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Red mud as aluminium source for the synthesis of magnetic zeolite

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ABSTRACT

Zeolite synthesis typically requires batch systems (precursor mixture) in which aluminate and silicate solutions are first mixed and then subjected to hydrothermal treatment. In this study, FAU and GIS types zeolite with wool ball-like morphology were synthesized using colloidal silica and red mud as an alternative aluminium source. The addition of aluminium powder to the precursor mixture composed by colloidal silica and red mud resulted in the crystallization of pure GIS-type zeolite with a cactus-like morphology. The crystalline products (GIS and FAU zeolites) were thoroughly characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and nitrogen adsorption. In addition, the magnetic properties of the zeolites were studied since the red mud used as aluminium source is mainly containing a mixture of magnetic iron-based oxides. The magnetic zeolites will be further considered for wastewater treatment, as they can be easily separated using an external magnetic field.

1. Introduction

Zeolites are hydrated aluminosilicate minerals with a three-dimensional open structure consisting of aluminium and silicon tetrahedra linked by shared oxygen atoms. Zeolites have been synthesized using a variety of initial materials [1–13]. Some research has been focused on the use of natural minerals such as clays, pure aluminate and silica sources and waste materials mainly represented by coal and biomass ashes as well as red mud. The zeolite synthesis using natural sources is considered as not expensive process since it is using raw materials naturally available at low cost. A thermal pre-activation to convert the mineral sources into activated silica and aluminate is required prior their use in zeolite synthesis, and this significantly could reduce the economic benefits. Moreover, since the chemical composition of natural sources from different locations is not identical, the zeolite synthesis conditions need to be additionally optimized. On the other hand, during the last few years, the synthesis of zeolites using waste material has also attracted significant interest. Wastes composed by large amount of aluminosilicate and silicate phases (coal and biomass fly ash) are considered as sources for zeolite syntheses. The process diverts the waste materials from disposal sites and transforms them into useful secondary products. The waste materials in some cases contain toxic elements which depend on the mode of their occurrence and could restrict them from certain applications [13].

Both FAU- and GIS- type zeolites have been prepared by direct transformation of natural sources [1,14–21], pure chemicals [22–25] and waste materials [4,26–31]. Recently alkaline pre-fusion and microwave heating have been applied for the synthesis of zeolites [32–39]. Among these synthesis methods, the process requiring organic compounds as structure directing agents has been largely used mainly to direct the crystallization process of nanocrystalline and high silica zeolites [40–44]. Template-free synthesis [45–48] using pure aluminate and silicate suspensions, a seed growth approach [49], and multi-step synthesis [50–53] approaches have been wildly applied for the preparation of zeolites.

In this study, FAU and GIS types zeolite with different morphologies using colloidal silica (Ludox HS-30) and an alternative aluminium source (red mud) were synthesized. Red mud (RM) is a waste material formed during the production of alumina when the bauxite ores are subjected to caustic leaching. It is mineralogically characterized by the presence of iron oxy-hydroxides (i.e., primarily hematite and goethite) with a minor percentage of aluminium hydroxides (i.e., boehmite). The red mud containing iron-based oxides with magnetic properties is expected to induce a magnetic behavior to the final synthetic zeolites. The possible application of the magnetic zeolites will be in wastewater treatments, as they can be easily separated from the medium using an

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Table 1
Chemical composition of red mud (major costituents - %).

Sample	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe
RM	2.99	0.128	6.07	3.68	0.379	2.52	2.88	0.171	25.7

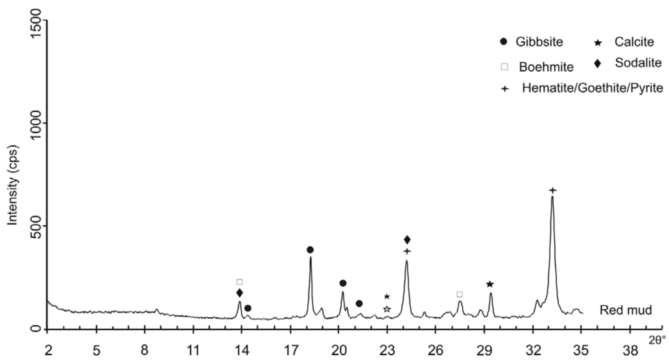

Fig. 1. XRD pattern of red mud (RM).

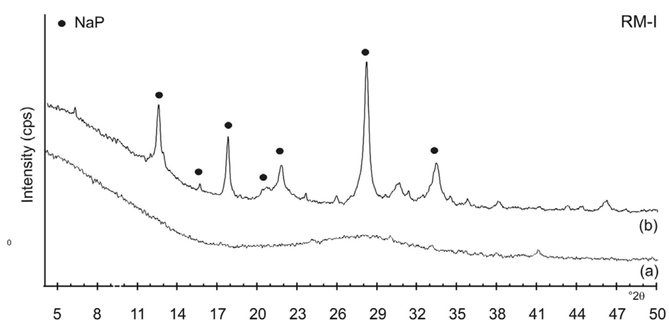

Fig. 2. XRD pattern of sample RM-I synthesized for four days at 40 °C (a), and after additional treatment for three days at 90 °C (b).

