Intersurface Ion-Imprinting Synthesis on Layered Magadiite Hosts

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A new methodology has been developed to provide effective functionalization of the *intersurface*s of ordered, crystalline, layered magadiite via an imprinting synthesis. Although the surface imprinting has been conducted successfully on a variety of substrates, no report has appeared on imprinting synthesis on the *inter*galleries of the layered materials. This methodology has resulted in a simplified experimental procedure for functionalizing layered silicates with good control of the distributions of functional ligands on magadiite. Our results demonstrate that the imprint-functionalized magadiite has better selectivity and a higher capacity for metal-ion templates than the nonimprinted analogue. The possibility of continuous variation of the basal spacing and the crystalline structures of the layered materials highlight a new opportunity for conducting imprinting synthesis.

Introduction

Host−guest composites based on the intercalation of guest molecules into inorganic layered hosts represent a new class of premier functional materials.[1] They have the unique chemical and physical characteristics that can be utilized for their potential applications in designing novel catalysts, new sensing materials, and advanced separation media.[2,3] Notably, Clearfield and co-workers have successfully developed a synthetic technique to incorporate crown ethers in the galleries between layered zirconium phosphonates for the selective adsorption of metal ions.[4] A novel use of layered materials for sensor applications has been demonstrated by Mallouk and Gavin.[3] Pinnavaia and co-workers have conducted systematic investigations into the uses of layered silicate clays as novel hosts for catalysts as well as the synthesis of novel composite materials through the space-confined polymerization processes.[5] Corma and co-workers pioneered the use of delaminated layered materials for surface immobilization of enzymes.[6] The remarkable activity and stability of the final products have been found.

We[7] and others[8−15] have been interested in conducting molecular imprinting[16−19] on nanostructured porous materials. Imprinting synthesis has been carried out on mesoporous and zeolitic materials through conventional surface imprinting,[7b,c,8] hierarchical imprinting,[7a,d] and "ship-in-bottle" imprinting[7e] methods. The pivotal technique of all imprinting synthesis methodologies involves the incorporation of a template into a host matrix by combining it with host monomers that polymerize around the template.[16−18] Subsequent removal of the template results in a material that contains imprint cavities with a favorable size, shape, and chemical environment to selectively rebind the template. The imprinting approach based on organic polymer hosts was first developed by Wulff and Sarhan who used this technique to produce polymers for the resolution of racemic mixtures.[20] Herein, we report a new approach for the synthesis of surface ion-imprinted sorbents using

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Scheme 1
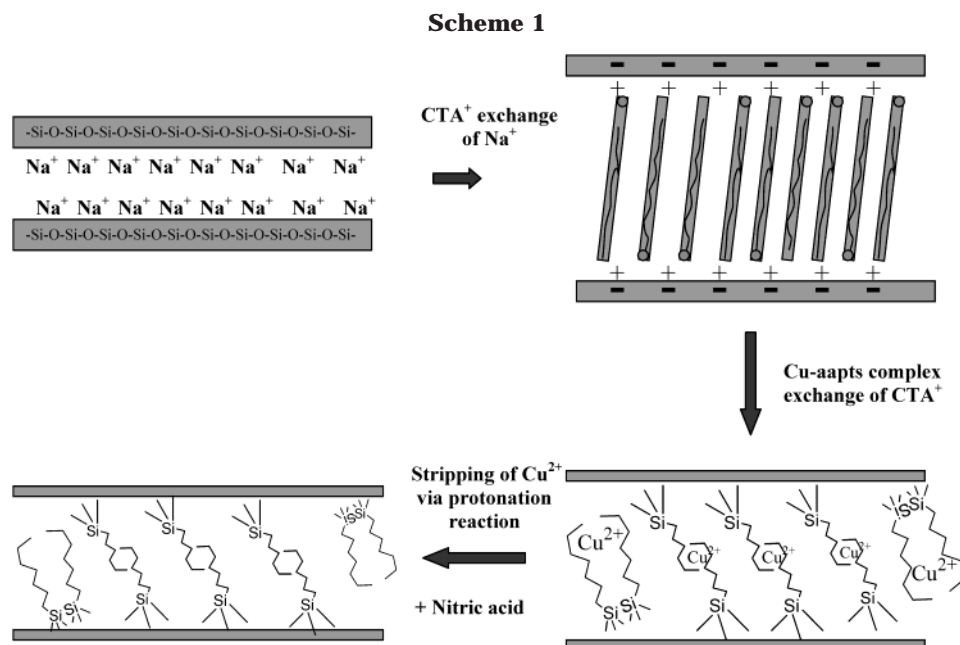
a layered nanomaterial as a host. The unique features of the layered materials are (a) that the gallery spacing can be tuned according to the size and stereochemistry of the intercalate molecules and (b) that the layer structures are crystalline. These unique properties are ideal for surface imprinting synthesis, which benefits from a tunable spacing but stable crystalline host.

