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A new class of hybrid mesoporous materials with functionalized organic monolayers for selective adsorption of heavy metal ions

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Thiol- and amino-functionalized SBA-15 silicas with uniform mesoporosities were prepared and employed for removing heavy metal ions from waste water; the thiolated SBA-15 adsorbent exhibited a higher complexation affinity for Hg^{2+}, while the other metal ions (Cu^{2+}, Zn^{2+}, Cr^{3+} and Ni^{2+}) showed exceptional binding ability with its aminated analogue.

To synthesize improved adsorbents for the removal of toxic heavy metal ions from waste water is a continuing research objective of environmental pollution control processes. Considerable efforts have been devoted to the preparation of mesoporous silica-based adsorbents due to their unique large surface area, well-defined pore size and pore shape and well-modified surface properties.[1–5] This application generally requires the materials to exhibit specific binding sites for heavy metal ions, but most mesoporous materials themselves do not have such surface properties. Accordingly, an efficient approach has been developed so that functional monolayers are chemically bonded to the surfaces of supports. The functionalized hybrid materials show great adsorption capacity and specificity for metal ions. For instance, a few metal ion adsorbents have been prepared by grafting thiol ligands onto the surface of a MCM-41 support, which are extremely efficient in removing mercury and other heavy metal ions.[1,2] The effectiveness of such adsorbents has been ascribed to the complexation chemistry of grafted ligands with metal ions. Continuing our efforts in synthesizing and improving the hydrothermal stability of mesoporous materials and in investigating their applications,[6–8] we prepared in this study two novel thiol- and amino-functionalized SBA-15 materials and investigated their complexation affinities for heavy metal ions. The more regular structure and much thicker silica walls of SBA-15 (31–64 Å) may impart significant hydrothermal stability in comparison to MCM-41. In addition, amino groups grafted on an SBA-15 support are expected to show considerably higher binding ability to relatively harder metal ions such as Cu^{2+}, Zn^{2+}, Cr^{3+} and Ni^{2+}.

Synthesis of the parent mesoporous SBA-15 was achieved by the use of a triblock copolymer surfactant in acidic media.[9] The calcined material has a surface area of 814 $m^2\ g^{-1}$ and an average pore size of 76 Å, as determined using the nitrogen adsorption technique and transmission electron microscopy (TEM). The X-ray powder diffraction pattern of this material shows a very intense peak (100) and two additional high order peaks with lower intensities, indicating a significant degree of long range ordering of the structure and well formed hexagonal pore arrays of the sample. SBA-15 functionalized with 3-mercaptopropyl groups [SBA-15(SH)] (5.6% C, S_{BET} 461 $m^2\ g^{-1}$ and V_t 0.66 $m^3\ g^{-1}$) and primary 3-aminopropyl groups [SBA-15(NH_2)] (9.5% C, S_{BET} 279 $m^2\ g^{-1}$ and V_t 0.45 $m^3\ g^{-1}$) were obtained through the treatment with chloroform solution of 3-mercaptopropyltriethoxysilane and 3-aminopropyltriethoxysilane, respectively. It was found that, upon functionalization, the surface area, total pore volume and pore size decreased significantly, revealing that the surface modification indeed occurred inside the primary mesopores of the SBA-15. However, the XRD analysis indicated that, in addition to a very intense peak (100), two higher order peaks were still observed. Therefore, the chemical bonding procedure did not diminish the structural ordering of SBA-15.

The ^{29}Si and ^{13}C NMR spectra and peak assignments for functionalized samples SBA-15(SH) and SBA-15(NH_2) are depicted in Fig. 1 and 2, respectively. In the ^{29}Si NMR spectrum of SBA-15(SH) (Fig. 1(a)), the three peaks at −113.8, −105.6 and −96.3 ppm are attributed to silicon in the siloxane binding environment without hydroxyl groups [$(SiO)_4\mathit{Si}$], isolated silanol groups [$(SiO)_3\mathit{Si}$-OH] and to geminal silanol groups [$(SiO)_2\mathit{Si}$-$(OH)_2$] of the silica support. In addition to these signals, two additional signals can be observed at −71.9 and −63.4 ppm, which correspond to two different environments for the siloxane groups in the functionalized monolayers:[10] (i)

