

The Synthesis of Zeolites A, X and HS from Natural Iranian Kaolinite and the Study of the Transformation of Zeolites X to HS and Zeolites Y to P by X-ray diffraction and Scanning Electron Microscopy.

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Abstract

Zeolites A, X and HS were synthesized from natural Iranian Kaolinite by alkaline fusion, followed by refluxing the mixture. The transformation of zeolites X to HS and Y to P were studied at different time intervals by X-ray diffraction and Scanning Electron Microscopy (SEM). It was revealed that in solution, zeolites HS and P are more stable than zeolites X and Y respectively.

Introduction

The silica and alumina tetrahedra are combined into more complicated secondary units, which form the building blocks of the framework zeolite crystal structures. The tetrahedra are arranged so that the zeolites have an open framework structure, which defines a pore structure with a high surface area. Zeolites have been used as water softeners and cation exchangers, as well as vehicles for the separation of molecules according to shape and size called molecular sieves. Zeolites have been employed as industrial catalysts and recently have led to new developments in shape selective heterogeneous catalysis. (1-4)

Zeolites are formed by hydrothermal synthesis, typically under mild conditions. Zeolite can be formed either by reactive aluminosilicate or by clay minerals as kaolinite. Reports⁵ on kaolinite reveal that zeolite is formed by mixing activated kaolinite and sodium hydroxide at 100°C (hydrothermally). The yield of reaction is around 50-80% and reaction time is considerable.

Here we report, the preparation of zeolites X, A and HS from natural Iranian Kaolinite by alkaline fusion followed by refluxing the mixture and also zeolites Y and P were prepared from Hamedan silica. These processes revealed that temperature and pH are important factors in product formation. Furthermore, the transformation of zeolite X to HS, and Y to P were studied by X-ray

diffraction (XRD) and Scanning Electron Microscopy (SEM).⁶

Experimental Section

Starting Materials

The kaolinite which has been used for the synthesis of zeolites is a natural kaolinite of Salafchehen (Anal. Calcd: SiO₂ 70%. Al₂O₃, 26%; Fe₂O₃ < 1% with a trace amount of CaO and MgO). XRD spectra revealed the presence of some silica (α - Quartz).

The silica which has been used is named Hamedan silica (α - Quartz, with 98% purity).

In order to increase purity, it was washed twice with (1:1) hydrochloric acid.

Instrumentation:

All X-ray diffraction spectra of synthesized zeolites were obtained by X-ray diffraction (Philips, with Cu - Tube). The pictures of zeolites Y and P were taken with a Scanning Electron Microscope.

Methods

Preparation of Zeolite X, Na₈₆(AlO₂)₈₆(SiO₂)₁₀₆ 26H₂O

For the preparation of zeolite X, natural kaolinite was mixed with sodium hydroxide at a weight ratio of (1 to 2.5). The mixture was heated to 500 °C, then cooled and distilled water was added at a weight ratio of (5 to 1). Again the

mixture was heated to the boiling point and then sodium hydroxide solution 1N was added (pH, 12–14). The mixture was refluxed for 2½ hrs, and a white solid product was obtained. It was washed with distilled water and dried. The XRD spectra (Table 1) shows the formation of zeolite X with high purity (yield ~ 100%)

Preparation of Zeolite A, Na₁₂(AlO₂)₁₂(SiO₂)₁₂ 27H₂O

The starting materials and the method of experimentation for the preparation of zeolite A were similar to the preparation of zeolite X, except when heated no sodium hydroxide was added. Distilled water as a weight ratio of (20 to 1) was added to the mixture, and then it was refluxed for 1½ hrs. The product was washed and dried. The XRD spectra (Table 2) shows the formation of zeolite A with a high purity content (yield ~ 100%).

