

## THE ROLE OF AMINES IN THE SYNTHESIS OF ZEOLITES BY WATER-ORGANIC VAPOR PHASE TRANSPORT

Man-Hoe Kim<sup>†</sup>, Man-Kyu Jung\* and Hyun-Ku Rhee\*\*<sup>†</sup>

Dept. of Chemistry, Air Force Academy, Chungbuk 363-849, Korea

\*Cosmo Corporation Ltd., Songjung, Chungju, Chungbuk 360-290, Korea

\*\*Dept. of Chem. Eng., Seoul National Univ., Seoul 151-742, Korea

(Received 8 August 1994 • accepted 25 April 1995)

**Abstract**—A number of articles have been published to illustrate the role of amines for the synthesis of zeolites and porosils. Some of the results are contradictory on the role of amines. In this study, the roles of amines are investigated by water-organic vapor-phase transport method. This method is attractive because the dilution effects by mother liquid can be avoided and the composition of the synthesized zeolite is equivalent to that of the parent gel. Thus, the relation between the gel and amine can be explained clearly. In the zeolite synthesis, the templating effect of amine is less plausible, whereas the molecules with higher dipole moment and appropriate dimension such as propylamine have higher effectiveness. The protonated amines cannot work as active cations independently but amines activate the inactive cations (organic and alkali) in the gel by means of reinforcement of the pH level in the gel.

**Key words:** Zeolite Synthesis, Vapor-phase Transport, Amine Effects, Crystallization

### INTRODUCTION

The molecular sieving properties of zeolite have been utilized in various chemical and physical processes such as heterogeneous catalysis and gas separation [Garwood et al., 1989; Moscou, 1991]. Because of the multiplicity of properties possessed by zeolite molecular sieves, extensive attempts for synthesis have been made for a long time. In the early alkali aluminosilicate synthesis of the low silica zeolites, it has been proposed that the hydrated alkali cation templates or stabilizes the formation of the zeolite structural sub-units. The addition of quaternary ammonium cations to alkali aluminosilicate gels was tried in the early 1960's to produce intermediate silica zeolites and subsequently led to the discovery of the high silica zeolites.

In the late 1970's, amines and quaternary ammonium ions instead of alkali metals was introduced to the synthesis of  $\text{AlPO}_4$ -based molecular sieves [Flanigen, 1991]. Xu et al. [1900] and Dong [1992] reported a new method for synthesizing zeolites, the vapor phase method, where an amorphous aluminosilicate gel is transformed into ZSM-5, ZSM-35, and ZSM-48 in the vapors of water and amines. Amines are often employed for the zeolite synthesis as well as for the porosil synthesis [Gie and Marler, 1992]. These authors stressed the importance of the amine consumption and zeolite productivity.

However, there is a very important issue raised up by this work, i.e., what kind of roles can be done by amines in the crystallization of zeolites is a very interesting question. Although the structure directing effect of the organic cation on the synthesis of zeolite has been studied in detail, the role of amines used in zeolite synthesis is not clear and certainly bears further investigation.

A number of articles have been published to illustrate the role

of amines for the synthesis of zeolites and porosils. M. G. Howden [1993] found amino functional groups would not feature as the main structure-directing agent. However, diaminoctane (DAO) and diaminoheptane (DAH) are superior templating agents for the synthesis of ZSM-5 and ZSM-11, respectively, because of their molecular sizes. In addition, diaminopropane (DAP), diaminobutane (DAB), and diaminopentane (DAP5) molecules are too small to function as structure-directing agents. Similarly, Gies and Marler [1992] examined the structure-controlling role of organic molecules in the simplified system of  $\text{SiO}_2$ /template/ $\text{H}_2\text{O}$ . They found the structure-controlling role of the guest molecules and the close correspondence between the size and shape of the guest molecules and the framework pore housings, considering the fact that the chemical characters of the guest molecules give no influence on the type of porosil structure. It can be deduced that van der Waals type of interaction exists between the  $\text{SiO}_2$  host framework and the guest molecule. It is observed that more or less globular templates will stabilize clathrasils with cage-like voids and further that the size of the guest molecule determines the cage volume. To be more specific, long chain amines and polyamines will favor zeosils having 1-dimensional channel system, and the diameter of the chain determines the pore opening of the channel. Chain-like molecules having long side chains will stabilize zeosils with an intersecting channel system.

