt% aqueous solution of TEAOH, Merck) and morpholine (Merck), teriethylamine (Merck) were used as the organic templates. The preparation procedure of SAPO-34 samples was explained in previous work [10].

2-2. Catalyst characterization
The X-ray diffraction (XRD) patterns of catalysts were obtained by powder X-ray diffractometer (Bruker D8) using CuKα radiation (λ=1.54 Å). For zeolite SAPO-34, the relative crystallinity was determined from the main peak intensities at $2\theta \approx 9.6$, 13.0, and 20.6 [11] on the base of SAPO-34 catalyst prepared with 0.5MOR:0.5TEA:1TEAOH molar ratio possessing the highest XRD intensities among other samples. Therefore, the relative crystallinity of the samples was calculated by Eq. (1):

$$\% \text{ relative crystallinity} = \frac{\Sigma I}{\Sigma I_2} \times 100 \qquad (1)$$

Where I is the line intensity of the sample and I_2 is the line intensity of the S2 sample. The crystal size and Morphology were

analyzed using Philips XL30 scanning electron microscope (SEM). Diffuse reflectance FTIR was conducted using a Bruker Tensor-27 spectrophotometer. IR spectra of the samples in the region of the framework stretching vibrations (450–4000 cm^{-1}) were measured. The BET specific surface areas of calcined samples were acquired from isotherm data of nitrogen adsorption–desorption at −196°C using Micromeritics ASAP-2010 analyzer. The chemical composition of the catalysts was determined by TESCAN system (VEGA model) scanning electron microscope equipped with an energy dispersive X-ray (EDX) spectrometer. The catalyst acidic properties were measured by temperature programmed desorption of ammonia (NH$_3$-TPD) using Micromeritics 2000. About 0.06 g of the catalyst was pretreated to remove adsorbed water at 300°C for 3 h and was subsequently cooled to the adsorption temperature of 100°C. After purging with helium for 20 min, the analysis was carried out at a heating rate of 10 mL/min from 100 to 600°C.

2-3. Catalyst performance test

Methanol conversion to olefins was tested under atmospheric pressure and at a temperature of 410˚C. The SAPO-34 catalyst weighing 1 g and 2.5 g silicon carbide (as an inert) [12] were packed in the center of stainless steel reactor (internal diameter: 6mm, length: 8cm) and heated by a tubular furnace. The catalysts were pretreated with 150 mL/min flow of N$_2$ at 550˚C for 1 h, then a liquid mixture of methanol in water (30% white) with a weight hourly space velocity (WHSV) of 6.5 1/h was fed by a syringe pump into the reactor. The gas product was analyzed by using a Hewlett-Packard 5890 gas chromatograph with FID detector. The conversion of methanol was determined from the outlet liquid sample as the percentage of methanol consumed in the MTO reaction using fractional distillation of outlet liquid. The experimental setup of MTO reaction used in tarbiat modares university laboratories is shown in Fig. 1.
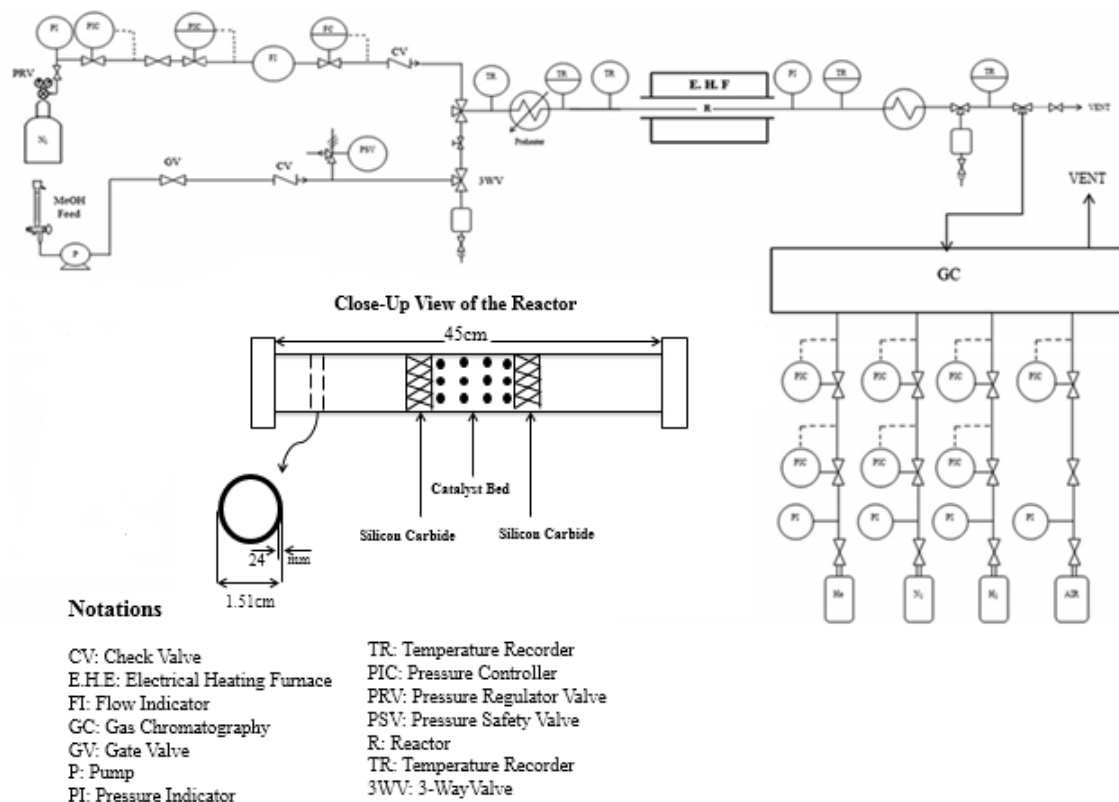
Figure 1. Experimental setup for MTO reaction.