The layered material used in this investigation is polysilicate magadiite ($Na_2Si_{14}O_{29} \cdot nH_2O$), which is composed of one or multiple negatively charged sheets of SiO_4 tetrahedra with abundant silanol-terminated surfaces, whose negative charges are balanced by either Na^+ or H^+ in the interlayer spacing. Various chemical species (charged or neutral) have been intercalated into the galleries of magadiite to form the corresponding intercalation compounds for various applications.[3] For example, organic functional groups can be covalently grafted on the silanol-terminated interlayer surfaces through the use of organosilanes containing the functional ligands.[21] Magadiite has been shown to exhibit novel guest-binding properties as sorbents for the adsorption of *n*-alkyl alcohols. A novel class of the hybrid nanocomposites with elastomeric properties has been prepared by intercalating paraffin-like molecules into the galleries of magadiite.[22] The tensile properties of the polymer matrix were improved greatly by the reinforcement effect of the silicate interlayers. Although many novel materials have been derived from magadiite and related layered materials, no previous applications of these materials as *tunable* hosts for conducting surface imprinting synthesis have been, to our knowledge, developed.

Experimental Section

Synthesis. The major reactions employed in our intersurface imprinting using the magadiite host are schematically

shown in Scheme 1. The target metal ion used to demonstrate this imprinting synthesis is Cu^{2+}, which can form strong dative bonds with amine ligands.[7] The amine silane bifunctional ligand used in this study is 3-(2-aminoethylamino) propyltrimethoxysilane (AAPTS). This ion-imprinting system has been extensively used as a model system to demonstrate several ion-imprinting principles because of its simplicity and ease in implementation.[7] The Na^+–magadiite host was synthesized by a hydrothermal reaction of 60.0 g of silica gel with 300 mL of 1.11 M NaOH solution at 150 °C for 50 h according to previously published methods.[23] Since the imprinting complex [$Cu(AAPTS)_2^{2+}$] is too big to be effectively intercalated into the galleries of the Na^+–magadiite host via ion exchange, a stepwise approach was employed.[3,7e,24] This methodology first involved the exchange of Na^+ by a much bigger CTA^+ cation (cetyltrimethylammonium), which was then followed by exchanging CTA^+ cations with $Cu(AAPTS)_2^{2+}$. This exchange strategy utilizing the bulk cation-exchanged form of the layered materials as the intermediates has been adopted in synthesizing other layered compounds, such as the layered materials intercalated with crown ethers.[3] Briefly, the intercalation of CTA^+ ions was conducted by an ion-exchange process between the Na–magadiite host and an aqueous cetyltrimethylammonium bromide (CTAB) solution.[25] The resulting CTA^+–magadiite was suspended in 100 mL of a methanol solution containing a mixture of 1.0 g of $Cu(NO_3)_2 \cdot$ $2.5H_2O$ and 2.4 mL of AAPTS (3-(2-aminoethylamino)propyltrimethoxysilane) (Cu^{2+}:AAPTS molar ratio = 1:2.5). The suspension was refluxed for 24 h. The product was recovered by filtration and washing with distilled water to remove excess ligands. The air-dried sample was then washed with a copious amount of 1 M HNO_3 to remove the target template ions (Cu^{2+}). The resulting product was placed in deionized water and titrated with 2.03 M NaOH to pH 7.6. The purpose of the titration is to recover the coordination ability of diamine groups after we had removed Cu^{2+} from the as-synthesized samples using 1 N HNO_3. The control blank sample was prepared using an identical procedure but without the addition of $Cu(NO_3)_2 \cdot$ $2.5H_2O$. This synthesis protocol has been repeated many times with reproducible results.