On the contrary, Mintova and Valtchev [1993] found that molecules with higher dipole moment have a shorter induction period to expedite crystallization, and the high dipole moment and the appropriate dimension of the propylamine (PA) are the reasons for its higher effectiveness among propylamine, dipropylamine (DPA) and tripropylamine (TPA). Conversely, the low dipole moment due to the geometric configuration of the organic templates explains the longer period of nucleation and the slower crystallization process. Several alkyldiamines such as ethylenediamine, diaminopropane, diaminobutane, diaminopentane, and diaminohe-

<sup>†</sup>To whom all correspondences should be addressed.

xane are investigated as potential templates. Ethylenediamine having the minimum ionization potential, the highest dipole moment, and the shortest dimension exhibits the best effect on the crystallization process among alkylamine used. Diaminohexane is inappropriate because of its high ionization potential, lower dipole moment, and longer molecular length.

As mentioned above, some of the results are contradictory on the role of amines. The objective of this work is to investigate the roles of amines in the zeolites synthesized by water-organic vapor-phase transport method. This method is attractive because of the following positive points. First, the ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of the synthesized zeolite is nearly equivalent to that of the parent gels. In case of the traditional hydrothermal liquid phase synthesis, the very complex patterns of mutual interactions are expected between the mother liquid and the chemical species involved. The effect of one component in a synthetic mixture is not simple because of the complexity of the interactions among various components involved. As a result, the influence of a particular guest molecule cannot be revealed clearly and some of the results are controversial.

In the vapor-phase transport method [Xu et al., 1990; Kim et al., 1992] the dilution effects by mother liquids can be diminished. Thus, the complexity of the system considered can be decreased. Secondly, amines can be transported into the solid gel phase and thus the relation between the gel composition and amine can be explained clearly.

## EXPERIMENTAL

NaOH (Aldrich Chemical Co.) and/or  $\text{NaAlO}_2 \cdot 1.5\text{H}_2\text{O}$  (EM science) are used as  $\text{Na}^+$  ion sources and  $\text{Al}(\text{OH})_3$  (Fisher Scientific Co.),  $\text{Al}(\text{NO}_3)_3$  (EM Science),  $\text{NaAlO}_2 \cdot 1.5\text{H}_2\text{O}$  are used as Al atom sources. Cab-O-sil (grade EH-5, Cabot Corporation), Ludox AS-40 and HS-40 (DU PONT), Syloid 74 (Davison Chemical), and tetraethylorthosilicate (TEOS) (Aldrich Chemical Company Inc.) are used as silica sources. Tetrapropylammoniumbromide (TPABr) (Aldrich Chemical Co.), tetrapropylammoniumhydroxide (TPAOH) (Johnson Matthey Electronics),  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{OH}$  (J.T. Baker Inc.) are also tested as cation sources in the zeolite crystallization.

First of all, the gels are prepared by adding the Na sources such as  $\text{NaAlO}_2 \cdot 1.5\text{H}_2\text{O}$  and NaOH to 30 g of distilled deionized water. Secondly, the Al source  $\text{Al}(\text{OH})_3$ , if needed, is added to the previous solution with stirring. Next, 3.0 g of Cab-O-Sil as  $\text{SiO}_2$  source are added and the resulting mixture is stirred to a homogeneous state for 2 h at room temperature. The resulting mixture is dried into a cake inside a hood at room temperature for 4 days. The cakes are crushed into fine powders with a mortar and pestle. These powdered gels are put into a teflon sample holder located at the upper position of the vessel. The liquid phase solution is in the bottom of the vessel as shown in Figure 1. Pure water (10 g) or a mixture of 7 g water and 3 g amine such as tripropylamine (TPA), dipropylamine (DPA), propylamine (PA), ethylenediamine (EDA), triethylamine (TEA), methylamine (MA) and diaminopropane (DAP) (Aldrich Chemical Company Inc.) is used as the liquid phase.

To avoid seeding effects of the inorganic materials in the zeolite synthesis, every sample holder and supporter is made of Teflon. When pure water is used as the liquid phase, a new Teflon liner is employed to eliminate the effect of organoamine absorbed in the Teflon liner. A Teflon bar is used to support the sample holder and to separate the solid phase from the liquid phase. The

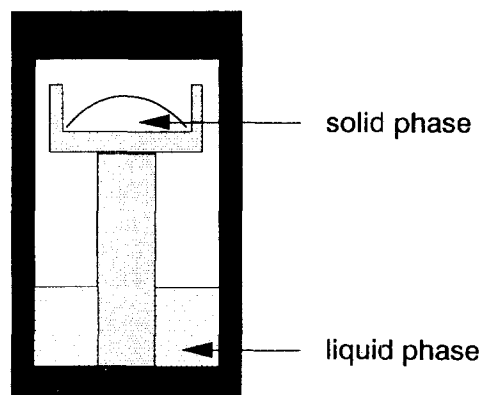


Fig. 1. Experimental setup for the vapor phase transport method.

bombs containing the Teflon vessel is placed in the air-heated oven at  $175^\circ\text{C}$  for an appropriate periods (3-7 days). After synthesis, the bomb is cooled down in air. The samples obtained are dried at  $110^\circ\text{C}$  for 1 h without washing. X-ray powder diffraction (XRD) data were collected on a Scintag XDS 2000 diffractometer using  $\text{CuK}\alpha$  radiation and a solid-state Ge detector cooled with liquid nitrogen.

