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Synthesis of nano-porous molecular sieve from some natural materials

F. Narimani*
M. Kharamesh

School of geology, College of science, University of Tehran, Tehran, Iran.

ABSTRACT

Zeolites due to their structures can be used as molecular sieves for purification of materials and solutions. Zeolites with PHI and SOD structure are so common and applicable for this purpose. Hydroxy sodalite and phillipsite are the more abundant members of zeolites which display good selectivity for very small molecules and some ions such as Sr, Pb, Zn, Cu and Rb. There is not any pure natural deposit of these zeolites and purify methods are not cost-effective. Therefore, introducing an effective method to prepare these zeolites is necessary. In this study, hydroxy sodalite and phillipsite have been synthesized respectively from clinoptilolite and volcanic ash at hydrothermal conditions in the presence of alkaline solutions. Mineralogical studies show that K, Na and Cl ions are necessary in SOD and PHI structure. The effect of K^+ concentrations and temperature in the presence of constant value of Na^+ and Cl^- are being considered as the variable parameters in the present experiment. NaCl used as source of Na^+ and Cl^- ions. Alkaline solutions were prepared by using 2 to 12 grams KOH powder and synthesize mixture were heated at temperatures of 100 and 150˚C. Results of this study show that phillipsite is synthesized at 100 and 150˚C in all runs. Hydroxy sodalite is appeared just in 150˚C by using clinoptilolite as initial material. Analcime formed as by-product of volcanic ash phase transition at 150˚C.

INTRODUCTION

Molecular sieves can separate molecules on basis of molecular dimensions. Zeolites because of their 3D porous structure have been nominated as first molecular sieve groups. Material separation and decontaminating and purifying of solutions and waste waters involve a lot of industrial applications that zeolites play important roles on them. The purification processes accomplish by two techniques: Continuous processing and Batch processing.

* Corresponding author:
Fatemeh Narimani
School of geology, College of science, University of Tehran, Tehran, Iran.
Tel +989124017344
Fax +982188575662
Email fnarimani@khayam.ut.ac.ir

In continuous processing, zeolitic membranes are used as the major component but in the batch processing, purification performs by zeolitic powders or tabs. In last decade, many of scientific researches and industrial applications have focused on zeolitic membrane investing and manufacturing. Because of technical challenges and scientific complexities in industrial membranes, manufacturing of zeolitic absorbents by using natural or synthetic zeolites are more economical and accessible.

Zeolites are microporous hydrated aluminosilicates of alkali and alkaline earth cations with open and rigid three-dimensional structures. The three-dimensional framework consists of AlO_4^{5-} and SiO_4^{4-} tetrahedral units which linked through their shared oxygens. There are several systematic channels in zeolite structures.

Among zeolite group minerals, phillipsite and hydroxy sodalite are common zeolitic mineral and suitable for use in wastewater treatment systems. Phillipsite with the chemical composition $K_2(Ca_{0.5},Na)_4(Al_6Si_{10}O_{32}).12H_2O$ is structurally built up by layers of tetrahedra with eight- and four-rings forming double crankshafts roughly perpendicular to *a*-axis [1]. In addition to its rare natural occurrence, there are several experimental and theoretical studies on synthesizing and stability limits of phillipsite. It has been synthesized from conversion of chabazite [2], alumino-silicate glass [3], pumice [4], and fly ash [5]. Between zeolitic materials, hydroxy sodalite gain particular position in academic researches and industrial applications. The mineral sodalite with the chemical composition $Na_8 [Al SiO_4]_6Cl_2$ was first discovered by Thomson [6] and its structure was described by Pauling [7]. Hydroxy sodalite is a crystalline (tecto) aluminosilicate which belongs to the group of clathrasils. Due to its small aperture size (2.2–2.8 Å) and hydrophilic nature (Si/Al ratio of 1), it have enough potential for using in separation processes. Dehydration cause partial collapse of the framework and transition hydroxy sodalite to sodalite [8].

