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Synthesis of SAPO-34 molecular sieves by varying synthetic parameters and study of its effect on Biginelli reaction

Sunita Barot[1], Kalpana C. Maheria[2], Rajib Bandyopadhyay[1*]

[1]*School of Technology, Pandit Deendayal Petroleum University, Gandhinagar, Gujarat, India*
[2]*Department of Applied Chemistry, Sardar Vallabhbhai National Institute of Technology, Surat, Gujarat, India*

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**Corresponding author:E-mail: Rajib.bandyopadhyay@sot.pdpu.ac.in (+91 9909991602 / 079 23275440)*

Abstract

SAPO-34 being a microporous crystalline material; its morphology is greatly influenced by synthetic parameters. The aim of present investigation is to employ SAPO-34 synthesized under varying synthetic conditions to study its effect for Biginelli reaction. SAPO-34 molecular sieve was successfully synthesized in presence of four different organic templates (DEA, TEA, TEAOH and morpholine) and two different silica sources (colloidal silica and fumed silica). To achieve the SAPO-34 phase in its purest form, the template concentration was optimized by eliminating the competing phases. Synthesized catalyst samples were characterized by XRD, SEM, TG, FTIR and Total acidity analysis. The DEA and morpholine templated SAPO-34 samples (colloidal silica as silica source) were found to be more acidic and hence were tested for synthesis of Biginelli condensation products such as dihyropyrimidinons. The reaction is studied further in terms of catalyst concentration and solvent effect.

Keywords – SAPO-34, Biginelli reaction, Organic template, Diethylamine

1. Introduction

Small-pore SAPO-34 with chabazite (CHA) structure and pore diameter of approximately 0.38 nm is considered important catalyst in petro-chemical reactions especially methanol to olefin transformation [1]. SAPO-34 is microporous material with mild acidity and high hydrothermal stability giving almost complete conversion of methanol with high selectivity towards light olefins. The catalytic activity of zeolitic material is largely dependent on parameters such as porosity, morphology and crystal size. These parameters are influenced by synthetic conditions like source of precursors, composition and content of materials in initial gel, crystallization time, temperature, templating agents etc. [2, 3]

Aluminophosphate ($AlPO_4$) frameworks are constructed from an alternating set of AlO_2^- and PO_2^+ tetrahedra, therefore the resulting frameworks are neutral. Introduction of silicon atom in place of phosphorous atoms creates negative charges in the framework. Hydroxyl group arised from organic structure directing agents (SDA) during calcination generate Brønsted acidic sites by neutralizing these negative charge centers. Therefore acidity in these materials can be tuned by adjusting the amount and source of silicon atoms. Certain zeolites can be synthesized from many different templates by varying synthetic conditions, while others require very specific templating species.

Some attempts have been made to explore the crystallization from the gel to SAPO-34 [4-6]. The crystallization of nano-SAPO-34 by using tetra ethyl ammonium hydroxide (TEAOH) as organic template has been reported by Hirota et al.[7] Another group of researchers Vistad et al. have explored the crystal growth of SAPO-34 by morpholine as SDA [8]. Guangyu Liu and group have reported the crystallization and silicon incorporation mechanism in SAPO-34 templated by triethylamine (TEA) and diethylamine (DEA). This group has also stated that silicon content of SAPO-34 synthesized with DEA was higher than those with TEA and TEAOH, even though the initial gel had similar composition [9].

The number of literatures has reported synthesis of SAPO-34 but its application in multicomponent reactions to synthesize dihydropyrimidinone (DHPM) has not been reported so far. This paper focuses on synthesis of SAPO-34 by tuning four templates and two silica sources followed by characterization by XRD, SEM, TG, Total Acidity and FTIR Analysis. The DEA and morpholine templated SAPO-34, being more acidic, were studied further for Biginelli reaction to synthesize DHPMs. 3,4-Dihydropyrimidin-2(1H)-ones and its derivatives which are commonly termed as Biginelli condensation products, are known to exhibit a wide range of biological activities such as antiviral, antitumour, antibacterial and anti-inflammatory actions, calcium channel blockers etc.[10-12] The reaction is known to be catalyzed by various solid acid catalysts such as polyoxometalate [13], heteropoly acids [14], silica sulfuric acid [15], or zeolites like H-Y, H-ZSM-5, MCM-41[16-17]. Silicoaluminophosphate (SAPOs) have not been tried so far for Biginelli reaction to the best of our knowledge. We are reporting the use of SAPO-34 for Biginelli reaction for the first time.

