Hydrothermal Synthesis of Low Silica Zeolites From Natural Clays

S. Kayiran Beyaz

Department of Chemistry, Kocaeli University, Kocaeli, Turkey
Fax: (90)(262)3032003; Tel: (90)(262)3032012
E-mail: saadetkayiran@kocaeli.edu.tr

Synthetic low silica zeolites are used for adsorption based air separation processes. This work is devoted to find a cost saving method for the synthesis of low silica zeolites from clay sources as bentonite and kaolin. The bentonite sample has been activated by alkaline fusion and has been calcinated in Na_2CO_3 media to be used as reagent for the synthesis of low silica zeolites. The thermal transformation of kaolin extrudates to metakaolin and its alkaline fusion with bentonite constitutes a source for the crystallization of low-silica zeolites of A type. The morphologic and structural characterizations of synthesized materials have been done by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Key Words: Zeolite, Clay, Bentonite, Kaolin, Synthesis, Characterization.

INTRODUCTION

Natural clays are low-cost materials and can be found in a number of soils. Chemically they are hydrated aluminosilicates compensated by iron or magnesium cations. The chemical composition of natural clays indicates that they could be modified chemically to form synthetic zeolites[1,2]. The conversion of kaolinite and metakaolinite to zeolite by alkali attack is a well known and widely practiced procedure. When kaolinites were used without additives, zeolites with a Si/Al ratio of 1 are the main products[3]. Studies of zeolites and porous carbons indicate that these materials may be used as adsorbents for retaining different types of inorganic and organic species from solutions and gaseous media[4,5]. Low (Si/Al ● 2) and intermediate (2 < Si/Al ● 5) silica zeolites[6] are used as ion exchangers and have also found great importance for separation of gases by adsorption processes. In particular the synthetic zeolites as the low silica faujasite-type zeolite and linde type A zeolites are used for air separation for the production of nitrogen and oxygen and hydrogen purification in order to have high pure hydrogen for using in fuel cells[7-11]. Synthesis of low and intermediate silica zeolites are usually performed under hydrothermal conditions using reactive alkali-metal aluminosilicate gels at low temperatures (*ca.* 100 ℃ and autogenous pressures). The synthesis procedure involves combining alkali hydroxide, reactive forms of pure silica and alumina and water to form a gel.

Crystallization of the gel to the zeolite phase occurs at a temperature near 100 ºC. Two most important zeolites prepared by this approach are zeolites A and X, which are very important for commercial applications[12]. The framework topology of zeolite A has not been found in nature. Zeolite X is compositionally different but topologically the same as mineral faujasite[13]. Using pure form of silica and alumina for A and X type zeolite synthesis increases the cost of the produced material. Other sources of silica and alumina like clay minerals may be used as reactants for synthesis process. This work is devoted to find a cost saving method for the synthesis of low silica zeolites from clay sources as bentonite and kaolin which could be found in numerous soils like center and west Anatolia in Turkey. The bentonite sample has been activated by alkaline fusion and has been calcinated in Na_2CO_3 media to be used as reagent for the synthesis of low silica zeolites. Finally by mixing the metakaolin and the bentonite in Na_2CO_3 media high pure and crystalline zeolite A is obtained.

EXPERIMENTAL

The chemical analysis of the kaolin from Fluka (SiO_2: 46 %, Al_2O_3: 39 %) and Na-bentonite from Alfa Aesar are carried out at Solaize-CNRS FRANCE. The X-ray powder diffraction pattern of the zeolite sample was collected with a STOE STADI P diffractometer using ($K\alpha1$) Cu radiation. SEM was carried out on a field emission scanning microscope model Jeol JSM-6700F.

RESULTS AND DISCUSSION

The chemical analysis results of the kaolin and bentonite are presented in Table-1. First, the reactivity test of the bentonite (B) by alkaline fusion and aging at long time for obtaining a gel starting from this source is done. The bentonite sample has a Si:Al ratio of 3.33. Aluminium in the form of $NaAlO_2$ (Carlo Erba) has been mixed for obtaining a gel with lower Si:Al ratio. The stoichiometric composition of the prepared gel is: Al_2O_3:2.8SiO_2:5.73Na_2O:1.43K_2O:312H_2O. The synthesis procedure consists on preparing two basic solutions which are mixed under stirring. The gel is kept at room temperature and then crystallized at 361 K. Table-2 shows the different synthesis conditions in term of aging and crystallization time and temperature for obtaining low silica zeolites. The bentonite sample is left for one night at 423 K in oven before the synthesis. The kaolin, because of its chemical stability, must be transformed into metakaolin by calcination at 973 K, before its incorporation in the synthesis system. Dehydration by a heat treatment converts the kaolin into metakaolin which is semi crystalline and more reactive than the starting material. The calcination of the kaolin is made according to the protocol described as earlier[2]. Initially the reactivity of the gel by aging it at room temperature has been tested. After 48 h no visible difference with the initial bentonite is observed (BS1). Traces of zeolites X and A have appeared after one week (BS2). At this stage the reaction medium was not very reactive and the synthesis has evolved slowly with time. BS3 and BS4 samples have been crystallized according to the Basso method[14] at 361 K

