



SYNTHESIS OF P_B ZEOLITE FROM SODIUM ALUMINO SILICATE GEL

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ABSTRACT

The P_B Zeolite has wide variety of application include separation and recovery of normal paraffin hydrocarbons, catalysis of hydrocarbon reactions, drying of refrigerants, separation of air components, carrying catalysts in the curing of plastics and rubber, removing radioactive ions from radioactive waste solutions. The mixture of two solutions of sodium silicate and sodium aluminate is carried out to obtain homogeneous gel. After continuous stirring and separating water, the discontinuous crystallization is carried out and particle size is controlled. We observed that the mixture is a thick milky gel. After processing, the gel is crystallized into smooth white fine powder. From XRD, IRS and EM Graphs it is clear that the sample is P_B type Zeolite. Comparing the results with standard characteristic spectrum, the material can be identified and value of lattice parameter is determined which shows good agreement with the reported value.

Key words: Zeolite, Sodium slumino silicate, Gel, XRD, IRS.

INTRODUCTION

Zeolites are crystalline aluminosilicates with a tetrahedral frame work structure, which are made up of [(Si, Al)_nO₂] networks. They possesses cavities in them into which gases like CO₂, NH₃ etc. and the liquids like water, ethyl alcohol etc. can enter and absorbed. These materials have an ability to adsorb selectively molecules other than water on the basis of molecular size they are commonly called as molecular sieves. The term 'molecular Sieve' was first given by MC Bain in 1932. By the early 1930s X-ray Diffraction studies were revealing the zeolites to be crystalline materials having within each crystal a system of precisely arrayed cavities and pores. The uses of zeolites are being explored in many scientific disciplines like modern Inorganic and organic chemistry, physical chemistry, colloidal chemistry, biochemistry, mineralogy, geology, surface chemistry, oceanography, Crystallography, Nanotechnology, Catalysis and in all types of Chemical engineering process technology. The wide variety of application include separation and recovery of normal paraffin hydrocarbons, catalysis of hydrocarbon reactions, drying of refrigerants, separation of air components, carrying catalysts in the curing of plastics and rubber, removing radio active ions from radioactive waste solutions. Cracking catalysts containing crystalline zeolite molecular sieves were first used in 1962 (1,2) and at present close to 95% of the installed capacity employs zeolite

catalysts.(3) The first experimental observation of the adsorption of gases on Zeolite and their behavior as molecular sieves was conducted on Zeolite minerals. The first definitive experiment on the separation of mixtures using the dehydrated Zeolite mineral chabazite as a molecular sieve was performed by Barrer in 1945.(4) He classified Zeolites into three groups based upon their ability to adsorb or exclude molecular species of different sizes. The classification defined the approximate interchannel dimensions.

EXPERIMENTAL

Properties of zeolites

Zeolites are crystalline, hydrated aluminosilicates of group I and group II elements, in particular, Sodium, Magnesium, Calcium, Strontium and Barium, Structurally, the Zeolites are “framework” aluminosilicates which are based on infinitely extending three - dimensional network of AlO₄ and SiO₄ tetrahedra linked to each other by sharing all the oxygens. Zeolite may be represented by the empirical formula



In this oxide formula p is generally equal to or greater than 2 since AlO₄ tetrahedra are joined only to SiO₄ tetrahedra, n is the cation valence. The framework contains channels and interconnected voids which are occupied by the cation and water molecules. The cations are quite mobile and may usually be exchanged, to varying degrees, by other cations. Intra crystalline “Zeolite” water in many Zeolites, is removed continuously and reversibly. In many other Zeolites, (natural and synthetic), cation exchange or dehydration may produce structural changes in the framework. This results into the modification of the structural formula. The structural formula of a Zeolite is best expressed for the crystallographic unit cell as



Where M is the the cation of valence n, w is the number of water molecules and the ratio y/x usually has values 1 to 5 depending upon the structure. The sum (x + y) is the total number of tetrahedra in the unit cell. The portion within (5-8) represents the frame work composition.

Although there are 45 species of zeolite minerals and more than 100 types of synthetic zeolites, only a few have practical significance at the present time. Many of the zeolites, after dehydration are permeated by very small channel systems which are not interpenetrating and which may contain serious diffusion blocks. In other cases dehydration irreversibly disturbs the framework structure and the positions of metal cations, so that the structure partially collapses and dehydration is not completely reversible. The molecule sieves the structure of a Zeolite, after complete dehydration must remain intact.

Table 1: Classification of Zeolites

Group	Secondary building unit	Members
1	Single 4 - ring S4R	Analcime, Harmotome, Philipsite
2	Single 6 - ring S6R	Erionite, Offretite, Levynite
3	Double 4-ring D4R	A, N-A, ZK-4
4	Double 6-ring D6R	Faujasite, X, Y, Chabazite, Gmelinite, Zk5, L
5	Complex Unit 4-1, T5O10	Natrolite, Scolecite, Mesolite
6	Complex Unit 5-1, T8O16	Mordenite, Dachiardite, Ferrierite
7	Complex Unit 4-4-1, T10O20	Heulandite, Clinoptilolite, Stilbite

Method of preparation of Pb zeolites

A series of synthetic Zeolite P has been reported which exhibit rather subtle difference which are referred to as the P Zeolites (14,15) and as Zeolite B (16). These Zeolites have been referred to as Philipsite like, Harmotome like, or Gismondine like. This is due to close similarities in the X-ray powder patterns of synthetic Zeolites with those of the minerals. The two most common types are the cubic Zeolite, referred to as Zeolite PB or PC. And a tetragonal type called Pt. Zeolite P is readily synthesized in the Na₂O - Al₂O₃ - SiO₂, H₂O system. The structure first proposed was based upon a BCC arrangement of D4R units of eight tetrahedra. But this has been shown to be incorrect and the framework structure has been shown to be the same as that of Gismondine. There appears to be no basic difference in the frame work structures of cubic P and tetragonal P.

