Applied Clay Science 129 (2016) 102–107

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Study on synthesis and characterization of ZSM-20 zeolites from metakaolin-based geopolymers

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ARTICLE INFO

Article history:
Received 17 January 2016
Received in revised form 9 May 2016
Accepted 10 May 2016
Available online 16 May 2016

Keywords:
ZSM-20 zeolites
Geopolymers
Metakaolin
In situ hydrothermal process

ABSTRACT

This paper presents a novel method for the synthesis of ZSM-20 zeolites. This method based on in situ transformation from a metakaolin-based geopolymer gel is more effective than the traditional hydrothermal method. The crystalline phase, micromorphology and microstructure of the geopolymers and the ZSM-20 zeolite samples were investigated using SEM, XRD and an N_2 adsorption apparatus. The experimental results showed that pure ZSM-20 zeolite crystals were obtained without any by-product and with a large BET surface area of 78.52 m^2/g under optimal conditions. Key factors of the in situ transformation process were studied, such as the alkalinity of the geopolymer gel, the curing conditions and the hydrothermal conditions. The optimum observed conditions were as follows: the modulus of sodium silicate solution (SiO_2/Na_2O molar ratio) was 1.1, H_2O/Na_2O molar ratio = 7.5, the geopolymers should be cured at 40 °C for 3 days, and the hydrothermal conditions should be kept at 140 °C for 10 h.

1. Introduction

Geopolymers, first named by Davidovits in 1978, are non-crystalline or quasi-crystalline inorganic polymer gels with a three-dimensional network structure (Davidovits, 1989). Generally, geopolymers are prepared from natural minerals and solid wastes through the polymerization of SiO_4 and AlO_4 tetrahedra. Previous work (Provis et al., 2005) indicated that there are nanocrystalline zeolite structures in geopolymers and that the geopolymer gels should convert into zeolites under suitable conditions. Many researches have confirmed this assumption. He (He et al., 2013) fabricated a high-strength, self-supporting NaA zeolite membrane from geopolymers through in situ hydrothermal processing, which could be used in organic solvent dehydration processes or seawater desalination. Tang (Tang et al., 2015) fabricated porous P-type zeolite spheres from metakaolin-based geopolymers using a dispersion solidification method combined with an in situ hydrothermal process, and the porous spheres provided a possible way for continuous-mode water treatment to remove Ca^{2+} and Mg^{2+}. Many studies (Ge et al., 2014; He et al., 2012; Zhang et al., 2014) have also shown the feasibility of preparing zeolites using geopolymer gels. As this method avoids adding template agents, it is simpler than the traditional method.

ZSM-20 zeolite is considered to resemble faujasite in certain structural aspects, but it has a higher silica/alumina ratio (typically 4.2) than faujasite (Ciric, 1976). ZSM-20 zeolite could be used as an adsorbent or employed as a catalyst in a wide variety of hydrocarbon conversion reactions, such as polymerization, aromatization, cracking and hydrocracking because of its large pore capacity. ZSM-20 was first synthesized by Ciric (Ciric, 1976) in 1976 using tetramethylorthosilicate, tetraethylammonium hydroxide, sodium aluminate and water. This method required a few weeks for the aging and crystallization processes to produce ZSM-20 zeolite. Tuan (Tuan et al., 2006) synthesized ZSM-20 zeolite in the $Na_2O—Al_2O_3—SiO_2—H_2O$ system with tetraethylammonium hydroxide as a template agent and determined the critical processing condition for its synthesis. S. Ernst (Ernst et al., 1987) synthesized ZSM-20 zeolite using $NaAlO_2$, tetramethylorthosilicate and tetraethylammonium hydroxide under steam conditions.

There are very few reports on the synthesis of ZSM-20 (Ciric, 1976; Ernst et al., 1987; Kosslick et al., 1994; Miessner et al., 1993; Ramesh and Abraham, 1992; Tuan et al., 2006). In addition to that most of them were based on the use of template agents. One of the inconvenient of this technique is the need of high temperature (above 500 °C over 10 h) to remove the template agents before the use of the obtained zeolite as adsorbent or catalyst. The crystallization products of ZSM-20 also tended to be impure, accompanied by zeolite β and other co-crystallization products. Finally, the synthesis period was at least 4 days, and in most reports, it was as long as a few weeks. Previous studies show that the above issues may be solved by in situ conversion methods from geopolymers.

Based on former works, this paper proposes a novel and simple method to fabricate ZSM-20 zeolites from geopolymer gels with three-dimensional networks. By adjusting the reaction conditions and

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http://dx.doi.org/10.1016/j.clay.2016.05.011
0169-1317/

the formula of the raw materials, the target ZSM-20 zeolites were obtained. Compared with other methods, this method has the advantages of non-organic template agents and shorter synthesis time.

2. Experimental procedure

2.1. Raw materials

Kaolin (obtained from Beihai in Guangxi Province, China) was calcined at 800 °C for 2 h to produce metakaolin. The chemical composition of the metakaolin as measured by XRF was (mass %): SiO_2 = 56.8, Al_2O_3 = 42.5, Fe_2O_3 = 0.24, K_2O = 0.46. A sodium silicate solution (Modulus: M = SiO_2/Na_2O molar ratio = 3.32, solid content = 37.2 mass %) was modified by NaOH. The H_2O/Na_2O molar ratio could be adjusted with distilled water.

