COMMUNICATION

ChemComm
www.rsc.org/chemcomm

1-Allyl-3-propylthiourea modified mesoporous silica for mercury removal

Valentyn Antochshuk and Mietek Jaroniec*

Department of Chemistry, Kent State University, Kent, Ohio 44242, USA. E-mail: jaroniec@kent.edu

Received (in Purdue, IN, USA) 28th September 2001, Accepted 2nd November 2001
First published as an Advance Article on the web 14th January 2002

1-Allyl-3-propylthiourea modified mesoporous silica has high adsorption capacity for mercury ions and its regeneration can be accomplished by washing with 10% thiourea in aqueous 0.05 M HCl.

Environmental pollution as a result of rapid technological development is a serious concern for ecology. Heavy metal ion contamination represents a significant threat to the ecosystem and especially to people due to the severe toxicological effects on living organisms.[1,2] Water (the most important component of the ecosystem) and its purification with adsorbents and ion-exchangers for heavy metal ion removal is an important topic for many scientific disciplines.[2] Several different types of materials, among them resins, carbons and clays, just to mention a few, have been studied and proposed for adsorption of heavy metal ions.[3–5]

Any efficient adsorbing material should consist of a stable and insoluble porous matrix having suitable active groups (typically organic groups) that interact with heavy metal ions. The most common solid support for organic groups is silica (an inorganic material, non-swelling and stable under acidic conditions), which can be prepared with desired porosity and high surface area. The recently discovered mesoporous silica[6] possesses a well developed surface and high concentration of surface silanol groups suitable for modification.

The hard–soft acid–base theory[7] indicates that a strong interaction between mercury(II) ion, a soft acid, and an adsorbent can be achieved when a complementary ligand, a soft base, is attached to the matrix surface. Also, according to this theory, common environmental metal ions such as Ca^{2+}, Mg^{2+}, Na^+ and K^+, that are classified as hard acids, would not interact with sulfur containing ligands, that are soft bases, and consequently would not interfere with mercury removal. The theoretically estimated maximum adsorption of mercury ions on mercaptopropyl grafted silica is *ca.* 0.7 g Hg^{2+} per gram of functionalized material, which is about 40% higher than the result reported for the material considered to have an unprecedented 100% ligand coverage.[8] Because of the existing limitation in ligand loading, a search for new heavy metal ion adsorbents should also be focused on the improvement of their stability and regeneration properties.

The current work is focused on the synthesis and regeneration of a mesoporous adsorbent having high adsorption capacity with respect to mercury ions. We propose to use a low molecular weight ligand, such as 1-allyl-3-propylthiourea, which has been previously utilized for analytical purposes in relation to gold(III) and platinum(IV) ions.[9] A potentially weaker bond between mercury and the thiocarbonyl group (in comparison to thiol group) could make the mesoporous silica with attached 1-allyl-3-propylthiourea a very promising adsorbent for mercury removal from aqueous and non-aqueous solutions as well as being convenient for regeneration under mild conditions, which could be accomplished by washing the adsorbent with 10% aqueous thiourea solution. In addition, the attached allylthiourea ligand seems to be useful for removal of other heavy metal ions.

A large pore (5.0 nm) mesoporous MCM-41 silica was used for adsorbent preparation.[10] Aminopropyl silica was prepared by reaction of (3-aminopropyl)triethoxysilane with the MCM-41 material according to the conventional procedure. The grafted 1-allyl-3-propylthiourea silica was synthesized *via* reaction between primary amine (mesoporous aminopropyl silica) and allyl isothiocyanate, which typically proceeds to completion.[11] A typical procedure included reaction of 2 g of aminopropylsilica with 0.50 ml of allyl isothiocyanate (25% excess) in toluene as solvent. In each step the resulting solids were filtered off, washed with 50 ml of toluene and 50 ml of isopropanol and dried under vacuum for 5 h at 90 °C. The final sample with attached thiourea functionalities had a light yellow color. The samples studied were designated as MCM-41 (unmodified mesoporous silica), MCM-41NH$_2$ (mesoporous silica with aminopropyl functionality), and MCM-41ATU (thiourea derivatized mesosilica).

The aforementioned successive modifications caused a gradual decrease in the total pore volume, BET surface area and BJH[12] pore diameter (Table 1). The decrease in the pore size caused by reaction with aminopropyltriethoxysilane and allyl isothiocyanate are 1.0 and 0.8 nm, respectively (Fig. 1). Both the initial and modified MCM-41 samples exhibited narrow pore size distributions.

