Aminopropyl–Glucose Sequentially Grafted Mesoporous Silica Nanocomposite as a Novel Boron Adsorbent

Masataka Yasui, Masataka Ikeda, Kazuo Takimiya, Joji Ohshita, Shoji Yamanaka, and Kei Inumaru*
Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8527

(Received September 16, 2004; CL-041093)

Aminopropyl groups and glucose molecules were sequentially grafted on mesoporous silica (ca. 5 nm in diameter) to synthesize a glucamine group analogue in the nanospaces. The grafted nanocomposite material showed a high capacity for adsorption of boric acid/borate from water.

Grafting of organic groups on inorganic porous materials is a powerful method for creating organic–inorganic nanostructures with new functions.[1–4] Recent studies successfully functionalized nanometer-sized pores of mesoporous silicas (MCM-41 or FSM-16)[5,6] as catalysts,[7,8] photo-controllable molecular storage material,[9] materials for molecular recognition,[10,11] molecular selective photocatalysts for organic pollutants,[12] and heavy metal ion adsorbents.[13–16] To develop adsorbents for ions such as Hg^{2+}, Cd^{2+}, and CrO_4^{2-}, researchers have grafted small functional groups such as mercaptopropyl and aminopropyl groups on mesoporous silicas. It is expected that it will be difficult to uniformly graft large functional groups in the nanospaces because of the limited diameter of the pores.

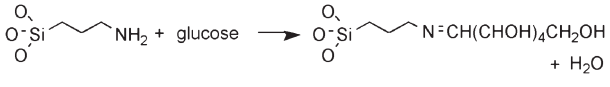
Boron is recognized as a harmful element and new adsorbents need to be developed for purification of water. It is known that *N*-methyl-D-glucamine resins adsorb boric acid/borate in water. Recent precise investigation by Yoshimura et al.[17] revealed that the *N*-methyl-D-glucamine groups act in a bifunctional way, in which the "glucose" part forms chelate complexes with boron species forming C–O–B bonds and the methylamine part buffers the pH inside the resin. Therefore, both the "glucose" and "methylamine" parts are indispensable for the adsorbent. However, direct grafting of *N*-methyl-D-glucamine into the nanospaces of mesoporous material would be difficult due to the bulkiness of the group, and there have been no reports on such a material.

Here we report for the first time the synthesis and performance of a boric acid/borate adsorbent based on organo-grafted mesoporous materials. A bulky glucamine group analogue was introduced in nanospaces by a two-step procedure. First the amino part was anchored on the mesoporous silica, and then glucose molecules were grafted on the amino groups to form a large functional group. This two-step synthesis allowed us to anchor a large amount of the bulky glucamine analogue in the nanospaces of mesoporous silica. The material showed a high performance for removal of boric acid/borate anion from aqueous solutions.

Mesoporous silica, HMS, was prepared using *n*-octadecylamine as a template according to the procedure described by Pinnavaia et al.[13,14,18] 1 g of HMS (dehydrated at 473 K) was added to a solution containing 0.02 mol of 3-aminopropyltriethoxysilane and a 30 cm^3 of freshly distilled toluene, and the reaction mixture was refluxed for 48 h. The solid was separated by filtration, washed with toluene and then methanol in an Ar-filled glove box (H_2O was kept less than 1 ppm to prevent undesired reactions of the excess silane). This material is designated by N-HMS. Grafting of glucose molecules onto the aminopropyl groups was carried out in an ethanol solvent: 0.3 g of N-HMS was added to a solution that contained 1 g of D-glucose and 60 g of ethanol at ambient temperature, under stirring. After 40 min of reaction, the solid was filtered and was dried in ambient atmosphere to obtain "glucamine"-grafted HMS (designated by G-N-HMS). The reaction scheme is shown in Scheme 1. For comparison, purely siliceous MCM-41 and non-porous silica (Aerosil 200) were used instead of HMS. These materials are denoted by N-MCM-41 (aminopropyl-grafted MCM-41) and G-N-SiO_2 ("glucamine"-grafted Aerosil 200). The preparation of MCM-41 was described elsewhere.[10c] Each product was analyzed by N_2 adsorption (77 K), elemental analysis of C, H, and N, and IR spectrometry. For boron adsorption measurements, 150 mg of sample was typically added to 30 cm^3 of boric acid aqueous solution (10 ppm as boron, pH = ca. 6). After standing for enough time to equilibrate the adsorption (ca. 2 h), the residual boron in the solution was measured by ICP analysis.

