Available online at www.sciencedirect.com
ScienceDirect
Microporous and Mesoporous Materials 101 (2007) 355–362
MICROPOROUS AND MESOPOROUS MATERIALS
www.elsevier.com/locate/micromeso

Incorporation of hybrid elements into microporous titanosilicate ETS-10: An approach to improving its adsorption properties toward Pb^{2+}

L. Lv, F. Su, X.S. Zhao *

Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117576, Singapore

Received 19 July 2006; received in revised form 23 November 2006; accepted 25 November 2006
Available online 16 January 2007

Abstract

In this study, B-, Al-, and Ga-substituted microporous titanosilicate ETS-10 (designed as ETBS-10, ETAS-10, and ETGS-10, respectively) were synthesized under hydrothermal conditions. The adsorption kinetics and equilibria of Pb^{2+} ions on the ETS-10 (without substitution), ETBS-10, ETAS-10, and ETGS-10 samples were measured in a batch mode. Upon isomorphous substitution of B, Al and Ga for the Si(4Si) sites, the resulting solids exhibited more surface-negative charges as revealed by Zeta potential profile. The kinetic data showed a similar adsorption rate of Pb^{2+} on the four samples because of the same crystalline structure and the similar particle sizes of the four samples. However, the equilibrium results demonstrated that the maximum adsorption capacities of Pb^{2+} ions on samples ETBS-10, ETAS-10, and ETGS-10 were increased about 11%, 16.9%, and 12.5%, respectively, in comparison with ETS-10 because of the substitution of Si atoms by the trivalent elements.

Keywords: Microporous titanosilicate ETS-10; Isomorphous substitution; Heavy metal lead; Adsorption

1. Introduction

Pollution of waters by heavy metal lead emitted from a variety of sources such as storage batteries, mining, plating, and the ceramic glass industries [1] is of a great human concern. All over the world, guidelines set the maximum acceptable concentration of lead in surface water at very low levels because the presence of excess lead can cause damages to the nervous system, kidneys, and livers [2,3]. The control over the level of lead in aqueous solutions has been thus received a great deal of attention. Adsorption over zeolites has been demonstrated to be a very efficient method because of many virtues of zeolites, such as high adsorption capacity, wide availability, low cost, and excellent stabilities [4–6].

Microporous titanosilicate ETS-10 [7] is constituted from orthogonal TiO_6 octahedra chains and SiO_4 tetrahedra linked by corner-sharing oxygen atoms [8], forming a three-dimensional pore system. Each Ti atom in a six-coordinated state carries two negative charges, which are balanced by exchangeable alkali cations, normally Na^+ and K^+ [7,8]. Thus ETS-10 has been demonstrated to display unique adsorption properties towards divalent metal ions [9], especially Pb^{2+} ions [10].

When a trivalent element, M, is substituted for a tetrahedral Si atom in the framework of ETS-10, one more negative charge is generated in the resultant material. This would favor the adsorption of heavy metal ions because of the enhanced surface-negative charge density upon incorporation of M. Kuznicki and Thrush [9] indeed observed an enhanced adsorption capacity of lead on Al-substituted ETS-10 materials. However, very recently, Choi et al. [11] reported that the adsorption capacities of Pb^{2+} and Cd^{2+} ions on ETS-10 solids were not improved upon

---

* Corresponding author. Tel.: +65 65164727; fax: +65 67791936.
E-mail address: chezxs@nus.edu.sg (X.S. Zhao).

1387-1811/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2006.11.030

Al substitution because of the simultaneous substitution of Al for both octahedrally coordinated Ti and tetrahedrally coordinated Si atoms. Whether or not incorporation of M into the ETS-10 framework favors heavy metal adsorption deserves a further study.

On the other hand, if the incorporation of M element favors the adsorption of heavy metal ions, then it would be desirable to incorporate M into the framework of ETS-10 as high as possible. However, a previous study has shown that a hybrid element would exclusively substitute for the Si atoms of non-neighboring with the TiO_6 chains [12], limiting the content of the hybrid element that can be incorporated into the framework of ETS-10. Subsequent studies have shown that the maximum molar ratio of M/Ti in M-substituted ETS-10 materials is about 0.35 [13–16].