3. Results & discussion

3-1. Characterization

The X-ray diffraction pattern of synthesized catalysts prepared by different gel composition is shown in Fig. 2. All synthesized samples confirmed the structure type of SAPO-34 [11]. There is no additional peak of impurity phase in any of the samples,which shows that SAPO-34 was successfully crystallized. According to XRD patterns [10], reflection intensities of each peak varied by changing the type of templates and also the molar ratios of templates. The peak intensities of S-2 sample synthesized using mixing of three templates with molar ratios of 0.5MOR:0.5TEA:1TEAOH are the highest. So this sample is applied for determining the crystallnity of other samples.
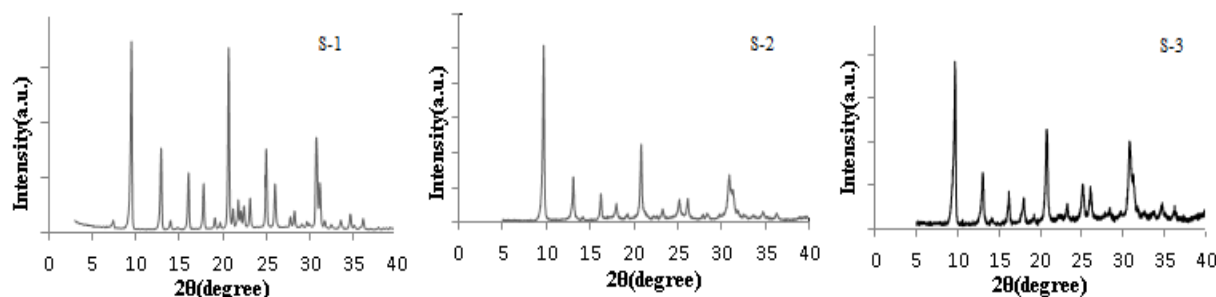

Figure 2. XRD patterns of SAPO-34 samples.