Preparation of Zeolite HS, Na₆(AlO₂)₆(SiO₂)₆ 7.5H₂O

Preparation of zeolite HS is similar to the zeolite A, except that after alkaline fusion, the melted material was diluted with water and then hydrothermally crystalized (2 – 7 days). The crystals were washed several times with distilled water and dried. The XRD spectra (Table 3) shows the formation of zeolite HS with high purity (yield ~ 100%).

Results and Discussion

As mentioned before, kaolinite is one of the starting materials, which can be used for the preparation of zeolites. According to literature⁵, kaolinite is usually mixed with sodium hydroxide and zeolite A is formed. When 10 grams of Natural Iranian Kaolinite (N. I. K) was mixed and heated (refluxed) with different concentrations of sodium hydroxide (1, 2.5, 3.75 moles) at different time intervals,

14.47	3.83	5.74	8.8	d _{exp}
14.465	3.808	5.731	8.845	d _{ASTM}
100	21	18	18	I

Table 1: Comparison of experimental data and ASTM data for Zeolite X

12.26	2.98	3.70	8.66	d _{exp}
12.29	2.987	3.714	8.71	d _{ASTM}
100	55	53	69	I

Table 2: Comparison of experimental data and ASTM data for Zeolite A

6.28	2.09	2.57	3.64	d _{exp}
6.28	2.10	2.56	3.63	d _{ASTM}
80	80	80	100	I

Table 3: Comparison of experimental data and ASTM data for Zeolite HS

the XRD spectra revealed that zeolite was not formed, and kaolinite was not changed. In another experiment, when kaolinite was heated to (500° – 600°C) and (925° – 950°C) a weight loss of about 13.5% occurred and the XRD shows that metakaolinite I and II were formed. When metakaolinite I and II were refluxed with sodium hydroxide, zeolite was not formed even after considerable time. By adding sodium hydroxide or a mixture of sodium silicate and sodium aluminate, again no zeolite formation occurred.

As a result of this, it was realized that the kaolinite crystals (layered silicate) converted by alkaline fusion to an amorphous aluminosilicate gel and then after refluxing different types of zeolites are formed.

Transformation of Zeolite X to HS

During the formation of zeolite X, samples were taken from the reaction flask at different time intervals. After washing and drying, the XRD spectra were studied (Fig.1). The results revealed that zeolite X is gradually transformed to zeolite HS.

Inspection of the spectra revealed that, the peak intensity of zeolite X decreased as time increased and the peak intensity of zeolite HS gradually increased. During a period of 0–48 hrs. no transformation of zeolite X was observed, but after 48 hrs. transformation of zeolite

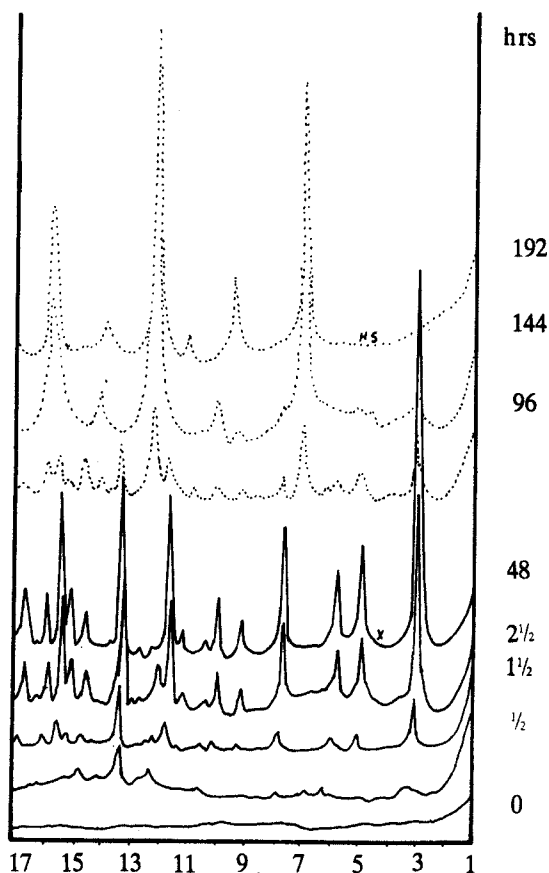


Fig. 1: Transformation of zeolite X to HS at different time intervals.

