



Trade Science Inc.

# Materials Science

An Indian Journal

## Full Paper

MSAIJ, 2(6), 2006 [250-253]

### Synthesis Of High Aluminum Zeolite X With Domestic Resources



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Received: 19<sup>th</sup> December, 2006Accepted: 3<sup>rd</sup> January, 2007Web Publication Date : 27<sup>th</sup> December, 2006

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#### ABSTRACT

High aluminum zeolite 13X with Si/Al molar ratio between 1 and 1.1 was synthesized from mixing sodium aluminate and sodium silicate solutions at temperatures 70 - 100°C. Effects of aging, temperature and composition of the reaction mixture on the formation of zeolite X were investigated. The crystalline product was characterized by scanning electron microscopy, X-ray diffraction and chemical analysis. In this work, attempts were made to synthesis high aluminum zeolite X suitable for use in separation and ion-exchange processes. © 2006 Trade Science Inc. - INDIA

#### KEYWORDS

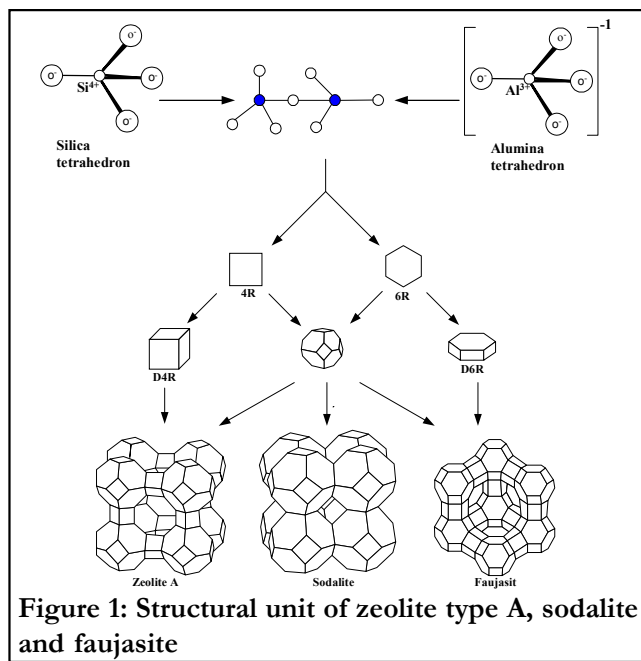
High aluminum;  
 Zeolite 13X;  
 Molecular sieve.

#### INTRODUCTION

Zeolites are porous crystalline aluminosilicates of regular skeleton structures formed by alternating silicon-oxygen and aluminum-oxygen tetrahedrons. The negative charges of aluminum-oxygen tetrahedron are compensated with cations, which are not rigidly fixed to the skeleton of zeolite so that they are capable of interchanging. Silicon-oxygen and aluminum-oxygen tetrahedrons in the zeolites of the type A, X and Y form a complex structural unit of cubooctahedron. The combination of such units

forms the structure of type A, X and Y<sup>[1]</sup>. The difference between them consists in the fact that they are interconnected by means of different number of member rings (i.e., eight membered ring(A), twelve membered ring (X, Y)) (Figure 1). The chemical difference of zeolites is defined by the ratio of Si/Al. For zeolite A this value is in the range of 0.95-1.05 and for faujasite (X, Y) 1-3. Zeolites A, X and Y are the most important ones to be used in industry.

Zeolites with different structure are known to be obtained by synthesis<sup>[2-6]</sup>. Zeolites are either synthesized from aluminosilicate hydrogel or by con-



version of clay minerals. The hydrogel can be prepared from different sources of silica and alumina.

The types of starting materials and the method of mixing them, determine the structure of the resulting gel.

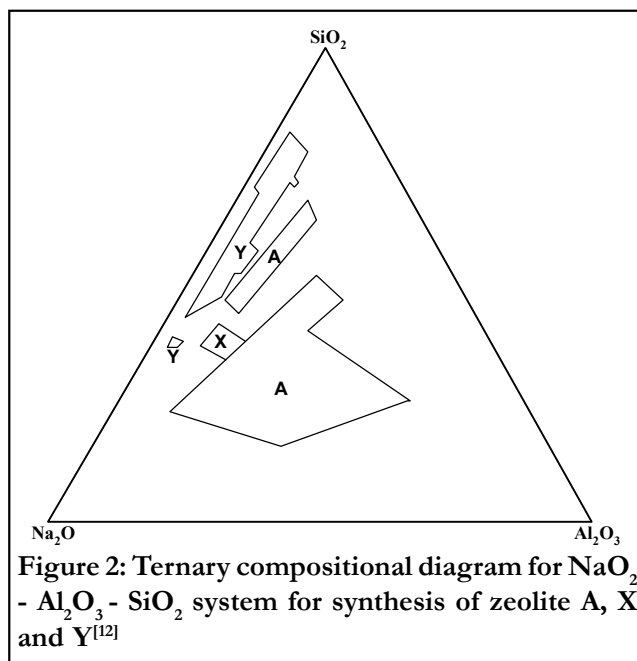
The nature of the gel, influences the rate of the subsequent crystallization, which affects the particle size distribution, and the formation of impurities<sup>[7]</sup>.