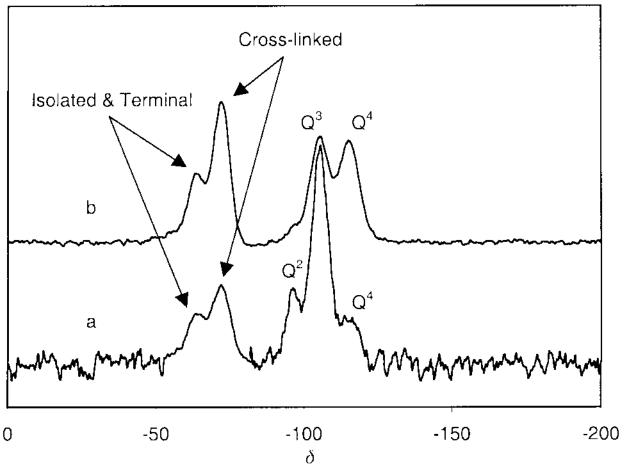

Fig. 1 ^{29}Si NMR spectra of organic monolayers on SBA-15: (a) SBA-15(SH) and (b) SBA-15(NH_2).

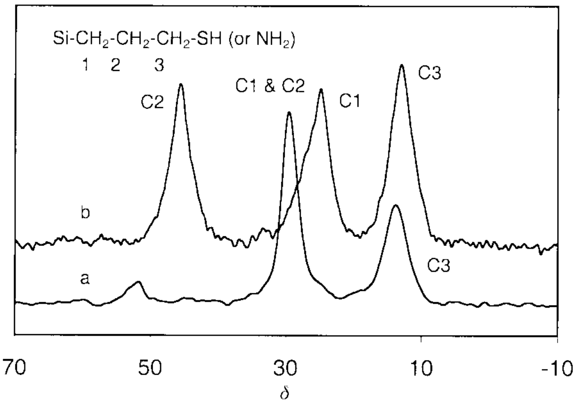

Fig. 2 ^{13}C NMR spectra of organic monolayers on SBA-15: (a) SBA-15(SH) and (b) SBA-15(NH_2).

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Table 1 Analyzed concentrations of toxic metal ions in waste water solutions before and after adsorption treatment (concentration in ppm)[a]

	Hg	Cu	Zn	Cr	Ni
No treatment	10.1	5.21	10.1	5.21	10.2
After treatment with SBA-15	10.2	5.12	10.2	5.13	10.3
After treatment with SBA-15(SH)	0	3.18	9.91	4.72	5.10
After treatment with SBA-15(NH_2)	2.15	0.01	0	0	0

[a] 10 mL of waste solution was mixed with 100 mg of adsorbent at room temperature with agitation overnight. The remaining metal concentrations in solution were analyzed using inductively coupled plasma spectroscopy (ICP).

cross-linked groups bound to two neighboring siloxanes and (ii) isolated groups and terminal groups bound to only one neighboring siloxane. In the case of sample SBA-15(NH_2) (Fig. 1(b)), only two distinguishable peaks at −115.0 and −105.5 ppm were recorded for the silica support. An increase of the Q^4 peak intensity was also observed, along with a reduction in the signal intensity of the Q^3 site. In agreement with higher coverage of amino monolayers for SBA-15(NH_2) (9.5% C), these observations indicate that, compared with the mercaptopropyl groups in SBA-15(SH) (5.6% C), more aminopropyl groups have been grafted onto Si-OH groups of the silica support, and thus more Q^4 silica sites are subsequently formed. It should be noted that relative peak intensities in the ^{29}Si NMR spectra are not strictly quantifiable due to differences in relaxation behavior. In the ^{13}C NMR spectrum of SBA-15(SH) (Fig. 2(a)), the peak at 13.8 ppm is ascribed to the methylene carbon group C3 that is directly bonded to the silicon atom. The strong signal at 29.6 ppm is attributed to the other two methylene carbons (C2 and C1). However, for sample SBA-15(NH_2), three distinct peaks are clearly observed at 13.1, 24.9 and 45.6 ppm, which can be assigned to the carbons C3, C1 and C2, respectively. We believe that the better resolution of the peaks for the three carbons in SBA-15(NH_2) is associated with the higher ordering orientation of the carbon chains with respect to the silica surface.[1]