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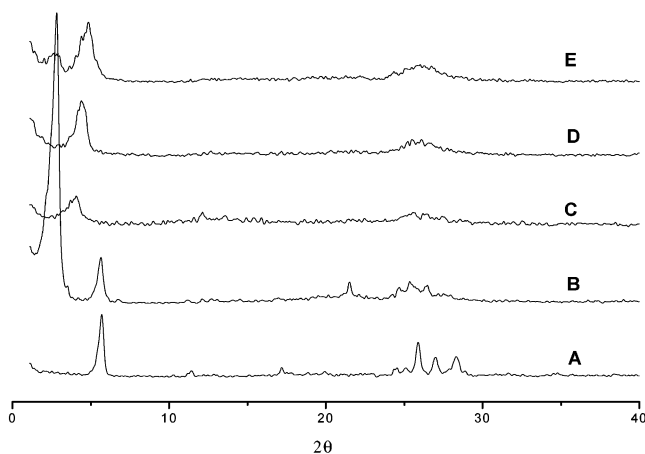
Figure 1. XRD patterns of a series of magadiite materials: (A) layered magadiite, (B) CTA$^+$−magadiite, (C) Cu−AAPTS-functionalized magadiite, (D) imprint-functionalized magadiite, and (E) control blank magadiite.

Characterization. The powder X-ray diffraction patterns of the samples were recorded using a SIEMENS D5005 X-ray diffractometer, where Cu Kα (wavelength = 0.154 nm) was used as the X-ray source operating at 40 kV and 40 mA. Solid state ^{29}Si NMR spectra were recorded on a Bruker MSL 100 spectrometer, operating at 2.35 T, using standard ^{1}H−^{29}Si cross-polarization/magic-angle spinning (CP/MAS) techniques and the following parameters: ^{1}H, 101.111 MHz; ^{29}Si, 19.883 MHz; ^{1}H rf amplitude, 64 kHz (3.9 μs 90 pulse) held constant for ^{1}H excitation, cross polarization, and dipolar decoupling; 2.5-ms cross-polarization contact time; 4-s pulse delay; MAS = 3050 ± 20 Hz. The Hartmann−Hahn cross-polarization match condition was optimized at the first upper sideband position by varying the ^{29}Si rf field amplitude. Chemical shifts are reported with respect to TMS (δ = 0 ppm) using dodeca-methylcyclohexasilane as a secondary standard (δ = −41.9 ppm). UV−visible spectra were measured with a Cary 5000 (Varian, Inc.) spectrophotometer equipped with a diffuse reflectance attachment.

Adsorption Test. The Cu(II) ion solution was buffered to a specific pH with sodium acetate/acetic acid (0.05 M). In a typical run, 0.1 g of sorbent and 10 mL of metal ion solution were placed in a capped P.E.T. vial. The solution was then sonicated for 1 h. The equilibrated solution was filtered, and the concentration of the resulting filtrate was measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; IRIS, Thermo Jarrell Ash).