2. Materials and methods

2.1. Catalyst synthesis

SAPO-34 was synthesized via conventional hydrothermal synthesis. The reaction mixture was prepared by using aluminum isopropoxide (97%, SD Fine chemicals) as aluminium source, phosphoric acid (85% SD Fine chemicals) as phosphors source and colloidal silica (40 % aq. Solution, Visa Chemicals) or fumed silica (Cab-O-Sil M5, cabot sanmar limited) as silica source. Diethyl amine (99.5%, SD Fine chemicals), Triethyl amine (99.5 %, Merk), Tetra ethyl ammonium hydroxide (35 % aq.solution, SigmaAldrich) and Morpholine (99.5 %, SD Fine chemicals) were varied as organic templates.

In typical procedure, aluminium isopropoxide was mixed with deionised water and stirred for half an hour to form paste. Diluted phosphoric acid was added dropwise to this solution and stirred for an hour to make uniform mixture. Silica source and template was subsequently added and whole mixture was stirred for 60-80 min. until it became homogeneous. The mixture was sealed in a teflon-lined stainless-steel autoclave and heated at 190 ^{o}C under autogenous pressure for 48 h. After synthesis, solid product was recovered by filtration, washed with water and dried in oven at 95 ^{o}C for 24 h followed by calcination in air at 450 ^{o}C for 8 h to remove organic template. The detailed synthetic parameters and molar gel composition of initial gel are presented in Table 1.

Table 1: Molar gel composition of synthesized SAPO-34 batches

Sample No.	Molar gel composition	Silica source	Temp. (^{o}C)	Time (h)	Relative cryst. (%)
S1	Al_2O_3:0.8P_2O_5:0.6SiO_2:2.0DEA:50H_2O	CS	190	48	100
S2	Al_2O_3:0.8P_2O_5:0.6SiO_2:2.0DEA:50H_2O	FS	190	48	98
S3	Al_2O_3:0.8P_2O_5:0.6SiO_2:3.0 TEA:50H_2O	CS	190	48	90
S4	Al_2O_3:0.8P_2O_5:0.6SiO_2:2.0TEAOH:50H_2O	CS	190	48	88
S5	Al_2O_3:0.8P_2O_5:0.6SiO_2:3.0Morpholine:50 H_2O	CS	190	48	95

(CS: colloidal silica 40%; FS: Fumed silica; DEA: Diethylamine; TEA: Triethylamine; TEAOH: Tetraethylammonium hydroxide)

2.2. Catalyst characterization

Crystallinity and phase purity was determined by powder X-ray diffraction using CuKα radiation over PANalytical X'Pert. The particle size and morphology was evaluated by SEM images taken over FE-SEM (ZEISS). FTIR was recorded over PerkinElmer's spectrometer model 'Spectrum Two'. Thermal studies were conducted on Mettler Toledo Star^e system.

2.3. Biginelli reaction procedure

Catalyst was activated at 100 ^oC for 120 min. in oven prior to reaction. All reactions were carried out in round bottom flask attached with reflux condenser over magnetic stirrer under heating in an oil bath. In a typical reaction procedure appropriate amount of benzaldehyde (2 mmol) and defined amount SAPO-34 as heterogeneous catalyst were added to a solution of ethyl acetoacetate (2 mmol) and urea (3 mmol) in toluene. The reaction mixture was refluxed for 5-6 hr at 110^{o}C. The completion of reaction was monitored by TLC. The spent catalyst was separated by filtration and washed with ethanol. Crude product was recovered by evaporating the solvent under reduced pressure. The product obtained was purified by recrystallization from ethanol to afford pure product 5-(1-ethoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one having melting point 204 ^{o}C (reported, 205 ^{o}C) [18].