Zeolite X is widely used in many applications such as separation of gases in permanent gas-flow<sup>[8]</sup>, air cleaning, natural gas sweetening, mercaptane-elimination<sup>[9]</sup> and especially in detergents as a water-softening builder<sup>[10]</sup>.

In detergents as water softening agent zeolite A is normally used in combination with another softening agent such as sodium tripolyphosphate (STPP).

These softening agents are needed to remove hardness ions (calcium, magnesium and iron). Zeolite A is ineffective for removing large ions (magnesium) due to its small pore size. High aluminum (low silica) zeolite X that is called LSX has a larger pore size than zeolite A and is suitable to remove large hardness ions from aqueous solution. It is also reported that the mixtures of zeolites A and X, containing an appropriate weight percent of each, exhibit a synergistic effect in the sequestering by ion exchange of calcium and magnesium ions in hard water<sup>[11]</sup>.

By decreasing Si/Al ratio of starting mixture,



region in which crystallization of zeolites A and X overlap was approached (Figure 2). In this work attempt was made to selectively synthesis zeolite X. For this purpose, effects of a number of parameters such as: i) aging, ii) crystallization temperature and iii) composition of starting reaction mixture were investigated.

## EXPERIMENTAL

### Reagents

Reagents used in this work were sodium silicate (water glass) with  $\text{Na}_2\text{O}$ :  $2.9\text{SiO}_2$  molar ratio, aluminum hydroxide (57.7 wt%  $\text{Al}_2\text{O}_3$ , 1.65 wt%  $\text{Na}_2\text{O}$ ) and sodium hydroxide (98%).

The sodium, silica and aluminum content of the reagents were analyzed by following methods:

-Silica and sodium in water glass (UOP - method 627-85)

-Aluminum in molecular sieves or catalysts (UOP - method 633-82)

### Zeolite synthesis

The reaction mixture was prepared by adding the sodium silicate solution (5.23 wt%  $\text{Na}_2\text{O}$ , 8.67 wt%  $\text{SiO}_2$ ) to the sodium aluminate solution (4.11 wt%  $\text{Na}_2\text{O}$ , 2.46 wt%  $\text{Al}_2\text{O}_3$ ) under vigorous agitation.

The hydrogel was stirred vigorously for 30 min-

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utes to produce a homogeneous mixture. The mixture was then aged for 4 - 20 hours at temperatures ranging from 20 to 50°C. The mixture was transferred into an autoclave and kept in an oven at temperature 70 - 100°C. Crystallization was continued until completion, the crystalline solid product was filtered, washed with plenty of distilled water until the pH of the filtrate was below 10. The solid sample was left in an oven at temperature of 120°C over night.

### Characterization

Philips X-ray diffractometer model PW 1840 (Cu K $\alpha$ , APD - software package and JCPDF - search files) were used for the qualitative phase analysis, determinations of the degree of crystallinity and unit-cell dimensions. The data obtained were evaluated by ASTM methods (D 3942 and D 5357) using reference samples.

Micrographs were taken using a Cambridge Stereoscan scanning electron microscope model 360. Particle size analysis of the same samples was done by Cambridge Image Analyzer model Quantimet 570.

Ion exchange capacity was also measured by the standard test method, D1782 (11.02), ASTM.

## RESULTS AND DISCUSSION

### Aging

It was found that a preliminary aging of the reaction mixture at temperatures ranging from 20 to 50°C followed by subsequent crystallization at higher temperature improved the crystallization process<sup>[13]</sup>. Aging of the gel at 25°C for 20 hours and then crystallization at 100°C for 5 hours prevented the formation of zeolite A and yielded a zeolite X with high purity and crystallinity.

Stirring reaction mixture during aging time significantly decreased the required synthesis time.

### Crystallization temperature

Larger crystals were formed at high temperature. This effect implies that temperature affect the crystal growth rate.