Results and Discussions

The powder X-ray diffraction (XRD) patterns for each phase along with that of the original Na$^+$−magadiite host are given in Figure 1. On the basis of the 2θ values corresponding to the (100) diffraction peak, the basal spacing of the CTA$^+$−magadiite is 3.16 nm, which is much larger than that of the Na$^+$−magadiite (1.56 nm). This big shifting of the (100) peak indicates that Na$^+$ ions were successfully replaced by CTA$^+$ ions with a concomitant expansion of the corresponding gallery spacing. It is very difficult to determine the exact amount of the intercalated CTA$^+$ ions because of the difficulty in the differentiation of the intercalated and the externally adsorbed CTA$^+$ in the present experiments. The basal spacing of the magadiite intercalated by Cu(AAPTS)$_2$$^{2+}$ is 2.26 nm, which is consistent with the fact that the length of Cu(AAPTS)$_2$$^{2+}$ is shorter than the chain length of CTA$^+$. The peak position shifts to a higher angle at the spacing 2.02 nm after stripping of Cu^{2+} via a protonation reaction. The basal spacing of
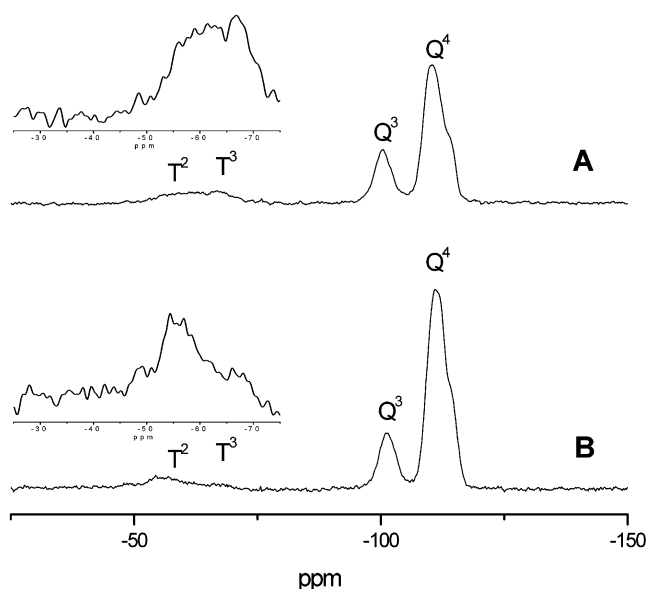
Figure 2. ^{29}Si MAS NMR spectra of (A) imprint-functionalized magadiite and (B) control blank magadiite (inset expansion spectrum between −25 and −75 ppm).

control blank magadiite is 1.81 nm. There is still a peak displayed near 3.16 nm, which indicates that the CTA$^+$ ions were only partially exchanged by AAPTS groups under the same experimental conditions as those for the imprinting functionalization. The resulting partially exchanged layered material has a similar double-basal structural feature as those reported previously with the exchange of CTA$^+$ in magadiite by smaller cations.[26] This observation implies that the functionalization yield for the imprinting method with metal ions is much more than that of the conventional surface functionalization. This enhancement can be attributed to the facilitation by the cation-exchange reaction of the precursor complexes with the cationic surfactant cations in the imprinting functionalization. In this approach, the surfactant ions are used as a unique vehicle to transport cationic metal complexes inside the galleries.[7c] The unique property of this ion-exchange technique is that the precursor metal complexes are deposited and functionalized *only* inside the galleries.