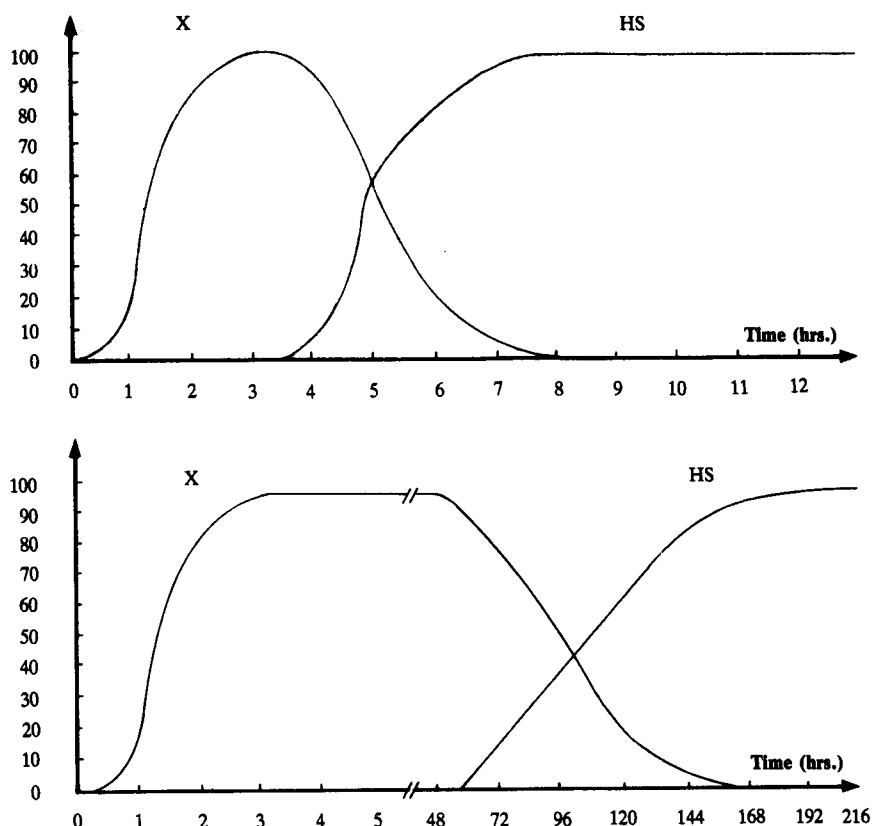


Fig. 2: Rate of crystallization of zeolite X and HS are shown, A: By refluxing method, B: By hydrothermal method

X occurs, and finally after 192 hours, only zeolite HS remains in the solution.

In Fig. 2 (A,B), the rate of crystallization of zeolites X and HS versus time are shown in refluxing and hydrothermal condition respectively.

On the basis of kinetic study on phase transformation it was found that zeolite HS was a more stable phase relative to zeolite X in solution. In fact, building units of zeolites X and HS are sodalite cages. When sodalite cages are joined together by hexagonal faces, zeolite HS with 2.2 Å pore size is formed and when they join by hexagonal prisms, zeolite X is formed. Because of this it is possible for zeolite X to transform to zeolite HS.

It was also observed that when zeolite X (solid form) was heated to 700°C or more, no change in the crystal structure resulted.

In addition to this, it was found that when zeolite X was refluxed in an approximately neutral solution (pH 9) no change in the crystal structure occurred. As a result, it may be said that the transformation of zeolite X to HS occurs in an alkaline solution.

Study of the Transformation of Zeolite Y to Zeolite P

In this study, Hamedan silica (α-Quartz) was used for the preparation of zeolite Y. First attempts were made to mix silica, sodium aluminate and sodium hydroxide (hydrothermally) according to the references (7,8). The XRD spectra show no zeolite was formed. Therefore, silica

was converted to sodium silicate and then according to the ratios of table (4), they were mixed at 20° to 70° C.

