Preparation of porous material from talc by mechanochemical treatment and subsequent leaching

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Abstract

Synthesis of porous silica via mechanochemical treatment of talc and subsequent acid leaching was investigated by X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and N_2 adsorption techniques. Raw talc was ground for different times and then leached with 4 M hydrochloric acid (HCl) at 80 °C. Grinding for 6 h and subsequent leaching for 2 h of raw talc produced the porous silica with a specific surface area of 133 m^2/g and total pore volume of 0.22 ml/g. The increase in specific surface area (S_{BET}) of the porous silica reflected the formation of micropores of 1.2~1.8 nm and mesopores of 4.0~5.5 nm in diameter inside the porous structure. The number of micropores decreased with prolonged leaching time, which can be attributed to a condensation reaction. The characteristic of hysteresis loop indicated mainly slit-shaped pores. The apparent activation energy for the leaching process was calculated to be about 21.6 kJ/mol, indicating that the kinetic process of talc leaching was the diffusion-controlled reaction. Mechanochemical treatment may promote the amorphization of talc, being greatly favorable to the subsequent leaching.

1. Introduction

Many special properties and broad application fields of porous materials, especially average pore size being nanometer quantity level, caused far-ranging appreciation of many scientists and enterprisers (Schüth and Schmidt, 2002). A new family of mesoporous materials is M41S which was synthesized firstly by Mobil Oil Company (Kresge et al., 1992; Chen et al., 1993; Herino, 2000). But the techniques to prepare this material need expensive organic raw materials and rigorous reaction conditions, so it is very difficult to be widely applied.

Silicate minerals are excellent raw materials for preparing porous materials because of their special structures. Much work has been done to prepare molecular sieves from zeolite type minerals which have been applied on a large scale in oil and chemistry industries (Kenneth et al., 2002; Claude, 1998; Xu and Zhu, 2003). So layer silicate minerals were used to

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produce cheaper porous materials because of their abundant reservations. Among these layer silicate minerals, montmorillite (Veda and Krishnan, 2002; Temuujin et al., 2004) and kaolinite (Temuujin and Okada, 2002) were paid more attention.

Preparation of porous materials from silicate minerals by mechanochemical activation and subsequent leaching involves the distortion of mineral structure and the removal of metallic ions through acid leaching, leaving pores within the mineral structures. Porous materials prepared via this technique show potential applications including catalyst supports, catalyst, adsorbents and agents for organic molecule separations (Aznar et al., 1996; Suquet et al., 1991; Corma and Perez-Pariente, 1987; Gonzales et al., 1984; Okada et al., 1999). There are some examples of using acid leaching method to prepare porous silica from silicate minerals, such as metakaolinite (Okada et al., 1998), montmorillonites (Shinoda et al., 1995), antigorite (Kosuge et al., 1995), chrysotile (Suquet, 1989), phlogopite (Kaviratna and Pinnavaia, 1994), vermiculite (Temuujin et al., 2003a) and so on. The S_{BET} of leached products varies greatly from a maximum value of 670 m^2/g for vermiculite (Temuujin et al., 2003a) to about 20 m^2/g for phlogopite (Kaviratna and Pinnavaia, 1994). But no report has been focused on the kinetic behavior of the leaching process.

Clay minerals can be classified into three types: 1:1, 2:1 and 2:1:1 according to their structures and the maximum obtainable surface area. Porous materials have been prepared mainly from 1:1 and 2:1 types of clay minerals by simple acid leaching. Since the S_{BET} of the porous materials obtained from 2:1 type clay minerals are generally higher than those from the 1:1 type, the former is considered to be more desirable as raw materials for preparing porous silica. On the other hand, almost no substitution occurs in the tetrahedral layers of 2:1 clay minerals such as talc and pyrophyllite. These minerals are very resistant to acid attack (Perez Rodriguez et al., 1985; Temuujin et al., 2003b), possibly due to their unstrained structures and the presence of oxygen atoms solely between the layer surfaces. Distortion of the layer structure of talc caused by grinding may significantly promote its leaching behavior. In the present paper, the syntheses of porous silica from talc and kinetic behaviors were primarily investigated.

2. Experimental

Natural talc from Guilin, China was used as raw material. The main chemical compositions of the talc were as follows (wt.%): 62.45 SiO_2, 31.16 MgO, 0.63 Fe_2O_3, 0.08 Al_2O_3 and 0.1 TiO_2. Mechanochemical treatment was performed for different times (2, 4, 6, 8 h, respectively) in a KM-10 type planetary mill at 600 rpm at room temperature with batches of 30 g samples and 10 mm diameter stainless steel balls at a ball-to-sample weight ratio of 10:1. After batch grinding, a 2 g sample was treated with 200 ml of 4 M hydrochloric acid (HCl) at 80 °C for various times. After leaching, 100 ml of distilled water was added and the sample was allowed to cool for 30 min. The suspension was filtered and then dried at 80 °C overnight. The samples were designated as TnGmL, where n and m correspond to grinding time (h) and leaching time (h), respectively.

The crystallinity of the samples was determined by XRD (Shimadzu Labx XRD-6100). The chemical compositions were measured using X-ray fluorescence using a Rigaku RIX spectrometer. The infrared (IR) spectra were recorded with a Shimadzu FTIR 8120 spectrometer using KBr disc technique. The morphology of the samples was observed by SEM using a JEOL JSM-5310 electron microscope at an acceleration voltage of 10, 15 or 20 kV. Nitrogen gas adsorption–desorption isotherms were measured at 77 K using a Quanta Chrome Autosorb-I instrument. The specific surface area was calculated by the Brunauer–Emmet–Teller (BET) method. The total pore volume was obtained from the maximum amount of nitrogen gas adsorbed at partial pressure (p/p_0) = 0.999. Isotherm data can be derived from either desorption or adsorption isotherm to calculate the pore size distribution. A pore size distribution is defined as the distribution of pore volume with respect to pore diameter of the sample. The Kelvin equation is only suitable for pores >2 nm. Mesopore size calculations were made using the Kelvin equation. Desorption isotherm was used to determine the pore size distribution using the Barrett–Joyner–Halenda (BJH) method through the AUTOSORB software. The HK model relates relative pressure (p/p_0) to a micropore radius described by a Lennard–Jones potential. Isotherm data at very low pressure in the region of micropore filling $(p/p_0 < 0.01)$ is necessary for the HK model to obtain reliable data. Micropore size distribution was derived from physisorption isotherm data according to the assumed slit-shaped pores. BJH and HK have been the commonly accepted methods to calculate the mesopore size distribution and micropore size distribution, respectively.

3. Results and discussion

3.1. Effect of milling on the talc structure

Mechanical grinding has great effect on the crystal structure of talc powder. During the grinding process, the powder surface was struck, cut and fell to pieces because of striking between the steel balls and chamber wall, which made the particle size of the powder smaller, the surface area and surface energy much higher. On the