3. Results & Discussions

3.1. Effect of template

The organic template has unique role in zeolite chemistry as SDA, space filler and charge compensator [3, 15]. Four different organic templates DEA, TEA, TEAOH and Morpholine were comparatively used under the same time and temperature conditions. The XRD patterns given in Figure 1 show that all the templates gave pure SAPO-34 phase.

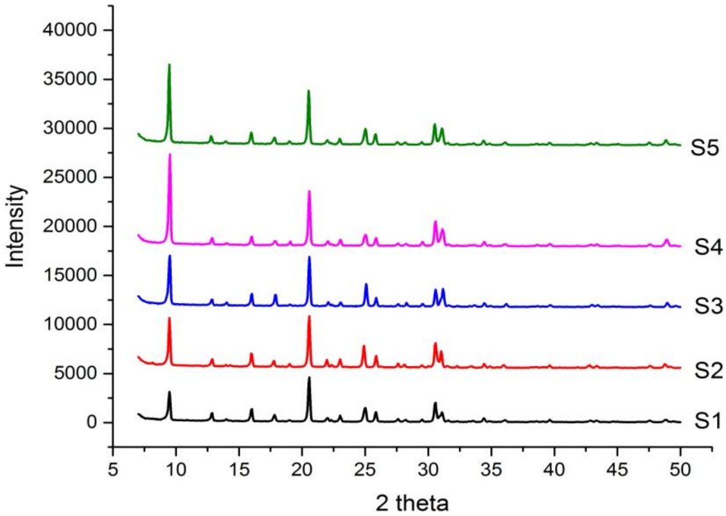


Figure 1: XRD patterns of as synthesized SAPO-34

The concentration of organic template was optimized to eliminate the competing phases of SAPO-5 and SAPO-18. DEA (Batch S1) amongst all templates gave very good crystallinity and dense phase only if used in the proportion of DEA /Al_2O_3 molar ratio greater than or equal to 1.5 or else it gives SAPO-11 peaks as impurity. In case of TEA as SDA, with lower concentration of template SAPO-5 is predominantly formed with irregular crystallinity and minor SAPO-34 phase. It is noted that TEA can be used as template for both SAPO-5 and SAPO-34, and less amount of SiO_2 in the gel favors formation of SAPO-5. In order to obtain pure SAPO-34 with uniform size, TEA / Al_2O_3 ratio must be greater than 2.5. In current studies we could obtain pure SAPO-34 (Batch S3) with TEA/ Al_2O_3 ratio 3. Literature studies have reported relatively smaller sized particles with

TEAOH [3], but that results into the phase impurity, similar results are reported in our studies also. Pure SAPO-34 with relatively smaller particle size (20-30 µm) was obtained at TEAOH / Al_2O_3 molar ratio 2 (Batch S4). TEAOH / Al_2O_3 molar ratio below 2 gives SAPO-5 and SAPO-18 peaks as impurity. Lower concentration of morpholine (Batch S5) leads to the impurity of cristobalite in the phase. However this impurity can be reduced by increasing concentration of template. Therefore, the concentration of template agent has significant effect on phase purity and crystal morphology. SEM results in Figure 2 (A), (B), (C) and (D) display that the sample synthesized with DEA, TEA, TEAOH and Morpholine respectively.