As shown in Fig. 3, all the samples had cubic like particles with different sizes [10]. The results indicated that crystal size has been decreased by increasing TEAOH template in synthesis gel. Also, increasing the number of templates in synthesis gel causes of the number of small nuclei to increase according to the role of templates as space filling. So, S-2 sample that was synthesized with different molar ratios of three templates showed smallest crystal size (0.64 µm). The relative crystallnity and mean crystal size of samples are given in Table 1.
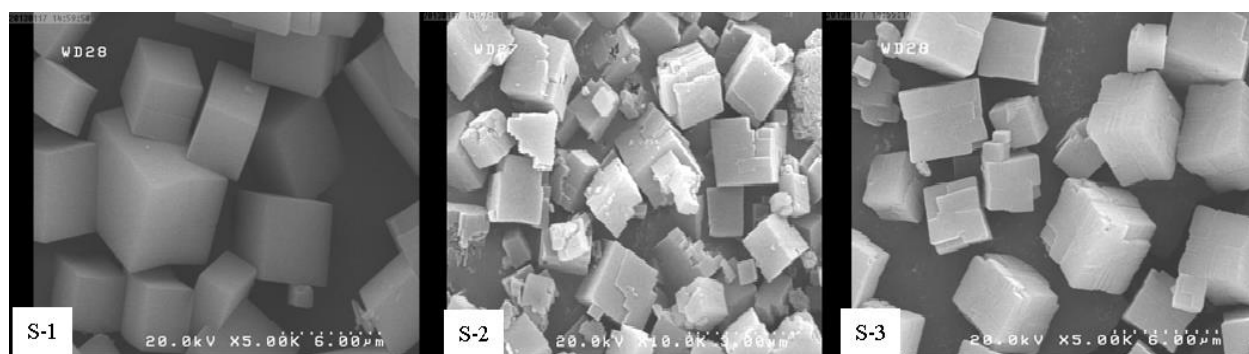

Figure 3. SEM image of SAPO-34 catalysts.

Infrared spectra of the samples [10] are shown in Fig. 4. It is obvious that there are no characteristic peaks of the amorphous phase in the samples. The characteristic absorption bands of the SAPO-34 are in good agreement with the published data [13,14]. There were two hydroxyl stretching, vibration bands at 3600 and 3625 cm^{-1}, which were assigned to –SiOHAl- groups. These are active sites for acid catalyzed reaction. The band at 1635 cm^{-1} is assigned to the bonding vibrational mode of water weakly adsorbed in the SAPO-34 cages. Bending around 1100 cm^{-1} and 730 cm^{-1} correspond to asymmetric and symmetric stretch of O-P-O. Furthermore, absorption peaks at 640, 580, 530 and 480 cm^{-1} indicated the bend of double 6-ring, PO_4, AlO_4 and SiO_4, respectively [15]. S-2 sample prepared with the mixture of three templates indicated higher concentration of the strong acidic hydroxyl groups.

The acidity and strength of acid sites of the catalysts were characterized by NH_3–TPD technique and shown in Fig. 5. The area under the curve indicates the total amount of NH_3 desorbed which is proportional to acidity. NH_3–TPD profiles showed two peaks at 150-210 and 370-420°C as low and high temperature desorbtion sites.
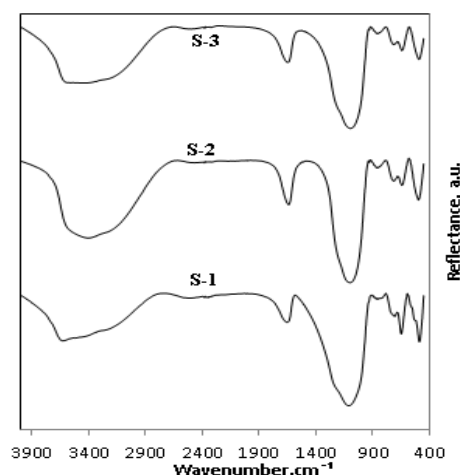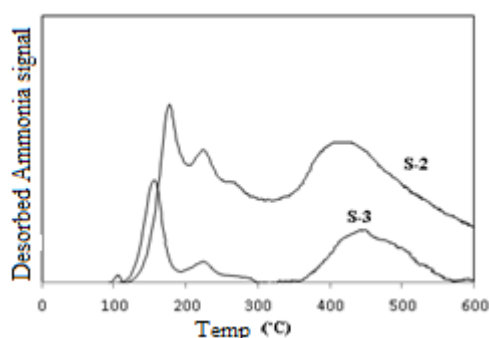

Figure 4. FTIR spectra of SAPO-34 samples.

Table 1

Molar ratios, relative crystallinity (%) and mean crystal size of SAPO-34 samples.

