Microporous and Mesoporous Materials 201 (2015) 134–140

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Synthesis and characterization of analcime using quartz syenite powder by alkali-hydrothermal treatment

Xi Ma [a,b], Jing Yang [a,*], Hongwen Ma [a,*], Changjiang Liu [a,b], Pan Zhang [a,b]

[a] School of Materials Science and Technology, China University of Geosciences, Beijing 100083, PR China
[b] Blue Sky Technology Corporation, Beijing 100083, PR China

ARTICLE INFO

Article history:
Received 27 July 2014
Received in revised form 17 August 2014
Accepted 7 September 2014
Available online 16 September 2014

Keywords:
Analcime
Quartz syenite
Alkali-hydrothermal method

ABSTRACT

Analcime was successfully synthesized for the first time via a hydrothermal treatment of quartz syenite powder and NaOH solution. The experiments were carried out at the temperature from 240 °C to 260 °C for 2–8 h using different concentrations of NaOH solution and mass ratio of NaOH/syenite. The as-prepared samples were characterized by X-ray fluorescence, X-ray powder diffraction, scanning electron microscopy, and Fourier transform infrared spectroscopy. The results indicate that the crystalline analcime can be prepared using natural quartz syenite as an economic raw material.

1. Introduction

Zeolites are three-dimensional crystalline aluminosilicates with corner-sharing $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra frameworks forming channels and cages in the structures. Analcime ($NaAlSi_2O_6{\cdot}H_2O$, ANA) is one of microporous zeolites with irregular channels formed from four, six, eightfold rings [1]. Recently, ANA was reported to be an absorbent in the treatment of wastewater [2–4]. In addition, the metals-modified ANA is used as heterogeneous catalyst in the selective adsorption reactions [5–7].

ANA zeolites were normally synthesized by chemical reagents sodium silicate and aluminate [8]. It is also well known that ANA can be prepared using other economic aluminosilicate materials, such as rice husk ash and kaolin [2,9], natural clinker [10], coal fly ash [11], palygorskite [12], and perlite [13]. Although these raw materials contain different impurities, all of them are highly reactive. Besides, rice husk ash and coal fly ash, used as the aluminosilicate source materials, have extra advantage of being inexpensive and alleviating environmental pollution challenges. Preparation of zeolites with high purity from natural raw materials, such as clay minerals, is an important way for synthesis of zeolites in the future [14].

Compared to other natural minerals and rocks mentioned above, quartz syenite, which is composed of main phase of microcline, 5–20% of quartz, and a small quantity of melanocratic minerals, is a promising raw material for synthesizing zeolites. It not only offers aluminosilicate and alkali metal source for the preparation of zeolite but also possesses rich K_2O which can be used to prepare potassium salts. Quartz and microcline, which are tectosilicate minerals, are difficult to be dissolved in the lower concentration of alkaline solution at lower temperature [1]. Quartz syenite is rich in silicon and aluminum elements and can be used as the raw material for synthesis of ANA. Meanwhile, the insoluble potassium can be extracted from microcline (K_2O wt. 16.91%) [15–18].

In this work, we report the synthesis of ANA zeolite using quartz syenite as raw material via a hydrothermal alkaline process for the first time. The effects of mass ratio of NaOH/syenite, NaOH concentration, reaction temperature, and reaction time on the synthesized samples were investigated. The as-prepared samples were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR).

2. Experimental

2.1. Materials

The starting material used in this work was quartz syenite, which was obtained from Guishan, Nanling country in Anhui province, China. The quartz syenite powder (QS) for the synthesis of zeolite was prepared by crushing and grinding procedure. Most of particles are smaller than 75 μm in size. The biotite was separated from the quartz syenite via the magnetic separation. NaOH solution was prepared using the chemical reagent sodium hydroxide (analytical reagent grade, ⩾96%) and distilled water.

* Corresponding authors. Tel.: +86 10 82323201, +86 10 82323374.
E-mail addresses: yjcl@cugb.edu.cn (J. Yang), mahw@cugb.edu.cn (H. Ma).

http://dx.doi.org/10.1016/j.micromeso.2014.09.019
1387-1811/

2.2. ANA synthesis

ANA synthesis was carried out by hydrothermal treatment of the quartz syenite powder in NaOH solution. Hydrothermal reactions were performed in a stainless steel autoclave with a wide range of experimental conditions, such as mass ratio of NaOH/syenite, NaOH concentration, reaction temperature, and reaction time. After the hydrothermal treatment, the mixtures were removed from the oven and cooled in water to room temperature. The as-prepared samples were filtered and washed with distilled water, and then dried at 105 °C for 16–24 h. The dried samples were weighed and kept in plastic bags for characterization. Table 1 shows the experimental conditions used for ANA synthesis and the mineral phases obtained in the hydrothermal reactions.

2.3. Characterization

The chemical compositions of QS and as-prepared samples were investigated by XRF in an ARL ADVANTXP XRF spectrometer. The XRD patterns of QS and as-prepared samples were recorded by a SmartLab (Rigaku) X-ray diffractometer with Cu Kα radiation. The morphologies of as-prepared samples were examined by Sirion 200 scanning electron microscopy under the analytical conditions of EHT = 5.00 kV and Signal A = SE. FT-IR spectra of as-prepared samples were collected by Perkin Elmer 2000 in the 4000–400 cm^{-1} region using potassium bromide as the diluent and binder.

