

# Review Article: The Amines Applied in SAPO-34 Synthesis: Investigating Crucial Factors in Templating Behavior of Amines

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## ABSTRACT

SAPO-34 has emerged as a highly versatile and valuable substance with exceptional capabilities across a wide range of industries, including the production of light olefins. Its high pore volume, excellent shape selectivity, suitable acidity, and superior hydrothermal stability make it a highly sought-after material. Amines, as structure-directing agents, play a vital role in the synthesis of SAPO-34. A diverse array of amines have been proposed for the synthesis of SAPO-34, each with a different templating behavior that can significantly impact the physiochemical properties of the resulting material. This review comprehensively investigates the templating behavior of amines based on pivotal factors such as size, shape, alkalinity, polarity, volatility, and environmental friendliness. This article provides a detailed overview of the most popular amines used for the SAPO-34 synthesis and examines the effects of the characteristics of each of these amines on the properties of synthesized SAPO-34, including crystallinity, purity, acidity, and surface area. This analytical view of the issue can aid in the targeted selection of amines for synthesizing SAPO-34 with desired characteristics.



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## Content

1. Introduction
2. Amine Properties
  - 2.1 Size and shape
  - 2.2 Basicity and protonation ability
  - 2.3 Polarity and hydrophilicity
  - 2.4 Volatility
  - 2.5 Toxicity and corrosiveness
3. Amines in SAPO-34 Synthesis
  - 3.1 Primary amines
  - 3.2 Secondary amines
  - 3.3 Tertiary amines
  - 3.4 Alkanolamines
4. Conclusion

### 1. Introduction

**A**luminophosphates are microporous structures composed of alternating  $\text{PO}_4$  and  $\text{AlO}_4$  tetrahedra. The combination of firm and directed covalent bonds along with flexible and non-directed ionic bonds enables the sharing of oxygen atoms and the formation of complex porous frameworks. The possibility of incorporation of different elements (T) in the  $\text{AlPO}_4$  lattice depends on parameters such as atom electronegativity, oxidation state, and the stability and nature of an element in a tetrahedral framework. In addition to the intrinsic properties of the elements, the properties of the reaction mixture including pH, viscosity, polarity, and batch compositions can effectively impact on the formation of tetrahedral structures and thus crystallinity [1].

Owing to the flexibility of  $\text{AlPO}_4$  frameworks, various elements can isomorphically substitute through different mechanisms and form various structures, namely SAPO (S: Si), and MeAPO/MeAPSO (Me: Mg, Mn, Fe, Co or Zn, etc.) [2]. Some monovalent, divalent, and trivalent cations can replace the Al and form a T-O-P bond (SM Ia, SM Ib, and SM Ic mechanisms, respectively). Some tetravalent and pentavalent cations are able to substitute P

and form the T-O-Al linkage (SM II a and SM II b mechanisms, respectively). Silica is the only element that, in addition to the SM IIa mechanism, can replace P and Al at the same time and form Si-O-Si islands (SM III mechanism). Isomorphic substitutions of SM I (a and b), and SMIIa generate the negative framework charge balanced with entrapped templates [3].

In contrast to many zeolites, the use of organic templates is essential in the synthesis of  $\text{AlPO}_4$ , MeAPOs, and MeAPSOs. These templates play two main roles in the synthesis process: space-filling and charge-compensating. In addition, as the primary alkaline substance in the composition, templates have a significant impact on the pH of the reaction gel. To date, over 100 templates have been identified for the synthesis of zeolites and zeotypes. These templates are primarily quaternary ammonium compounds and various organic amines, including primary, secondary, and tertiary alkylamines, cyclic amines, and alkanol amines. Uncharged template molecules, such as tetraalkylammonium hydroxide molecules or unprotonated amines, are Van der Waals-bonded with the framework, filling the cavities and increasing the thermodynamic stability of the structure. On the other hand, organic ammonium cations or protonated amines

neutralize the charge of  $\text{AlPO}_4$  structures that become negatively charged with anionic ligands (hydroxide, fluorides, and phosphates) or with isomorphic substitutions of SM I (a and b), and SMIIa. In such cases, there is usually a stoichiometric relationship between template molecules and structural elements [1, 4].

Among the types of  $\text{AlPO}_4$ -derived structures, SAPO-34 has been studied extensively as a promising catalyst and adsorbent [5]. The crystal structure of SAPO-34 closely resembles that of chabazite, exhibiting a three-dimensional pore system with a diameter size of  $3.80 \times 3.80 \text{ \AA}^2$  and a large cage of  $11 \text{ \AA} \times 6.7 \text{ \AA}$  [6]. Its unique structure, excellent shape selectivity, appropriate acidity, and superior thermal and hydrothermal stability have rendered this zeotype an outstanding catalyst for methanol-to-light olefins conversion and  $\text{CO}_2$  hydrogenation [7]. It has also been researched for its potential use in gas separation, particularly for the removal of  $\text{CO}_2$  from air and natural gas [7, 8]. Its high adsorption capacity for  $\text{CO}_2$  has demonstrated potential for carbon capture and storage (CCS) and hydrogen purification [8-10]. Like many zeolite and MOF structures [11-15], SAPO-34 can be employed further for adsorption-based processes such as gas storage, gas drying, and removal of volatile organic compounds (VOCs) from air or water. The adsorption properties of SAPO-34 can be customized by modifying its framework or incorporating different cations [7, 16]. The ion exchange properties of SAPO-34 enable it to selectively exchange cations with surrounding solutions, making it useful for applications such as water softening, removal of heavy metal ions from water, and separation of ions in various chemical processes [7, 17]. Furthermore, its high surface area and intricate microporous structure offer a hopeful avenue for the medical field functioning as a biomaterial for the engineering of hard tissues [18].