Figure 1 shows N_2 adsorption isotherms of the organo-grafted samples prepared from HMS and MCM-41. For both mesoporous silicas, the sequential grafting of aminopropyl groups and glucose molecules brought about step-by-step decreases in pore volumes and pore diameters, demonstrating that the organic groups were grafted into the nanospaces. Table 1 lists some properties derived from the N_2 isotherms of these samples. G-N-HMS showed considerable N_2 adsorption and the pore volume was 0.52 $cm^3\,g^{-1}$, showing that large spaces were left in the nanopores after the grafting of glucose. On the other hand, G-N-MCM-41 showed very low N_2 adsorption and no capillary condensation in the isotherm. This means that nanospaces are blocked up at 77 K by the organic moiety in G-N-MCM-41. The differences between G-N-HMS and G-N-MCM-41 are attributable to the difference in pore size between HMS and MCM-41.

The amounts of aminopropyl groups and glucose molecules in the nanocomposite materials were able to be determined by the elemental analysis: The amounts of aminopropyl groups were directly estimated from the nitrogen contents. The glucose contents were calculated from the increases in carbon contents arising from the glucose grafting. The results of the elemental analysis are shown in Table 1. Among the samples synthesized



Scheme 1.

Table 1. Properties and adsorption performances of the nanocomposite materials prepared in this study

Sample	BET surface area /$m^2\ g^{-1}$	Pore volume /$cm^3\ g^{-1}$	Pore diameter /nm	Grafted amine /10^{-4} mol g^{-1}	Grafted glucose /10^{-4} mol g^{-1}	Organic group surface density /molecule nm^{-2}	B adsorption /10^{-4} mol g^{-1}
HMS	526	0.97	5.3	—	—	—	0 (10)[a]
N-HMS	472	0.82	4.1	13	—	1.7	0 (10)
G-N-HMS	400	0.52	3.3	13	9.7	1.7	1.7 (1.7)
MCM-41	920	0.83	2.7	—	—	—	0 (10)
N-MCM-41	650	0.53	1.5	12	—	1.3	0 (10)
G-N-MCM-41	60	—	—	11	7.7	1.3	1.1 (8.4)[b]
G-N-SiO2	200[c]	—	—	4.6	4.5	1.4	0.6 (6.2)

[a]The values in parentheses show the equilibrium concentration as boron in ppm. [b]Adsorbent, 50 mg. [c]Surface area of the silica.

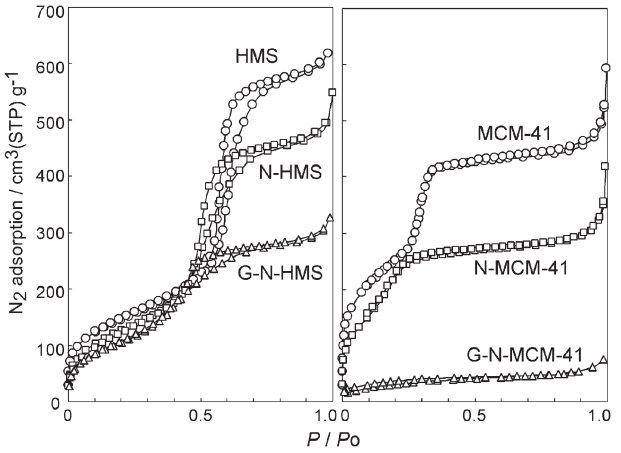


Figure 1. N_2 adsorption isotherms for mesoporous silicas and organo-grafted nanocomposite samples.

in this study, G-N-HMS had the largest amount of grafted glucose. G-N-SiO_2 had a smaller amount of grafted glucose because of its lower surface area. These results demonstrate that HMS is a suitable organic framework for preparing the glucamine analogue nanocomposite by the sequential grafting method.

The results of the boron adsorption experiments are also listed in Table 1. G-N-HMS showed a large boron anion adsorption capacity. This is the first example of a good boric acid/borate adsorbent based on organo-grafted mesoporous materials. Note that the aminopropyl-grafted samples (N-HMS and N-MCM-41) showed no adsorption, indicating that the formation of "glucamine" groups is indispensable for adsorption of the boron species. The adsorption capacities of G-N-MCM-41 and G-N-SiO_2 were smaller than that for G-N-HMS due to the smaller amount of grafted glucose in these samples.