SiO ₂	
—	9 - 12
Al ₂ O ₃	
Na ₂ O	
—	1 - 11
SiO ₂	
H ₂ O	
—	150 - 300
Na ₂ O	

Table 4

The XRD spectra showed that, the gel of aluminosilicate completely crystallized and the product was a mixture of two different types of zeolites, similar to Y and P which are formed by amorphous aluminosilicate gel reaction (1,2).

$$\text{NaAlO}_2 + \text{Na}_2\text{SiO}_3 (\text{aq}) \xrightarrow{25-70^\circ\text{C}} \text{Na}_a (\text{AlO}_2)_b (\text{SiO}_2)_c$$

$$\text{NaOH} \cdot \text{H}_2\text{O} (1) \text{Na}_a (\text{AlO}_2)_b (\text{SiO}_2)_c, \text{NaOH} \cdot \text{H}_2\text{O} \xrightarrow{80-100^\circ\text{C}} \text{Na}_6 (\text{AlO}_2)_6 (\text{SiO}_2)_6 \cdot 15\text{H}_2\text{O} (\text{Zeolite P}) + \text{Na}_{56} (\text{AlO}_2)_{56} (\text{SiO}_2)_{136} \cdot 25 \text{H}_2\text{O} (\text{Zeolite Y}) (2)$$

* (a,b,c) are unknown factors which depend on the chemical composition of the gel.

