COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Novel nanoporous hybrid organic–inorganic silica containing iminodiethanol chelating groups inside the channel pores

Chunqing Liu,[a] Nathaniel Naismith,[a] Lei Fu[b] and James Economy*[a]

[a] *Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA. E-mail: jeconomy@uiuc.edu; Tel: 217-333-9260*

[b] *Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA*

Received (in Cambridge, UK) 11th April 2003, Accepted 12th June 2003

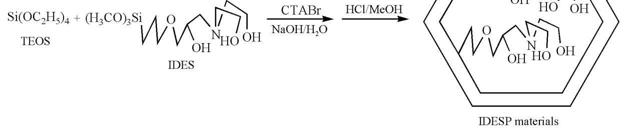
First published as an Advance Article on the web 27th June 2003

Novel nanoporous hybrid organic–inorganic silica with covalently bound iminodiethanol chelating groups inside the channel pores has been synthesized by template-directed co-condensation of tetraethoxysilane (TEOS) and organotrimethoxysilane $(CH_3O)_3SiR$ [IDES, R = $(HOCH_2CH_2)_2NCH_2CH(OH)CH_2O(CH_2)_3$], and is shown to be very efficient in recovery of germanium and antimony oxides from water.

In the past few years, a new family of ordered mesoporous silica materials, MCM-41 and related transition-metal oxide analogues, has attracted wide attention due to their high surface area and well-ordered porous structures.[1–5] However, the purely inorganic materials formed by this procedure have limited applications in environmental and industrial process due to the lack of organic functional groups. A second generation of materials containing organic groups on the surfaces of nanoporous or mesoporous silicas was produced by grafting or anchoring of organic guests onto the pore channel surface[6] or by the direct incorporation of organic groups through co-condensation of organotrialkoxysilanes.[7,8] However, only a few organic chelating functional groups such as mercaptyl,[7,8] ethylenediamine,[9] or cyclam moiety[10] have been covalently incorporated into the nanoporous or mesoporous silicas up to now.

Iminodiethanol (IDE) has been shown to be an efficient chelate-forming group for germanium and antimony oxides.[11] Here, we report the successful incorporation of IDE chelating groups into nanoporous silica through covalent bonds by co-condensation of varying molar ratios of TEOS and IDE-containing $(HOCH_2CH_2)_2NCH_2CH(OH)CH_2O(CH_2)_3Si(OCH_3)_3$ (IDES) in the presence of a structure-directing surfactant, cetyltrimethylammonium bromide (CTABr) (Scheme 1). We show that the nanoporous material IDESP-5% is extremely efficient in recovery of germanium and antimony oxides. The chelating precursor IDES was synthesized from the reaction of an epoxy group-containing 3-(2,3-epoxypropoxy)propyltrimethoxysilane with diethanolamine in isopropanol.

In a typical synthetic procedure for nanoporous hybrid silica (IDESP-5%), the molar ratio of the mixture was: IDES : TEOS : H_2O : NaOH : CTABr = 0.05 : 0.95 : 130 : 0.5 : 0.12. 7.87 g of CTABr (Aldrich) was dissolved in a solution of 3.96 g of NaOH and 346.68 g of high purity water. The solution was stirred at 40 °C for 30 min in a closed flask. 35.6 g of TEOS and 3.55 g of a mixture of IDES (3.1 g) and isopropanol (0.45 g) were added to the solution. The solution was stirred for 24 h at room temperature, and cured for an additional 24 h at 80 °C. The solid product was collected by filtration, washed thoroughly with high purity water and methanol, and air-dried under ambient conditions. The extraction of the surfactant template was performed by stirring a suspension of the solid product (8.9 g) in a mixture of methanol (1500 g) and concentrated HCl (89 g) at 50 °C for 2 h. The surfactant-extracted material was filtered, washed with copious amounts of methanol and dried for 24 h at 80 °C *in vacuo*.



Scheme 1 Synthesis of iminodiethanol chelating group-containing IDESP materials.

The nature and extent of IDE chelating moiety incorporation into the nanostructured materials were determined by solid state ^{13}C and ^{29}Si NMR of the as-synthesized and surfactant-extracted IDESP materials. The C–O and C–N carbon resonances are found in the region δ 50–80, and the Si–*C* and Si–C–*C* carbon resonances are found at δ 8.8 and 21.2, respectively, in the solid state ^{13}C NMR spectrum of the surfactant-extracted IDESP-5% material (Fig. 1). The surfactant resonances disappeared and the chelating group resonances increased in intensity from IDESP-5% to IDESP-20%. The solid state ^{29}Si NMR spectra of IDESP-10% and IDESP-20% samples show a broad signal at δ −61.9 attributed to T^3 $(CSiO_3)$ substructures, as well as two other signals at δ −100.6 and −110.1 attributed to Q^3 and Q^4 substructures, respectively. The increasing intensity of the T^3 peak from IDESP-5% to IDESP-20% is consistent with the increasing proportion of IDES units. These results indicate that IDES chelating groups can be covalently linked into silica structures by co-condensation in the presence of surfactant templates, and the chelating functional groups remain intact after surfactant extraction.