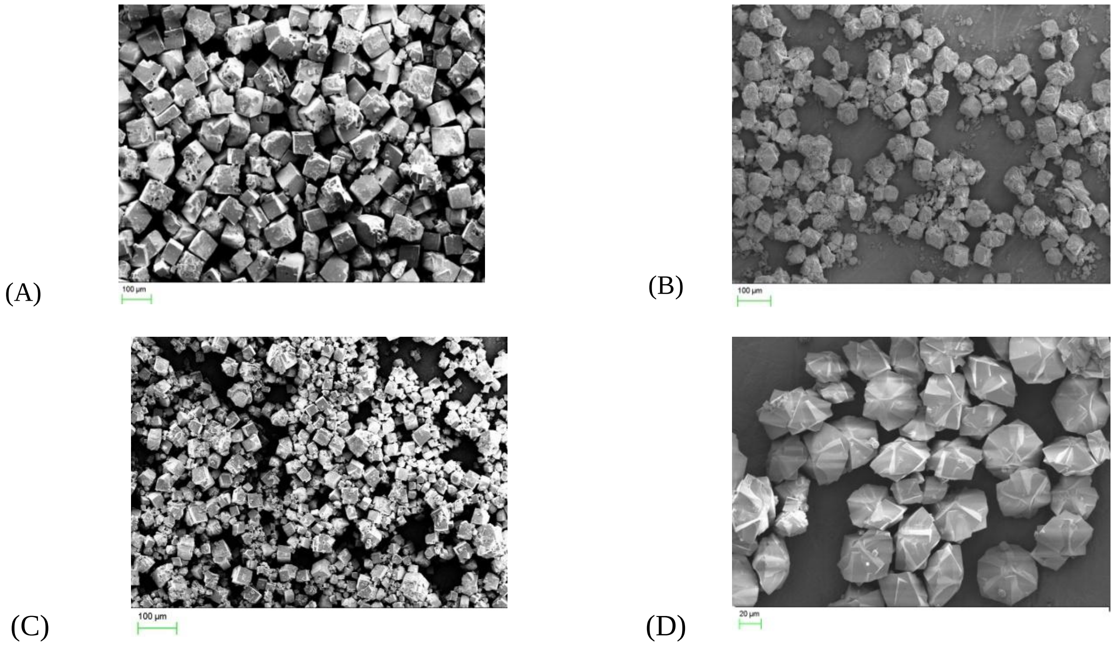


Figure 2: SEM images of samples synthesized using various templates (A) DEA (B) TEA (C) TEAOH (D) Morpholine

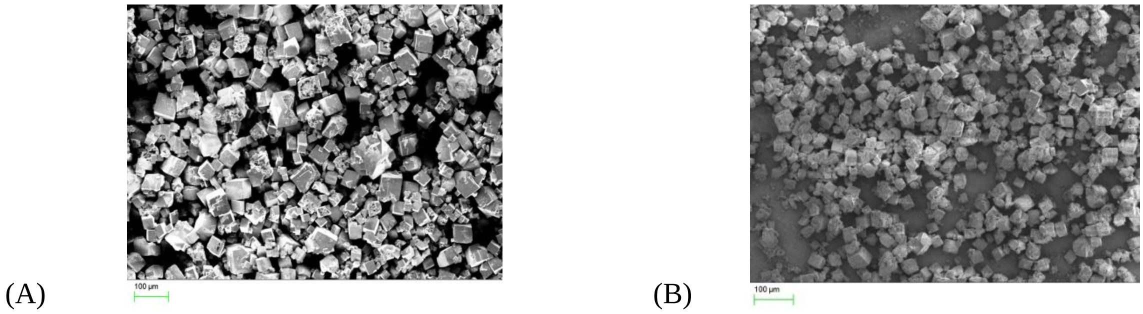


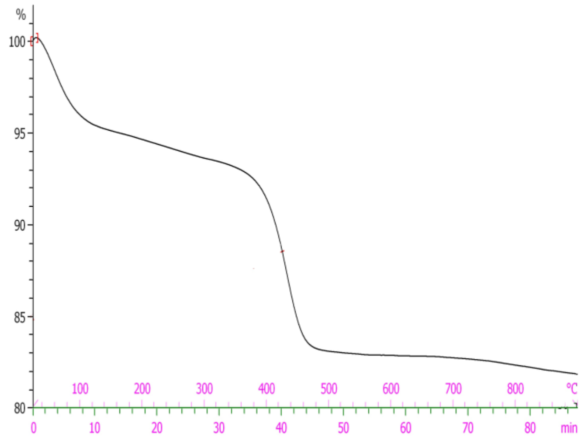
Figure 3: SEM images of samples synthesized using DEA as template with different silicon sources (A) Fumed silica (B) Colloidal silica