The ^{29}Si CP/MAS NMR spectra of imprint-functionalized magadiite (A) and control blank magadiite (B) are shown in Figure 2. The ^{29}Si resonance peaks in A and B at ca. −103 and −114 ppm are assigned to the ^{29}Si nuclei of Q^3 and Q^4 environments, respectively. The relative narrow peak widths indicate that the crystalline structure of the magadiite framework is retained during the functionalization reactions. The resonance peaks at ca. −56.5 and −67.5 ppm arise from the (−O)$_2$Si(OH)R and (−O)$_3$SiR species assigned to T^2 and T^3, respectively. The presence of the T^2 and T^3 bands indicates that the AAPTS functional groups are covalently bonded to the magadiite surface.[27] As seen from Figure 2, the integrated intensity of the T^2 and T^3 peaks in A is larger than that in B. This observation validates the above XRD results that the functionalization yield for the
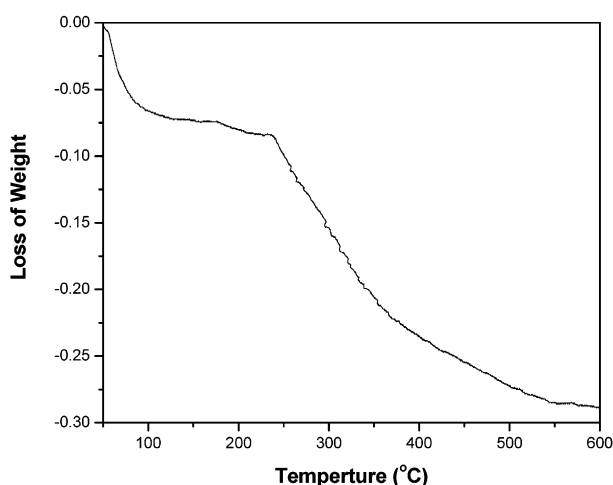
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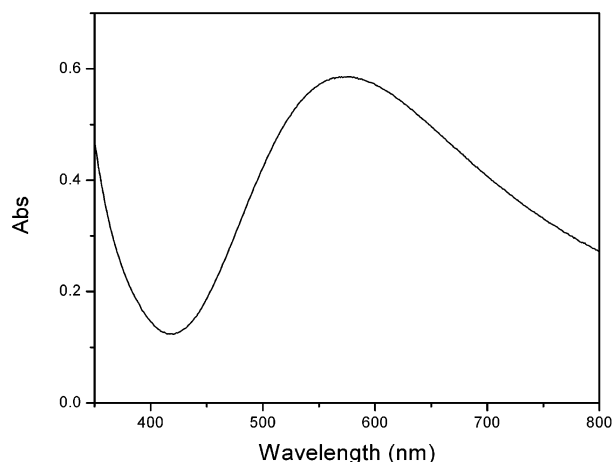
Figure 3. Diffuse-reflectance UV−vis spectrum of Cu−AAPTS-functionalized magadiite.

Figure 4. TGA curve of the imprint-funtionalized magadiite.

imprinting method is more than that of the conventional surface functionalization. The reason probably comes from the difference between the Cu−AAPTS complex and AAPTS in its ion-exchange role with C$_{16}$TMA−magadiite.

The ultraviolet−visible (UV−vis) diffuse reflectance spectra were measured on a CARY-4E spcetrophotometer. The maximum band position of the d−d transition from Cu(II) can be correlated with the coordination environment of copper ions in the imprint-functionalized magadiite.[28] As seen from Figure 3, the maximum band position is located at 581 nm, which is consistent with the coordination environment of Cu(II) with approximately two diamine ligands.[7a]

The thermogravimetric analysis (TGA) curve of the imprint-functionalized magadiite is displayed in Figure 4. This curve shows three distinct stages of weight loss: 25−200, 200−400, and above 400 °C. The first weight loss is mainly due to the desorption of water (about 5.1%).[29] A minor weight loss at ~175 °C might be attributed to the release of the minor nitrate component. This nitrate component might result from the residue of sodium nitrate used in synthesis. The

second weight loss arises mainly from the combustion and decomposition of functional ligands in air (about 11%). The loading of the functional ligands is very close to those of the mesoporous silica materials functionalized via imprint-coating synthesis.[7b] The third stage may be related to water loss via condensation of silanol groups to form siloxane bonds (about 4%). This weight loss behavior is very similar to that found for inorganic−organic nanocomposites derived from organoalkoxysilane and methyl methacrylate by a sol−gel process.[30]