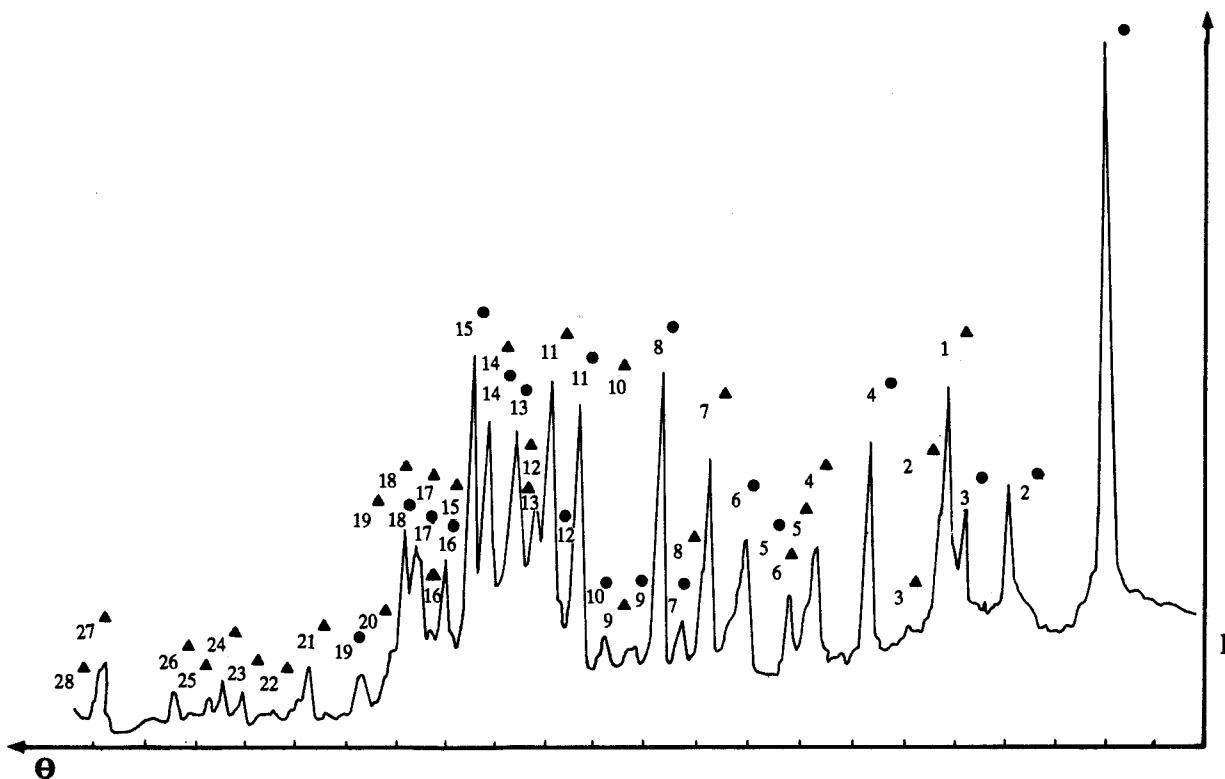


Fig. 3: XRD spectra of the mixture of zeolite Y and P (peaks of zeolite Y and P are labeled by ● and ▲ respectively).

Peak No.	⁴ Exp	⁴ ASTM	I	hkl
1	14.4	14.29	100	111
2	8.8	8.75	9	220
3	7.4	7.46	24	311
4	5.7	5.68	44	331
5	4.76	4.76	23	511,333
6	4.35	4.38	35	440
7	3.9	3.91	12	620
8	3.77	3.775	47	533
9	3.57	3.573	4	444
10	3.45	3.466	9	711,551
11	3.32	3.30	37	642
12	3.22	3.222	8	731,553
13	3.03	3.024	16	733
14	2.9	2.917	21	822,640
15	2.85	2.858	48	751,555
16	2.76	2.767	20	840
17	2.7	2.717	7	911,753
18	2.64	2.638	19	664
19	2.59	2.595	11	631

Table 5: Comparison of experimental data of zeolite Y (Fig. 3) with ASTM data for zeolite Y

The XRD pattern reveals the presence of both zeolite Y and P in solution (Fig. 3, Table 5,6).

At this time, attempts were made to observe and record zeolite crystallization. During this study, samples were taken at different time intervals (0, 1, 2, 3, 8, 14, 25, 30, 48, 96, 120, 144, 168, 192 and 216 hrs). Then their XRD spectra were studied. These spectra revealed that no crystallization

occurred during a (0 – 24) hr. period and the mixture was an amorphous aluminosilicate gel. Crystallization began after 30 hrs. and zeolites Y and P formed together after 48 hours. One interesting point is that zeolites Y and P are formed together during the reaction time, and at the end of the reaction, zeolite P was the final product in the solution (Fig. 4).