## RESULTS AND DISCUSSION

### 1. Gel Chemistry

It is necessary to examine the solid gel properties to find the effects of amines. NaOH and/or  $\text{NaAlO}_2 \cdot 1.5\text{H}_2\text{O}$  are easily dissolved in distilled, deionized water. Cab-O-Sil is added to the stirred solution of NaOH and/or  $\text{NaAlO}_2 \cdot 1.5\text{H}_2\text{O}$ . As soon as a silica source is added to the solution of NaOH and/or  $\text{NaAlO}_2 \cdot 1.5\text{H}_2\text{O}$ , the solution is changed to sticky clods. The sticky clods lose viscosity with continuous kneading and mixing. The decrease of the viscosity of the gel mixture with kneading and mixing is also observed at the dissolution of Cab-O-Sil to distilled, deionized water. The particles settled down in the mixture are not dissolved by additional water. It is believed that the viscosity of the mixture is decreased due to the water released from the condensation reaction between hydroxyl groups of silicates and/or aluminosilicates at room temperature.

The gel mixtures are dried into a cake form at room temperature. The cakes obtained are crushed into powder gels. These gels are used for the solid phase in the vapor phase method. Because of the difference in the starting materials between the traditional hydrothermal method and the vapor phase transport method, several experiments on the gels are carried out to find the kinds of changes occurring during the gel formation and the physical properties of the gels. The mixing and aging effects are examined by synthesis experiments. The resulted materials are quite different from one another because of the different conditions of the starting materials as shown in Table 1. The powder gels are exposed to air at room temperature for 24 h for TGA experiment. Desorption of water is detected from the gels as shown in Table 2. Most of water desorption occurs below  $150^\circ\text{C}$ . When the pure  $\text{SiO}_2$  gel having 54.3 weight percent of moisture is washed with acetone and dried at room temperature, this gel has only 5.5% weight loss below  $150^\circ\text{C}$ . Thus, the weight loss from the pure  $\text{SiO}_2$  gel can be regarded as bulk water absorbed on the hydrophilic hydroxide groups.

**Table 1. The effect of mixing and aging of the solid sources. The resulted crystals are obtained from the vapor-phase transport method at 175°C for 5 days**

Phase I (solids)	Phase II (liquid)	Results
40/10 <sup>a</sup> gel, mixing & aging (liquid)	H <sub>2</sub> O	ZSM-5
40/10 gel, powder mixing	H <sub>2</sub> O	Quartz, Mordenite
40/10 (NaOH, NaAlO <sub>2</sub> , SiO <sub>2</sub> ) just added	H <sub>2</sub> O	Quartz

<sup>a</sup>ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/ratio of SiO<sub>2</sub>/Na<sub>2</sub>O

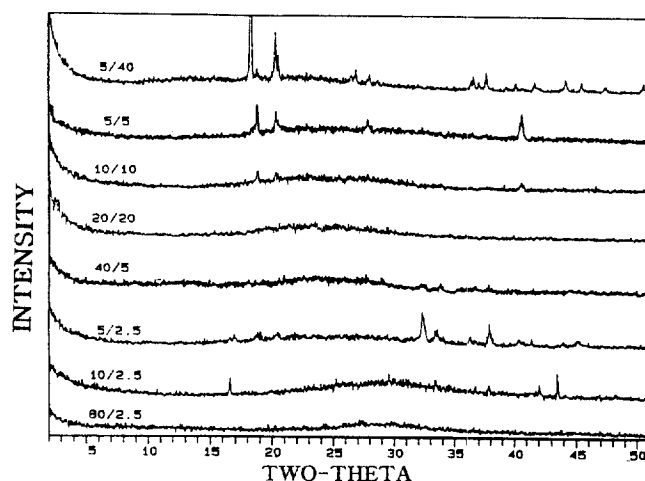
**Table 2. The content of moisture (wt%) in the gels in atmosphere at room temperature**