Table 1 Adsorption and surface properties of mesoporous silica and functionalized samples

Sample	BET specific surface area/m^2 g^{-1}	Total pore volume/ cm^3 g^{-1}	Pore diameter (BJH)/nm	Ligand bonding density/ mmol g^{-1}	Max. Hg^{2+} adsorption capacity/ mmol g^{-1}
MCM-41	900	1.00	5.0	—	0.0
MCM-41NH$_2$	490	0.46	4.0	1.95	—
MCM-41ATU	320	0.24	3.2	1.70	1.5 (0.75)[a]

[a] Value after regeneration in parentheses.

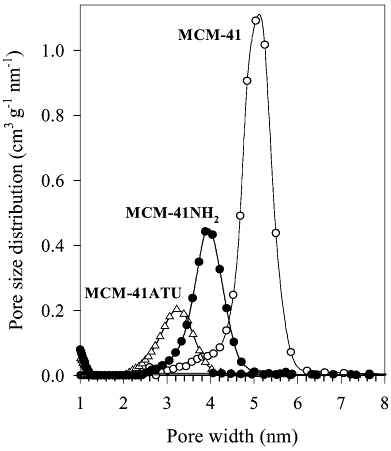

Fig. 1 Differential pore size distributions calculated from nitrogen adsorption isotherms for the calcined mesoporous silica (MCM-41) and materials functionalized with aminopropyl (MCM-41NH$_2$) and 1-allyl-3-propylthiourea groups (MCM-41ATU).

DOI: 10.1039/b108789d

This journal is © The Royal Society of Chemistry 2002

The introduction of aminopropyl groups on the silica surface and their further transformation into 1-allyl-3-propylthiourea functionalities was proved by means of ^{13}C CP-MAS NMR† (Fig. 2). Chemical modification of the silica surface with aminopropylsilane results in a group of signals with chemical shifts in the range 10–60 ppm.[14] The subsequent reaction with allyl isothiocyanate gave new signals (see Fig. 2) which correspond to the carbon atoms of allyl (*ca.* 20, 115 and 135 ppm) and thiocarbonyl (182 ppm) groups. There is a small amount of unreacted ethoxy groups from the first modification step with aminopropyltriethoxysilane but the presence of these groups after the second modification step confirms that they do not interfere with allyl isothiocyanate.

The results of elemental analysis support the presence of bonded aminopropyl groups and their successful subsequent reaction with allyl isothiocyanate. The concentrations of the attached ligands are shown in Table 1. More than 87% of the attached amino groups were successfully converted into the 1-allyl-3-propylthiourea functionalities.

Mercury adsorption was studied under static conditions from aqueous solutions. The test solution was prepared by dilution of a standard 0.145 M mercury(II) nitrate solution in water (Aldrich). In a typical determination, 0.05 g of the adsorbent was slowly agitated for 40 min with 10 ml of the solution containing mercury nitrate of the following concentrations: 1.8×10^{-2} M, 4.5×10^{-3} M and 1.8×10^{-4} M (Hg^{2+} : ligand ratios 2 : 1, 1 : 1 and 1 : 50). After filtration the adsorbent was washed with 5 ml of deionized water, and the filtrate and rinsing water were collected and diluted to 25 ml.

Mercury(II) concentration was measured spectrophotometrically with dithizone used as a complexing agent.[15] The mercury uptake was determined as the difference between the initial and equilibrium concentrations. In a similar fashion the mercury uptake experiments were repeated with regenerated adsorbent. For comparison purposes adsorption experiments were performed for unfunctionalized mesostructured silica using the same amounts of the sample and solutions.

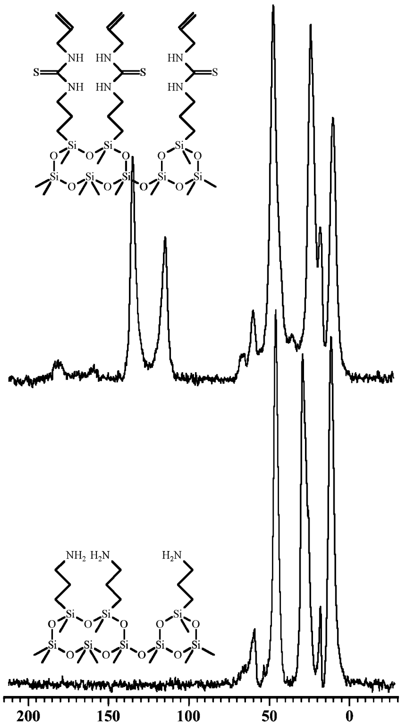

Fig. 2 ^{13}C CP-MAS NMR spectra for the mesoporous materials functionalized with aminopropyl (MCM-41NH$_2$) and 1-allyl-3-propylthiourea (MCM-41ATU) groups. Chemical shifts are in ppm with respect to TMS standard.