Due to lack of any pure deposition of hydroxy sodalite and phillipsite or economically method to purify them, effective method to phillipsite synthesis is needed. The present study experimentally explores the possibility of phillipsite and hydroxy sodalite synthesis from available natural materials such as clinoptilolite and volcanic

ashto achieve an economically method to synthesize these molecular sieves.

EXPERIMENTAL

Initial sample

Volcanic ashes used in this study were collected from Damavand Mountain, Iran. The volcanic ashes were sieved with 150μ meshes separating some dark minerals and then used in experiments. XRD pattern of powdered volcanic ash sample shows reflection of plagioclase (albite) and alkali feldspar (sanidine) (Figure 1). The clinoptilolite sample used in this study was collected from Semnan area, Iran. The initial sample was powdered in an agate mortar and was used for synthesis without any purification. X-ray diffraction (XRD) pattern of powdered sample shows reflection of clinoptilolite and albite (Figure 2). X-ray fluorescence (Philips PW 14800) analysis of the initial samples is shown in Table 1 and Table 2.
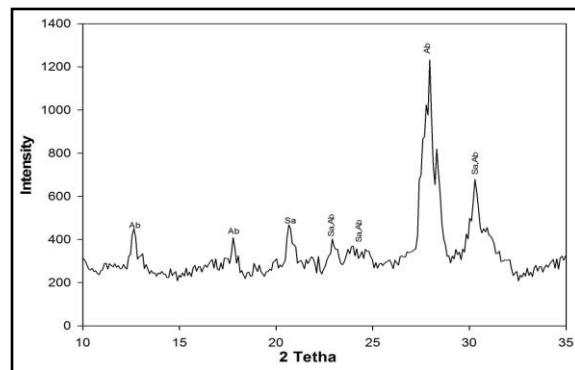

Fig. 1. XRD pattern of volcanic ash sample (VAsh). Ab: albite and Sa: sanidine.
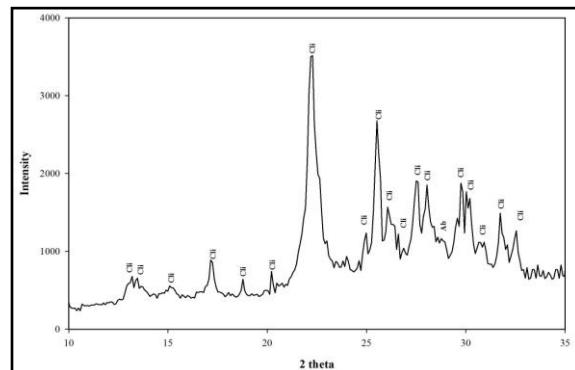

Fig. 2. XRD pattern of clinoptilolite sample (Clino). Clin: clinoptiloliteand Ab: albite.

Syntheses were performed at temperatures 100 and 150°C in the presence of alkaline solution. KOH is source of K^+ and OH^- and NaCl is the source of Na^+ and Cl^-.

Table 1. Chemical composition (wt %) of clinoptilolite sample

Sample	VAsh
SiO_2	62.654
Al_2O_3	16.72
Fe_2O_3	4.11
CaO	3.01
Na_2O	3.91
K_2O	5.11
MgO	1.72
TiO_2	0.923
MnO	0.052
P_2O_5	0.412

Table 2. Chemical composition (wt %) of the volcanic ash.

Sample	Clino
SiO_2	73.45
Al_2O_3	13.13
Fe_2O_3	0.75
CaO	4.31
Na_2O	0.83
K_2O	0.98
MgO	0.63
TiO_2	0.164
MnO	0.008
P_2O_5	0.003

Experimental method

The powdered initial sample(s) (4g) was mixed with 80 ml distilled water by magnetic stirrer for 2 min at room temperature. Then KOH and NaCl powders add to the mixture (according to Table 3) and stirred for another 3 min. The produced mixture was transferred to Teflon autoclave. Finally, the autoclave was sealed and heatedfor 120 hours. The obtained solid was filtered and washed with distilled water and dried in air.