The most commonly used template for the SAPO-34 synthesis is tetraethylammonium hydroxide (TEAOH). However, due to its high toxicity, potential corrosiveness, and high cost, researchers have explored the use of amines as structure-directing agents (SDAs) [19, 20].

Various amines have been investigated in the SAPO-34 synthesis, each leading to the production of crystals with different phases, crystallinity, and physicochemical properties. To the best of our knowledge, despite the extensive experimental study of the performance of amines in the SAPO-34 synthesis, no work concretely categorizes the various key factors affecting the efficacy of an amine. The purpose of this review-analytical study is initially to take an analytical look at the effective factors in templating behavior of amines in the SAPOs synthesis, and then provide an overview of the most common amines suggested in the synthesis of SAPO-34. The infographic in **Figure 1** displays the important properties of amines that affect the SAPO-34 properties. Understanding these properties can help improve the efficiency of the catalyst in the MTO process.

## 2. Amine Properties

### 2.1 Size and shape

The dimensions of the template molecules should be proportional to the cage sizes of SAPOs. Nevertheless, there is not necessarily a direct relationship between the size of the template and size of cages [21]. Due to the flexibility of the carbon chains, molecules can fit into different structural cages [22]. Lewis *et al.* opined that the small size of the template causes several molecules to be trapped in an intracrystalline cage (**Table 1**), consequently increasing the time and temperature of crystallization and leading to the formation of competing phases [23]. The presence of two template molecules in a cage increases Si(4Al) environments (generated by the SMII mechanism) [24]. In other words, the size of template can affect the Si distribution in the structure and consequently the density and acid strength of SAPO-34 [25]. The formation of larger silica islands reduces acid density, but increases acid strength at the borders of the island [26]. Fan *et al.* [27] synthesized CHA-SAPO by aminothermal method with different amines. SAPO synthesized by hexamethyleneimine has more Si(4Al) compared to Di-iso-propylamine due to the



**Figure 1.** An infographic of the most important properties of amines affecting SAPO-34 properties and the MTO process

higher charge compensating centers occluded in its CHA cavities. Cao *et al.* [28] also reported that Cu-SAPO-34 synthesized with a larger template molecule such as TPAOH shows better stability against moisture, which is due to the lower concentration of Si(4Al) and as a result, less Brønsted acids and lower moisture adsorption. However, size is not the only determining factor, playing an electronic role in directing a specific structure, templates should have also the appropriate energy interaction with the framework in addition to geometric matching. As cases in point, n-hexylamine and n-butylamine are proportional to the structural dimensions of SAPO-11 in terms of size, however, they are not efficient templates for it [29].

The size of amines plays a role in the mechanism of nucleation and crystallization as well. It is implied that the large size of the

template increases the nucleation rate. Chatterjee *et al.* showed that large TPAOH molecules have less dynamic freedom in the ZSM-5 structure compared to amines and alcohols, which improves the nucleation process [22]. Zones *et al.* suggests that a larger template molecule if it fits into the CHA cavity, will accelerate the crystallization rate [30]. In an effort made for the rational design of efficient templates using computer modeling, it was found that increasing the molecule size in a family of templates (i.e. increasing and not changing the atom types) enhances the favorable host-guest interactions, as a result, improves templating efficacy [31]. A favorable short-distance interaction between the inorganic framework and organic charged templates plays a vital role at the nucleation stage [32]. On the other hand, the large size of the template hinders the growth rate. It was inferred that a large size and high C/N ratio of

amines make the positive charge of the nitrogen atom less easily accessible to the anionic species in the synthesis mixture and impede the zeolite crystallization. It also decreases the solubility of the template in water and disrupts the crystal growth process [21]. Investigation of nucleation and crystallization of SAPO-5 synthesized with TPAOH and alkyl amines ( $\text{Pr}_3\text{N}$ , DEA, and  $\text{Et}_3\text{N}$ ) showed that amine-synthesized samples have faster nucleation but slower crystal growth rate due to smaller size and more hydrophobic nature of amines [33, 34].

The shape of a template molecule also has an impact. Templates with linear shapes tend to create straight channels in the structure while spherical ones usually lead to cage-like voids [35]. Primary amines have a high probability of forming lamellar phases due to their linear structure [36]. In secondary amines, compounds such as DEA and DPA, which have linear carbon chains, can form structures with straight channels, including AEL. It means that precise control of the synthesis conditions is important to achieve pure SAPO-34 using these amines [37-41].

### *2.2 Basicity and protonation ability*

The templating power of amines is significantly influenced by their basicity and protonation ability, which play an important electronic role. In the SAPO synthesis process, the pH of the reaction mixture is primarily controlled by the template [42]. To achieve proper space-filling and charge compensation of  $\text{AlPO}_4$  and SAPO structures, a certain critical amount of amines is required, with a minimum ratio of  $1\text{Al}_2\text{O}_3:1\text{template}$  [38, 43]. However, an excess amount of template can lead to an increase in pH, which subsequently affects the crystallization behavior [44]. The pH of the reaction medium has a significant impact on various aspects of the synthesis process including: 1) the nature of building species, 2) the condensation mechanism, 3) the coordination of the cations, and 4) the charge density of amines [35, 45]. The mixture contains various groups of silica ( $\text{Si-O-Si}$ ,  $\text{Si-OH}$ , and  $\text{Si-O}^-$ ) and alumina ( $\text{Al-OH}$ ,  $\text{Al-OH}_2^+$ , and  $\text{Al-O}$ ) at different pH levels [46]. An increase in pH

leads to the ionization of silanol groups and the breaking of siloxane bonds, thereby increasing the silica solubility. Furthermore, alumina is solubilized as  $\text{Al(OH)}_4^-$  anions, which serve as building species for tetrahedral structures. However, a high pH range can disrupt the condensation mechanism [1].