In the present work, we investigated the incorporation of trivalent elements B, Al, and Ga into the framework of ETS-10 by hydrothermal synthesis. The content and local structure of the incorporated hybrid elements were characterized by means of field-emission scanning electron microscope (FESEM), N_2 adsorption, inductively coupled plasma atomic emission spectroscope (ICP-AES), X-ray diffraction (XRD), Raman spectroscope, solid-state nuclear magnetic resonance (MAS NMR), and Zeta potential techniques. The adsorption isotherms and kinetics of heavy metal lead ions on the substituted ETS-10 materials were examined.

2. Materials and methods

2.1. Incorporation of hybrid elements into ETS-10

A pure ETS-10 was hydrothermally synthesized as described previously [17]. The incorporation of trivalent elements B, Al, and Ga was conducted by adding the corresponding metal sources into the synthesis gels, of which the compositions are shown in Table 1. A typical synthesis procedure is described as follows. An alkaline solution was first prepared by mixing NaCl (Adrich), KCl (Adrich), and sodium silicate solution (Merck, Na_2O 8 wt%, SiO_2 27 wt%) in deionized water under stirring for 0.5 h. Then, the Ti source, namely Degussa P25 (containing 76 wt% anatase and 24 wt% rutile) and an M source, namely $NaAlO_2$ (Strem), or B_2O_3 (Aldrich), or $Ga(NO_3)_3$ (Adrich) were combined in an aqueous solution of NaOH (Merck) under stirring for 1 h. Subsequently, the alkaline silicate solution and the Ti/M mixture were combined under vigorous stirring for 2 h. The resulting white opaque gels were sealed in a Teflon-lined stainless autoclave and placed in an oven for crystallization at 503 K for 60 h. The resultant products, named as ETAS-10, ETBS-10, and ETGS-10, respectively, were collected by filtration, washing with deionized water until the pH of the filtrate was below 10, and dried at 373 K overnight.

2.2. Characterization

The chemical compositions of the synthesis gels and final products were determined with ICP-AES on a Perkin–Elmer ICP Optima 3000DV spectrometer by digesting the samples with a dilute HF solution. The FESEM images were obtained on a JEOL JSM-6700F. The XRD spectra were collected on a Shimadzu XRD-6000 diffractometer (CuKα radiation). The Raman spectra were collected at room temperature on a FT-Raman spectrometer (Bruker Equinox 55) at a power of 200 mW and an excitation wavelength of 1064 nm. The ^{29}Si, ^{11}B, ^{27}Al, and ^{71}Ga MAS NMR spectra were obtained on a Bruker MSL-400 spectrometer. The M/Ti and Si/M molar ratios of the samples were also estimated using the ^{29}Si MAS NMR data by curve deconvolution into Gaussian functions with a software Origin 6.10. The pore structure characteristics were measured by nitrogen adsorption on an automatic volumetric sorption analyzer (Quantachrome, Autosorb-1). The specific surface areas (S_{BET}) were determined according to the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.2.

2.3. Measurement of Zeta potential

A suspension containing 100 mg L^{-1} solid sample and 0.001 M NaCl was shaken for 12 h at room temperature, followed by oscillation in an ultrasonic bath for 10 min. The pH of the suspension was adjusted from 2 to 10 by using a 0.1 M HNO_3 or 0.1 M NaOH solution. Then the supernatants were used to measure the electrophoretic mobility on a Brookhaven Zeta-plus 4. An average of eight experimental runs was taken to minimize the experimental error. The measured electrophoretic mobility of the colloidal particles was converted to Zeta potential ζ (mV) by using the Smoluchowski equation [18].

Table 1
Molar compositions in parent gels and atomic ratios of final products

	Composition in parent gels						NMR deconvolution		Chemical analysis	
	Na_2O	K_2O	SiO_2	TiO_2	M_2O_3[a]	H_2O	M[a]/Ti	Si/Ti	M/Ti	Si/Ti
ETS-10	3.36	1.41	5.68	1.00	–	187	–	5.03	–	4.97
ETBS-10	3.43	1.38	4.95	1.00	0.37	123	0.23	4.82	0.29	4.70
ETAS-10	3.32	1.42	5.02	1.00	0.33	128	0.36	4.69	0.35	4.62
ETGS-10	3.41	1.42	4.99	1.00	0.29	122	0.34	4.72	0.31	4.63

[a] M denotes B, Al, and Ga in the corresponding materials.