3.2. Effect of silica source

Figure 3(A) and (B) represents the SEM images of samples synthesized with fumed silica and colloidal silica as silica sources with DEA as template. Fumed silica is introduced to the reaction mixture in its solid form. Therefore its solubility plays an important role in synthesis. On the other hand colloidal silica is already in its hydrolyzed form and hence can be easily incorporated in aqueous reaction medium. Moreover fumed silica leads to the wider particle size distribution as compared to colloidal silica as shown in Figure 3 (A) & (B) respectively. Lin and group have synthesized SAPO-34 nanoparticles under microwave heating using colloidal silica and solid SiO_2 powder. They have reported sheet like morphology with colloidal silica which changed into the irregular spheres when tetra ethyl ortho silicate is used as silica source [19]. Choice of silica source is considered as one of the influential parameter in determining crystal size distribution.

3.3. Thermal studies

The thermo gravimetric (TG) profile of SAPO-34 sample S1 is given in Figure 4. TG profile shows two major weight losses. The first weight loss of around 2.7 % below 100 ^{o}C temperature region is due to desorption of surface adhered water. The second weight loss of around 11.3 % in the temperature region of around 100 to 450 ^{o}C is due to the combustion of organic template from the framework. It can be seen from the TG curve that there is no significant weight loss or exothermic peak beyond 500 ^{o}C due to structural collapse of zeolite framework. This suggests the good thermal stability of SAPO-34 synthesized in present studies [20-22].



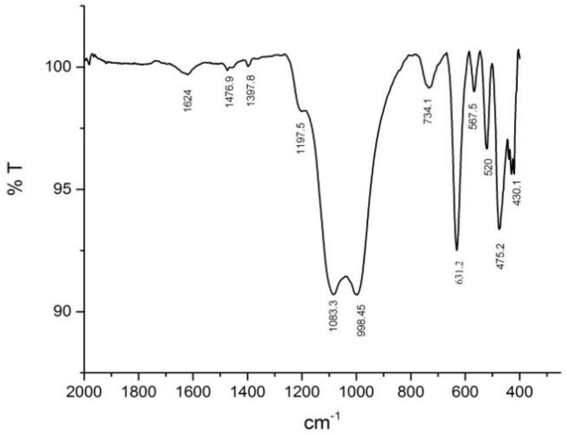


Figure 5: FTIR spectra of SAPO 34 sample synthesized with DEA and colloidal silica

3.4. FTIR Analysis

FTIR spectrum of as synthesized sample of SAPO-34 (Batch S1) is presented in Figure 5. As per the literature [6, 9] absorption peaks can be assigned as follows; peaks observed 1197 cm^{-1}, 1083 cm^{-1} and 998 cm^{-1} are due to the asymmetric stretching of T-O tetrahydra. Peak at 734 cm^{-1} is due to symmetrical stretching of T-O tetrahydra. The peaks observed at 631 cm^{-1} and 567 cm^{-1} are corresponding to the vibration of double-6 rings, while peaks at 520, 475 and 430 cm^{-1} are due to the bending vibration of T-O bond. In addition to above mentioned peak few more peaks are seen in the region of 1400-1600 cm^{-1} which can be assigned to vibrational frequencies of template molecule.

3.5. Determination of acidity

Acidity of all SAPO-34 samples was determined by acid-base titration. Weighed amount of catalyst sample was dispersed in (N/100) NaOH solution and stirred for 2 hours. Solid catalyst was then separated by filtration and change in base strength of alkali was measured by titrating it against (N/100) oxalic acid solution [23]. The reported acidity of all samples is given in Table 2.