The functionalized materials exhibited unique selective affinity for binding heavy metal ions. Table 1 lists the ion concentrations of simulated waste water solutions before and after treatment with SBA-15(SH) and SBA-15(NH_2). It can be seen that a single treatment with SBA-15(SH) reduced the mercury concentration to below the detection limit, but it exhibited little or no affinity for other metal ions. On the other hand, the aminated SBA-15 adsorbent efficiently removed the metal ions from the waste solution with the exception of Hg^{2+}. Note that no significant concentration change for all metal ions was observed when unmodified SBA-15 was directly treated with the waste water solution under identical conditions. Thus, the concentration change is indeed attributed to the complexation reactions between metal ions with grafted ligands. It has been well recognized that softer transition metal ions are prone to forming stable complexes with ligands carrying softer donor atoms, and *vice versa*. Sulfur has been regarded as a softer donor atom compared with nitrogen, and therefore it is understandable that the thiolated adsorbent exhibited higher complexation affinity for the softer metal ion Hg^{2+}, while the other relatively harder metal ions (Cu^{2+}, Zn^{2+}, Cr^{3+} and Ni^{2+}) demonstrated considerably higher binding ability with its aminated analogue.

The hydrolytic stability was tested by treating mercury-loaded SBA-15(SH) and copper-loaded SBA-15(NH_2) in water at 70 °C for 12 h. Elemental analysis indicated that only a very small amount of metal was released during this process (0.5% Hg and 0.8% Cu were released from SBA-15(SH) and SBA-15(NH_2), respectively). To regenerate the used adsorbents, the metal-loaded functionalized SBA-15 adsorbents were washed with conc. HCl, resulting in complete removal of the loaded metal. The regenerated SBA-15(SH) and SBA-15(NH_2) materials were treated with $Hg(NO_3)_2$ and $Cu(NO_3)_2$ solutions, respectively. An Hg loading of 292 mg g(SBA-15(SH))$^{-1}$ and a Cu loading of 46 mg g(SBA-15(NH_2))$^{-1}$ were obtained, corresponding to about 60% of the original loading capacities. Similar results were obtained for a third regeneration and reuse cycle. These results indicated that both adsorbents remained effective even after extended regeneration and reuse cycles. In good agreement with the results, BET analyses of the regenerated adsorbents indicated that the surface area and pore volume for both adsorbents only slightly decreased (*ca*. 5% decrease), while the pore size essentially remained unchanged [68 Å for SBA-15(SH) and 63 Å for SBA-15(NH_2)]. IR spectra showed that the bonds corresponding to grafted ligands were still present. This result clearly demonstrates that both the mesoporous SBA-15 silica and the organic monolayers appear to essentially retain their structures even after extended use.

For the purpose of comparison, thiolated and aminated MCM-41 were also prepared and tested in this study. The effectiveness of these adsorbents is comparable to their SBA-15 analogues. However, the regeneration process resulted in a significant decrease in surface area and pore volume for both functionalized MCM-41 adsorbents: the surface area and pore volume of the regenerated MCM-41(SH) are 465 (665) $m^2\ g^{-1}$ and 0.41 (0.61) $cm^3\ g^{-1}$; for MCM-41(NH_2), 282 (460) $m^2\ g^{-1}$ and 0.26 (0.41) $cm^3\ g^{-1}$ (the corresponding original values are indicated in parentheses). This result is in good agreement with the report that SBA-15 is much more stable than MCM-41.[9] A great loss in adsorption capacity to heavy metal ions was observed accordingly: an Hg loading of 160 mg g(MCM-41(SH))$^{-1}$ and a Cu loading of 28 mg g(MCM-41(NH_2))$^{-1}$ were obtained, corresponding to about 35% of the original loading capacities.

Less attention has been focused on the synthesis and applications of SBA-15 mesoporous silica since it was discovered in 1998.[11–13] However, we believe that this unique mesoporous material can provide more possibilities for the design and synthesis of open pore structures because of its high surface area and easily controllable uniform pore size that may be extended to *ca*. 300 Å. In addition, compared with MCM-41, the more uniform pore structure and thicker silica walls of SBA-15 (31–64 Å) are shown to impart significant stability to the material under hydrothermal conditions.[9]

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