In conclusion, we synthesized, for the first time, a good boron adsorbent using organo-grafting on mesoporous materials. The sequential grafting of aminopropyl groups and glucose molecules in mesoporous silica was proved to be advantageous for grafting the large functional groups, the glucamine analogues, into the nanospaces. Although the adsorption performances of these materials did not exceed that of *N*-methyl-D-glucamine resins in practical use (ca. 5×10^{-4} mol g^{-1}), this study highlights that grafting of large functional groups into mesoporous materials by sequential grafting methods is a promising strategy for developing new nanostructured adsorbents.

References and Notes

1 A. Sayari and S. Hamoudi, *Chem. Mater.*, **13**, 3151 (2001).
2 R. Anwander, *Chem. Mater.*, **13**, 4419 (2001).
3 C. W. Jones, K. Tsuji, and M. E. Davis, *Nature*, **393**, 52 (1998).
4 A. Katz and M. E. Davis, *Nature*, **403**, 286 (2000).
5 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992).
6 a) T. Yanagisawa, T. Shimizu, K. Kuroda, and C. Kato, *Bull. Chem. Soc. Jpn.*, **63**, 988 (1990). b) S. Inagaki, Y. Fukushima, and K. Kuroda, *J. Chem. Soc., Chem. Commun.*, **1993**, 680. c) S. Inagaki, A. Koiwai, N. Suzuki, Y. Fukushima, and K. Kuroda, *Bull. Chem. Soc. Jpn.*, **69**, 1449 (1996).
7 A. P. Wight and M. E. Davis, *Chem. Rev.*, **102**, 3589 (2002).
8 A. Corma, H. Garcia, A. Moussaif, M. J. Sabater, R. Zniber, and A. Redouane, *Chem. Commun.*, **2002**, 1058.
9 N. K. Mal, M. Fujiwara, and Y. Tanaka, *Nature*, **421**, 350 (2003).
10 a) K. Inumaru, J. Kiyoto, and S. Yamanaka, *Chem. Commun.*, **2000**, 903. b) K. Inumaru, Y. Inoue, S. Kakii, T. Nakano, and S. Yamanaka, *Chem. Lett.*, **32**, 1110 (2003). c) K. Inumaru, Y. Inoue, S. Kakii, T. Nakano, and S. Yamanaka, *Phys. Chem. Chem. Phys.*, **6**, 3133 (2004).
11 V. S. Y. Lin, C. Y. Lai, J. Huang, S. A. Song, and S. Xu, *J. Am. Chem. Soc.*, **123**, 11510 (2001).
12 a) K. Inumaru, M. Murashima, T. Kasahara, and S. Yamanaka, *Appl. Catal., B*, **52**, 275 (2004). b) T. Kasahara, K. Inumaru, and S. Yamanaka, *Microporous Mesoporous Mater.*, in press.
13 Y. Mori and T. J. Pinnavaia, *Chem. Mater.*, **13**, 2173 (2001).
14 L. Mercier and T. J. Pinnavaia, *Adv. Mater.*, **9**, 500 (1997).
15 X. Feng, G. E. Fryxell, L. Q. Wang, A. Y. Kim, J. Liu, and K. M. Kemner, *Science*, **276**, 923 (1997).
16 H. Yoshitake, T. Yokoi, and T. Tatsumi, *Chem. Mater.*, **14**, 4603 (2002).
17 K. Yoshimura, Y. Miyazaki, F. Ota, S. Matsuoka, and H. Sakashita, *J. Chem. Soc., Faraday Trans.*, **94**, 683 (1998).
18 For preparation of HMS with wormhole-like mesopores, 2.4 g of *n*-octadecylamine was dissolved in ethanol (10 g) and then water (120 g) was added at 333 K. 8.3 g of tetraethoxysilane was added and the solution was aged for 72 h at 333 K. After filtration of the precipitate, the template was removed by extraction with ethanol using a Soxhlet extractor.

Published on the web (Advance View) November 13, 2004; DOI 10.1246/cl.2004.1582