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Hydrogen adsorption on natural and sulphuric acid treated sepiolite and bentonite

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ABSTRACT

In this study, hydrogen (H_2) adsorption on sepiolite and bentonite and those of acid treated forms were studied at 77 K using volumetric apparatus up to 100 kPa. Both clay minerals were treated with 100 ml of 0.5, 1.0, 2.0 and 4.0 M H_2SO_4 solutions at 80 °C for 5 h. Differences in the structures of the sepiolite and bentonite samples before and after the acid treatments were determined by XRD, XRF, TG, DTA and N_2 adsorption methods. The level of H_2 adsorption of original and acid treated sepiolite samples (1.332–2.252 mmol/g) was higher than those of the bentonite samples (0.341–1.003 mmol/g). The variation in the H_2 adsorption capacities during the acid treatment was also discussed.

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Introduction

The clay minerals are hydrous aluminum phyllosilicates with industrial importance [1]. Although the basic building blocks of smectite and sepiolite are similar, the difference in the arrangement and content of the tetrahedral and octahedral sheets leads to the important structural differences between these two clay minerals [2]. Smectite is three-layer mineral having central octahedral sheet sandwiched between two silica tetrahedral sheets [2]. A charge imbalance is created by the considerable substitution in the octahedral sheet of Fe^{2+} and Mg^{2+} for Al^{3+} and in the tetrahedral sheet of Si^{4+} by Al^{3+} [2,3]. The term bentonite is used for any clay which was dominantly composed of a smectite [4]. In addition to the structural properties, the high surface area gives a smectite a high gas adsorption capacity for many gases, making it very effective in various industrial applications.

Sepiolite has 2:1 inverted structure with a general formula $(OH)_4(OH)_4Mg_8Si_{12}O_{30} \cdot 8H_2O$ [2,5]. The octahedral sheets are continuous in only one dimension and the tetrahedral sheets are divided into ribbons by the periodic inversion of rows of tetrahedrons [2]. The internal arrangement of the tetrahedral and octahedral layers of sepiolite results in channels throughout the structure [2,5]. When adsorbed water from external surfaces and zeolitic water from within the channels are lost by heating the surface area and thus the adsorption capacity of the sepiolite is increased. In order to increase the specific surface area, porosity and adsorption capacity of gases, clay minerals are generally activated by using nitric, hydrochloric or sulphuric acid solutions. This treatment causes the replacement of exchangeable cations with H^+ , the dissolution of some impurities such as calcite and gypsum and the removal of some aluminum ions from the tetrahedral layer and some iron, aluminum, and magnesium ions from

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the octahedral layer. The main mineral component of the sample as well as the type and amount of other clay and non-clay minerals present plays an important role in the gas adsorption properties [2].

The adsorption of hydrogen on bentonite and sepiolite type clay minerals [6–13] has been investigated worldwide. Gil et al. [6] investigated the hydrogen adsorption at 77 K on alumina pillared Gador montmorillonite. H₂ adsorption capacity of (GAmont-Al) 473 sample was found as 0.5 mmol/g up to 14 kPa. Gil et al. [7] measured the hydrogen capacity of various alumina pillared montmorillonite from Tsukinuno at 77 K. They proposed the presence of the relation between the microporous volume and the hydrogen uptake of the pillared clays. Didier et al. [8] investigated the hydrogen adsorption on Na synthetic montmorillonite-type clays and CO_x clayrock using gas chromatography method at 90 and 120 °C. Edge [9] stated that laponites with 3 wt% H₂O rapidly physisorbed 0.5–1 wt% H₂ at 77 K and 80 bar. Mondelli et al. [10] synthesized sodium montmorillonite (Na-Mt) for investigating the adsorption and diffusion of hydrogen gas at pressures up to 90 bar and at 363 K. Sandi et al. [11] synthesized the pure carbon-based material using sepiolite clay. The hydrogen storage capability was found ca. 2.2% w/w for the carbon nanofibers at room temperature and 10 MPa. Back et al. [12] investigated the hydrogen sorption on novel Pd-doped sepiolite-derived carbon nanofibers. Ruiz-Garcia [13] investigated the hydrogen adsorption properties of clay-graphene nanomaterials prepared using caramel from sucrose and two types of natural clays (montmorillonite and sepiolite). Erdoğan Alver [14] obtained the hydrogen adsorption isotherms of bentonite from Ünye and that of K⁺, Li⁺, Ag⁺ and Mg²⁺ exchanged forms at 77 K and pressures up to 100 kPa. H₂ gas adsorption capacity of these samples was found in the range of 0.522–0.388 mmol g⁻¹. Large deposits of bentonite and sepiolite are widespread in Turkey, however the studies on hydrogen [14] adsorption on these materials are limited. Moreover, most of the previous studies do not take into account the effect of the sulphuric acid activation on the structural properties of these two different clay minerals under the same conditions. For this reason, the main objective of this study is to investigate the effect of sulphuric acid treatment on structural, thermal and hydrogen adsorption properties and to evaluate their capacities in the storage of hydrogen for possible energy applications.