Gel content	wt%	Gel content	wt%	Gel content	wt%
(Al <sup>F</sup> /Na <sup>F</sup> ) <sup>a</sup>	54.3				
Al <sup>F</sup> /96	18.0				
Al <sup>F</sup> /80	5.9	(80/80) <sup>b</sup>	46.4	80/80	46.4
Al <sup>F</sup> /40	7.3	80/40	41.7	40/80	7.3
Al <sup>F</sup> /20	9.2	80/20	21.0	20/80	8.8
Al <sup>F</sup> /10	12.4	80/10	28.3	10/80	10.8
Al <sup>F</sup> /5	19.6	80/5	37.4	5/80	13.1

<sup>a</sup>Al free/Na free gel, <sup>b</sup>ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/ratio of SiO<sub>2</sub>/Na<sub>2</sub>O

There is a correspondence between the gel composition and the amount of water absorbed. After the calcination, the gels were exposed to atmosphere to absorb moisture from air. Although the amount of initial desorption is as large as 54.3 weight percent in the pure SiO<sub>2</sub> gel, the amount of reabsorbed moisture is only 2.6 weight percent. It is believed that the pure SiO<sub>2</sub> gel has the largest number of unreacted terminal hydrophilic hydroxyl groups, i.e., the lowest degree of condensation and the smallest particle size. These hydrophilic functional groups are transformed into hydrophobic siloxanes by the condensation reactions induced by the calcination. When a little amount of NaOH is added to the amorphous SiO<sub>2</sub> and water mixture (Al free/80 means the gel of Al free and of SiO<sub>2</sub>/Na<sub>2</sub>O=80), the amount of the water desorbed is sharply decreased from 54.3 wt% to 5.9 wt%. It is considered that NaOH promotes the condensation reaction between the hydroxyl groups of the silicates even at the room temperature. However, if the same amount of Al as that of Na<sup>+</sup> is supplied (80/80 means the gel of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=80 and SiO<sub>2</sub>/Na<sub>2</sub>O=80) in the form of NaAlO<sub>2</sub>·1.5H<sub>2</sub>O, the amount of desorbed water increases from 5.9 wt% to 46.4 wt%. Comparing the amounts of water desorbed from the two gels (80/80 and Al free/80), the species of Na<sup>+</sup>, OH<sup>-</sup>, and Al are controlling the condensation reaction.

Both the cation Na<sup>+</sup> and the basic condition catalyze the condensation between the hydroxyl groups. However, the monomeric Al anions restrict the activities of the Na<sup>+</sup> and OH<sup>-</sup> ions, in particular, the activity of Na<sup>+</sup>. It is well known that spectroscopic studies of the liquid phases of aluminosilicate gels used for synthesis of zeolites show that, as in silicate solutions, various silicate particles are observed and that the aluminate particles are always present in the form of monomeric aluminate ions as in alkali aluminate solutions [Szostak, 1989]. In general, the data in Table 2 show a trend that the desorbed amount is steeply decreased with increasing Na<sup>+</sup> and OH<sup>-</sup> contents in the gels, and then slowly increased with increasing Al species and Na<sup>+</sup> species due to hy-



**Fig. 2. XRD patterns of the gels before synthesis.**

**Table 3. The weight (%) of the soluble portion in the gels**

Gels	5/5 <sup>a</sup>	10/1	20/20	40/20	40/10	40/5
wt %	34	10	6	2	7	18

<sup>a</sup>ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/ratio of SiO<sub>2</sub>/Na<sub>2</sub>O

drophilic properties of these elements. If we define the difference between the amount of initial desorption and that of reabsorbed moisture as irreversible desorption, this irreversible desorption is related to the amount of unreacted hydrophilic hydroxyl groups.

From the N<sub>2</sub> adsorption experiment, the extent of condensation can be compared indirectly. The total adsorption volume of the pure amorphous SiO<sub>2</sub> gels is twice as large as that of the gel composition 86/20 (43 cm<sup>3</sup>/g). Also, the pore size of the pure SiO<sub>2</sub> gel is relatively larger than that of the 86/20 gel. These results imply that the gel having higher degree of condensation has lower surface area and smaller pore size.

The XRD patterns of the starting gels are shown in Figure 2. The Al rich gels (5/40) have XRD patterns of Al(OH)<sub>3</sub>. The gels having same number of Al and Na<sup>+</sup> (20/20, 40/40, 80/80) show no crystallinity. By comparison, the XRD patterns of some intermediate structures are observed from the Na<sup>+</sup> rich and OH<sup>-</sup> gels (5/2.5, 10/2.5, 40/5). These results imply that the Na<sup>+</sup> and OH<sup>-</sup> species contribute to the formation of some intermediate secondary building units and that the activities of Na<sup>+</sup> and OH<sup>-</sup> are restricted by the presence of Al species. When NaCO<sub>3</sub>, NaCl, NaCH<sub>3</sub>COO, and NaNO<sub>3</sub> instead of NaOH are employed as Na<sup>+</sup> source, condensation or crystallization does not proceed in the gels due to the lower pH.

