Available online at www.sciencedirect.com

SCIENCE DIRECT®

Applied Clay Science 30 (2005) 116–124

Applied CLAY Science

www.elsevier.com/locate/clay

Preparation of porous silica from chlorite by selective acid leaching

Kiyoshi Okada[a,*], Naoki Arimitsu[a], Yoshikazu Kameshima[a], Akira Nakajima[a], Kenneth J.D. MacKenzie[b]

[a]*Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo 152-8552, Japan*
[b]*School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600 Wellington, New Zealand*

Received 21 May 2004; received in revised form 30 March 2005; accepted 4 April 2005
Available online 23 May 2005

Abstract

Porous silica was prepared by selective leaching of chlorite and the influence on the porous properties of the product of the acid type and acid concentration, solution temperature and leaching time were investigated. After leaching, only SiO_2 remained, the other components being selectively leached from the sample in the order $MgO < Fe_2O_3 < Al_2O_3$. The specific surface area of the product obtained by H_2SO_4-leaching was greater than with HNO_3- and HCl-leaching. The highest specific surface area (394 m^2/g) was obtained by leaching the chlorite with 5 N H_2SO_4 at 90 °C for 1.5 h. The pore size distribution of the products showed a maximum at about 5 nm with a pore size much larger than would be expected for selective leaching of the octahedral chlorite sheets. The ^{29}Si MAS NMR spectra of the products showed a stronger Q^4 peak (related to a framework structure unit) than the Q^3 peak (from a layer structure unit), suggesting the presence of a framework structure similar to silica gel rather than the original layered structure. The resultant structure of the silica product results in a lower specific surface area than found in leached vermiculite and phlogopite.

Keywords: Selective leaching; Chlorite; Porous material; Acid treatment

1. Introduction

The wide use of porous materials in environmental applications has led to the development of a variety of preparation methods. These are of two types, i.e. assembly from component structures, and leaching methods. Selective leaching of clay minerals with acid is a well-known longstanding technique which provides a simple and cost-effective method for preparing porous silica from various clay minerals including kaolinite (Okada et al., 1998), antigorite (Kosuge et al., 1995), chrysotile (Suquet, 1989), phlogopite (Okada et al., 2002), montmorillonite (Shinoda et al., 1995), vermiculite (Temuujin et al., 2003), sepiolite (Balci, 1999), etc. In this process, all the components of the clay minerals except SiO_2 are leached out by the acid and the leached spaces become pores in the product. The porous properties

* Corresponding author. Tel.: +81 3 5734 2524; fax: +81 3 5734 3355.
E-mail address: kokada@ceram.titech.ac.jp (K. Okada).

0169-1317/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.clay.2005.04.001

of the leached products vary widely according to the structures and components of the starting clay minerals.

In the case of the 2:1 type clay minerals, both the octahedral sheets and interlayers are sandwiched by tetrahedral sheets and are leached by the acid, leaving the tetrahedral units on the surfaces of the platy clay particles. It is therefore important to know whether the tetrahedral sheets consist solely of SiO_4 or whether partial substitution by AlO_4 tetrahedra occurs, since the latter are leached by acid. The leaching of AlO_4 from the tetrahedral sheets opens up pathways for acid attack on the octahedral sheets and interlayers by both gallery access and edge access, enhancing selective leaching of the starting material. By contrast, the acid attacks only by edge access in the absence of substitution of tetrahedral AlO_4 for SiO_4. Most of the 2:1 type clay minerals are of the former type whereas a limited number of clay minerals, including talc, pyrophyllite and montmorillonite, are of the latter type.

We have investigated preparation and properties of silica products from various 2:1 type clay minerals (talc (Okada et al., 2003a), phlogopite (Okada et al., 2002) and vermiculite (Temuujin et al., 2003)) by selective acid leaching. The leaching rates of the various clay minerals were found to differ considerably, in the following order of leachability: talc $\ll$ phlogopite$\leq$vermiculite. Since there is no AlO_4 substitution in the SiO_4 tetrahedral sheets of talc, but partial AlO_4 substitution in phlogopite and vermiculite, tetrahedral AlO_4 substitution clearly exerts considerable influence on the leaching rate. The porous properties of the silica products from talc were also distinctly different from those of the other minerals, being non-porous with a maximum specific surface area of only 38 m^2/g even after hydrothermal treatment at 150 °C for a long time in strong acid. By contrast, the products obtained from phlogopite and vermiculite were porous, with specific surface areas of about 530 and 670 m^2/g, respectively. The measured specific surface areas increase in the order talc $\ll$ phlogopite $<$ vermiculite, as does their interlayer spacings (0.93, 1.0 and 1.4 nm, respectively), suggesting that higher specific surface areas may be obtained from clay minerals with larger interlayer spacings.

It is therefore interest to examine the porous properties of the product from leached chlorite, which has a 2:1:1 type sheet structure with an interlayer spacing of about 1.4 nm. In the present work, silica products were prepared from chlorite by selective leaching and their porous properties were determined. The effect of the structure and chemical composition of the starting clay mineral on the resulting silica product is also discussed.

2. Experimental

2.1. Preparation

Chlorite from Wanibuchi, Shimane, Japan (Iwao, 1969) was used as the raw material. This mineral occurs in association with gypsum ore deposits from which it was purified by elutriation.

In the initial leaching experiments, powdered chlorite samples were treated with nitric acid, sulfuric acid and hydrochloric acid to optimize the selective leaching procedures to produce products with the highest specific surface areas. Samples (1.5 g) were reacted with 75 ml of each acid (2 N) at 90 °C for 2 h, washed once with the same diluted acid (0.2 N), followed by three washings with distilled water. The product was then centrifuged and dried at 110 °C overnight. Based on the results of the initial leaching experiments, further selective leaching experiments were carried out with sulfuric acid at acid concentrations of 2, 5 and 7 N, reaction temperatures of 70, 80 and 90 °C, reaction times of 0.5, 1, 1.5 and 2 h. The aim of these experiments was to determine the optimal conditions for obtaining the highest specific surface areas.

2.2. Characterization

The chemical compositions were determined by X-ray fluorescence using a Rigaku RIX2000 spectrometer. X-ray diffraction (XRD) patterns were recorded on a Shimadzu LabX XRD-6100 diffractometer using monochromated Cu Kα radiation to identify the crystalline phases in the samples. The DTA–TG curves were recorded up to 1300 °C at a heating rate of 10 °C/min in a dynamic atmosphere of dry air using a Rigaku Thermoplus TG8120 instrument. Solid-state ^{29}Si and ^{27}Al MAS NMR spectra were obtained at 11.7 T using a Varian Unity 500 spectrometer and