Samples	Molar composition	Relative crystallinity (%)	Mean crystal size (μm)
S-1	Al_2O_3:0.4SiO_2:1P_2O_5:1.5 MOR:0.5TEA	85	3.25
S-2	Al_2O_3:0.4SiO_2:1P_2O_5:0.5MOR:0.5TEA:1TEAOH	100	0.64
S-3	Al_2O_3:0.4SiO_2:1P_2O_5:1.5MOR:0.5TEAOH	83	2.92

The first desorbtion peak of TPD curves corresponding to weak acid sites was related to P-OH hydroxyl groups not fully linked to AlO_4 tetrahedral, SiOH and AlOH, and the second peak is related to Si-OH-Al hydroxyl groups as strong bronsted acid sites which should be activated for MTO reaction [16,17]. Acid strength distribution of samples is given in Table 2. S-2 sample that was prepared with three templates indicated higher amounts of strong acid sites and also showed higher concentration of the strong acidic hydroxyl groups.

According to Table 2, BET surface areas were increased by addition of TEAOH in the gel synthesis such as crystalline and using three templates indicated higher BET surface area. The final product composition based on $(Al_xP_ySi_z)O_2$ Formula was obtained from the results of EDX analysis. Compared to Si/(Al+P+Si)=0.091 belonging to all starting gels, this ratio in products was higher which means a greater amount of Si was incorporated into the framework of SAPO-34 samples. For S-2 sample with high crystallinity, more Si content was incorporated into the framework in the crystallization process.

Figure 5. NH_3–TPD profiles of synthesized samples.

Table 2

Physico-chemical properties of synthesized SAPO -34 samples.

| Sample	Composition in product	%Si content	Si incorporation*	BET Surface area (m²/g)	Acid site concentration (%)	
					strong	weak
S-1	-	-	-	-	-	-
S-2	$Al_{0.5521}Si_{0.1043}P_{0.4110}O_2$	10.05	1.14	625.8	70	30
S-3	$Al_{0.5301}Si_{0.0964}P_{0.3976}O_2$	9.41	1.03	598.9	48	52

*Si incorporaton is defined by : $\dfrac{\left[\frac{Si}{Al+P+Si}\right]product}{\left[\frac{Si}{Al+P+Si}\right]gel}$

3-2. MTO reaction performance

The performance of catalysts was tested at 410°C with a feed WHSV of 6.5 1/h. The yield of ethylene and propylene (wt%) of SAPO-34 catalysts in the MTO reaction is presented in Fig. 6. The product distribution over three synthesized catalysts is presented in Tables 3-5. The products yield was obtained at different times: 60,110,160, 210, 260 min.
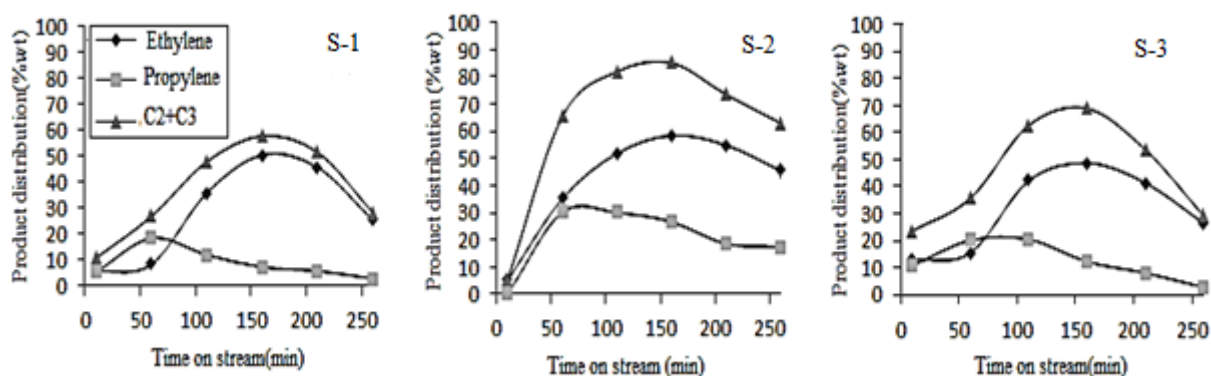
Figure 6. Products distribution in the MTO reaction over SAPO-34 catalysts at 410°C and WHSV=6.5 1/h.

