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Microporous and Mesoporous Materials 88 (2006) 220–231

MICROPOROUS AND MESOPOROUS MATERIALS

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Cr(III) exchange on zeolites obtained from kaolin and natural mordenite

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Received 9 March 2005; received in revised form 13 September 2005; accepted 15 September 2005
Available online 3 November 2005

Abstract

Zeolites with high Cr(III) exchange capacity were synthesized from kaolin and natural mordenite. The intermediate phases and final products were characterized by X-ray diffraction, FTIR spectroscopy, scanning electron microscopy, thermogravimetric analysis, N_2-adsorption and chromium exchange capacity (CrEC). In addition, precise zeolitic phases were identified using the TOPAS program based on Rietveld refinement. Hydrothermal synthesis from kaolin leads to the formation of a mixture of zeolites-X and A. At higher hydrothermal treatment period, zeolite-X (space group *Fd-3*) appears as the dominant phase. In the synthesis from natural mordenite a mixture of zeolite-Y (*Fd-3m*) and orthorhombic zeolite-P2 (*Pnma 62*) is formed, obtaining a more pure zeolite-P with the increase in reaction time. The differences in the course of the crystallization/transformation process in both systems are explained in terms of the differences in the dissolution rate of the starting materials in alkaline medium. The CrEC of synthesis products was determined by the type of zeolite and the fraction of amorphous phase in the solid product. It was found that the highest CrEC is obtained for synthesis products containing FAU-type zeolites. The chromium exchange on FAU zeolites is favored due to the larger pore opening, which facilitates the diffusion of large hydrated chromium ions into the internal cation exchange sites. Synthesized zeolite products presented higher Cr(III) exchange capacity than commercial zeolites. These results suggest that the use of these synthesized materials in Cr(III) removal from industrial wastewater could be promising.

Keywords: Zeolite synthesis; Cr(III) exchange; Kaolin; Natural mordenite; Zeolite transformation

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1. Introduction

Zeolites are materials widely known for their ion exchange properties [1]. Zeolitic materials are a good example of how the structure at an atomic scale can determine macroscopic properties, and how a detailed knowledge of structure can favor performance prediction. The Si/Al framework ratio of the zeolite determines its maximum ion exchange capacity; however the real capacity may be lower if a proportion of the charge compensation cations are inaccessible for the exchanging ion [2]. The aperture dimensions control exchanging ion entry into zeolite cavities, and may be a limiting factor during the ion exchange process [3]. Chromium (III) has the largest hydrated ionic radius of any known heavy metal [4] and its exchange in zeolitic materials requires a favorable pore opening. The study of the Cr(III) exchange in zeolites is interesting from an environmental point of view: the use of zeolitic materials in the control of pollution has received increasing attention [5–12] due to their good selectivity for cations such as Cr(III) from tannery effluents and the relatively low cost when using zeolite packed beds.

Cr(III) removal using several commercial synthetic and naturally occurring zeolites have been studied in previous

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1387-1811/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2005.09.007