Run products were characterized by a Bruker D-8 X-ray diffractometer with Ni-filtered Cu-Kα radiation (40Kv, 30mA) and changeable diaphragm at the Faculty of Science, University of Damghan, Iran. Analyses of XRD Patterns were occurred by diffracted and powderX softwares. Microphotographs images of synthesized phases are prepared by aVega Tscan Scanning Electron Microscope (15kv) at Razi Metallurgical Research Center, Tehran, Iran.

RESULTS AND DISCUSSION

XRD patterns of samples heated at 100 and 150°C, show structural break down of initial materials which is accompanied by the appearance of the new peaks indicating the formation of new phase(s). Results show that after dissolving and reaction of volcanic glass whit hydrothermal fluid some initial minerals such as albite and sanidine approximately remained without change. In K^+ bearing environments PHI structure is suitable framework to form in any temperatures. Phillipsite formation cause a decreasing in silica, alumina and K^+ ions in reaction environment and will prepare conditions for formation zeolitic structure with lower content of Si, Al and K ions. At 150°C the concentration of Na^+ and Cl^- ions in hydrothermal solutions have critical role in hydroxy sodalite and analcime formation. In lower concentration of these ions just phillipsite form as synthesized product. But by increasing in ions concentrations, in runs with volcanic ash as initial material analcime and in runs with clinoptilolite as initial material hydroxy sodalite peaks appear in XRD patterns and peaks intensities dramatically elevate by increasing ions concentrations (Figures 3, 4, 5 and 6).SEM images of samples shows hydroxy sodalite, phillipsite and analcime appear as new phases (Figures 7 and 8).