Zeolite cannot be synthesized from the Na<sub>2</sub>O-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> gel without water by the vapor phase transport method. From this observation, it can be deduced that crystallization proceeds through the liquid phase transformation involving soluble species in the gels. To see the correlation between the solubility and the composition of the gel, the soluble portions in the gels are measured. The soluble portions are defined as follows. Distilled water of 20 g is added to the gel of 1.00 g dried at 110°C for 24 h. The mixture is put aside at room temperature for 24 h and centrifuged to remove the clear solution over the solid gel, and then dried at 110°C for 24 h. The soluble portion means the weight loss from this treatment. The amount of soluble portion of the gel is related

to the contents of Na and Al as shown in Table 3.

When the gel calcined at 500°C is used as the synthetic source for ZSM-5, the synthesis of ZSM-5 structure is successful. This implies that the density of the gel is not a controlling factor in zeolite synthesis.

## 2. Composition Effects

If gels have proper Al and Na<sup>+</sup> contents and basicity, the ZSM-5 structure is easily obtained from the gel of Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O in the presence of H<sub>2</sub>O vapor only. The cations in the zeolite frameworks compensate the negative charges on the aluminum-oxygen tetrahedra. In general one Na<sup>+</sup> cation is balanced by the negative charge of one Al site in the zeolite framework. But more than one cation per one aluminate anion are needed to compensate the negative charge balance in the early stage of the crystallization. Thus, crystallization can occur under the conditions that the contents of Na<sup>+</sup> and OH<sup>-</sup> ions are no less than twice of that of Al atoms in the solid phase [Kim et al., 1992].

Now, although enough alkali cations compared to the aluminum species exist in the gels, if the pH of the gel is lower than the relevant level, the gel is not changed into a crystal structure. In addition, solid state gels are extracted from the sol dissolved state due to the lower solubility at lower pH. It is considered that although the alkali cations balancing the negative charges have no activity for the formation of ZSM-5 structure at lower pH, these cations could be transformed into an active form at higher pH. This result is confirmed by a number of synthesis experiments, where the gels containing Na<sup>+</sup> cations supplied from NaCO<sub>3</sub>, CH<sub>3</sub>COONa, NaNO<sub>3</sub>, NaCl, and Na<sub>2</sub>SO<sub>4</sub> are used. No crystallization occurs in these gels due to the lower pH of the gels.

The zeolite structures obtained are sensitive to the amounts of Na<sup>+</sup> and OH<sup>-</sup> ions as well as Al species. Crystallization can occur in the gels consisting of only NaOH and SiO<sub>2</sub> in water vapor, although the gel has no Al species. However, crystallization does not progress without cations, with lower NaOH composition compared to the Al content in water vapor due to lower pH. From these results, it may be concluded that the presence of cations is essential for the crystallization and the activity of Na<sup>+</sup> is restricted by the Al species or by the lower pH in the gel. If the Al content is increased in the gel, the resulted structures are changed from magadiite to quartz, ZSM-5, mordenite and NaP1 in the presence of water vapor.

## 3. Amine Effects

The vapors of amine and water are transferred from the liquid solution into the micropores of the gels when the vessel is heated within the air-heated oven at 175°C. The existence of organic substances within the crystals formed can be confirmed by TGA experiment and <sup>13</sup>C NMR test. Besides these experiments, the vapor pressures and mole fraction of the vapor phase of amines at the synthetic condition can be simply calculated using relevant equations and data. The theoretical partial pressures of amines, e.g., PA and DPA, at the synthetic conditions, are 262 KPa and 35 KPa, respectively. And the mole fractions of PA and DPA in the vapor are 0.25 and 0.041, respectively. It is confirmed that water and amines are transferred from the liquid solution at bottom to the gel phase at upper position.

Besides acting as counterions to balance the zeolite framework charge, cations in a reaction mixture have a pronounced effect on both the nucleation and the crystal structure, morphology and its size [Szostak, 1989]. Crystallization occurs in regions where the number of Na<sup>+</sup> cations are no less than twice of that of Al