works [13–15]. It was found that the commercial synthetic Na-X zeolite exhibits the highest Cr(III) exchange capacity. The structure of faujasite zeolites (natural faujasite and synthetics analogs X and Y) is one of the most open of all zeolites and are composed of significantly large openings of ∼0.74 nm. FAU-type zeolites are synthesized from pure reactive, such as solutions of sodium aluminate, sodium silicate, colloidal silica and triethanolamine (TEA). However, when zeolite is used for ion exchange units, it needs to have a competitive price with respect to other ion exchangers, since water purification processes consume large amounts of the exchanger material. For this reason, it is preferable to synthesize zeolites from more economical sources, such as natural aluminosilicates. De Lucas et al. [16] have reported the synthesis of zeolite X from calcined kaolin using silicate solution as an additional silica source and under normal pressure conditions. The variables were optimized to obtain zeolite-X with the established specifications for its use in detergent formulation. Rees and Chandrasekhar [17,18] have studied the formation of zeolite from kaolinite, metakaolinite and sodium aluminosilicate gel, using a sodium hydroxide medium and fluoride-containing medium at autogenous pressure. Kaolinite gave partially rehydrated non-basic hydroxysodalite, whereas zeolite 4A is produced from metakaolinite and sodium aluminosilicate gel. When a fluoride medium was used, kaolinite gave zeolite-P directly without any intermediate meta-stable phase; whereas zeolite-X was the stable intermediate from metakaolinite. The transformation of kaolin to low-silica X zeolite (LSX) was studied by Akolekar et al. [19], where metakaolin is converted to zeolite X plus a small amount of zeolite A in alkaline solution. The amount of zeolite-A decreases with increasing synthesis time, but there is an overall increase in product crystallinity and surface area. Chilean kaolinites have been used for the synthesis of Na-A zeolite with builder properties in powdered detergents [20]. No adverse effects have been found with respect to the presence of abundant coaly matter in the initial materials. Zeolites may also be obtained from starting materials such as volcanic glass [21], diatomite [22] and recently from fly ash [23,24]. Another form of zeolite synthesis is the transformation of one zeolite type into other zeolite types. Some zeolites represent metastable structures that may, under given conditions, be transformed into other more stable phases [2]. Subotić et al. [25] studied the kinetics of the transformation of synthetic zeolite-A into zeolite-P, showing that the processes take place by nucleation and crystal growth of the solution. The transformations of zeolite-X to HS and zeolite Y to P also have been studied [26]. Studies on transformation of well-known natural zeolites, such as mordenite, clinoptilolite or erionite into faujasite, have not been found in the literature. Highly occurring zeolites, such as mordenite and clinoptilolite, could be transformed under specific conditions into faujasite, a zeolite rarely found in nature.

The objective of this work is the synthesis of zeolites with high Cr(III) exchange capacity (CrEC) using kaolin and natural mordenite as starting materials, and to evaluate the effect related to the reaction time on the crystallization/transformation process and on product CrEC. The intermediates phases and final products were characterized by XRD, FTIR, SEM, N_2-adsorption and TG/DTG. Additionally, precise zeolitic phases analyzed by XRD were identified using the TOPAS program based on the Rietveld refinement.

2. Experimental

2.1. Materials

The starting materials used for the synthesis were kaolin (Sigma) and natural mordenite. Table 1 shows the chemical composition of the natural materials obtained by X-ray fluorescence. The mordenite zeolite was obtained from a natural deposit near the locality of Parral, situated about 300 km south of Santiago, Chile. To obtain a more reactive phase, kaolin and natural mordenite were used after calcination at 900 °C for 30 min.

2.2. Experimental

The synthesis experiments were carried out using a reaction mixture with the following molar composition: $3.75Na_2O:1.0Al_2O_3:2.5SiO_2:243.7H_2O$. This reaction mixture was prepared by mixing the calcined starting materials (metakaolin or calcined mordenite) with sodium hydroxide pellets and deionized water in a Teflon vessel (100 ml) at room temperature. The SiO_2/Al_2O_3 ratio of the reaction mixture was adjusted by adding appropriate amounts of sodium metasilicate salt ($Na_2SiO_3 \cdot 5H_2O$, BDH) and aluminiumoxide (Al_2O_3, Merck) for experiments with metakaolin and natural mordenite, respectively. The resulting mixtures were immediately placed in a Teflon-lined stainless steel reactor and kept in an oven for hydrothermal synthesis. The hydrothermal period was carried out at 100 °C under autogenous pressure and static conditions. The influence of the crystallization time on the type of formed

Table 1
Chemical composition of the starting materials (wt.%)

	SiO_2	Al_2O_3	TiO_2	MgO	CaO	Fe_2O_3	Na_2O	K_2O	MnO	Molar SiO_2/Al_2O_3
Kaolin	45.4	38.5	1.60	0.03	0.15	0.50	0.20	0.10	–	2.00
Natural mordenite	70.66	12.69	0.30	0.68	3.35	1.21	1.47	1.10	0.20	9.45