The primary source of aluminum typically exhibits octahedral coordination in the initial solution, thereby enabling the synthesis of amorphous or dense aluminophosphate. Upon the introduction of phosphoric acid, the octahedral aluminum undergoes a conversion to an unstable tetrahedral coordination. Upon the addition of amines to the reaction solution, they form bonds with the tetrahedrally coordinated aluminum and phosphorus species, creating a hydrophobic shell that shields the aluminum from exposure to water and prevents its conversion to octahedral coordination [1, 34].

In contrast to ammonium cations, amines are inherently uncharged. Their role in this context is limited to space-filling and increasing the stability of the structure. To neutralize the charges caused by Si substitution in the structure, amines should be initially protonated [34, 41]. Consequently, the protonation strength of amines can significantly impact the distribution of Si in the structure. When the amount of ammonium to amine in the solution is low, less  $\text{Si(4Al)}$  is formed in the structure. Neutral amines tend to be surrounded by less polar  $\text{Si-O-Si}$  particles and form more silica islands [26, 46]. Amines with moderate basicity in aqueous synthesis at neutral pH are usually slightly protonated. The addition of HCl and HF can enhance their protonation ability [44, 46]. The basicity and the protonation ability of amines are primarily governed by their electronic nature and steric effects. The electronic effects can be categorized into two types: inductive and resonance. Inductive effects suggest that the introduction of electron-releasing groups, such as RO- and alkyl groups, to the nitrogen atom of an amine, leads to an increase in its base strength. Furthermore, the electron-donating nature of OH, OR, and alkyl groups strengthens the amine basicity through



**Table 1.** Comparison of the characteristics of the most common alkylamines used in the SAPO-34 synthesis with TEAOH

Amine (Abbreviation)	Molecular volume <sup>a</sup> (Å <sup>3</sup> )	Molecule per cage <sup>b</sup> [Ref]	pK <sub>a</sub> <sup>d</sup>	H <sub>am</sub> <sup>e</sup>	Category Oral LD50 (mg/kg) <sup>6</sup>	Category Dermal LD50 (mg/kg) <sup>6</sup>	Category Vapor LC50 (mg/l) <sup>f</sup>
Tetraethylammonium Hydroxide (TEAOH)	162.31	1 [47]	pH >13 (20 °C)	-	2 <sup>7</sup> (5-50)	3 (200-1000)	- =>20
n-propylamine (PA)	74.09	2 [36]	10.6 (20 °C)	65,907	4 (370)	3 (400)	3 (6.32)
Isopropylamine (IPA)	73.87	1 <sup>c</sup> [48]	10.6 (25 °C)	68,186	3 (122)	3 (>400)	3 (8.7)
n-butylamine (n-BA)	90.89	2 [36,49]	10.8 (20 °C)	74,757	4 (366)	3 (>1110)	3 (4.7)
Diethylamine (DEA)	91.76	2 [47,50,51]	11.0 (20 °C)	839,029	4 (540)	3 (582)	4 (17.3)
Dipropylamine (DPA)	125.37	1 [40,49,52]	10.9 (25 °C)	1,079,491	4 (300)	3 (1250)	3 (4.4)
Diisopropylamine (DIPA)	124.94	1 [40,49]	11.1 (25 °C)	1,155,449	4 (770)	- (2000)	3 (5.35)
Morpholine (MOR)	90.39	2 [47,50,51]	8.5 (25 °C)	903	4 (1050)	3 (310)	3 (>8000ppm)
Piperidine (PPR)	98.20	2 [53]	11.1 (25 °C)	89,322	4 (337)	3 (0.32ml/kg)	3 (1390 ppm)
Triethylamine (TEA)	125.51	1 [47,51]	10.75 (25 °C)	4,457,060	4 (460)	3 (415)	3 (>1250ppm)

<sup>a</sup>Molinspiration.com<sup>b</sup>Values are rounded off<sup>c</sup>Calculated for CoSAPO-34<sup>d</sup>Pubchem.ncbi.nlm.nih.gov<sup>e</sup>Henry's law constant of amines predicted from Nguyen's model [54] and used as an indicator of amine volatility and polarity. larger H<sub>am</sub> means more volatility and less polarity<sup>f</sup>Thermofisher.com (safety data sheet)<sup>g</sup>For 35% w/w aqueous solution

their positive resonance effects. The basicity of amines is also influenced by steric parameters, which can be classified into primary and secondary effects. The primary effect is the net effect of bulky groups on weakening the base,

while the secondary effect is a hindrance to solvation. The low basicity of tertiary amines in solution, as compared to primary and secondary ones, is attributed to the steric effect [44, 55].

### 2.3 Polarity and hydrophilicity

The balance between hydrophilicity and hydrophobicity is a crucial characteristic that should be taken into account when selecting templates for zeolite synthesis. The appropriate dissolution of the template in the solvent is a critical intermediate step in this process, as it facilitates the interaction of template molecules with anions and crystal surfaces, leading to nucleation and crystal growth [21, 56]. Moreover, the capacity of amines to undergo protonation is associated with their hydrophilic nature. Nevertheless, the interaction between the template and the solvent (water in the hydrothermal method) should not be so strong as to disturb the condensation mechanism [57]. Augmenting the C/N ratio heightens hydrophobicity, whereas the inclusion of an aromatic group enhances hydrophilicity [54]. Consequently, hydrophilicity can be linked to the dimensions and configuration of the template. In this study, the Henry's Law constant was calculated to determine the polarity and hydrophilicity of amines commonly used in the synthesis of SAPO-34 according to the equation (1) and are presented in **Table 1**.

$$H_{amine} \text{ at } 313.15 \text{ K} = \text{EXP}(17.5 + \sum k_j \times n_j) \quad (1)$$

Where,  $k_j$  is the parameter value for functional group  $j$  and  $n_j$  is the number of group  $j$  in an amine structure [54]. The parameter values for different groups are listed in **Table 2**.