In methanol to olefin process over SAPO-34 catalysts, it is widely accepted that methanol is first dehydrated to DME, then DME can easily be converted to light olefins over strong acid sites of catalysts until the cages inside the SAPO-34 catalysts are occupied by coke. Therefore, after deactivation of the catalysts, conversion of methanol to DME can still take place at the weak acidic sites [3,18]. According to the Tables below, the production of heavier molecules increases over the time and deactivation is caused by the formation of coke from the heavier hydrocarbons that were entrapped within the cages of SAPO-34 catalyst during the process.

According to the Fig. 5, at the first propylene yield reached a maximum then leveled off, whereas production of ethylene monotonically increased. After activation of the catalyst with a propene pulse, ethylene is able to form stably. Product distribution in MTO reaction is affected by diffusion limitation of propene within pores of SAPO-34 with particle size of >0.5μm. The maximum yield of light olefins of S-1 and S-3 was 70 and 69 wt%. Compared with synthesized samples, S-2 sample possessed the smallest crystal size, about 0.6 μm, resulting in minimizing the possibility of inhomogeneous coke distribution. S-2 sample possessed the highest yield of light olefins (88.7 wt%) and the total yield of $C_2^=$ $– C_3^=$ maintained at higher than 60% after 250 min.

Table 3

yield of products over S-1 catalyst.

Product	t=10	t=60	t=110	t=160	t=210	t=260
CH_4	75.1	50.45	40.58	20.48	8.85	11.57
C_2H_6	0.77	3.18	1.54	0.98	1.25	0
C_2H_4	5.48	8.36	35.9	50.5	45.75	25.35
C_3H_8	0.04	0	2.35	1.54	2.14	1.25
C_3H_6	5.37	20.48	12.01	7.28	5.82	2.88
i-Butane	0	5.48	0	0	0	0
n-Butane	0	0	0	0	0	0
Propadien	0	0	0	0	0	0
C_2H_2	0	0.01	0	0	0	0
T_2-Butene	0	0	0.03	0	0	0
1-Butene	0	0.01	0	0	0	0.04
Iso-Butene	0.01	0	0.04	0.03	0	0.05
C_2-Butene	0	0	0	0.01	0	0
I-Pentane	0.01	0.01	5.02	0	0.04	0.04
1.2 Butane	0	4.5	0	0	0	0
n-Pentan	1.57	5.23	0	0	0	0
MA	2.5	0.04	0.27	0	0.58	9.25
heavier	9.15	2.25	2.26	19.18	35.57	49.57

Table 4

yield of products over S-2 catalyst.

products	t=10	t=60	t=110	t=160	t=210	t=260
CH_4	93.65	20.65	10.68	3.22	3.58	3.02
C_2H_6	0.1	1.24	2.25	0.42	0	0.12
C_2H_4	5.31	35.24	51.83	58.46	54.91	45.54
C_3H_8	0	2.56	1.5	1.19	0.1	1.56
C_3H_6	0.3	30.21	30.1	26.67	18.62	17.54
i-Butane	0	0.01	0	0	0	0.52
n-Butane	0.01	0.05	0	0.82	0	0
Propadien	0	0	0	0	0	
C_2H_2	0	0	0	0	0	
T_2-Butene	0	0.03	0	0	0	0
1-Butene	0	0.25	0.01	0.31	0	0.01
Iso-Butene	0	0	0	0	0.04	0
C_2-Butene	0	0	0	1.54	2.45	0
i-Pentane	0	0	0	0	0	0
1.2 Butane	0	0	0	0	0	0
n-Pentan	0	0	0	0.03	0	0.15
MA	0	0	1.05	0.12	0	0.2
heavier	0.63	9.76	2.56	5.35	20.3	31.34

Table 5

yield of products over S-3 sample.