**Table 4. The cation effects on the zeolite synthesis at 175°C**

Upper phase (solid phase)	Lower phase (liquid phase)	Periods (day)	Product
Al free/8-27	H <sub>2</sub> O	3	magadiite
Al free/42-96	EDA or DAP, H <sub>2</sub> O	3	ZSM-48
Al free/42-96	EDA or DAP, H <sub>2</sub> O	7	tridymite
TEOS <sup>a</sup>	EDA, TPA, H <sub>2</sub> O	5	amorphous
	TEOS, TPAOH, H <sub>2</sub> O	4	ZSM-5
	Cab-O-sil, TPAOH, H <sub>2</sub> O	4	ZSM-5
	Cab-O-sil, TBAOH, H <sub>2</sub> O	3	ZSM-5(s) <sup>b</sup>
	Cab-O-sil, TEAOH, H <sub>2</sub> O	3	amorphous
TEOS	TPAOH, H <sub>2</sub> O	4	amorphous
TEOS, TPABr	H <sub>2</sub> O	4	amorphous
	TEOS, TPABr, H <sub>2</sub> O	4	amorphous
TEOS	TPABr, EDA, H <sub>2</sub> O	4	amorphous
	TEOS, TPABr, NH <sub>4</sub> OH, H <sub>2</sub> O	4	amorphous
	TEOS, TPABr, EDA, H <sub>2</sub> O	4	ZSM-5
	TEOS, TPABr, EDA, H <sub>2</sub> O	4	ZSM-5
TEOS, TPABr	EDA, TPA, H <sub>2</sub> O	3	ZSM-5

<sup>a</sup>tetraethyorthosilicate, <sup>b</sup>very poor crystalline

atoms. When the gel has the same number of Al atoms and Na<sup>+</sup> cations, they are not normally transformed into zeolite structures by the presence of water vapor [Kim et al., 1992]. Only the gel of 2.5/2.5 has changed into zeolite because the gel is basic enough by the addition of basic NaAlO<sub>2</sub>·1.5H<sub>2</sub>O. In particular, the activity of the cations balancing the negative charge at the lower Na<sup>+</sup> content or at lower pH can be enhanced by the supply of amine vapor to the gel. The reason for this is that the activity of Na<sup>+</sup> cations can be increased by the increased basicity. Also, the basicity of the gel can be increased by the amine vapors such as TPA, DPA, PA, and DAP as Kim et al. [1992] reported. The region of the gel compositions for crystallization is proportionally extended with the basicity of the amines.

However, the gel mixtures having no cation sources show no crystallization in the synthesis as shown in Table 4, even though various amines are supplied with water vapor. This indicates that amines do not replace the role of cations. ZSM-5 crystals can be successfully synthesized in the presence of TPAOH and SiO<sub>2</sub>. But the combination of TPABr and SiO<sub>2</sub> does not make any crystal because of the neutral pH. When EDA is supplied to the mixture, ZSM-5 can be formed. Tetrapropylammonium ion (TPA<sup>+</sup>) does not contribute to ZSM-5 synthesis in the neutral pH; however, this ion becomes active in the enhanced basicity by adding EDA or OH<sup>-</sup>.

There is one interesting question that the combination of EDA and TPABr works while the combination of NH<sub>4</sub>OH and TPABr does not as shown in Table 4. The reason for this is also most likely due to the effect of pH of reaction conditions. The protonated amines should be stable in the liquid phase to give the basicity at the elevated temperature. Comparing the high basicity (pH 10.5) and the high boiling point (118°C) of EDA with those of NH<sub>4</sub>OH, the EDA is very soluble and stable in the aqueous solution. In contrast, although the aqueous ammonia has high basicity (pH 10.5), the solubility of ammonia is very low due to its lower boiling point (-33.3°C). As a result, the increase in the basicity of the liquid phase is negligible. It is regarded that NH<sub>4</sub>OH cannot give basicity to the liquid phase within the gel. We also confirm that crystallization occurs in the condensed liquid phase within the pores of the gel. The presence of moisture and Na<sup>+</sup> cation, and basicity are needed for the crystallization.

**Table 5. The pH of the aqueous solutions of various amines**

Aqueous solutions (3.0 g amine + 1.0 g water)	pH
Ammonium hydroxide	10.5
Methylamine	11.10
Propylamine	10.5
Diethylamine	10.1
Dipropylamine	9.9
Tripropylamine	9.0
Ethylenediamine	10.4
Diaminopropane	10.8
Diaminobutane	9.9
Tetraethylorthosilicate	6.7

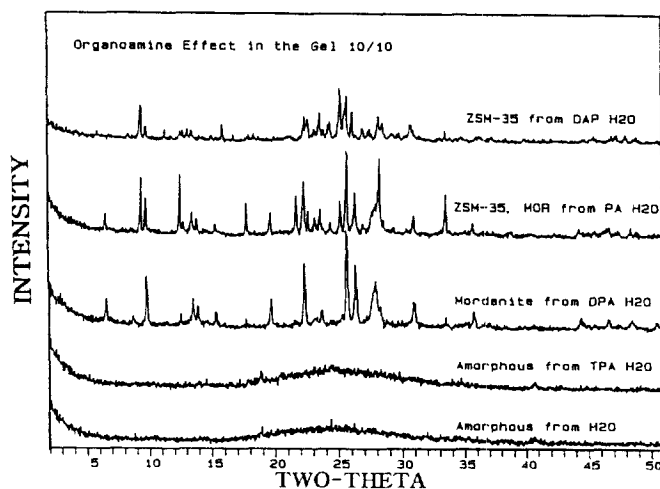
**Table 6. The amounts of DAP occluded in the ZSM-5 in the vapor-phase transport method**