2.2. Characterization methods

A Hitachi scanning electron microscope S-3400 was used at an accelerating voltage of 10 kV to observe the morphology of samples (SEM). Surface area and pore structure calculations of metakaolin geopolymer and ZSM-20 zeolite block were performed using a Micromeritics surface area analyzer (Gemini VII 2390) using N_2 gas as adsorbate. Before performing the surface area analysis, the samples were dried at 105 °C for 4 h. The crystalline phase of the samples was analyzed by X-ray diffraction using a Rigaku D/MAX 2500 v instrument (XRD), and the crystallinity was calculated with the peak separation method using Rigaku-provided software (Du et al., 2001).

2.3. Preparation process of ZSM-20 zeolites

In this work, ZSM-20 zeolites were synthesized in situ from metakaolin-based geopolymers, which were prepared using sodium silicate solutions and metakaolin as raw materials, according to the steps given in Fig. 1. The two-part procedure consisted of part I, preparation of the metakaolin-based geopolymer, and part II, the crystallization process. During part I, sodium silicate solutions (Modulus = 0.9–1.2) and metakaolin were fully mixed to obtain a homogeneous slurry according to the composition designed as ZSM-20 zeolite (Si/Al molar ratio = 2.0). This slurry was then cast in cylindrical molds (d = 40 mm). The molds were sealed and then cured under varying conditions (30–60 °C, 1–7 days). After the curing process, the geopolymer gel was obtained. During part II, the geopolymer gels were placed in a Teflon hydrothermal synthesis reactor with distilled water and kept under certain hydrothermal conditions. After a hydrothermal process (130–160 °C, 8–14 h), the geopolymer gel converted into ZSM-20 or other zeolites.

3. Results and discussion

3.1. Characterization of the geopolymer gel

The XRD spectra of the geopolymer gel and metakaolin are shown in Fig. 2. As seen in curve (A-b), the geopolymer gel had an amorphous structure. After a series of geopolymerization reactions, a broad hump moved from 20–25° (in metakaolin) to 28° (in geopolymer) (Davidovits, 2011). Compared to the pattern of metakaolin, the emergence of dispersing diffraction peaks at 20°–40° indicates the conversion from metakaolin to geopolymer, and the disappearance of peaks at 17°–25° indicates that metakaolin dissolved under alkaline conditions during the geopolymer preparation reaction (Heah et al., 2012). The diffraction peak at 26° is the characteristic peak of SiO_2, demonstrating that unreacted SiO_2 remains in the geopolymer.

From Fig. 2 (B), it can be clearly seen that geopolymer gels exhibited an irregular structure, corresponding to the amorphous structure in the XRD analysis. The amorphous structure had high reactivity and was beneficial to the hydrothermal reaction in part II.

To determine the optimal preparation conditions for ZSM-20, the influences of the alkalinity, the curing conditions and the hydrothermal conditions on the products were investigated. The as-prepared samples were characterized by XRD, SEM, surface and pore structure analyses.

3.2. Alkalinity of the reaction system

During the synthesis of ZSM-20 from geopolymer gel, the modulus of the sodium silicate solution and the H_2O/Na_2O molar ratio are the critical indices of the alkalinity. The lower the modulus and H_2O/Na_2O molar ratio, the higher the alkalinity in the reaction system.

During both the synthesis of geopolymer gel and the hydrothermal transformation from geopolymer to zeolite, alkalinity has a great impact. Different alkalinities lead to different degree of polymerization of

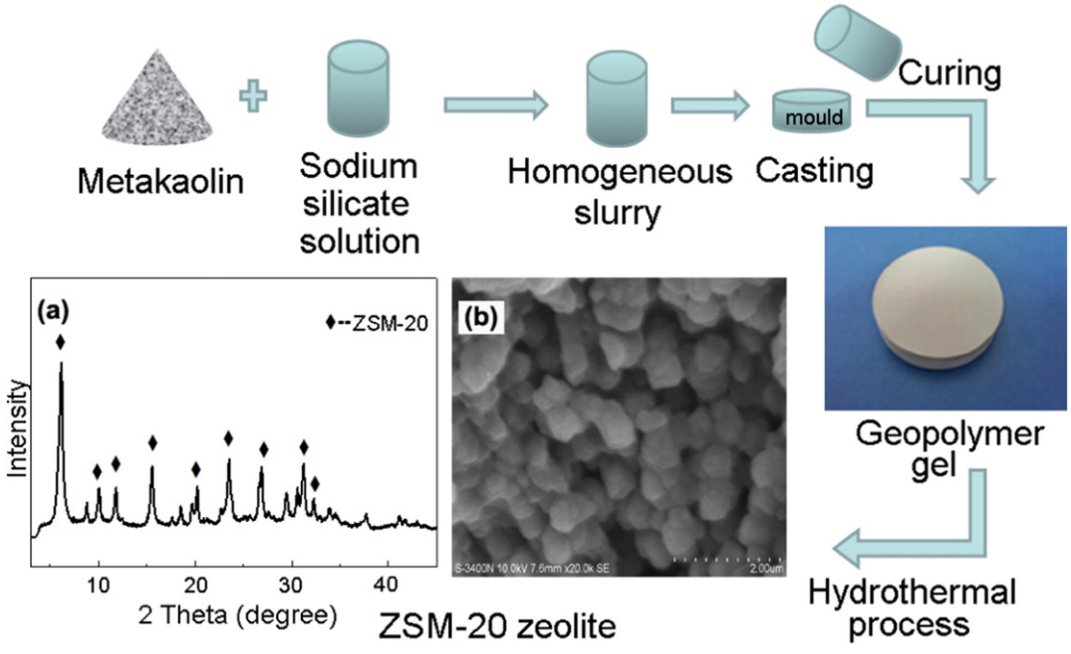

Fig. 1. Schematic fabrication process of ZSM-20 zeolite and the XRD pattern (a) and SEM image of ZSM-20 zeolite (b).