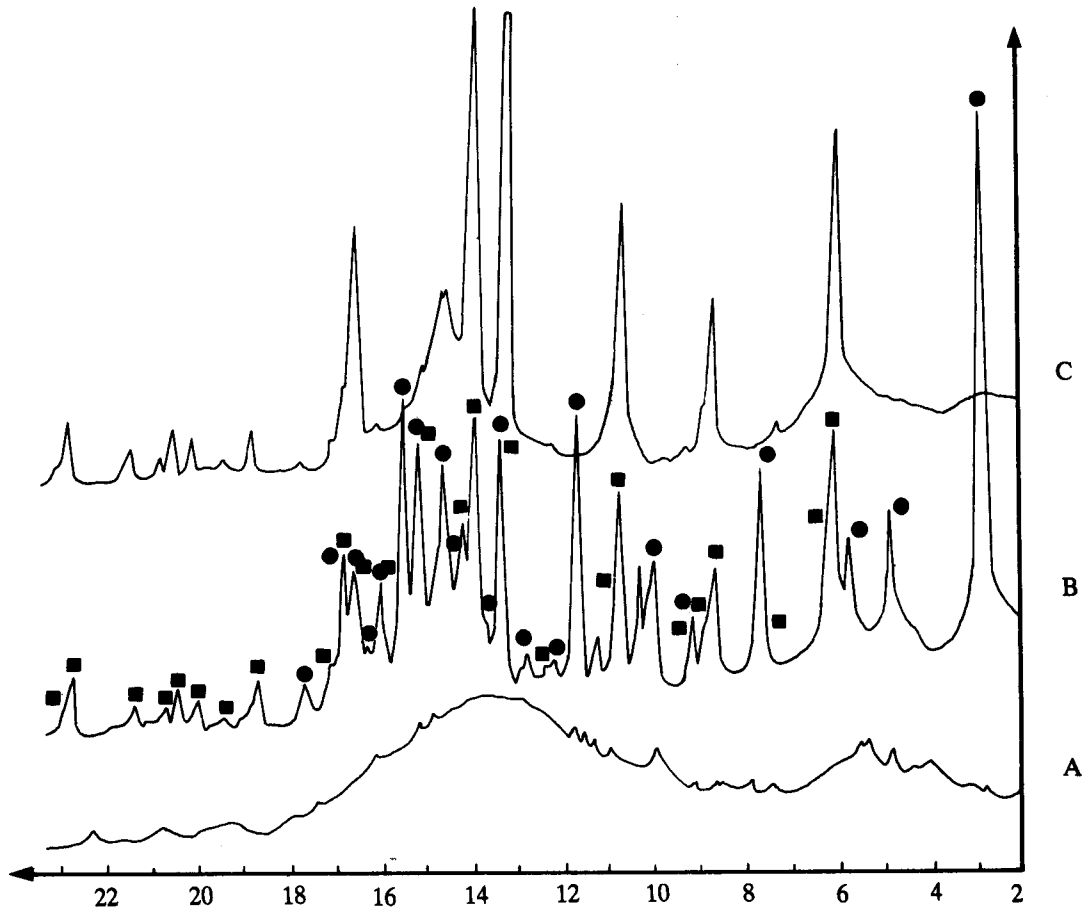


Fig. 4: XRD Spectra of zeolite X at different time intervals; A: At the beginning of crystallization; B: after 48 hrs. zeolites Y and P are formed; C: After 192 hrs. zeolite P (Peaks of zeolites Y and P are labeled by ● and ■ respectively).

Peak No.	d_{Exp}	d_{ASTM}	I	hkl	Peak No.	d_{Exp}	d_{ASTM}	I	hkl
1	7.15	7.132	85	110	15	2.77	2.776	3	302
2	7.05	7.047	83	101	16	2.75	2.750	5	203
3	5.8	5.776	5	111	17	2.69	2.694	46	321
4	5.05	5.048	51	200	18	2.67	2.679	28	312
5	4.92	4.914	26	002	19	2.65	2.653	21	313
6	4.5	4.420	8	102	20	2.54	2.531	6	400
7	4.1	4.108	94	211	21	2.4	2.435	5	322
8	4.05	4.049	22	112	22	2.16	2.387	4	104
9	3.25	3.527	4	202	23	2.24	2.257	2	430, 402
10	3.30	3.328	18	212	24	2.19	2.206	2	421
11	3.19	3.194	100	310	25	2.15	2.159	2	214
12	3.11	3.117	64	103	26	2.05	2.055	1	422
13	3.03	3.036	10	311	27	1.98	1.982	2	510
14	2.9	2.979	5	113	28	1.96	1.966	2	413

Table 6: Comparison of experimental data of zeolite P (Fig. 3) with ASTM data

The results in table 7 are obtained from the crystallization of zeolite Y and P at different time intervals.

When the crystallization of zeolite Y was studied by SEM, it was observed that when zeolite Y is formed, its crystal is octahedra (micrograph 1) and the size of the

crystal is 10μ ($1 \mu = 1 \times 10^4 \text{ \AA}$). It is possible that zeolite Y crystals transform into zeolite P crystals which are spheres (micrograph 2). Finally, at the end of the reaction only zeolite P existed in the reaction flask (micrograph 3). The size of crystals were 10μ .