Burkett and Davis demonstrated that propyl chains in TPA<sup>+</sup> selectively interact with the hydrophobic silicate particles through Van der Waals forces, resulting in inorganic-organic

structures that facilitate nucleation and crystal growth. Conversely, such an interaction between TMA<sup>+</sup> and silicate particles was not observed, and it is incapable of serving as a template for Si-ZSM-5 [56]. In the SAPO-5 synthesis, which is known to be synthesized with high amounts of silica, Weyda *et al.* have suggested that amines exhibit faster nucleation as compared to TPA<sup>+</sup> due to their smaller size and higher hydrophobicity. However, they also observed a slower crystal growth rate due to the harder sorption of amines on the surface of growing crystals [33]. Although the hydrophilicity of the template may pose a challenge in the synthesis of high-silica zeolites/Zeotypes, it is important to note that the interaction between the hydrophilic amine heads with polar Al and hydrophilic SiOH, and anionic framework is crucial in the SAPOs synthesis.

Alkanolamines exhibit greater hydrophilicity than alkylamines due to the presence of hydroxyl groups in their molecular structure. This increased polarity enhances the bonding between alkanolamines, as well as with the anionic framework, leading to higher template density within each cage [58]. Consequently, mesopores and larger crystals can form in microporous zeolite structures [59]. However, the high hydrophilicity of alkanolamines can limit their structuring-directing effects in the synthesis of ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=30-100). At lower crystallization temperatures and OH-/SiO<sub>2</sub> ratios, the amorphous phase may prevail [59]. Therefore, it is recommended to balance the hydrophilicity/hydrophobicity of amines based on the specific zeolite type and structural characteristics.

**Table 2.** Group parameter values for Nguyen's model

Group*	N	NH	NH <sub>2</sub>	N <sub>cy</sub>	O	OH	O <sub>cy</sub>	C <sub>cy</sub>	CH <sub>2</sub> - (R)	CH <sub>2</sub> - (OH/N/O)	CH <sub>3</sub> - (R)	CH <sub>3</sub> - (OH /N/O)	CH <sub>3</sub> - (N <sub>cy</sub> )
k <sub>j</sub>	- 18.9	- 15	- 12.1	- 7.57	- 13.8	- 10.8	- 4.3	0.294	0.126	5.41	0.16	4.48	1.85

\* CY: Cyclic and R: can be CH<sub>3</sub>, CH<sub>2</sub>, and CH

## 2.4 Volatility

Reactor pressure has a significant impact on both the thermodynamics and crystallization kinetics of zeolites and zeotypes. The hydrothermal method is the most commonly employed synthesis technique for SAPOs, where crystals are produced at high temperatures and under autogenous pressure. Pressure enhances the solubility of precursors and promotes collision between reacted molecules in the gel, thereby affecting the supersaturation of the system and, consequently, the rate of nucleation and crystallization [60-62]. However, it is essential to regulate autogenous pressure in consideration of safety measures, taking into account the synthesis temperature, volatility of the components, and their interactions. Notably, amines exhibit higher volatility than tetraalkylammoniums, which can potentially enhance the rate of crystallization and solid yield. Nevertheless, it is imperative to exercise caution during both gel preparation and hydrothermal treatment.

The volatility of amines in aqueous solutions is distinct from their pure form and does not necessarily correspond to their boiling point. For example, at 40 °C, DGA exhibits a higher saturated vapor pressure than MDEA, while the aqueous solution of MDEA is more volatile. Therefore, the interaction between amine and water should be considered a primary factor in the volatility of aqueous solutions [54]. Nguyen conducted a study to measure amine volatility in water for 19 alkanolamines and 8 alkylamines at 40 °C and developed a general model to estimate Henry's constant and consequently, amine volatility in water using structural parameters [54]. The results indicated that the presence of polar groups reduces the volatility of aqueous solution of amine due to increased interaction with water. The hydrophilicity of different polar groups was ranked as follows:  $O < OH < N < N_{cyclic}$ . Moreover, an increase in alkyl groups increases the volatility of amine due to its non-polarity. The strength of the hydrophobicity of alkyl changes depending on the adjacent group in the following order:  $C < C_{cyclic} < CH_3-(C) < CH_3-(N) <$

$CH_3-(N_{cyclic})$ . Consequently, diethylamine has a lower volatility in aqueous solution compared to triethylamine, despite its lower boiling point. Furthermore, morpholine, with high polarity, possesses much lower volatility than these two, as listed in **Table 1**.

## 2.5 Toxicity and corrosiveness

In general, the toxicity of amines is dependent on various parameters, including pH, hydrophobicity, electronic properties (reactivity and propensity to be metabolically transformed), and steric properties. As presented in **Table 1**, the amines commonly proposed for the SAPO-34 synthesis exhibit lower toxicity and corrosiveness compared to TEAOH. Most alkylamines fall under categories 3 and 4 in terms of acute oral, dermal, and inhalation toxicity, indicating moderate to slight toxicity. Amines can interact electrostatically with membranes [63], and acute toxicity is directly related to their basicity, with an increase in pH leading to an increase in toxicity [64, 65]. However, an increase in pH reduces the nitrosation rate of the amine, which is a carcinogenic factor. Short-chained amines can be easily absorbed through the skin, gastrointestinal, and respiratory tracts while increasing the length of the alkyl chain reduces toxicity. The lungs are the only organ whose vulnerability increases with the alkyl length [65]. Hydrocarbon branching near the amino moiety and an increase in alkyl groups reduce interaction with the membrane and the formation of nitrosamine due to steric hindrance of reactivity [63, 66]. Therefore, tertiary amines exhibit less acute and chronic toxicity compared to primary and secondary amines. Replacing alkyl groups with aromatic rings increases reactivity towards nitrosation and carcinogenesis [66]. According to the safety data sheet, alkanolamines exhibit less acute toxicity compared to alkylamines. However, some analyses suggest that aminoalkanols exhibit more toxic potency than aliphatic amines due to the presence of several reactive centers [63].