Gel composition	wt%	Gel composition	wt%
40/40 <sup>a</sup>	7.3	80/80	3.86
40/20	6.1	20/80	4.46
40/10	5.6	10/80	4.86
40/5	5.6	5/80	5.50

<sup>a</sup>ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/ratio of SiO<sub>2</sub>/Na<sub>2</sub>O

The acidity of zeolite is coupled with the extent of polymerization, since it is known that the greater number of siloxane linkages and the fewer hydroxyl groups on the silicon atom, the stronger acidity [Szostak, 1989]. Theoretically, protonated tripropylamine cations can be formed by the reactions between the TPA in the vapor phase and the acid sites in the gels. A systematic experiment is carried out to investigate the effects of these protonated alkylamines. Although the gels contain the cations such as Na<sup>+</sup> and TPA<sup>+</sup>, the cations are inactive in the low pH or when the number of Al species included is greater than that of Na<sup>+</sup>. Under these conditions, the vapors of water and alkylamines such as TPA, DPA, PA, and DAP are supplied to the inactive gels, and crystallization occurs by the effects of organoamines. This means that amines can bring about significant changes to the gel conditions, although amines cannot play the roles of cations independently. There are three possible factors which can be exercised by the amines in the vapor phase transport method. The first one is the increased pH by the amines. The inactive Na<sup>+</sup> cations in the gels can be activated by the increased pH. Thus, crystallization can occur by the activated Na<sup>+</sup> cations. The amines giving higher pH (TPA < DPA < PA, DAP) can exert more positive effects to crystallization as shown in Table 5. The molecules of TPA, DPA, PA, and DAP have the lone pair electrons in the nitrogen atom. The driving force for protonation is proportional to the basicity of the amines. The basicity increases in the order of TPA, DPA, and PA. PA and DAP have small steric hindrance for the protonation and high solubility in water due to the hydrogen-bond.

The second one is the role of the protonated amine as weak cations. It is believed that the interaction between the protonated amine and gel is too weak to give the structure-directing effects, but the protonated amines could act as counterions to balance the negative framework charges of the Al atom sites. Thus, these protonated amines can be replaced with the inactive Na<sup>+</sup> cations balancing the negative framework charges. The incorporated a-

**Fig. 3. XRD patterns of the resulted materials from the gel (10/10) in the presence of different amines and water vapor.**

mines are detected by TGA as shown in Table 6.

The amines occluded in ZSM-5 channel structures are considered to be decomposed above the temperature 400°C. To see the relationship between the amount of DAP occluded in the ZSM-5 and the gel composition, a series of TGA experiments are carried out on the produced ZSM-5 in the presence of DAP and water vapor. The amount of the occluded DAP in the ZSM-5 structure is determined by measuring the weight loss between 320°C and 600°C. The water desorption is negligible in this region. To remove the adsorbed water effect on TGA, every sample is put in an oven at 110°C for 3 days and cooled down with sealing. The occluded amount of DAP is proportional to the Al content and disproportional to the Na<sup>+</sup> content. This means that the protonated DAP is employed as cations balancing the negative framework charges induced by tetrahedral Al sites. When the protonated amines are replaced with the inactive Na<sup>+</sup> balancing negative framework charges, the substituted Na<sup>+</sup> cations are changed into the active Na<sup>+</sup> cations in the synthesis. Crystallization may also occur by the substituted Na<sup>+</sup> cations.

The third one is the templating effect of the amine. If the molecular shape of the amine used is compared to that of TPA<sup>+</sup> cation that is believed to give the cation effect and the templating effect in the pure SiO<sub>2</sub> gels, the shape of TPA is the most similar to that of TPA<sup>+</sup> among DPA, PA, and DAP. However, the contribution of TPA is the smallest among the amines tested. Thus, the templating effect of the molecular shape and its size is less plausible. On the contrary, different structures such as moronite, a mixture of moronite and ZSM-35, and ZSM-35 are obtained from the same gel composition, when the different amines such as DPA, PA, and DAP are employed, respectively, as shown in Figure 3. Also, ZSM-48 structure can be synthesized with only diaminoalkane in the water-amine vapor-phase transport. These results admit following interpretations. That is, the difference in the pH level of amine results in the different structure. In other words, the structures resulted are changed from amorphous material to moronite, and ZSM-35 with increasing basicity. As a result, amino functional group having higher dipole moment is the major controlling factor in the vapor-phase transport method rather than the size and shape of the guest molecules.