A single treatment of aqueous mercury solution with the allylthiourea adsorbent lowered its concentration below 0.1 ppm. The mercury-loaded material did not release Hg^{2+} ions upon washing with water. Both 1-allyl-3-propylthiourea functionalized material and adsorbent loaded with mercury are thermally stable up to 130 °C. The maximum adsorption capacity is 1.5 mmol Hg^{2+} per gram of adsorbent or 0.3 g Hg^{2+} per gram of adsorbent.

Mercury desorption studies were performed for the samples loaded with mercury in the previous experiments *via* treatment with 10% thiourea in aqueous 0.05 M HCl. The regeneration was performed under static conditions by soaking 0.05 g of mercury-loaded adsorbent for 15 min in 10 ml of thiourea solution followed by filtration of the sample with an additional 20 ml of thiourea solution and subsequent rinsing with 10 ml of deionized water. Such mild treatment resulted in the restoration of over 50% of the initial capacity, which is higher than the previously reported result for thiol functionalized materials.[8] It is interesting to note that other complexing agents such cysteine or dithizone (chloroform solution) were suitable for regeneration but further studies are necessary to establish the optimal regeneration conditions such as pH and concentration of the complexing agent.

The exploratory studies of 1-allyl-3-propylthiourea modified mesoporous silica MCM-41 suggest that this material has high adsorption capacity towards mercury(II) ions and its regeneration can be accomplished under mild conditions, *e.g.*, by washing with 10% thiourea aqueous solution. This modified silica before and after mercury loading exhibits a relatively high thermal stability.

We acknowledge the National Science Foundation (grant CTS-0086512) for support of this research and Professor A. Sayari (University of Ottawa, Canada) for providing the MCM-41 sample.

Notes and references

† Solid state ^{13}C CP-MAS NMR experiments were performed on a Bruker 400DMX spectrometer operating at 100.54 MHz at a room temperature using a 7 mm zirconia rotor with a spinning frequency of 2.5 kHz. Spectra were acquired using the TOSS pulse sequence[13] with 2 ms contact time, high-power decoupling and a total number of 60000 scans.

1 S. E. Manahan, *Environmental Chemistry*, Lewis, Boca Raton, FL, 1994.
2 B. Hultberg, A. Andersson and A. Isaksson, *Toxicology*, 1998, **126**, 203.
3 C. Kantipuly, S. Katragadda, A. Chow and H. D. Gesser, *Talanta*, 1990, **37**, 491.
4 D. Mohan, V. K. Gupta, S. K. Srivastava and S. Chander, *Colloids Surf. A*, 2001, **177**, 169.
5 R. Celis, C. M. Hermosin and J. Cornejo, *Environ. Sci. Technol.*, 2000, **34**, 4593.
6 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.
7 R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533.
8 X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu and K. M. Kemner, *Science*, 1997, **276**, 923.
9 V. N. Losev, N. V. Maznyak, A. K. Trofimchuk and V. K. Runov, *Ind. Lab.*, 1998, **64**, 365.
10 C. P. Jaroniec, M. Kruk, M. Jaroniec and A. Sayari, *J. Phys. Chem. B*, 1998, **102**, 5503.
11 *Comprehensive Organic Functional Group Transformations*, ed. A. R. Katritzky, O. Meth-Cohn and C. W. Rees, Pergamon, New York, vol. 6, ch. 18, 1995.
12 M. Kruk, M. Jaroniec and A. Sayari, *Langmuir*, 1997, **13**, 6267.
13 W. T. Dixon, J. Schaefer, M. D. Sefcik, E. O. Stejskal and R. A. McKay, *J. Magn. Reson.*, 1982, **49**, 341.
14 S. G. Caravaja, D. E. Leyden, G. R. Quinting and G. E. Maciel, *Anal. Chem.*, 1988, **60**, 1776.
15 *AOAC Official Methods of Analysis*, ed. W. Horwitz, The Association of Official Analytical Chemists, Washington DC, 1990.