The structure of amines also affects the corrosion rate. Long-chained alkyl groups increase hydrophobicity, which repels water



molecules from the metal surface, thereby protecting it from corrosion. Furthermore, the corrosion rate can decrease as the number of –OH groups increases in the amine structure. In this case, the O atom chemically adsorbs onto the metal surface and decreases the open metal surface [67].

### 3. Amines in SAPO-34 Synthesis

#### 3.1 Primary amines

The primary amines commonly used for the SAPO-34 synthesis include *n*-PA, *i*-PA, and *n*-BA [36, 37, 48, 49, 68, 69]. It has been observed that *sec*-butylamine leads to the formation of a different type of CHA structure known as SAPO-47 [70, 71]. *n*-PA and *i*-PA are less efficient compared to *n*-BA due to their small size and increase the possibility of forming amorphous materials [36, 37, 72, 73] and are mostly used for the synthesis of MAPSO-34 and MAPO-34 [48, 68, 69]. In these structures, metal ions trapped in the cavities can act as charge-balancing entities and modify crystallization [74]. Although *n*-BA has been a more successful CHA-directing agent among primary alkylamines, however, due to the linear structure of this amine, the formation of

lamellar materials is quite possible, and the precise adjustment of the synthesis conditions, including the temperature of 200 °C and above (preferably at 240 °C) and a suitable range of Si ( $\text{SiO}_2/\text{Al}_2\text{O}_3=0.6-1.4$ ) is needed [36]. SAPO-34 crystals synthesized with primary alkylamines were typically smaller in size than those synthesized with secondary and tertiary alkylamines [75, 76]. **Table 3** summarizes the primary alkylamines that have been studied in the SAPO-34 synthesis. It is worth mentioning that further research is needed to fully understand the performance of these zeolites in the MTO (methanol-to-olefins) process.

#### 3.2 Secondary amines

The SAPO-34 synthesis has been extensively studied using secondary alkylamines such as DEA and MOR, which have been found to yield better results compared to other alkylamines [47, 51, 77]. This is due to the small size of these templates, which allows two molecules to fit into one CHA cage, resulting in higher Si incorporation and more Si(4Al) species [50]. Si content in DEA-directed SAPO-34 was usually more than the MOR-directed one [51]. According to the above discussion, the lower polarity of DEA compared to MOR can play a

**Table 3.** The primary alkylamines studied in the literature for SAPO-34 synthesis

Template [Ref.]	Phases	Aging/ Crystallization conditions	Molar Composition T:Al <sub>2</sub> O <sub>3</sub> :P <sub>2</sub> O <sub>5</sub> :SiO <sub>2</sub> :H <sub>2</sub> O
<i>n</i> -BA[36]	SAPO-34	-No aging -Stirring hydrothermal - 200/240 °C for 24 h	2.0:1.0:0.8:(0.6-1.4):50
<i>n</i> -BA[36]	SAPO-34	-No aging -Stirring Aminothermal -240 °C for 8 h	7.0:1.0:0.8:0.8:15
<i>n</i> -PA[36]	SAPO-34	-No aging -Stirring Aminothermal -240 °C for 24 h	7.0:1.0:0.8:0.8:15
<i>n</i> -BA[26]	SAPO-34	-No aging -Hydrothermal -200 °C for 24 h	2.0:1.0:0.8:(0.6-1):50 5% seeds
<i>n</i> -BA[75]	SAPO-34	-No aging -Stirring hydrothermal -200 °C for 24 h	2.0:1.0:0.8:1.2:50
IPA[37]	SAPO-34 Amorphous	-30 min aging -Hydrothermal -175 °C for 48 h	2.0:1.0:1.0:0.3:50

role in this regard. Moreover, it was reported that part of the MOR in the CHA cages is not charge-compensating [51]. This could be explained by the lower basicity and weaker protonation ability of this template compared to DEA. Therefore, providing conditions (mildly acidic pH) for proper protonation of this template can be important in the synthesis of SAPO-34. MOR-templated crystals also mainly have a much larger particle size compared to ones templated by other alkylamines [78, 79]. Containing an oxygen atom, morpholine establishes a strong interaction through hydrogen with Brønsted acid groups in the framework and accelerates crystal growth [80]. Pastore *et al.* showed that the CHA cages contain water-morpholinium (or morpholine) molecular complexes, which are connected as a chain along several cages with H-bonds between water molecules [70]. It may promote the growth of larger crystals.

DPA and DIPA are also other secondary amines that have been proposed for the SAPO-34 synthesis. Based on the shape and structure of DPA, this molecule exhibits a strong propensity to form structures with direct channels and has directed AEL and ATO structures [37, 39-41]. Pure DPA- SAPO-34 is obtained at high hydrothermal temperature and time (*i.e.* 200 °C, 120 h) [52] and a high amount of this template is recommended to

prevent the formation of SAPO-31 and SAPO-11 phases [40]. DIPA is known to be a more efficient template than DPA in structuring the low-silica SAPO-34. To establish a favorable electrostatic interaction with the CHA framework, DPA requires more silicon species to be incorporated into the structure, whereas DIPA has stronger non-bonding host-guest interactions and can stabilize the structure more efficiently, even with low amounts of silica [40].

