

THE ROLE OF AMINES AS TEMPLATES IN DIRECTING THE STRUCTURE OF ZEOLITES

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Abstract

In this article, we have investigated the role of dimethylamine (DMA), tributylamine (TBA), Triethanoleamine (TEA), Trishydroxymethylamine (TRIZMA), and Hexamethyleneterraamine (HMTA), in the formation of zeolitic compounds. The experiments were carried out in acidic and basic media using Si/Al<10 and Si/Al>10. The structure of the resulting synthetic zeolites were similar to Natro Davyne, ammonium sodalite, analcime, and mordenite. We also recognized that HMTA in basic media resulted in a new crystalline Compound.

Introduction

In the last two decades zeolites have played an important role in the petrochemical industry. Their regular structure of pores and cages cause them to act as good catalysts for conversion reactions, such as the methanol to gasoline (MTG) process by using ZSM-5 and SAPO's type, dehydrocyclooligomerization (conversion of low molecular weight of olefines and alkanes to aromatics [1] photocatalyzed oxidation of hydrocahons [2] and many more [3].

Therefore, the architecture of the zeolites remain a strategic point for scientists [4] The range of materials that can be utilized for this purpose are not restricted to positively charged species. Primary and secondary amines, diamines, alcohols, polyamines, alkanolamines, salt of organic acids and many other representatives of a variety of functional groups, have all been shown to be effective [5-18]. In this article we have studied the role of some secondary, tertiary and alkanolamines as directing

agents in zeolite structures.

Experimental Section

The sodium silicate solution (25.5-28.2% SiO₂, 7.5-8.5% Na₂O), aluminium hydroxide, sulfuric acid 98%, dimethylamine, tributylamine, triethanolamine, hexamethylenetetraamine were purchased from the Merck Chemical Company, trishydroxy methylamine was obtained from Sigma.

The crystallinity of materials were estimated from XRD patterns recorded on a Philips PW-1880 diffractometer, using Cu K_α radiation (Type of scan continuous, V= 40 KV, I= 30 mA). Vibration spectra were recorded by a Philips FT-IR, Pu 9800. TGA spectra were taken by TGA-2 Perkin Elmer (Heat rate 40°/min, chart speed 5 mm/min, T_{max} = 900°C, T_{in} = 50°C).

Preparation

In a typical reaction, the appropriate amount of sodium aluminate was slowly added to the mixture of sodium silicate, amine and distilled water under four different conditions (See Table 1). The resulting solutions were stirred to form a hydrogel, the reaction mixture (hydrogel) was then stirred for approximately 5 days at ambient temperature. Crystallization was carried out in 200 ml

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Table 1. Experimental conditions for systematic study

Condition	SiO ₂ /Al ₂ O ₃	Na ₂ O/Al ₂ O ₃	H ₂ O/Al ₂ O ₃	amine/Al ₂ O ₃	H ⁺ /Al ₂ O ₃
I	5.28	16.8	333	14.92	–
II	100	10	3700	43	–
III	100	10	3700	215	–
IV	100	10	3700	43	17.3

stainless steel autoclaves at a temperature between 140-180°C.

The reaction mixture was allowed to cool and the product was filtered, washed with a large amount of distilled water, and dried at 100°C.

Results and Discussion

According to the results of Table 2, Figure 1, when DMA and TBA were used as directing agents (runs 1,2), the products of these two runs were similar. In run 3, when no amine was used, the structure of the product was