Zeolite Y	The rate of crystallization		Time of crystallization (hrs)
	Zeolite P		
72%	28%		48
65%	35%		72
60%	40%		96
40%	60%		144
20%	80%		168
0%	100%		192
0%	100%		216

Table 7

Reports⁹ state that zeolite Y and P may form in the same overall composition field, but the type of reactant silica seems to control which species nucleates.

By XRD spectra and SEM it can be observed that zeolite Y transforms into zeolite P in solution. In fact zeolite P has a more stable phase than zeolite Y.

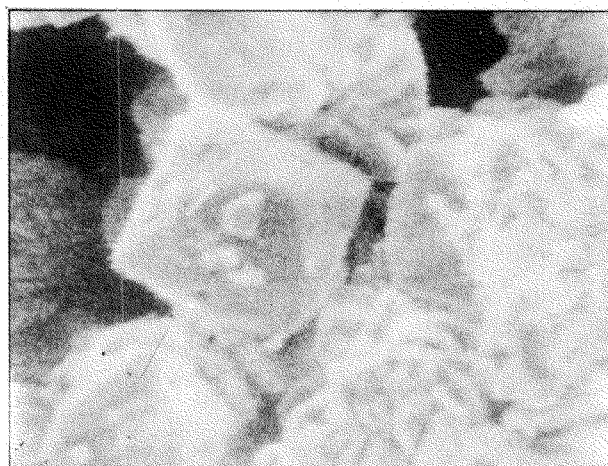
Conclusion

In comparison, the methods which have been used for zeolites X, A and HS, and the reactant for the preparation of these zeolites are the same, the only difference being the concentration of sodium hydroxide and experimental conditions. It should be mentioned that the alkaline fusion method has some advantages over the other procedures which are:

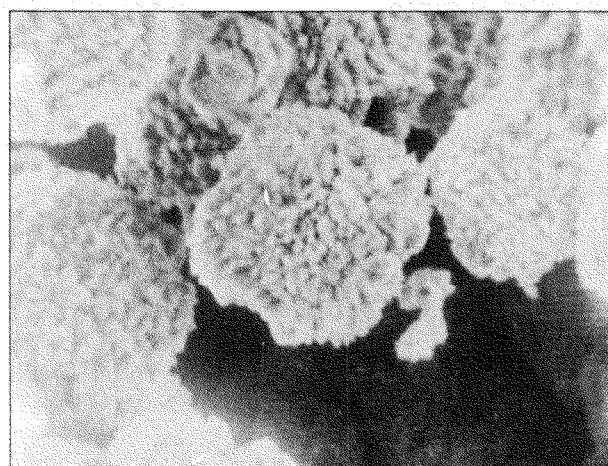
- A. increase in the yield of product.
- B. the formation of different types of zeolites.
- C. shorter reaction time, and finally it was found that zeolite HS and P have a more stable phase than zeolites X and Y respectively.

References

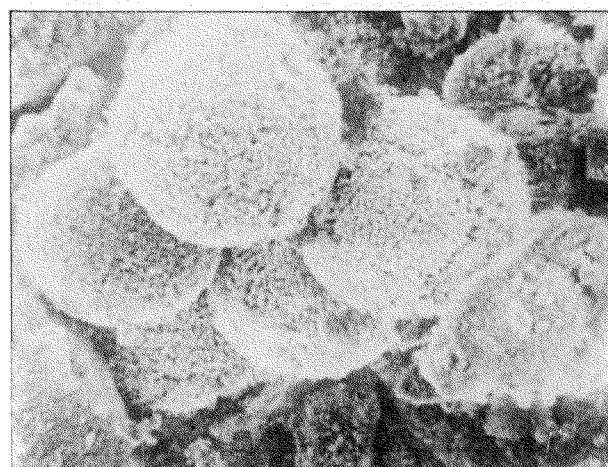
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8. Ref. 1, p. 278.
9. Ibid, p. 277 - 279 and references therein.



Micrograph 1 (2000X)



Micrograph 2 (2000X)



Micrograph 3 (2000X)