Synthesis, Characterization, and Boron Uptake of Organic–Inorganic Hybrid Mesoporous Materials

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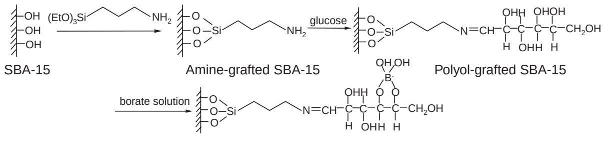
An organic–inorganic hybrid mesoporous material with polyol functional groups has been prepared by a two-step post-grafting method using mesoporous SBA-15 as the support, proven to be a promising adsorbent with the considerable uptake capacity, as well as the high selectivity towards boron.

Boron contamination is a wide spread environmental problem, since even a few ppm present in irrigation water can cause stunting of plant growth,[1] and boron has virulence for reproduction and causes disease in the nervous system of animals.[2] Unfortunately, boron is widely distributed in the environment, occurring naturally or from anthropogenic contamination mainly under the form of boric acid or borate, and there is yet no efficient and economical method for boron removal. A great deal of effort has been made to remove or recover boron from aqueous solutions by utilizing polymer-supported boron-specific chelating resins.[3] Vicinal diol groups on the resins are regarded as the most efficient ligands for the chelation of boron. However, drawbacks are associated with all organic resins, such as instability in harsh chemical environments, limited surface areas, uncontrollable pore structures, hydrophobicity, and thermal instability of polymer matrixes.[4] Recently, the development of hybrid functional mesoporous materials has been paid more attention to adsorption applications including the removal and recovery of heavy metal ions,[5] dyes,[6] oxyanions,[7] anionic complexes,[8] and bio-molecules.[9] In the present study, a polyol-functionalized SBA-15 with large pore diameters and uniform pore channels was prepared, proven to be promising for boron uptake.



Scheme 1. Schematic illustration of the two-step post-grafting method and the proposed structure of the boron-polyol complex.

A solution of Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Aldrich): cetyltrimethylammonium bromide (CTAB, Aldrich):2 M HCl: etraethoxysilane (TEOS, Fluka):$H_2O = 4.0:0.4:45:11.6:15$ (mass ratio) was prepared, stirred at 38 °C for 20 h, then heated at 100 °C for 24 h to synthesize SBA-15. The surfactants were extracted by hydrochloric acid–ethanol solution to obtain surfactant-free SBA-15 with enriched surface hydroxy groups. The first grafting process was performed with γ-(aminopropyl) triethoxysilane in xylene solvent at 80 °C for 6 h to obtain the white amine-grafted SBA-15. Then it was treated with methanol solution containing anhydrous glucose at 60 °C for 6 h to achieve yellow polyol-grafted SBA-15 (Scheme 1).

^{29}Si NMR spectra (Figure 1a) show the successful grafting of functional groups on mesoporous SBA-15. The silanols on SBA-15 are greatly reduced after functionalization, indicated by the decrease of the signal intensities of Q^3 and Q^2 [$Q^n = Si(OSi)_n\,(OH)_{4-n}$]. There exists residual silanols, suggesting that the surface of SBA-15 after functionalization remains hydrophilic. The new signals attributable to Si atoms attached to C atoms in the functionalized SBA-15 are observed at −66 ppm (T^3, $C–Si(OSi)_3$) and −59 ppm (T^2, $C–Si(OSi)_2(OC_2H_5)$).[7,10] Functional groups identified by FT-IR spectra (Figure 1b) confirm the mechanism of Scheme 1. The FT-IR spectra of the functional materials show the decrease in the band at 964 cm^{-1} ($\delta_{SiO–H}$),[11] suggesting the reduction of silanols on the surface of silicas, and the appearance of the new peaks at 2927 ($\nu_{C–H}$), 2857 ($\nu_{C–H}$), 1470 ($\delta_{C–H}$), 1562 ($\delta_{N–H}$), and 695 ($\delta_{C–H}$) cm^{-1},[5,12] suggesting the successful functionalization of SBA-15 with amine groups. The reduction of 1562 cm^{-1} shows the conversion of the amine groups into N=C groups and the successful grafting of polyol groups on the SBA-15 supports.

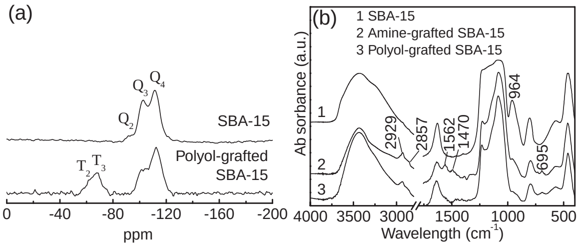


Figure 1. ^{29}Si NMR spectra (a) and FT-IR spectra (b) of the starting and functional SBA-15 materials.