The nitrogen adsorption–desorption isotherm of IDESP-5% (Fig. 2) is of a type I isotherm, indicating that the pore size of

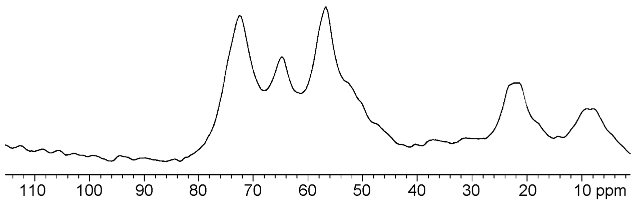


Fig. 1 Solid state ^{13}C NMR spectrum of surfactant-extracted IDESP-5% material.

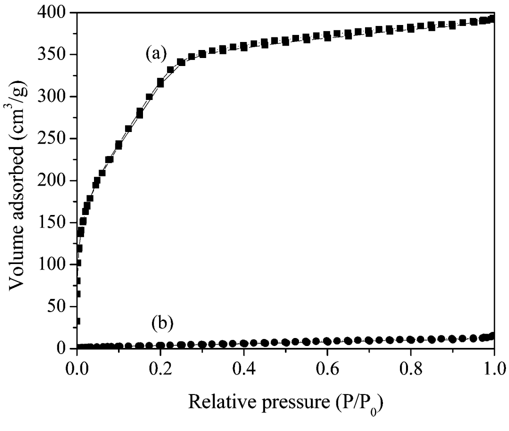


Fig. 2 Nitrogen adsorption–desorption isotherms of (a) IDESP-5% and (b) IDESP-20% materials.

DOI: 10.1039/b304057g

this material is in the nanopore ranges. The IDESP-5% material has a BET surface areas of 825 m^2 g^{-1} (Table 1) with a narrow pore size distribution centered at 1.94 nm calculated from the desorption branch by the BJH method (Fig. 3). However, the IDESP-20% material has a very low surface area of 7.6 m^2 g^{-1}, indicating that it is a nonporous material.

Table 1 displays the physical and surface properties of the IDESP materials obtained from their small angle XRD patterns and nitrogen isotherms. The powder XRD pattern of the surfactant-extracted IDESP-5% material (Fig. 4a) showed a single peak at 2.7 nm, which indicates some degree of structural correlation because of the uniformity of the pore channel diameters. However, the powder XRD pattern of the surfactant-extracted IDESP-20% material (Fig. 4b) did not show an apparent peak in the small angle region, indicating the disappearance of uniform nanopores in accordance with the nonporous feature of IDESP-20% measured from the nitrogen isotherm.

The adsorption properties of the nanoporous IDESP-5% material for germanium and antimony oxides were studied at different germanium and antimony concentrations in water (Table 2). It can be seen from Table 2 that a single treatment with IDESP-5% material reduces antimony concentration to well below 2 ppb. The germanium oxide could be reduced from 0.6 ppm to about 2 ppb, and from 7.8 ppm to about 40 ppb when treated with IDESP-5% material. The sorption kinetics of IDESP-5% material with germanium oxide (Fig. 5) indicates that this nanoporous chelating material could adsorb 98% of germanium from water in 10 min, and even more than 99% in 2 h. These adsorption results show that the iminodiethanol chelating group-containing nanoporous hybrid material IDESP-5% is ideal for the recovery of trace amounts of germanium and antimony ions from large volumes of environmental waters.

Table 1 Physical and surface properties of surfactant-extracted IDESP materials

Sample	*d* Spacing from XRD (nm)	BET Surface area/m^2 g^{-1}	Nanopore diameter/nm[a]
IDESP-5%	2.7	825	1.94
IDESP-20%	—	8	—

[a] Calculated from the adsorption branch by the BJH method.