3.6. Biginelli Reaction using SAPO-34

As shown in Table 2 SAPO-34 synthesized with DEA and morpholine were found to be more acidic than SAPO-34 synthesized with TEA and TEAOH. Moreover DEA and morpholine both exhibited the material with two different particle sizes (DEA: 80-90 μm and Morpholine: 40-50 μm) and morphology. DEA templated SAPO-34 showed regular cubic crystals whereas morpholine templated sample exhibited spherical flower like crystals and hence these two catalyst samples were chosen for further reaction studies. Biginelli reaction scheme using SAPO-34 is presented in Figure 6. DHPMs were synthesized in presence of various amounts of SAPO-34DEA, SAPO-34Morpholine and results are presented in Table 3. The maximum product yield of around 54 % was obtained in case of 7 wt % of SAPO-34DEA catalyst. SAPO-34Morpholine with same amount i.e. 7 wt % has given only 31 % product yield owing to its lesser acidity than the SAPO-34DEA.

Table 2: Acidity of SAPO-34 synthesized under varying conditions [* Fumed silica sample]

Sample No.	Catalyst	Acidity (mmol of NaOH/gm)
S1	SAPO-34DEA	0.94
S2	SAPO-34DEA*	0.67
S3	SAPO-34TEA	0.6
S4	SAPO-34TEAOH	0.55
S5	SAPO-34Morpholine	0.82

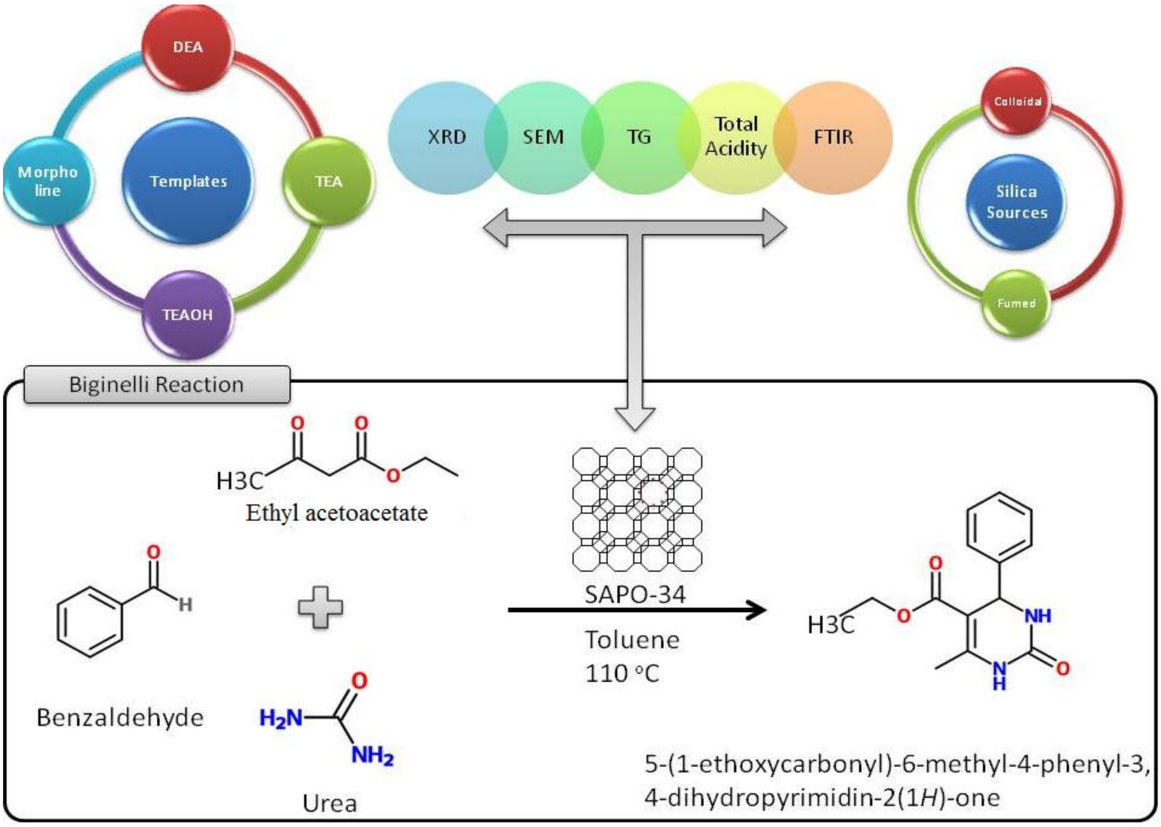


Figure 6: Biginelli reaction scheme using SAPO-34

Table 3: Optimization of catalyst concentration for synthesis of DHPM[a]