Piperidine is a secondary amine that is recognized for its ability to template ERI-type structures [81-83], which can also structure CHA-SAPO through careful control of the synthesis conditions [53, 84]. According to Dumitriu *et al.*, the synthesis of pure SAPO-34 using this template is highly dependent on batch compositions and reaction conditions, and can only be synthesized within a narrow range of compositions. A low amount of templates results in the synthesis of SAPO-17 and SAPO-35, while a high amount of templates leads to the emergence of the competing phase of SAPO-20 [53]. **Table 4** provides a summary of the secondary alkylamines that have been studied in the SAPO-34 synthesis. The performance of SAPO-34 prepared with these amines has been extensively evaluated in the MTO process.

**Table 4.** The secondary alkylamines studied in the literature for SAPO-34 synthesis

Template [Ref.]	Phases	Aging/ Crystallization conditions	Molar Composition T:Al <sub>2</sub> O <sub>3</sub> :P <sub>2</sub> O <sub>5</sub> :SiO <sub>2</sub> :H <sub>2</sub> O	Space velocity T (°C)/ Feed ratio	Light olefin selectivity	Lifetime (min)
DPA[75]	SAPO-34	-No aging -Stirring hydrothermal -200 °C for 24 h	3.0:1.0:0.8:0.4:100	-	-	-
DPA[37]	SAPO-34 SAPO-11 SAPO-5	-30 min aging -Hydrothermal -175 °C for 48 h	2.0:1.0:1.0:0.3:50	-	-	-
DPA[85]	SAPO-34	-4 h aging at T <sub>room</sub> -Static Hydrothermal -200 °C for 120 h	2:1:1:0.6:20	WHSV = 1.2 h <sup>-1</sup> 400 °C MeOH/N <sub>2</sub> = 1/1 mol	~85%	<3 h

Table 4. Continued

DPA [40]	SAPO-34	-No aging -Tumbled hydrothermal -200 °C for 48 h	(3-5):1.2:0.9:(0.5-0.75):40	WHSV = 4 h <sup>-1</sup> 450 °C MeOH/H <sub>2</sub> O = 2/3 wt.	81.4% <sup>e</sup>	89 min
DIPA[26]	SAPO-34	-No aging -Hydrothermal -200 °C for 24 h	2.0:1.0:0.8:(0.3-1.1):50 5% seeds for Si/Al <sub>2</sub> O <sub>3</sub> :1.1	-	-	-
DIPA[75]	SAPO-34	-No aging -Stirring hydrothermal -200 °C for 24 h	3.0:1.0:0.8:0.4:50	-	-	-
DIPA [40]	SAPO-34	-No aging -Tumbled hydrothermal -200 °C for 48 h	3:1.2:0.9:(0.3-0.75):40	WHSV = 4 h <sup>-1</sup> 450 °C MeOH/H <sub>2</sub> O = 2/3 wt.	87.2% <sup>d</sup>	208 min
DEA[37]	SAPO-34	-30 min aging -Hydrothermal -175 °C for 48 h	2.0:1.0:1.0:0.3:50	WHSV=1.59 h <sup>-1</sup> 400 °C MeOH/N <sub>2</sub> = 1.1/8.9	83.4 (mol%)	<200 min
DEA[86]	Ni-SAPO-34	-No aging -Static Hydrothermal -200 °C for 48 h	1.0:1.0:1.0:0.6:70 0.05 Ni	GHSV=4200 cm <sup>3</sup> /g.h 400 °C MeOH/H <sub>2</sub> O=1/9	>80 %	~6 h
DEA[85]	SAPO-34	-4h aging at T <sub>room</sub> -Static Hydrothermal -200 °C for 120 h	2:1:0.8:0.6:50	WHSV = 1.2 h <sup>-1</sup> 400 °C MeOH/N <sub>2</sub> = 1/1 mol	~65%	<2 h
DEA[47]	SAPO-34	-No aging -Static Hydrothermal -200 °C for 48 h	(1.5-4):1:0.8:(0.1-0.8):50	WHSV = 4 h <sup>-1</sup> 450 °C MeOH/H <sub>2</sub> O = 2/3 wt	78.8% <sup>a</sup>	52 min
DEA[51]	SAPO-34	-No aging -Static Hydrothermal -200 °C for 24 h	2:1:(0.7-1.4):0.6:(15:300) <sup>b</sup>	-	-	-
DEA[87]	SAPO-34	-No aging -Static Hydrothermal -100 °C for 24h then 200 °C for 72 h	2:1:1:0.6:53	WHSV = 1 h <sup>-1</sup> 425 °C MeOH/N <sub>2</sub> = 0.03 ml/60 ml	84.48%	115min
MOR[51]	SAPO-34	-No aging -Static Hydrothermal -200 °C for 24 h	2:1:0.8:0.6:50	-	-	-
MOR[79]	CeSAPO-34	-24 h aging at T <sub>room</sub> -Static hydrothermal -200 °C for 72 h	3:1:1:0.6:50 0.006 CeO <sub>2</sub>	GHSV= 4200cm <sup>3</sup> /g <sub>cat</sub> .h 400 °C MeOH/H <sub>2</sub> O = 1/9 mol	86.9%	9.8 h

Table 4. Continued

MOR [88]	SAPO-5 (92%) SAPO-34 (8%)	-25 h aging at $T_{\text{room}}$ -Stirring hydrothermal -120 °C for 12 h, and then 200 °C for 12 h	2:1:1:0.6:52	WHSV = 1 h <sup>-1</sup> 450 °C MeOH/He = 1 /10.89 vol%	89.9%	160 min
MOR[89]	SAPO-34 <sup>c</sup>	-24 h aging at 27 °C -Static hydrothermal -(150-220 °C) for (6-60) h	(0.5-3):1:1:(0.1-1):60	-	-	-
MOR[77]	SAPO-34	-24 h aging at $T_{\text{room}}$ -Static hydrothermal -180 °C for (0-24) h	1.5:1:1:0.6:52	-	-	-
Piperidine [53]	SAPO-34	-20-30 min aging -Stirring hydrothermal -200 °C for 4-8 days	1.1:1:0.6:0.8:100	-	-	-
Piperidine [84]	SAPO-34	-	2:1:1:0.25:50	-	-	-