## CONCLUSIONS

The condensation between the hydroxyl groups of the silicates or aluminosilicates occurs in the aqueous mixture of NaOH,  $\text{NaAlO}_2$ , and  $\text{SiO}_2$  at room temperature. The condensation seems to be promoted by the  $\text{Na}^+$  and  $\text{OH}^-$ . In other words, cations such as  $\text{Na}^+$  and  $\text{TPA}^+$  exert activities for the condensation under the relevant basic conditions. By comparison, the Al species restrict the activity of  $\text{Na}^+$  in the condensation. The surface area and pore size of the gel are decreased by the condensation at room temperature. The density of the gel phase does not affect the crystallization but the cation and its activity under basic conditions are the governing factors.

ZSM-5 structure can be easily synthesized from the mixture of  $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$  in the water vapor. When the gel has no cation sources, crystallization does not progress even if various amines are supplied with water vapor. The presence of cations and moisture in the gel is essential for crystallization. Crystallization can occur under the conditions that the content of NaOH ions is no less than twice of that of Al atoms in the solid phase. The cations can be restricted by Al atoms in the gel and activated in the basic aqueous solution. The resulted structure is sensitive to the  $\text{Na}^+$  content as well as Al content. With the increasing Al content, quartz, ZSM-5, mordenite, and NaP1 are formed in the presence of water vapor. Structure transform can occur by the added components in the presence of water vapor. Amine increases the pH of the gel, thus, the inactive cations for the crystallization can be activated by the supplied amine vapor such as DAP and PA,  $\text{H}^+$ ,  $\text{NH}_4^+$ , and the protonated amines cannot independently work as active cations. However, protonated amines could act as counterions to balance the framework negative charges. Comparing the shapes and sizes of amines to the structure obtained, the templating effect of amine is less plausible, whereas the molecules with higher dipole moment and appropriate dimension such as PA have higher effectiveness in zeolite synthesis. Thus, the results of Mintova and Valtchev [1993] are certainly in order.

## ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the

Korean Science and Engineering Foundation for this work.

## REFERENCES

- Dong, J., Dou, T., Zhao, X. and Gao, L., "Synthesis of Membranes of Zeolites ZSM-5 and ZSM-35 by the Vapor Phase Method", *J. Chem. Soc. Chem. Commun.*, 1056 (1992).
- Flanigen, E. M., "Introduction to Zeolite Science and Practice", Bekkum, H. Van, Flanigen, E. M. and Jansen, J. C., Eds, Elsevier, Tokyo, 28 (1991).
- Garwood, W. E., Dwyer, F. G. and Chen, N. Y., "Shape Selective Catalysis in Industrial Applications", Marcel Dekker, Inc., New York and Basel (1989).
- Gie, H. and Marler, B., "The Structure-controlling Role of Organic Templates for the Synthesis of Porosils in the System  $\text{SiO}_2$ /Template/ $\text{H}_2\text{O}$ ", *Zeolites*, **12**, 42 (1992).
- Howden, M. G., "Thermogravimetry of  $\alpha,\omega$ -Diaminoalkanes Used in Synthesizing ZSM-5", *Zeolites*, **13**, 315 (1993).
- Kim, M.-H., Li, H.-X. and Davis, M. E., "Synthesis of Zeolites by Water-organic Vapor-phase Transport", *Microporous Materials*, **1**, 191 (1992).
- Mintova, S. and Valtchev, V., "On the Crystallization Mechanism of Zeolite ZSM-5: Part 1. Kinetic Compensation Effect for the Synthesis with Some Diamines", *Zeolites*, **13**, 305 (1993).
- Moscou, L., Introduction to Zeolite Science and Practice, Bekkum, H. V., Flanigen, E. M. and Jansen, J. C., Eds, Elsevier, Tokyo, 1-8 (1991).
- Szostak, R., "Molecular Sieves" Van Nostland Reinhold, New York, NY, 73 (1989).
- Szostak, R., "Molecular Sieves" Van Nostland Reinhold, New York, NY, 143 (1989).
- Xu, W., Dong, J., Li, J., Li, J. and Wu, F., "A Noble Method for the Preparation of Zeolite ZSM-5 by the Vapor Phase Transport Method", *J. Chem. Soc. Chem. Commun.*, 755 (1990).