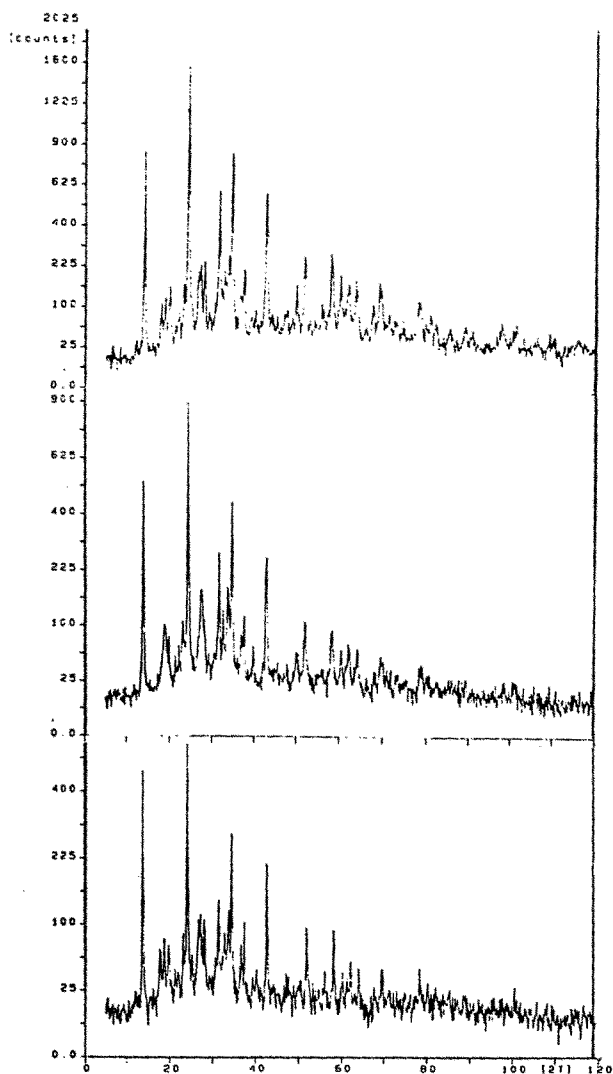


Figure 1. Comparison XRD spectra from runs 1 to 3 A) with DMA, B) with TBA, C) no amine.

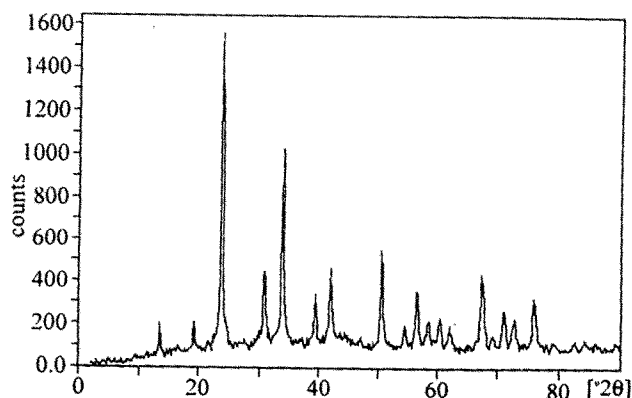


Figure 2. XRD Pattern of ZHM

exactly the same as run 1 and 2. (Fig. 1). Apparently DMA and TBA have no effect as directing agents on the zeolitic compound formation. The XRD pattern of run 4 was consistent with the pattern of the Natro Davyne type structure, and when TRIZMA was used, the XRD results were similar to the structure of ammonium sodalite.

Finally, when using HMTA, a new crystalline phase was formed. The XRD results are given in Figure 2. The TGA and FTIR are also shown in Figure 3 and 4, respectively.

Thermal decomposition patterns from 50°C to 750°C (Fig. 3) show two distinct weight losses for ZHM 50 ~350°C, 350 to 750°C. The first loss is due to desorption of water, the second from the decomposition of organic compound (amine).

According to the FTIR spectra (Fig. 4), the strong vibration mode at ~1000 cm⁻¹ is due to internal tetrahedral vibration of T-O stretching and the peak at ~400 cm⁻¹ is assigned to bending. Two bands in the region ~750-760 cm⁻¹ are related to the presence of double (D₄R) rings in

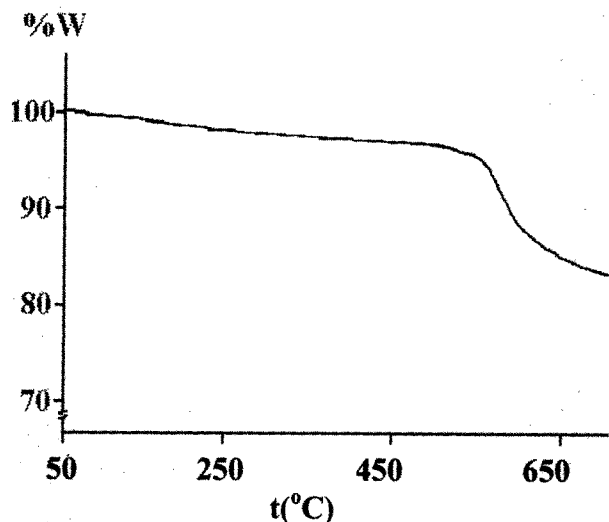


Figure 3. Thermogravimetric analysis of ZHM ($T_{in} = 50^{\circ}\text{C}$, $T_{max} = 750^{\circ}\text{C}$, heat rate $40^{\circ}\text{C}/\text{min}$, chart speed $10\text{mm}/\text{min}$)

the framework structures of as external linkages due to the symmetrical stretching of tetrahedral atoms. [19] The comparison of FT-IR spectra of HMTA in aluminosilicate beds are distinguishable.