On the basis of the above spectroscopic characterizations, the possible mechanism of the ion-imprinting process inside the layered magadiite host is consistent with the proposed Scheme 1. The key synthesis step involves the grafting of the precursor complex [Cu(AAPTS)$_2$$^{2+}$] on the intersurfaces of the magadiite host. The cationic charge of Cu(AAPTS)$_2$$^{2+}$ plays a key role in the ion-imprinting process. Because both CTA$^+$ and Cu(AAPTS)$_2$$^{2+}$ are positively charged, the intercalation process of Cu(AAPTS)$_2$$^{2+}$ inside the galleries via a methanol solution is enhanced by the ion-exchange process. The complexes exchanged into the galleries are then covalently attached to the surfaces through condensation reactions of silicon alkoxide groups in the bifunctional ligands with neighboring surface SiO$^-$ or SiOH groups. Accordingly, this reaction mechanism would result in efficient functionalization of the intersurfaces of the magadiite host. The high solubility of Cu(AAPTS)$_2$$^{2+}$ in methanol is the main reason for us to choose methanol as a solvent for this functionalization process.[31] In fact, methanol has been previously used as a solvent for graphing AAPTS on silica surfaces[31] and Cu(AAPTS)$_2$$^{2+}$ on mesoporous materials.[7b]

Table 1 summarizes the measured adsorption capacities of the imprint-coated and conventionally coated (control blank) magadiite sorbents for Cu^{2+} and Zn^{2+}. The selection of different concentrations of Cu^{2+} (0.0001 M) and Zn^{2+} (0.001 M) is based on the convenient comparison with our previous works to conduct competitive ion-binding experiments.[7] The affinity of Cu^{2+} toward amine ligands is much greater than that of Zn^{2+}. This difference in the affinity is a primary reason for us to use different concentrations of Cu^{2+} and Zn^{2+} to clearly see the improvement of the sorbents for binding Cu^{2+} via imprinting synthesis. As seen from Table 1, the imprinted sorbents exhibit higher effective capacities for Cu^{2+} than that of control blank magadiite. These batch measurements provide experimental data for the calculation of the distribution coefficient (K_d), selectivity coefficient (k), and relative selectivity coefficient (k') for the magadiite sorbents.[32] As seen from Table 1, the K_d value of the Cu^{2+}-imprinted sample is 3-fold greater than that of the control sample. The value of the relative selectivity coefficient k' (3.24) is >1, which indicates enhanced adsorption through the ion-imprinting synthesis. The capacity did not change after several cycles of loading and striping. Although the enhanced capacity for Cu^{2+} could also be induced by the greater loading of

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Table 1. Competitive Loading of M_1 (Cu^{2+}) and M_2 (Zn^{2+}) by Plain, Control Blank, and Copper-Imprinted Magadiite at pH 5.0 (Acetic Acid/Acetic Buffer) (Formula for Calculation of K_d, k, and k' Are According to ref 7a)

| | solution[a] | | | | | | | |
type	Cu(M_1)	Zn(M_2)	%Cu abs	%Zn abs	Cu K_d	Zn K_d	k	k'
magaditte[b]	0.0001	0.001	78.99	60.32	368	149	2.47	
nonimp-AAPTS[c]	0.0001	0.001	94.38	26.61	1572	34.57	45.47	
imp-AAPTS[d]	0.0001	0.001	98.07	26.71	5105	34.72	140.03	3.24

[a] Initial solutions. [b] Unfunctionalized magadiite. [c] nonimp = nonimprinted AAPTS-functionlized magadiite. [d] imp-AAPTS = imprinted AAPTS-functionlized magadiite.

the ligands in the imprinted sorbents, the increased selectivity is best rationalized with the imprinting effect.

In conclusion, a new methodology has been developed to provide effective functionalization of the *intersurface* of ordered, crystalline, layered magadiite via an imprinting technique. Although the surface imprinting has been conducted successfully on a variety of substrates,[7,8,10–13,33] no report has appeared on imprinting synthesis on the galleries of the layered materials. This methodology has resulted in a simplified experimental procedure for functionalizing layered silicate with good control of the distributions of functional ligands on magadiite. Our results demonstrated that the imprint-functionalized magadiite has better selectivity and a higher capacity for the metal-ion templates than the nonimprinted analogue. The possibility of the continuous variation of the basal spacing and the crystalline layered structures for the layered materials highlight a new opportunity for conducting imprinting synthesis.

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