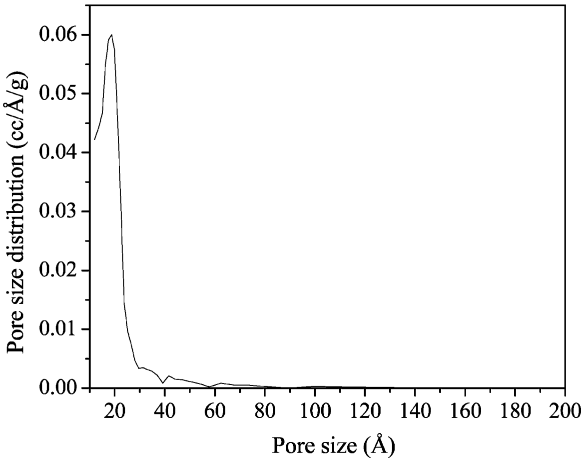


Fig. 3 Pore size distribution plot of IDESP-5% material.

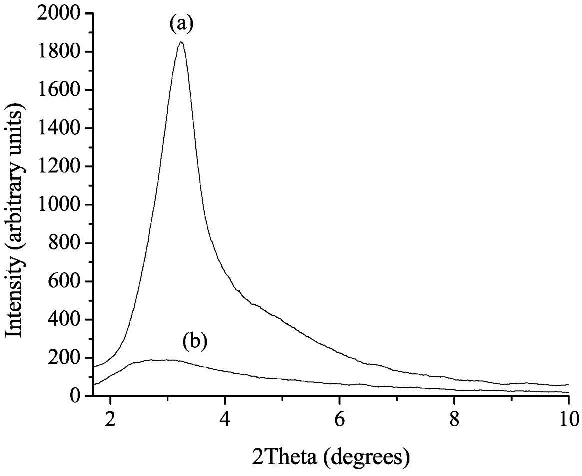


Fig. 4 Powder X-ray diffraction patterns of (a) IDESP-5% and (b) IDESP-20%.

Table 2 Analyzed concentrations of germanium and antimony ions in aqueous solutions before and after treatment with IDESP-5% material[a]

Metal concentration	Initial solution			Solution after treatment		
(ppm)	1	2	3	1′	2′	3′
Ge^{4+}	0.6	7.8	—	0.002	0.04	—
Sb^{3+}	—	—	0.5	—	—	< 0.002

[a] Experimental conditions: 0.1 g of IDESP-5% in 10 mL of aqueous solution, 2 h, room temperature.

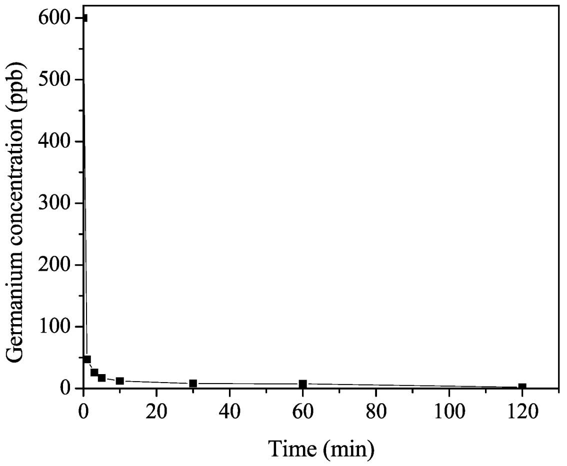


Fig. 5 Changes of germanium concentrations as a function of time in the sorption reaction of IDESP-5% material. Initial Ge concentration: 0.6 ppm in pH = 4 HCl aqueous solution, 10 mL solution, 0.1 g polymer.

This work is supported by the Science and Technology Center (STC) program of the National Science Foundation (NSF) under Agreement Number CTS-0120978.

Notes and references

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
3 G. A. Ozin, *Can. J. Chem.*, 1999, **77**, 2001.
4 G. S. Attard, J. C. Glyde and C. G. Goltner, *Nature*, 1995, **378**, 366.
5 P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Nature*, 1998, **396**, 152.
6 X. Feng, G. E. Fryxell, L. Q. Wang, A. Y. Kim and M. Gong, *Science*, 1997, **276**, 923.
7 M. H. Lim, C. F. Blanford and A. Stein, *Chem. Mater.*, 1998, **10**, 467.
8 L. Mercier and T. J. Pinnavaia, *Chem. Mater.*, 2000, **12**, 188.
9 S. Dai, M. C. Burleigh, Y. Shin, C. C. Morrow, C. E. Barnes and Z. Xue, *Angew. Chem., Int. Ed.*, 1999, **38**, 1235.
10 R. J. P. Corriu, A. Mehdi, C. Reye and C. Thieuleux, *Chem. Commun.*, 2002, 1382.
11 I. Ozawa, K. Saito, K. Sugita, K. Sato, M. Akiba and T. Sugo, *J. Chromatogr. A*, 2000, **888**, 43.