Products	t=10	t=60	t=110	t=160	t=210	t=260
CH_4	72.26	58.95	25.65	20.25	11.3	17.65
C_2H_6	0.25	1.26	0.03	0.54	0.21	0.5
C_2H_4	12.86	15.53	42.23	48.78	41.4	26.43
C_3H_8	1.26	2.35	1.53	0.49	0.59	0
C_3H_6	10.78	20.16	20.44	12.26	8.06	2.74
i-Butane	0	0	0	0	0.1	0
n-Butane	0	0	0.01	0	0	0
Propadien	0.2	0.15	0	0.58	0	0
C_2H_2	0	0	0	0.01	0.26	0.16
T_2-Butene	0.4	0	0.03	0	0	0
1-Butene	0	0	0.15	0	0	0
Iso-Butene	0	0	0	0	0.15	0
C_2-Butene	0	0.21	0	0	0	0.01
i-Pentane	0	0	0	0	0	0
1.2 Butane	0	0	0	0	0	0
n-Pentan	0	0	0	0	0.01	0
MA	0.01	0.02	0.01	1.26	2.68	7.25
heavier	1.97	1.37	9.92	15.83	35.24	45.26

3-3. Optimization

Central Composite Design (CCD) was applied to investigate the effect of two independent variables namely, TEA content (A) and TEAOH content (B) on maximum yield of light olefins. The five examined levels for each independent variable are shown in Tables 6.
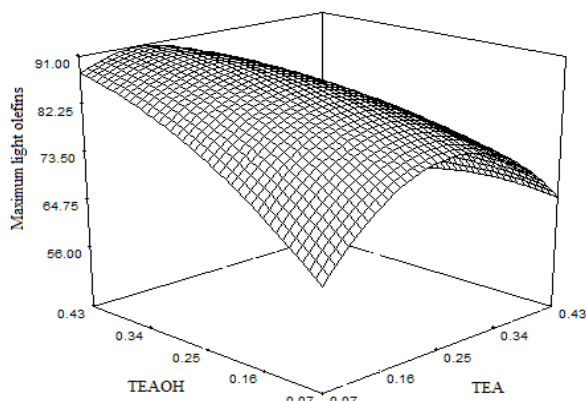
Table 6

Variables and their examined levels used in experimental design.

Factor	Level		
	-1	0	+1
A-x (TEA content)	0.07	0.25	0.43
B-y (TEAOH content)	0.07	0.25	0.43

Graphical representations of experimental design are shown in Fig. 7. According to this figure, the increasing TEAOH and decreasing TEA results in increase of light olefins yield.

Figure 7. Counters describing the response surface for light olefins yield as a function of TEAOH and TEA.

In order to validate optimum point, experiments were also done on samples with the molar ratio of X=0.17 and Y=0.34, based on the molar ratios that were obtained from experimental design. Maybe it can be said that in order to reach maximum yield of light olefins, the molar ratio of TEAOH should be two times more than the molar ratio of TEA. Experimental

values for ethylene and propylene yields in the molar ratios of TEA=0.34 and TEAOH=0.68 were 57.22 and 27.03 wt%, respectively. From Table 7, these results confirm that the predicted results match satisfactorily with experimental values and with 95% confidence level, this point is the optimum point.

Table7

Products yield at optimum point.

Response	prediction	95% Cl* low	95% Cl high
Ethylene yield	59.24	56.55	61.91
Propylene yield	30.02	26.78	33.30

*Confidence level

4. Conclusions

SAPO-34 catalysts were synthesized with three different molar ratios of TEAOH-MOR-TEA under hydrothermal conditions. The morphology of samples was similar to the cubic shape of typical SAPO-34. Increasing TEAOH in synthesis gel led to decreasing mean crystal size. The tri-templating sample with molar ratio of $Al_2O_3{:}0.4SiO_2{:}P_2O_5{:}0.5MOR{:}0.5TEA{:}1TEAOH{:}70H_2O$ indicated highest crystallinity, smallest crystal size. The catalyst synthesized by combination of tri-templates exhibited highest light olefins yield in 100% methanol conversion. The optimum values (X=0.17, Y=0.34) were related to the sample with molar ratios of $1Al_2O_3{:}1P_2O_5{:}0.4SiO_2{:}0.68$ TEAOH:0.34TEA:0.98morpholine:$70H_2O$.

These molar ratios were obtained by central composite design and response surface contour plots.

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