Table 2: Details of Zeolite PB

Structure group : 1

Chemical Composition

Typical oxide formula : Na₂O.Al₂O₃.2.O-5.O SiO₂.5H₂O

Typical Unit cell contents : Na₆ (AlO₂)₆ (SiO₂)₁₀. 15H₂O

Variations : Si/Al = 1.1 to 2.5

Crystallographic data

Symmetry : Near cubic

Density : 2.01 g/cc

Space group : 14/amd

Unit Cell Volume : 1015 Å³

Unit Cell Constants : a = 10.05 Å

RESULTS AND DISCUSSION

The process for the semi continuous preparation of Zeolite PB type which is a crystalline sodium alumino silicate of constant and homogeneous quality comprises continuously mixing with vigorous agitation, a solution of sodium silicate and a solution of sodium aluminate in a container in which the average retention time is from 30 seconds to 20 minutes and temperature is from 700 C to 1050C to form a gel which is subsequently matured over a period of 4 to 7 hours, at a temp. ranging from 800C to 950C. During maturing the precipitated particles of Zeolite are kept in suspension without any shearing force being exerted on them, or with just enough shearing force to ensure that the particles are kept in suspension. The actual process of preparation of PB Zeolite takes place in following steps.

Step - I: Preparation of Sodium Silicate Solution (Solution A)

The desired sodium silicate solution (Solution A) is obtained by dissolving crystalline commercial grade sodium silicate in distilled water at 500C. It has following characteristics:

- a) SiO₂ concentration ----- 138 gm per litre
- b) Na₂O concentration ----- 4.1 gm per liter and temperature = 500C at the moment of use. Thus SiO₂/Na₂O = 138/41 = 3.36

Step - II: Preparation of Sodium aluminate solution (Solution B) :-

The desired sodium aluminate Solution (Solution B) is obtained by dissolving hydrated alumina in concentrated soda at 1040C. It has following characteristics.

- a) Al_2O_3 concentration ----- 56 g/L
- b) Na_2O concentration ----- 80 g/L and temperature = 92^oC at the moment of use.

Thus $\text{Al}_2\text{O}_3/\text{Na}_2\text{O} = 56/80 = 0.7$

Step - III: Mixing of two solutions A and B

The two well prepared solutions are then heated on hot plate solution A goes upto 50^oC and solution B goes upto 920C. Both the solutions are then poured simultaneously in a big container under fast stirring in order to avoid the settling of reactants. The result of mixing is a thick (milky) white gel. The mixture is then kept on hot plate under minimum stirring speed upto 7 hours. The system should be completely closed. The temperature of hot plate is maintained between 80^oC and 95^oC. After ageing for 7 hours, the mixture is kept for settling overnight. This well settled mixture is then kept in centrifuge for 15 minutes at 1500 r.p.m. After 15 minutes it is taken out and washed with hot water and again put back to centrifuge under same conditions. The process is repeated for 5 times and the mixture is then kept in the oven for drying at about 100^oC for two hours. The sample obtained, this way, is a smooth white fine zeolite powder. Zeolite PB is important due to its pollution control significance which includes (a) Radioactive Waste disposal, (b) Sewage effluent treatment (c) Agricultural waste water treatment etc.

CONCLUSION

From the diffractograph of sample we comparing the results with standard characteristic spectrum and the material can be identified by X-ray Diffraction technique. We study the internal structure in the microcrystal of PB Zeolite, using infrared spectroscopy which exhibits the infrared spectrum of the sample. From the electron micrographs of the sample only 60% Zeolite is obtained which contains cubic and hexagonal crystal also the particle size is very fine.

REFERENCES

1. S. C. Estwood, R. D. Drew and F. D. Hartzell, Oil Gas J., **60**, 152 (1962).
2. K.M. Elliott and S.C. Eastwood, Oil Gas J., **60**, 142(1962).
3. E.J. Demmel, A.V. Perrello, W.A. Stoves and J.P. Shambaugh, Oil Gas J., **64**, 179 (1966).
4. R.M. Barrer, J. Soc. Chem Ind., **64**, 130 (1945).
5. R.M. Milton, Molecular Sieves, Society of Chemical Industry, London, **199** (1968).
6. A. Cronstedt, Akad. Naudl. Stockholm, **102** (1758).
7. L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca (1960).
8. L.L. Ames, Unclass Rept. Hy-62607, USAtomic Energy comm., **23** (1959).
9. L.L. Ames, Am. Min., 45, 689 (1960).
10. B.W. Mercer, Ore. Bin., 31, 209 (1969).
11. B. W. Mercer, L. L. Ames, C. J. Touhill, W. J. An Slyke and R.B. Dean, Fed., **42**, R95 (1970).

12. R. G. Kisperi, L. C. Anderson D. H. Walker and D. L. Wise NSF/RANN/SE/C Report, 827/PR/74/2, **176** (1974).
13. S. Ohtani, Japan Kokai, **72**, 046, 668, 6 (1972).
14. R.M. Barrer, F. W. Bultitude and I. S. Kerr, J. Chem. Soc., **1521** (1959).
15. R. M. Barrer, J. W. Baynham, F. W. Bultitude and W. M. Meier, J. Chem. Soc., **195** (1959).
16. R. M. Milton U. S. Pat., **3**, 008, 803 (1961).