TABLE-1
CHEMICAL COMPOSITION OF KAOLIN AND BENTONITE SAMPLES

Materials	% Al	% Si	% Na	% K	Si/Al	Na/Al	K/Al
Kaolin	18.97	22.50	320 ppm	2.64	1.14	-	0.096
Bentonite	7.75	26.89	2.31	0.76	3.33	0.35	0.060

TABLE-2
SYNTHESIS RESULTS. COLUMN 1: SAMPLE REFERENCES, COLUMN
2: ALKALINE FUSION CONDITIONS, COLUMN 3: AGING CONDITIONS, COLUMN
4: CRYSTALLIZATION CONDITIONS, COLUMN 5: IDENTIFICATION OF CRYSTALS
BY XRD (B: BENTONITE, X: LOW SILICA X, GIS: GISMONDINE)

Sample	Alkaline fusion	Aging	Crystallization	XRD
BS1	-	48 h	-	B
BS2	-	1 week	-	B + X + A
BS3	-	-	48 h; 361 K	B + X
BS4	-	-	1 week; 361 K	B + X + GIS + A
BS5	NaOH/KOH	-	16 h, 361 K	B + A + X
BS6	Na_2CO_3	-	16 h, 361 K	A + gel
BS7	Na_2CO_3+ metakaolin	-	20 h, 361 K	A

for 48 h and 1 week, respectively. Fig. 1 presents the SEM images of the sample BS4. It shows the formation of a mixture of three types of zeolites: X, A and GIS (gismondine, deduced from XRD) and the rest of bentonite which was not reacted. Bentonite is present as small flakes (Fig. 1a). The crystals of zeolites seem well crystallized (Fig. 1b) and are formed directly on the clay layers. That can let suppose that only complementary aluminium is in solution, the silicium migrating gradually from the layer towards zeolite during crystal growth. In order to increase the reactivity, an alkaline fusion was carried out. A mixture containing bentonite and half of the base necessary to the synthesis, are introduced either in the form of NaOH and KOH or in the form of Na_2CO_3. The reactants are mixed and the calcination was carried at 773 K for 1 h. The system is more reactive leading to a mixture of clay, zeolites A and X when alkaline fusion is carried out in the presence of NaOH and KOH (BS5). If the alkaline fusion is done with Na_2CO_3, formation of zeolite A, which is a more stable phase than zeolite X, is observed (BS6). Fig. 2 shows the SEM images of samples referenced as BS5 and BS6. The cubic zeolites A and orthorhombic zeolites X grown on bentonite surface could be seen. To reach the ratio of Si/Al=1, the Si/Al report of the bentonite (3.33) was corrected by adding to the bentonite sample the kaolin sample which has the Si/Al ratio of 1. The mixture then reacted with Na_2CO_3 at 773 K. The sample BS7 is obtained after the crystallization of this mixture at 361 K during 20 h. Zeolite A obtained from the starting mixture bentonite/kaolin seems correctly crystallized, without trace of impurity. Fig. 3a clearly shows the cubic morphology of zeolite A. The diameter distribution of the crystals is not uniform. The lattice constants of exchanged zeolites were calculated from the XRD of sample BS7 (Fig. 3b). The Na A unit cell parameter is equal to $a_0 = 24,550Å$ in conformity with the literature[15,16].
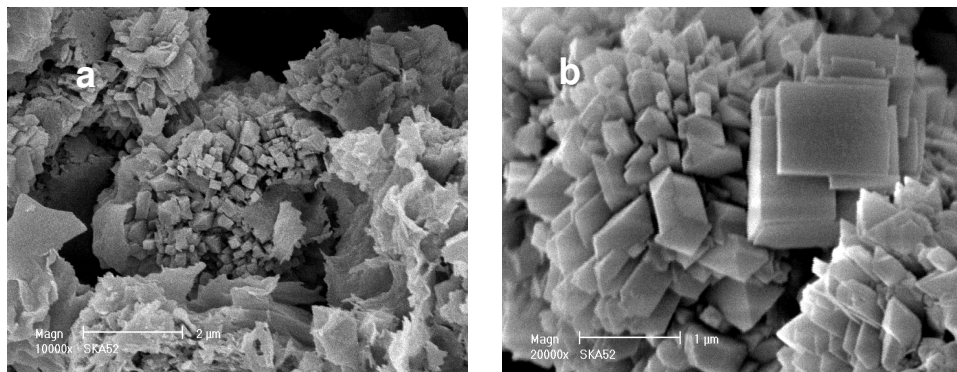
Fig. 1.   Formation of the zeolite crystals on the bentonite layers (a), well crystallized A and X zeolite on bentonite layer (b)
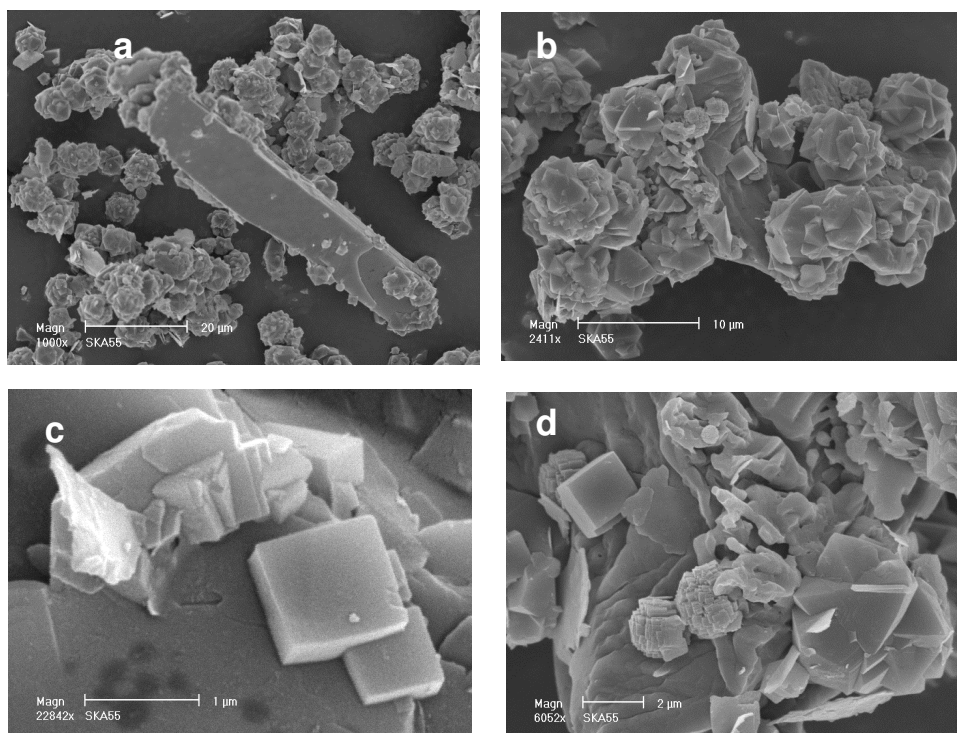