[[a]Reaction conditions: aldehyde (2mmol), Ethyl aceto acetate(2 mmol), urea (3mmol) under toluene reflux condition, Temp- 110^{O}C]

Entry	Catalyst amount (wt %)	Isolated yield %	
		SAPO-34DEA	SAPO-34Morpholine
1	2	34	12
2	5	44	23
3	7	54	31
4	10	30	33

3.7. Effect of solvents on catalytic activity of SAPO-34

The effect of polar and non-polar solvents on catalytic activity of SAPO-34DEA and SAPO-34Morpholine for synthesis of DHPMs was evaluated and results are presented in Figure 7. The mechanism of the Biginelli reaction has been investigated by several research groups. In this three components condensation reaction nucleophilic attack on benzaldehyde by urea is generally considered as rate-determining step of synthesis [24]. Solvent polarity is responsible for the tautomerisation equilibrium position of dicarbonyl group which in turn depicts the yield of reaction product [25]. In case of such heterogeneous catalyst system stability of metal – enolate intermediates decides rate and yield of reaction. In present study toluene and acetonitrile were used as solvents. Non-polar solvent toluene gave better performance giving 54 % product yield with SAPO-34DEA and 30 % with SAPO-34Morpholine. Acetonitrile on the other hand resulted into the lower product yield 32 % with SAPO-34DEA and 19 % with SAPO-34Morpholine.

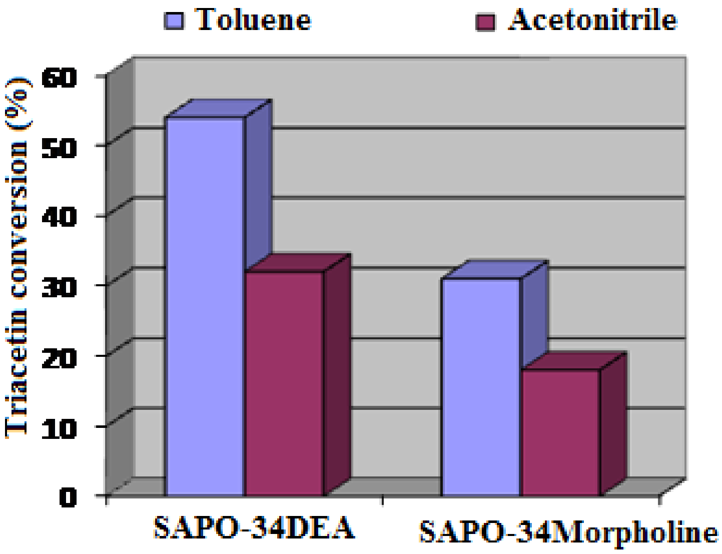


Figure 7: Effect of polar and non polar solvent on catalytic activity of SAPO-34 material in DHPMs synthesis [Reaction conditions: Benzaldehyde (2mmol), Ethylacetoacetate (2mmol), urea (3mmol), catalyst (SAPO-34DEA-7 wt%) under solvent reflux, 110 ^{o}C]

Conclusion

In present studies pure SAPO-34 could be successfully synthesized by varying four organic templates (DEA, TEA, TEAOH and Morpholine) and two silica sources (Colloidal silica and Fumed silica). The concentration of organic template is important in determining the phase purity and crystal morphology of SAPO-34 particles. Whereas silica source determines the particle size distribution in synthesized material. The nature of template decides the silicon distribution and acidity of resultant material, in that line DEA and morpholine templated SAPO-34 samples are found to be more acidic with unique morphology. Acidity of catalyst governs the product yield in Biginelli reaction and therefore more acidic SAPO-34DEA was found to be more effective than SAPO-34Morpholine. Biginelli reaction with SAPO-34 is more efficient in presence of non-polar solvents as compared to polar solvents. The studies provide future scope for the use of various types of silicoaluminophosphate in organic condensation reaction.

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