3. Results and discussion

3.1. Chemical and mineralogical properties of quartz syenite

Chemical and mineral compositions of the rock syenite have an important influence both on the potential application and comprehensive utilization of relevant by-product. The main chemical composition of the quartz syenite powder is SiO_2 68.20 wt%, Al_2O_3 15.64 wt%, K_2O 10.41 wt%, as well as a small quantity of Fe_2O_3, MgO, CaO, Na_2O (see Table 2). The quartz syenite powder has the main contents of SiO_2 and Al_2O_3 with the SiO_2/Al_2O_3 mole ratio of 7.41, appropriate for synthesis of low-Si zeolite materials [19–21]. Moreover, the quartz syenite powder could be a potassium resource as it contains 10.41 wt% of K_2O [15]. The XRD pattern of the quartz syenite powder is shown in Fig. 1. The peaks with high intensity correspond to quartz (ICDD 46-1045) and microcline (ICDD 19-0932), while the peaks with low intensity reflect the presence of traces of melanocratic biotie mineral (ICDD 10–0495). Based on the principle of the materials balance [22], the content of the main minerals in the quartz syenite powder is microcline 64.6 wt%, quartz 23.5 wt%, kaolinite 7.4 wt%, biotite 2.2 wt%, and other minerals 2.3 wt%.

Table 1
Experimental conditions for synthesis of ANA using quartz syenite and the mineral phases obtained.

Samples	NaOH/QS (mass)	NaOH concentration (mol/L)	Hydrothermal condition		Mineralogical composition of the samples
			T (°C)	t (h)	
GS-1	0.30	4.0	240	4	A, M, B
GS-2	0.45	4.0	240	4	A, M, B
GS-3	0.50	4.0	240	4	A, M, B
GS-4	0.55	4.0	240	4	A, F, M, B
GS-5	0.50	5.0	240	4	F, M, A, B
GS-6	0.50	6.0	240	4	F, M, B
GS-7	0.50	4.0	240	6	A, M, B
GS-8	0.50	4.0	240	8	A, M, B
GS-9	0.50	4.0	260	2	A, M, F, B

A, analcime; M, microcline; F, faujasite-Na; B, biotite; QS, the quartz syenite powder.

3.2. Synthesis of ANA zeolite

The hydrothermal conversion of quartz syenite into ANA zeolite mainly consists of the dissolution of the minerals quartz, kaolinite and microcline and the followed precipitation of ANA zeolite. The results showed that the mass ratio of NaOH/QS and NaOH concentration played an important role in forming ANA zeolite.

The XRD patterns of the samples with different NaOH/QS in 4 M NaOH solutions synthesized at 240 °C for 4 h are given in Fig. 2. In the reaction with NaOH/QS mass ratio of 0.30, ANA (ICDD 41-1478) was prepared with a large amount of microcline. When the mass ratio of NaOH and the quartz syenite powder was 0.45 and 0.50, the products included ANA zeolite with high crystallinity and a small amount of microcline and biotite impurities. When the NaOH/QS mass ratio was increased to 0.55, a new mineral (faujasite-Na ICDD 28-1036) was obtained. Chemical compositions of as-prepared samples are listed in Table 2. It was shown that the sample (GS-3) with SiO_2/Al_2O_3 mole ratio of 4.01 corresponds to the theoretical ratio of analcime. Our studies indicate that the quantity of NaOH has primary influence on dissolution of microcline and the structure of ANA zeolite. The optimized experimental condition for the preparation of ANA is 0.50 for the mass ratio of NaOH/QS.

The dissolution of the quartz syenite powder in 4, 5, 6 M NaOH solutions, respectively, was conducted at 240 °C for 4 h to study the effect of NaOH concentration on the preparation of ANA, which is illustrated in Fig. 3. With the increasing of NaOH concentration, the crystalline phase was transformed into faujasite-Na, while the amount of dissolved microcline reduced. When treated in the 6 M NaOH solutions, the product was faujasite-Na with some microcline phase, and no longer appearing analcime phase. The results reveal that high NaOH concentration is disadvantageous to the formation of ANA, which is in good agreement with relevant studies on the preparation of ANA in 2–4 M NaOH concentration [2,9].

The results about the effect of reaction time on the as-prepared products are shown in Fig. 4. ANA zeolite with a smaller quantity of microcline was obtained after reaction for longer time. The three as-prepared ANA products approach to the theoretical crystalline structure with SiO_2/Al_2O_3 mole ratio of 4.00 and M_2O/Al_2O_3 mole ratio of 0.93, 0.95, 0.97, respectively (see Table 2). The content of

Table 2
Chemical compositions of the quartz syenite powder and the as-prepared samples (wt%).

Samples	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Loss	Total	SiO_2/Al_2O_3	M_2O/Al_2O_3
QS	68.20	0.32	15.64	1.71	0.04	0.32	0.40	0.57	10.41	0.19	1.79	99.59	7.41	0.62
GS-2	54.12	0.39	21.35	2.36	0.05	0.39	0.58	8.27	5.97	0.22	5.54	99.25	4.31	0.94
GS-3	52.42	0.41	22.24	2.56	0.05	0.42	0.58	9.72	4.39	0.24	6.09	99.13	4.01	0.93
GS-7	52.35	0.41	22.42	2.58	0.06	0.42	0.59	10.12	4.29	0.24	6.14	99.62	3.97	0.95
GS-8	52.02	0.40	22.34	2.57	0.05	0.41	0.59	10.63	3.85	0.23	6.46	99.55	3.96	0.97

SiO_2/Al_2O_3, $(M_2O/Al_2O_3) = (Na_2O + K_2O)/Al_2O_3$, mole ratio.