Fig. 2. SEM images of sample BS5 (2a, 2b, 2d), sample BS6 (2c)

Conclusion

The hydrothermal synthesis of low silica A zeolite by using natural clays as sources is reported. Bentonite and kaolin natural clays are used as Al_2O_3 and SiO_2 sources. Although of very great stability, the bentonite seems to be able to constitute a source usable in the synthesis of zeolite. However without alkaline fusion the reactional
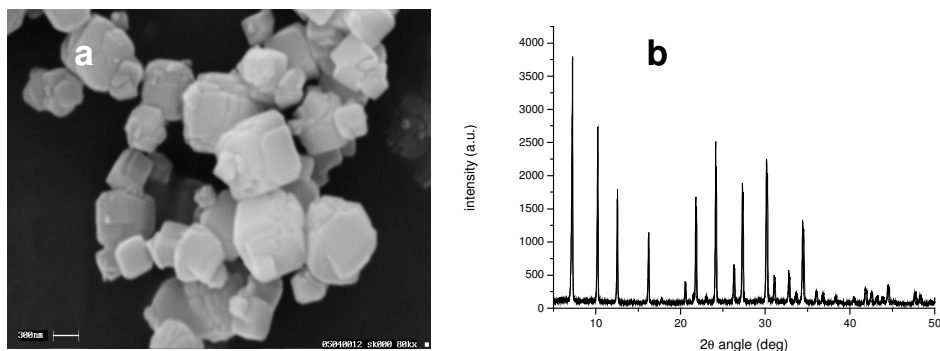
Fig. 3. SEM image of sample BS7 (a) and the XRD of sample BS7 (b)

mixture evolves slowly at room temperature and traces of zeolites X and A being observable only after 1 week. It does not seem either possible to completely react the bentonite at the temperature of 361 K. The synthesis of pure zeolite LSX starting from natural bentonite appears however difficult, undoubtedly because of a great heterogeneity of species concentration and reactivity of the synthesis medium thus formed. Alkaline fusion of the mixture of bentonite and kaolin increases the reactivity of clays leading to obtain a pure phase of zeolite A.

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