<sup>a</sup> $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3) = 0.6 / (n(\text{DEA})/n(\text{Al}_2\text{O}_3)) = 2$

<sup>b</sup>The relative crystallinity decreases when  $n(\text{H}_2\text{O}) > 50$

<sup>c</sup>Dense phase impurities at  $n(\text{SiO}_2) < 0.3$  and  $n\text{MOR} < 1$

### 3.3 Tertiary amines

Triethylamine (TEA) is the most commonly reported tertiary amine used in SAPO-34 synthesis, as indicated in **Table 5**. While TEA is considered a suitable template due to its bulkiness, its flexibility can introduce the possibility of different impurity phases [90-92]. SAPO-5 and SAPO-18 are the main competing phases that are typically obtained alongside TEA-SAPO-34, but their presence can be effectively controlled by adjusting the amount of silicon (Si) and the crystallization time [37, 51, 93-97]. Previous studies have shown that TEA, due to its larger size, can only accommodate one molecule within the CHA cage, resulting in less Si(4Al) compared to the other templates like MOR and DEA [51]. In addition, TEA-SAPO-34 exhibits a lower silica content and smaller particle size compared to secondary amines [40, 51]. This can be attributed to the reduced polarity and steric effects associated with TEA. It is concluded that the bulkiness of the molecule can improve nucleation, but the steric effects and less polarity hinder its bonding with the framework and the crystal's growth. Pyridine is another tertiary amine that has been proposed in a limited number of studies for the synthesis of AlPO<sub>4</sub>-34 and GaPO<sub>4</sub>-34 in the presence of

fluoride [98, 99]. However, due to its low *pK*<sub>a</sub>, it does not appear to be a suitable template for the SAPO-34 synthesis.

### 3.4 Alkanolamines

Alkanolamines have been investigated as a potential option for the synthesis of SAPO-34 due to their reasonable cost, low volatility, and favorable aqueous solubility. However, it has been observed that they primarily result in the production of one-dimensional channel systems, including SAPO-5, SAPO-11, or other CHA phases such as SAPO-47, in addition to SAPO-34. The alkanolamines commonly employed for hydrothermally/aminothermally synthesized CHA-structure include Diethanolamine [102], Diisopropanolamine [24], Triethanolamine [103, 104], N, N-dimethylethanolamine [24, 105, 106], N-Dimethylpropanolamine [107], N, N-diethylaminoethanol [24, 53], N-methyldiethanolamine [24, 58], and diglycolamine [24] (as listed in **Table 6**). These types of amines chelate aluminum with the hydroxyl groups, which impedes the incorporation of aluminum into the framework, thereby reducing nucleation and increasing crystal size. Due to intermolecular bonding, they are typically suitable templates for the synthesis of mesoporous structures [109].

**Table 5.** The tertiary alkylamines studied in the literature for SAPO-34 synthesis

Template [Ref.]	Phases	Aging/ Crystallization conditions	Molar Composition T:Al <sub>2</sub> O <sub>3</sub> :P <sub>2</sub> O <sub>5</sub> :SiO <sub>2</sub> :H <sub>2</sub> O	Space velocity T (°C)/ Feed ratio	Light Olefin selectivity	Lifetime (min)
TEA[37]	SAPO-34 SAPO-5	-30 min aging -Static Hydrothermal -175 °C for 48 h	2.0:1.0:1.0:0.3:50	-	-	-
TEA[85]	SAPO-34	-4h aging at T <sub>room</sub> -Static Hydrothermal -200 °C for 120 h	3:1:0.8:0.6:50	WHSV =1.2 h <sup>-1</sup> 400 °C MeOH/N <sub>2</sub> =1/1 mol	~70%	<1 h
TEA[47]	SAPO-34	-No aging -Static Hydrothermal -200 °C for 24h	3:1:0.8:(0.1-0.8):50	WHSV =4 h <sup>-1</sup> 450 °C MeOH/H <sub>2</sub> O =2/3 wt.	81% <sup>a</sup>	82 min
TEA[51]	SAPO-34	-No aging -Static Hydrothermal -200 °C for 24 h	2:1:0.8:0.6:50	-	-	-
TEA [40]	SAPO-34	-No aging -Tumbled hydrothermal -200 °C for 48 h	3.5:1:1:0.3:50	WHSV =4 h <sup>-1</sup> 450 °C MeOH/H <sub>2</sub> O =2/3 wt.	80.4%	123 min
TEA[100]	SAPO-34 <sup>b</sup>	-20min aging -Static hydrothermal -200 °C for 24 h	3:1:1:(0.025-0.6):50	-	-	-
TEA [97]	SAPO-5	-18h aging -Static hydrothermal -200 °C for 48 h	3:1:1:0.6:110	-	-	-
TEA[101]	SAPO-34 <sup>c</sup>	-30 min aging -Stirring aminothermal -160 °C for 0-48 h	7:1:0.9:0.35:15.7	-	-	-
TEA[101]	SAPO-34 <sup>d</sup>	-30 min aging -Stirring hydrothermal -160 °C for 0-48 h	3:1:1:0.3:50	-	-	-

<sup>a</sup>  $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3) = 0.6$ <sup>b</sup> SAPO-18 was formed when the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> was 0.025<sup>c</sup> The fully crystalline SAPO-34 is obtained after heating for 24 h<sup>d</sup> SAPO-34 appeared after 24 h