The chemical analysis of this compound, which we have named ZHM, showed 34.41% SiO_2 , 25.32% Al_2O_3 , 20.2% Na_2O , 7.02% C, ~5.1% N and 7.62% H_2O . It's empirical formula on the basis of chemical analysis is $3.3 \text{Na}_2\text{O}$, $2.5 \text{Al}_2\text{O}_3$, 5.7SiO_2 , 1HMTA , $2.7\text{H}_2\text{O}$. In general according to three investigations we found a new compound with HMTA (ZHM). Preliminary XRD results showed body centered cubic for ZHM.

According to the results of Table 2, TEA, TRIZMA,

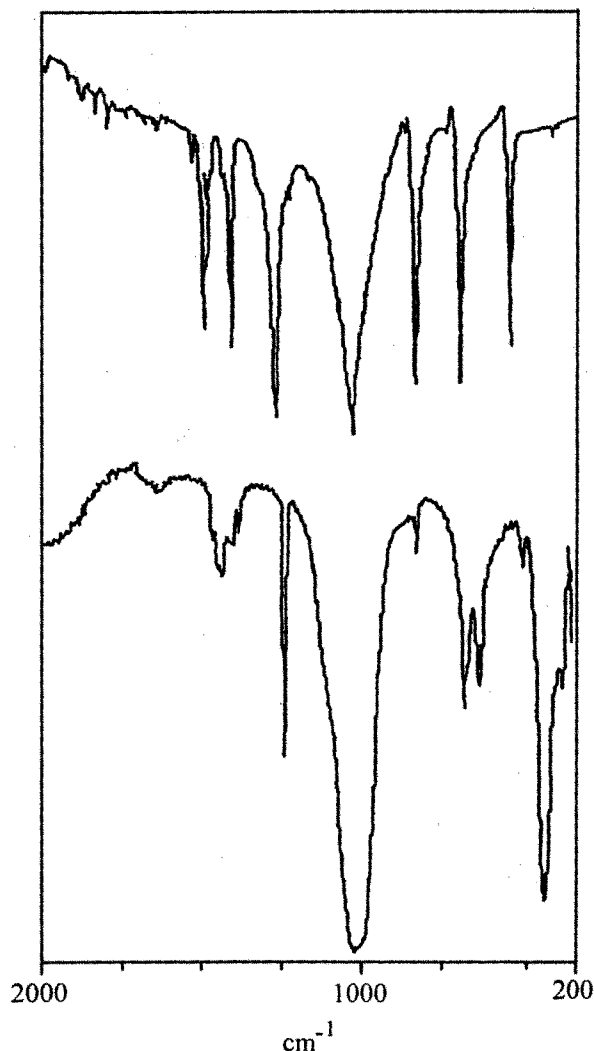


Figure 4. Framework i.r. spectra of A) HMTA, B) ZHM

Table 2. The effect of amine (Condition I) on product structure

Run	Organic Component	Crystalline Phase Obtained
1	DMA	a crystalline phase obtained ¹
2	TBA	same as above
3	no amine	same as above
4	TEA	a crystalline phase obtained ²
5	TRIZMA	a crystalline phase obtained ³
6	HMTA	ZHM (Cubic) ⁴

¹Similar to the crystalline phase of sodium aluminum cyanide hydrate

² Similar to the crystalline phase of the Natro Davyne

³ Similar to the crystalline phase of ammonium sodalite

⁴ ZHM (a new crystalline compound)

Reaction mixture= 10SiO_2 , $1\text{Al}_2\text{O}_3$, $16.8 \text{Na}_2\text{O}$, $333 \text{H}_2\text{O}$, 14.9amine , Temp. 140°C , Time 48h.