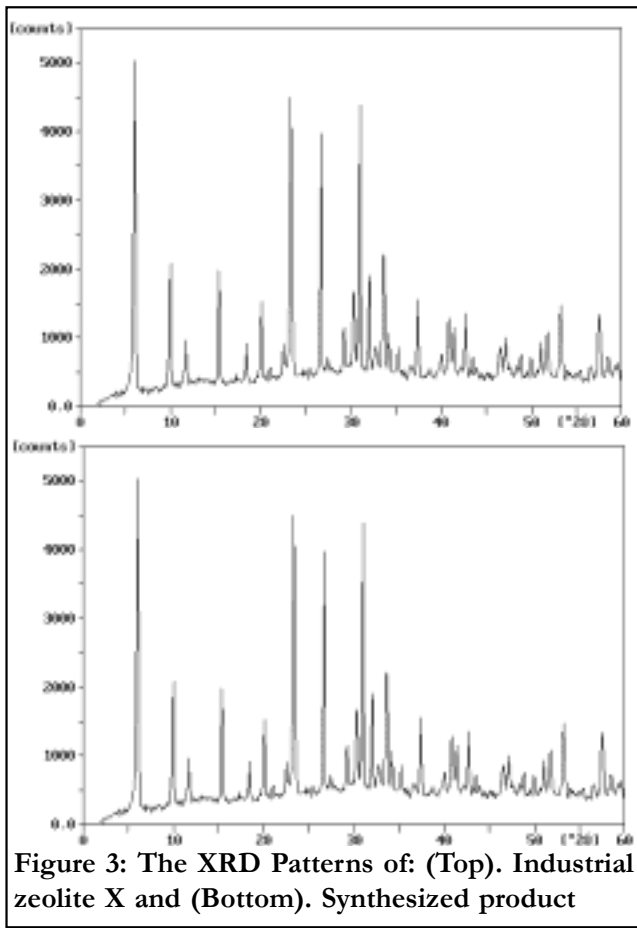


Figure 3: The XRD Patterns of: (Top). Industrial zeolite X and (Bottom). Synthesized product

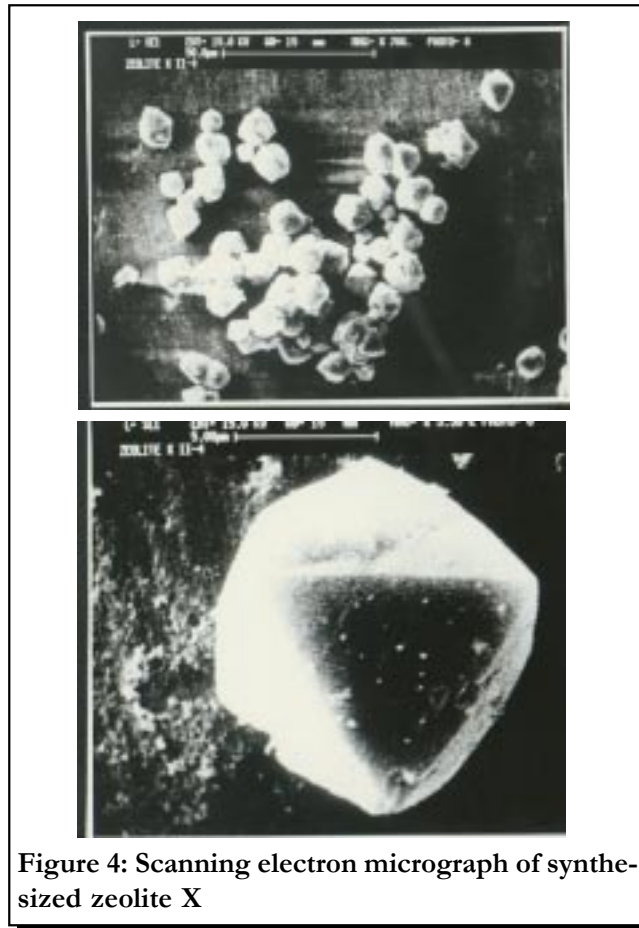


Figure 4: Scanning electron micrograph of synthesized zeolite X

Since zeolites with the most open structures nucleate at low temperature, it was observed that pure zeolite X crystallizes below 75°C easily. At higher temperature, the crystallization time decreased but zeolite A appeared in the final product. Crystallization temperature affected the selectivity of zeolite X formation.

### Composition of the starting reaction mixture

The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio in the starting reaction mixture significantly influenced the Si/Al ratio of the product. Pure zeolite X with Si/Al molar ratio between 1 and 1.1 was prepared from the reaction mixture having SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 2.5 - 3.5. In this condition it was observed that increasing H<sub>2</sub>O/Na<sub>2</sub>O molar ratio in the reaction mixture, decreased the formation of zeolite A. It was also found that decreasing Na<sub>2</sub>O/SiO<sub>2</sub> molar ratio had the same effect.

### CONCLUSION

Pure zeolite X was synthesized at temperature less than 75°C. At higher temperatures, formation of zeolite A as a co-existing phase occurred in the final product. Selective formation of zeolite X was controlled by factors, which affect the nucleation step. The aging of the synthesis medium at temperature less than 50°C considerably increased nucleation rate. The aging also shortened the crystallization time at higher temperatures.

Pure high aluminum X zeolite with the Si/Al molar ratio of 1.08 and with a unit cell parameter of 2.499 nm was obtained<sup>[14]</sup> from the reaction mixture of the following ratios:

4.5-5.5 Na<sub>2</sub>O : Al<sub>2</sub>O<sub>3</sub> : 2.5-3.5 SiO<sub>2</sub> : 250-400 H<sub>2</sub>O

The final product had a mean particle size of 5.9 mm and showed higher relative crystallinity than that of industrial one (Figure 3).

SEM of the sample is shown in figure 4. Ion exchange capacity of the sample was 140 mg CaO / g of zeolite.

### ACKNOWLEDGEMENT

We would like to acknowledge our thanks to Mr. A. Abbasi and Mr. A. Jebreili Jolodar for their help in this work.

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