**Table 6.** The alkanolamines studied in the literature for SAPO-34 synthesis

Template [Ref.]	Phases	Aging/ Crystallization conditions	Molar Composition T:Al <sub>2</sub> O <sub>3</sub> :P <sub>2</sub> O <sub>5</sub> :SiO <sub>2</sub> :H <sub>2</sub> O
Diisopropanolamine [24]	SAPO-34	-Stirring aminothermal -30 min aging -200 °C for 48 h	8:1:1:(0.2-1):15.4
N,N-dimethylethanolamine [24]	SAPO-34	-Stirring aminothermal -30 min aging -200 °C for 48 h	8:1:1:0.4:15.4
N,N-diethylethanolamine [24]	SAPO-34	-Stirring aminothermal -30 min aging -200 °C for 48 h	8:1:1:0.4:15.4
Diglycolamine [24]	SAPO-34 <sup>a</sup>	-Stirring aminothermal -30 min aging -200 °C for 48 h	8:1:1:(0.2-1):15.4
Diglycolamine [24]	SAPO-34	-Stirring hydrothermal -30 min aging -200 °C for 48 h	3:1:1:0.4:50
Triethanolamine [103]	Amorphous SAPO-34 & SAPO-5 <sup>b</sup>	-Static hydrothermal -12 h aging at T <sub>room</sub> -180 °C for 48 h	3:1:1:0.4:50
Triethanolamine [24]	SAPO-5	-Stirring aminothermal -30 min aging -200 °C for 48 h	8:1:1:0.4:15.4

<sup>a</sup>Amorphous impurities at n(SiO<sub>2</sub>)=0.2

<sup>b</sup>Aluminium hydroxide led to amorphous and aluminium isopropoxide led to 43% crystallin sa-po-34 with sa-po-5

#### 4. Conclusion

This contribution sheds light on the most critical factors that play pivotal roles in the efficacy of an amine for the synthesis of CHA-SAPO. Through an extensive review of the literature, the influence of each of these factors on the crystallization process, as well as the purity and physiochemical properties of the resulting crystals, was thoroughly examined:

**Size:** The flexibility of carbon chains in amines enables a diverse range of amine sizes and shapes to fit within the SAPO-34 cages. An assessment of the documented efficacy of various templates revealed that templates with a smaller volume than the dimensions of the SAPO-34 cavity are situated within the cavity in pairs, necessitating longer crystallization time and higher temperatures, and heightening the likelihood of competing phase formation.

However, due to their higher charge-neutralizing capabilities, small amines increase Si(4Al) environment and improve acid strength and density. In contrast, bulky amines accelerate nucleation rates and exhibit greater templating efficacy by establishing more favorable host-guest interactions. In addition, due to steric effects, they lead to a diminished crystal growth rate, which frequently results in the formation of smaller crystal particles and an enhanced specific surface area.

**Shape:** Amines featuring linear shapes have a tendency to generate straight channels within the structure, whereas those with spherical shapes typically result in cage-like structures.

**Basicity:** The findings indicate that the protonation of amines during the preparation of the synthesis mixture plays a crucial role. A low ammonium-to-amine ratio in the solution

leads to the formation of more silicon islands. Consequently, to enhance the protonation of amines with moderate or weak alkalinity, it is recommended to add HF or HCl. This can modify the silica incorporation and subsequently the acidity of the SAPO-34 structure.

*Polarity and hydrophilicity:* Henry's law constant was computed to estimate the polarity and hydrophilicity of commonly used amines in the SAPO-34 synthesis. The findings indicate that an increase in the polarity and hydrophilicity of the amines results in a higher density of the template within the cavities of the structure. In high polarity, such as when alkanolamines are employed, this can lead to the formation of mesopores and mesochannels in the microporous structure of the SAPO. Furthermore, it was discovered that amines with high polarity exhibit a higher rate of crystal growth, resulting in larger particle sizes and a wider distribution of particle sizes. However, it has been observed that high polar amines are not suitable for the synthesis of nearly electrically neutral structures, such as high-silica zeolites or  $\text{AlPO}_4\text{s}$ .

*Volatility:* The utilization of more volatile amines increases the system pressure, which in turn enhances the solubility of precursors and promotes the collision of reacted molecules within the gel matrix. This phenomenon influences the degree of supersaturation and consequently the crystallization rate. In the context of hydrothermal systems, the polarity of amines plays a pivotal role in determining their vapor pressure.

*Environmental friendliness:* Bulky, long-chained amines exhibit lower acute and chronic toxicity and repel water molecules from metal surfaces, protecting them from corrosion. However, the presence of aromatic rings in amine structures increases their reactivity toward nitrosation and carcinogenesis.

*Amines in SAPO-34 synthesis:* The influence of the aforementioned factors and their interactions can result in crystals with diverse physiochemical properties. Concerning these factors, we can make a well-informed and cost-

effective decision when selecting a template for the SAPO-34 synthesis. Synthesis using an inefficient amine necessitates precise control of conditions, which can be achieved by increasing the Si and pH of the mixture (high  $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$ , Template/ $\text{Al}_2\text{O}_3$ ). Primary amines, with small and linear structures, are suitable for MAPSO-34 and MAPO-34 synthesis due to the presence of metal, but may lead to lamellar materials in SAPO-34 synthesis. Secondary alkyl amines have demonstrated effective structuring performance in SAPO-34 synthesis. DEA produces crystals with smaller particles and more silica compared to MOR due to its polarity and basicity. DIPA is more successful in structuring the low-silica SAPO-34 compared to DPA due to better host-guest interactions. TEA, with its bulky molecule, is the most suitable tertiary alkyl amine, leading to smaller crystals with less silica content than secondary amines. Alkanolamines, due to their high polarity and chelation with aluminum, reduce the nucleation rate and may lead to the creation of mesopore structures within the SAPO crystals.

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