Table 3. The effect of amine (Condition II) on product structure

Run	Organic Component	Crystalline Phase Obtained	
		140°C	180°C
7	DMA	amorphous	analcime
8	TBA	amorphous	analcime
9	TEA	amorphous	analcime
10	TRIZMA	amorphous	analcime
11	HMTA	amorphous	amorphous

Analcime with formula $\text{NaAl}_2\text{Si}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$
 Reaction mixture: 100 SiO_2 , 1 Al_2O_3 , 10 Na_2O , 43 amine, 3700 H_2O
 Time: 48h

and HMTA are able to act as directing agents on the structure of crystalline compounds. Recently a special type of zeolite from the analcime family was synthesized using TEA which has an average size of 24μ .⁵

The results which are given in Table 3 indicate that by increasing the Si/Al ratio from 10 to 100, the type of amine has no role in the crystallization of the product. All solids formed after each run (7 to 11) were amorphous and by increasing the temperature from 140°C, the amorphous phase of run 7 to 11 converted to an analcime phase (Fig. 5), except for HMTA (run 11) which decomposed at this temperature, and therefore no crystalline phase was obtained.

According to the results of Table 4, in run (12-16) the

ratio of amine/ Al_2O_3 was increased to 215. DMA, and TBA had the same effect and the product in each case was analcime. But with alkanolamines, the product structures were similar to a wirakite type (cubic), Figure 6, and the product with HMTA was amorphous as mentioned earlier.

In addition, the effect of acid (H_2SO_4) on the reaction mixture was also investigated (Table 5). The XRD results of each solid product showed the formation of an amorphous phase and no crystalline compound was formed at 180°C. The amorphous phase changed to a crystalline phase as the temperature was increased to 220°C (Table 5).

Although using DMA and TBA yielded amorphous

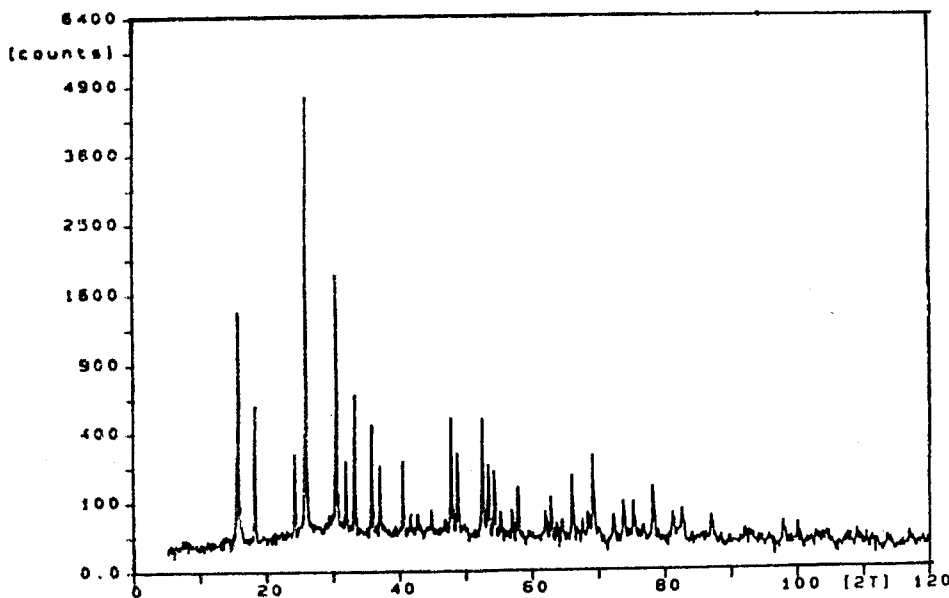


Figure 5. The XRD pattern of products of runs 7 to 11

Table 4. The effect of amine (Condition III) on product structure.

Run	Organic Component	Crystalline Phase Obtained
12	DMA	analcime
13	TBA	analcime
14	TEA	wirakite structure (cubic)
15	TRIZMA	wirakite structure (cubic)
16	HMTA	amorphous