Table 3. Experimental conditions and products

	Initial material	No.	t (h)	T (°C)	KOH (g)	NaCl (g)	Distilled water (mL)	Product(s)
Seri I	Volcanic Ash	NK1	120	100	2	2	80	Phi
	Volcanic Ash	NK2	120	100	4	2	80	Phi
	Volcanic Ash	NK3	120	100	8	2	80	Phi
	Volcanic Ash	NK4	120	100	12	2	80	Phi
	Volcanic Ash	NK5	120	150	2	2	80	Phi
	Volcanic Ash	NK6	120	150	4	2	80	Phi + Ana
	Volcanic Ash	NK7	120	150	8	2	80	Phi + Ana
	Volcanic Ash	NK8	120	150	12	2	80	Phi + Ana
Seri II	Clinoptilolite	NK9	120	100	2	2	80	Phi
	Clinoptilolite	NK10	120	100	4	2	80	Phi
	Clinoptilolite	NK11	120	100	8	2	80	Phi
	Clinoptilolite	NK12	120	100	12	2	80	Phi
	Clinoptilolite	NK12	120	150	2	2	80	Phi
	Clinoptilolite	NK14	120	150	4	2	80	Phi
	Clinoptilolite	NK15	120	150	8	2	80	Phi + Sod
	Clinoptilolite	NK16	120	150	12	2	80	Phi + Sod
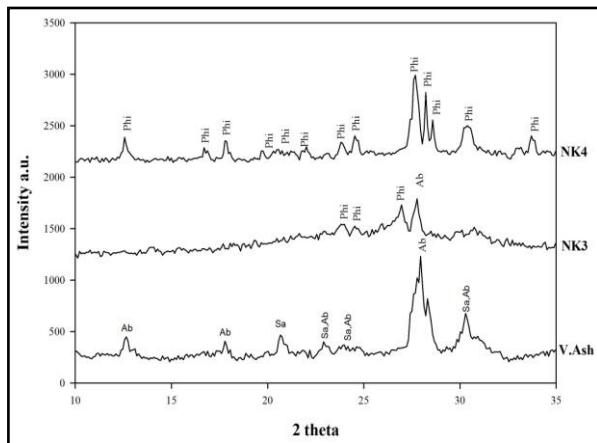
Fig. 3. XRD pattern of samples heated at 100°C (NK3 and NK4) compared with the volcanic ash as initial sample (VAsh).Ab: albite, Sa: sanidineand Phi: phillipsite.
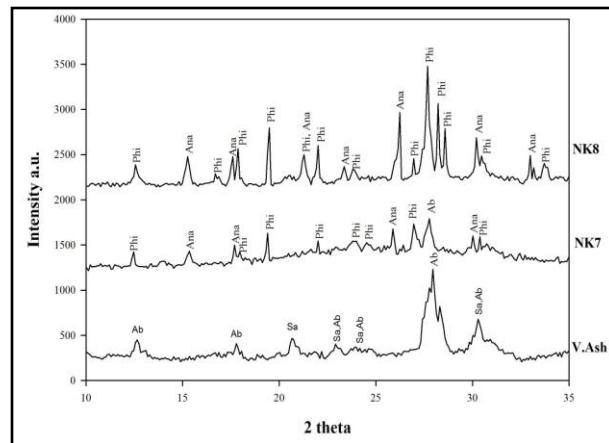
Fig. 4. XRD pattern of samples heated at 150°C (NK7 and NK8) compared with the volcanic ash as initial sample (VAsh). Ab: albite, Sa: sanidine , Phi: phillipsite and Ana:analcime
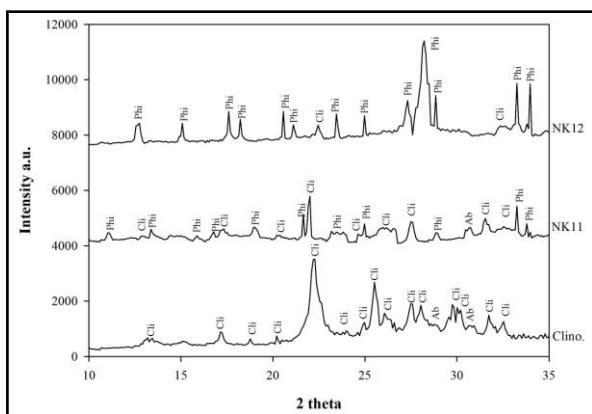
Fig. 5. XRD pattern of samples heated at 100°C (NK11 and NK12) compared with the clinoptiloite as initial sample (Clino). Cli: clinoptilolite, Ab: albite and Phi: phillipsite.
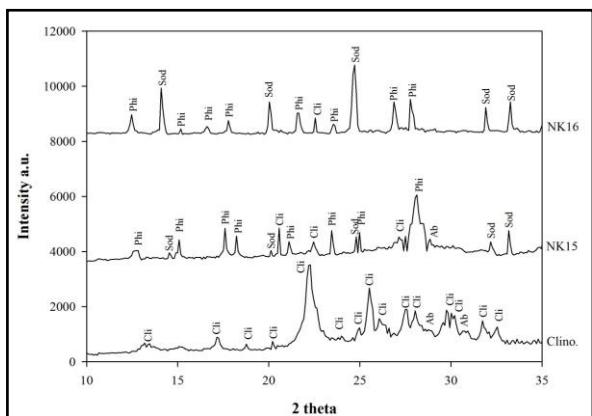