Experimental

Materials and methods

Sepiolite (S) from Sivrihisar and bentonite (B) from Ünye were used as the starting materials in this study. First, samples were crushed and sieved to obtain <90 µm fractions and then washed with 100 ml of de-ionized water at 80 °C for 5 h and dried at room temperature. In order to consider the effect of acid treatment on structural and gas adsorption properties of sepiolite and bentonite, 5 g of these clay minerals was modified with 100 ml of 0.5, 1.0, 2.0 and 4.0 M H₂SO₄ solutions at 80 °C for 5 h. After the acid treatment, the samples were separated and washed with hot deionized water at several

times. Before the experimental procedure, all samples were dried in an oven at 100 °C for 24 h. The resulting acid-treated sepiolite and bentonite samples were named as SH-05, SH-1, SH-2, SH-4, BH-05, BH-1, BH-2 and BH-4, according to their corresponding 0.5, 1.0, 2.0 and 4.0 M acid treatments, respectively.

Instrumentation

In this paper, XRD, XRF, TG, DTA and N₂ adsorption techniques were used for comparison of the sepiolite (S) and bentonite (B) samples before and after the acid treatment. Powder XRD patterns were obtained using a Bruker diffractometer (D8 Advance) in the range 3–40° 2θ, using CuK_α radiation at 40 kV and 40 mA. The samples were scanned with a step of 0.02° 2θ. The chemical analyses of the samples were carried out using a Panalytical-Zetium model XRF instrument. Simultaneous TG and DTA measurements performed with a Setsys Evolution Setaram instrument in the temperature range of 30–1000 °C with the heating rate of 10 °C min⁻¹. About 40 mg of sample was loaded into alumina pan. Both N₂ and H₂ adsorption isotherms of all samples were obtained by Quantachrome Autosorb 1 gas adsorption analyzer. Specific surface area values were determined from the B.E.T. method for the relative pressure (P/P₀) between 0.05 and 0.35. In addition, t-plot method was used for calculation of the micropore surface area and micropore volume values. All the samples were outgassed at 125 °C for 12 h prior to N₂ and H₂ adsorption measurements. High-purity (99.99%) nitrogen and hydrogen were used in gas adsorption measurements. All of the experimental runs were repeated to confirm the reproducibility of the obtained results.

Results and discussion

Elemental analysis

The results of XRF analyses of both natural and those of acid-treated forms are given in Table 1. Increasing concentrations of H₂SO₄ solutions caused increase in the relative SiO₂ content, due to its insolubility, and the progressive elimination of the significant amount of interlayer and octahedral cations from the bentonite structure. The presence of K₂O in BH-4 sample shows the relative resistance to acid attack of feldspar and illite impurities in the bentonite. Previous studies have also reported the similar changes [15,16]. Acid treatment of sepiolite also led to the significant changes in its chemical compositions. A large amount of octahedral cations were gradually removed, on the other hand SiO₂ content showed relative increase in the acid treated forms. Lazarevic et al. [17] and Gonzalez-Pradas et al. [18] also found the similar effect of acid treatment on the chemical composition of sepiolite.

X-ray analysis

The powder X-ray diffraction patterns of sepiolite and bentonite samples before and after acid treatments are given in Figs. 1 and 2, respectively. Both clay minerals were identified using the characteristic reflections of minerals [19].

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