Reaction mixture: 100 SiO₂, 1Al₂O₃, 10Na₂O, 215 amine, 3700H₂O

Temp: 180°C

Time: aging time 3 days, then kept in hydrothermal conditions for 2 days

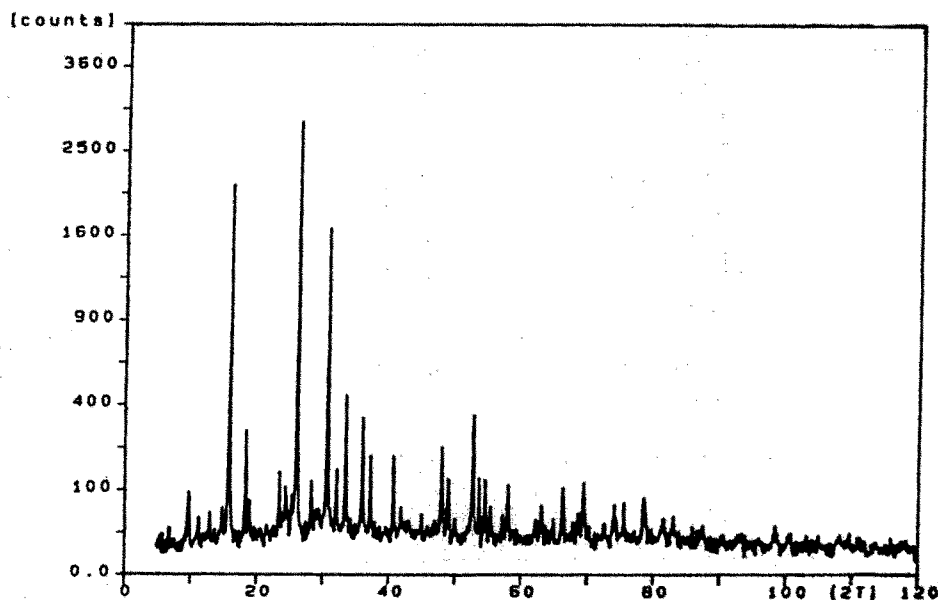


Figure 6. The XRD pattern of products of runs 14 and 15

Table 5. The effect of amine (Condition IV) on product structure.

Run	Organic Component	Crystalline Phase Obtained	
		180°C	220°C
17	DMA	amorphous	amorphous
18	TBA	amorphous	amorphous
19	TRIZMA	amorphous	mordenite+α Quartz
20	TEA	amorphous	mordenite+α Quartz
21	HMTA	amorphous	amorphous

Reaction mixture: 100 SiO₂, 1Al₂O₃, 10Na₂O, 43 amine, 17.3H₂SO₄, 3700H₂O

Temp: 140°C or 180°C

Time: aging time 3 days, then kept in hydrothermal conditions for 3 days

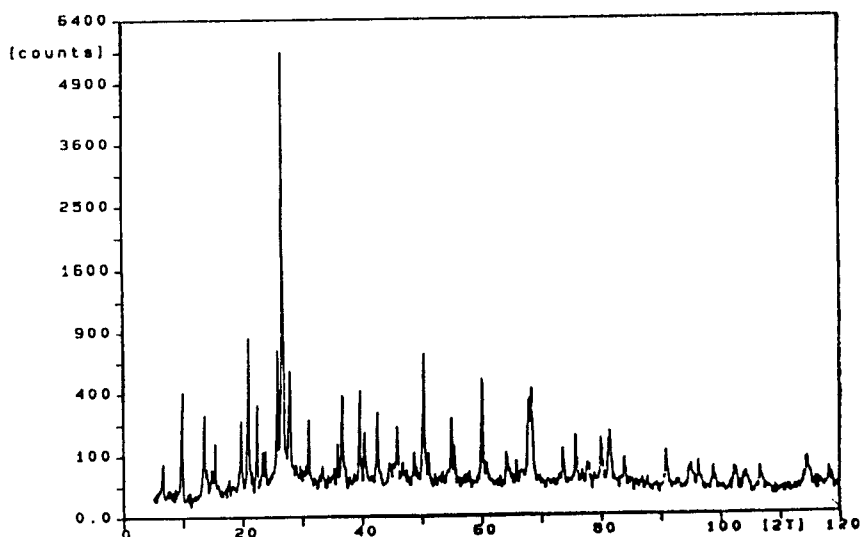


Figure 7. The XRD pattern of products of runs 19 and 20

products, with TRIZMA and TEA, a mixture of two crystalline products (mordnrite, α -Quartz) was obtained (Fig. 7).

Conclusion

1. DMA and TBA didn't show any effect on zeolite formation at low and high ratios of Si/Al, but alkanolamines such as TEA and TRIZMA act as directing agents at a Si/Al ratio equal to 10.

2. Using HMTA leads to the formation of a new crystalline phase of aluminosilicate since it is caged and symmetrical.

3. In order to reach a crystalline phase at a high ratio of Si/Al (~100) more energy (high temp). is needed than at a low ratio.

It can be concluded that alkanolamines (TEA, TRIZMA, and symmetrical type amine (HMTA) can act as directing agents in the formation of Crystalline Compounds.

Supporting Information Available

Comparison Table for XRD data of run 4 with d_{ASTM} of Natro Davyne Type Zeolite, run 5 with ammonium sodalite, runs 7 to 11 with analcime and 14, 15 with virakite and the results of run 6 can be obtained by corresponding with the authors.

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