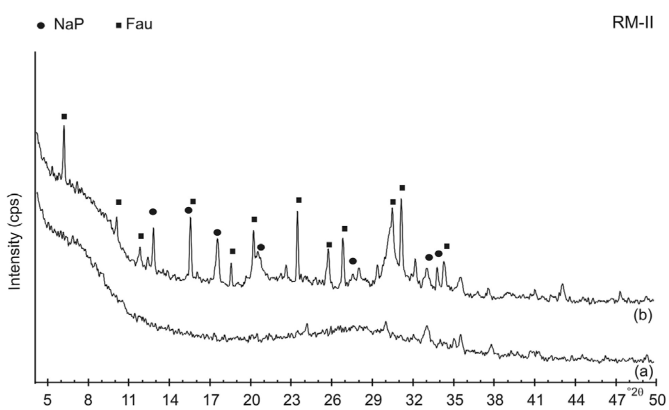

Fig. 3. XRD pattern of sample RM-II synthesized for four days at 40 °C (a), and after additional treatment for three days at 90 °C (b).

external magnetic field.

2. Experimental

2.1. Material

Red mud (RM) from aluminium extraction area of Podgorica, Montenegro, as the main aluminium source for the zeolite synthesis was used. The chemical composition of the RM is given in Table 1. Pure sodium hydroxide pellets (98%), Ludox LS-30 (30 wt% SiO_2), aluminium powder and deionised water for the preparation of the initial precursor suspensions were used. All chemicals of reagent grade were purchased from Aldrich Chemicals Ltd.

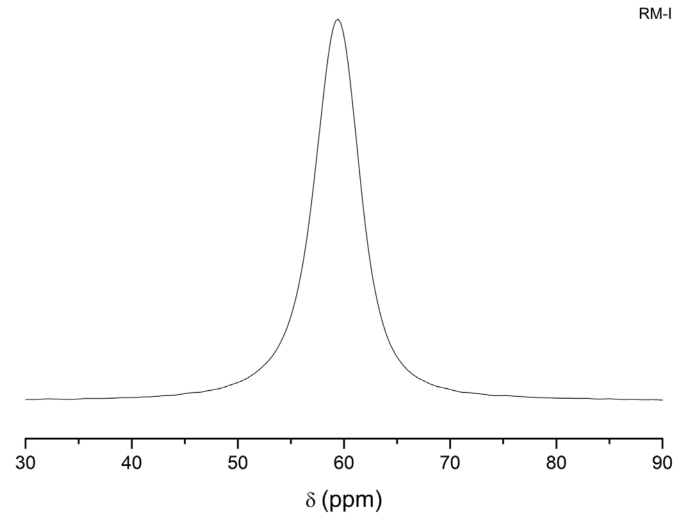

Fig. 4. ^{27}Al MAS NMR spectrum of sample RM-I.

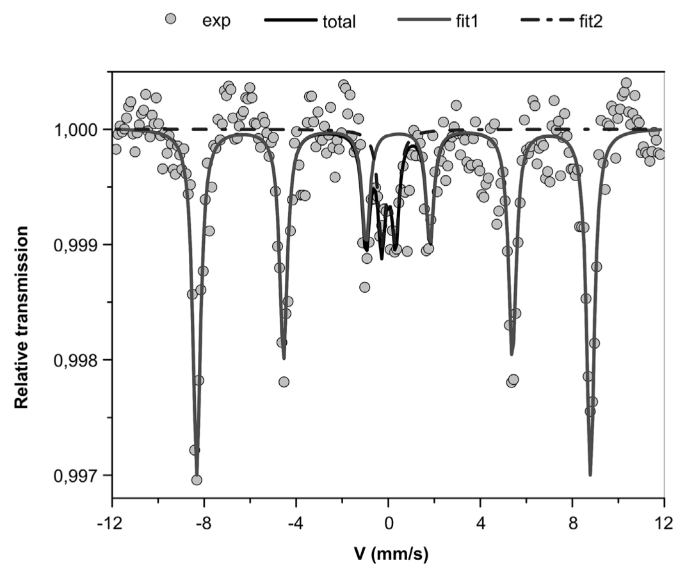

Fig. 5. ^{57}Fe Mossbauer spectrum of sample RM-I recorded at −196 °C (77 K).

Table 2
Mosbauer fitted parameters of sample RM-I.

	δ (mm/s)	2ε (mm/s)	B_{hyp} (T)	%
	± 0.01	± 0.01	± 0.5	± 2
Hematite	0.48	−0.19	52.9	88
Fe^{3+}/Fe^{4+}	0.17	0.43	0	12

Isomer shift (δ), Quadruple shift(2ε), Hyperfine field B_{hyp} (T), Percentage of different component (%).

2.2. Zeolite synthesis

Solution A was prepared by dissolving RM (2.00 g) and sodium hydroxide (9.50 g) in distilled water (8.00 g) at room temperature. Solution B was prepared by dissolving sodium hydroxide (0.50 g) in Ludox HS-30 (2.00 g) at 100 °C until clear suspension was obtained. Then solution A was quickly added into solution B under vigorous stirring. The resulted suspension was continuously stirred for 1 h, and