Fig. 6. XRD pattern of samples heated at 150°C (NK15 and NK16) compared with the clinoptiloite as initial sample (Clino). Cli: clinoptilolite, Ab: albite, Phi: phillipsite and Sod:hydroxysodalite.
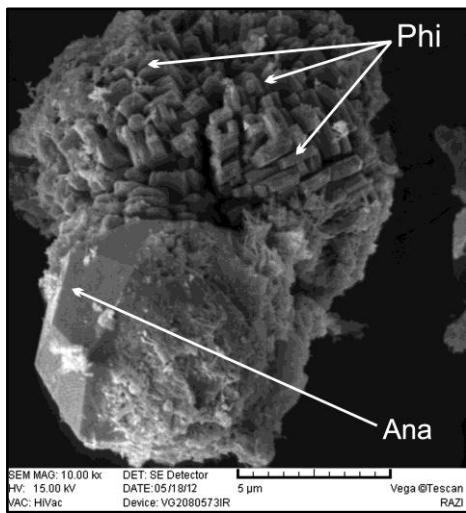
Fig. 7. SEM image of sample NK8.Phi: phillipsite and Ana: analcime.
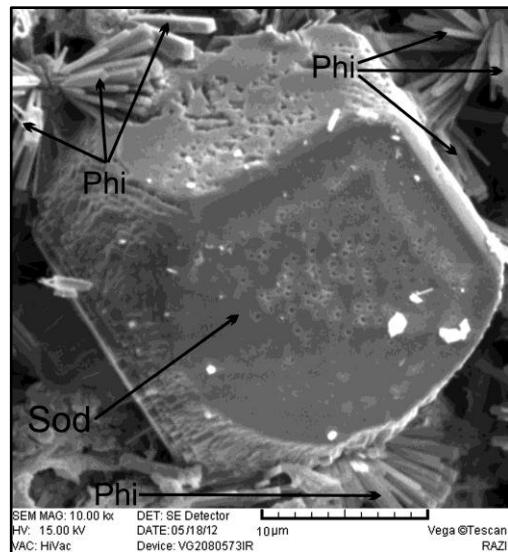
Fig. 8. SEM image of sample NK16., Phi: phillipsite and Sod:hydroxysodalite.

Powder diffraction studies have revealed a monoclinic (pseudo-orthorhombic) symmetry with the unit-cell parameters of: a: 9.90(8)Å, b: 14.28(5)Å, c: 14.41(2) Å, β: 90.60(8)º for phillipsite synthesized from clinoptilolite and unit-cell parameters of: a: 9.91(6) Å, b: 14.13(5) Å, 14.18(9) Å, β: 90.31(4)º for phillipsite synthesized from volcanic ash. Calculated lattice parameters in this study are similar to the measured unit cell parameters of phillipsite reported from natural occurrences (Table 4).

Table 4. Unit cell parameters of phillipsite synthesis in this study and parameters from another source.

	a (Å)	b (Å)	c (Å)	β (degree)
This work (Clinoptilolit as initial sample)	9.90(8)	14.28(5)	14.41(2)	90.60(8)
This work (Volcanic ash as initial sample)	9.91(6)	14.13(5)	14.18(9)	90.31(4)
[9]	9.88	14.30	14.34	89.30
[1]	9.874	14.306	14.362	90
[10]	9.994(4)	14.181(8)	14.225(5)	90.2(6)

In addition, Powder diffraction studies have revealed a cubic symmetry with the unit-cell parameters of a: 8.871(8) Å for hydroxy sodaliteand an orthorhombic (pseudo-cubic) symmetry with the unit-cell parameters of a: 13.754(9)Å, b: 13.736(4)Å, c: 13.792(7)Å for analcime. Calculated lattice parameters in this study are similar to the measured unit cell parameters of hydroxy sodalit and analcime from scientific report (Tables 5 and 6).

Table 5. Unit cell parameters of hydroxy sodalite synthesis in this study and parameters from another source.

	a (Å)
This work	8.871(8)
[8]	8.86
[11]	8.877(2)
[12]	8.880(3)

Table 6. Unit cell parameters of analcime synthesis in this study and parameters from another source.

	a (Å)	b (Å)	c (Å)
This work	13.754(9)	13.736(4)	13.792(7)
[9]	13.73	13.71	13.74

CONCLUSIONS

This study shows that synthesis of zeolites with PHI and SOD structure by using clinoptilolite and volcanic ash as precursors occurs at 100 and 150°C in the presence of alkaline hydrothermal solutions. phillipsite is synthesized at 100 and 150˚C from volcanic ash and clinoptilolite. Hydroxy sodalite is formed just in 150˚C by using clinoptilolite as initial material. Analcime formed as by-product of volcanic ash phase transition at 150˚C.

Concentration of K^+ and temperature has positive effects in initial material phase transitions. By increasing in concentration of alkaline cations and temperature, precursors break down rate increase and the amount of phillipsite and hydroxy sodalite increase significantly as a result of the transition of initial materials to new phases. In addition, temperature and initial samples have effect on the type of products.

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