The XRD patterns of the SBA-15 materials show that there are no significant changes upon amine and polyol immobilization except for the expected decrease in XRD peak intensity. The transmission electron microscopic (TEM) images show similar images with similar pore arrays except for the changes of channels and walls resulting from each of the modification steps (see Supplemental Information, Figure S1), suggesting that the orderness of the pore channels has not been completely changed after two modification steps. The N_2 adsorption–desorption isotherms of the materials are all type IV in nature and exhibit a H1 hysteresis loop, but the sharpness of the adsorption branches decreases with each of the grafting steps, indicating the shift and broadening of the pore size distributions. The physicochemical properties of the materials are reported in Table 1. It is noteworthy that the surface area, the total pore volume and the most frequent pore size of the materials decrease with each of the mod-

Table 1. Physicochemical property of SBA-15 materials

Sample	S_{BET} /m^2/g	V_p /ml/g	D_p^{a} /nm	NH$_2$^{b} /mmol/g	C/N molar ratio^b
SBA-15	755	0.94	5.6	—	—
Amine-grafted SBA-15	524	0.61	4.6	3.08	3.51 (3)^d
Polyol-grafted SBA-15	224	0.29	4.2	2.81^c	5.84 (9)^d

^{a}The most frequent pore size calculated from the adsorption branch by using BJH method. ^{b}Calculated from elemental analysis. ^{c}N molar content (including NH_2 and N=C groups). ^{d}Theoretical values in parentheses.

ification steps, as expected, which is consistent with the presence of a significant amount of organic groups on the surface of pore channels.

The C and N concentrations of the grafted SBA-15 are determined by elemental analysis carried out at randomly selected spots (Table 1). The nearly consistent C/N ratios of the functional materials suggest evenly distributed functional groups. After the first grafting step, the amine-grafted SBA-15 has the higher NH_2 contents of 3.08 mmol/g than that prepared by co-condensation method,[13] proving that the post-grafting method can maximize the number of functional groups on supports. The high NH_2 content is beneficial to the following functionalization and adsorption processes. The C/N molar ratio of the polyol-grafted SBA-15 is larger than that of the amine-grafted SBA-15, which confirms the second grafting reaction. The first grafting reaction is complete, while the second step is not complete according to the comparison of the experimental C/N molar ratio with the theoretical one of 9 (Table 1). This may be attributed to the unoptimizable experimental conditions and the steric hindrance effect during the second reaction process.

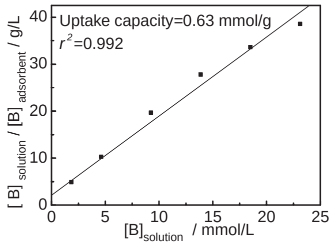


Figure 2. The adsorption isotherm of polyol-grafted SBA-15 at 30 °C. Solid line in isotherm represents the best fit according to the least-squares method. The uptake capacity is obtained by a reciprocal of the slope.

The polyol-grafted SBA-15 was tested for adsorption of boron through batchwise process, accomplished by shaking 0.25 g polyol-grafted SBA-15 with 10-mL borate solution containing certain amount of boron (from 20 ppm to 250 ppm) at 30 °C for 24 h. The concentration of boron in the solution phase was measured by ICP-OES. The maximum adsorption capacity is deduced from the adsorption isotherm (Figure 2). As the boron content increases, the capacity of the material for boron also increases, as expected. The adsorption isotherm is in good accordance with the Langmuir equation. The maximum uptake capacity of boron reaches 0.63 mmol/g, which is lower than that of commercial polymer-based resins of 0.91 mmol/g.[14] But it should be noted that this “maximum” capacity is the value when the grafting of polyol groups is not complete enough. So it can be inferred that the polyol-grafting SBA-15 should have larger capacity of boron uptake if it had more polyol functional groups after the second grafting process. Optimizing experimental conditions and controlling the physicochemical properties of the adsorbent may further increase the capacity of boron uptake. Further work on those subjects is in progress.

The boron selectivity of the polyol-grafted SBA-15 was investigated in a competitive environment.[15] It is found that the adsorbent doesn’t adsorb other metal ions such as Mg^{2+}, Ca^{2+}, K^+, Na^+, and Li^+ in the brine, indicating its high selectivity towards boron. The uptake capacity of boron in the brine is 0.54 mmol/g, only slightly lower than that in pure borate solution.

In summary, a novel boron-specific hybrid mesoporous material with the polyol functional groups by a two-step post-grafting method has been developed, which is a promising adsorbent with the high selectivity and the considerable uptake capacity of boron. The ordered mesoporous SBA-15 materials are selected as the supports because of their excellent characteristics of textural properties, hydrophilicity, stability, refunctionalization, and reusability for applicable adsorbents. The polyol-functionalized SBA-15 is also expected to be promising for the separation of boron isotopes.

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References and Notes

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14 A theoretical boron capacity of 0.6 mmol/L, i.e. 0.91 mmol/g has been described for Amberlite IRA743 (Rohm & Haas).
15 The solution was brine from Qinghai salt lake. The main compositions are Mg^{2+} (110 g/L), Ca^{2+} (8.9 g/L), K^+ (1.1 g/L), Na^+ (1.6 g/L), Li^+ (116 ppm) and B^{3+} (266 ppm), determined by ICP-OES.

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