Organosilica Copolymers for the Adsorption and Separation of Multiple Pollutants

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Benzene, diethylbenzene, and ethylenediamine-bridged bistrialkoxy precursors were used in the synthesis of multifunctional PMO copolymers for the adsorption of phenols and metal ions. Polyoxyethylene(10) stearyl ether (Brij 76) was used as the structure director with the surfactant template approach in the synthesis. The resulting PMO copolymers with two or more bridging groups have been characterized by nitrogen gas adsorption, powder X-ray diffraction, and ^{13}C and ^{29}Si solid-state NMR. These organosilicas exhibit large surface areas, narrow pore size distributions, large total pore volumes, and pore ordering consistent with well ordered, hexagonally packed *p6mm* structures. Minimal competitive effects were observed on the adsorption of *p*-chlorophenol to the copolymers in the presence of copper ions in solution. Similarly, the presence of *p*-chlorophenol in solution or adsorbed onto the copolymers did not interfere with copper adsorption. Replacement of a small portion of the benzene bridge in the 90:10 BENZ:EDA copolymer with diethylbenzene produced a copolymer 2.5-fold more efficient for *p*-chlorophenol adsorption. ICP analysis revealed that greater than 98% of adsorbed copper was removed during extraction with HCl, and this extraction process can be repeated with no difference in copper adsorption after regeneration.

Introduction

Periodic mesoporous organosilicas (PMOs) can play a key role in the effort to develop efficient, regenerable sorbents. PMOs are synthesized from bistrialkoxyorganosilane precursors using the surfactant template approach and are high surface area materials with narrow pore size distributions containing few bottlenecks or dead ends.[1−3] Having both structural rigidity due to the siloxane groups as well as functionality due to the organic bridging groups, these highly ordered pore networks allow for fast access of molecules and ions to the polymer functional groups in liquid or gas phase. Until recently PMOs have been successfully prepared with only a single type of organic bridging group[4−8] and the addition of multiple trialkoxyorganosilane groups in any appreciable amount via co- or post-synthetic grafting condensation resulted in a loss of pore ordering, restriction of pore openings, or uneven distribution of organic functional groups on the PMO surfaces.[9−13]

Our approach capitalized on the recently developed methodology in our laboratory for preparing PMO copolymers containing two or more functional groups incorporated into the material's walls with ordered porosity and the capability of adsorbing multiple types of analytes.[14,15] Here we have designed PMO sorbents containing both aromatic and metal chelating bridging groups capable of removing aromatic organic pollutants as well as metal ions with high adsorption capacity. Benzene (BENZ), diethylbenzene (DEB), and ethylenediamine (EDA)-bridged bistrialkoxy precursors were used in the synthesis of multifunctional PMOs.

Experimental Section

The 1,4-bis(triethoxysilyl)benzene monomer was synthesized in our laboratory following reported procedures,[16] while bis-(trimethoxysilylethyl)benzene and bis[(trimethoxysilyl)proyl]-ethylenediamine were obtained from Gelest, Inc. All other chemicals were obtained from Aldrich and used as received. Water used in all synthetic procedures was deionized to 18 MΩ cm. The PMOs were prepared using our Brij 76 templating method using the two different precursors in various ratios while keeping the total number of moles constant.[15] Details of the synthesis are given in the Supporting Information. Following hydrothermal treatment, the surfactant templates were extracted three times with acidified ethanol, to produce the mesoporous products. Gas sorption experiments were performed using a Micromeritics ASAP 2010. Nitrogen gas was used as the adsorbate at 77 K. X-ray diffraction measurements were made on an Enraf-Nonius FR591 rotating-anode operating at 13 kW. A singly bent graphite monochromator selected Cu K$_{\alpha}$ radiation and provided an in-plane resolution of 0.014 Å^{-1} full-width at half-maximum. Powder samples were placed in 1.0 mm quartz capillary tubes.

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TABLE 1: Physicochemical Properties of Periodic Mesoporous Organosilicas

PMO	d^a (Å)	BET surface area (m²/g)	total pore volume (cm³/g)	pore size^c (Å)
BENZ	57	974	0.80	35
EDA	b	190	0.62	13
90:10 BENZ/EDA	71	924	0.78	34
80:20 BENZ/EDA	84	950	1.05	39
85:10:5 BENZ/EDA/DEB	68	539	0.48	30

^{a} $d(100)$ spacing of the extracted products ($\pm$ 2 Å). ^{b} No order observed. ^{c} Calculated from adsorption isotherm.

Solid-state ^{13}C and ^{29}Si NMR experiments were performed at room temperature on a Bruker DMX 500 MHz at a resonance frequency of 125.77 and 99.36 MHz, respectively, with a 4.0 mm MAS probe. The samples were packed in 4 mm zirconia Bruker rotors fitted with Kel-F end caps for magic angle spinning at 10 kHz for ^{13}C MAS NMR and at 5 kHz for ^{29}Si MAS NMR. A two-pulse phase modulation (TPPM) decoupling sequence was used for proton decoupling.[17] A ^{13}C CP contact time of 3 ms was used for all the samples with up to 2000 scans and 4 s delay times. The ^{13}C reference was set to external tetrakis(trimethylsilyl)silane at 3.5 ppm with respect to TMS at 0 ppm. A ^{29}Si CP contact time of 3 ms was used for all the samples with up to 6000 scans and 2−5 s delays. The ^{29}Si reference was set to external tetrakis(trimethylsilyl)silane at −9.9 (SiMe₃) and −135.6 ppm ($T = 297$ K) with respect to TMS at 0 ppm.

For adsorption studies, each copolymer sorbent was added into a single sorbate solution (100 μM copper or 100 μM p-chlorophenol) or into a binary solution (100 μM copper and 100 μM p-chlorophenol) with 0.01 M phosphate buffer (pH = 7). The resulting mixtures were equilibrated for 1 h on a rotary shaker then centrifuged for 20 min at 2500 rpm. This solution was decanted and filtered through 0.2 μm PTFE Acrodisc filter prior to analysis via HPLC. Adsorbed aromatics and metal ions were extracted by adding 2 mL ethanol (for organic extraction) followed by 2 mL 1M HCl (for metals extraction) to solids from centrifugation of adsorption cycle and equilibrated on rotary shaker for 1 h, then centrifuged and the solution decanted. The supernatant was diluted and filtered through 0.2 μm PTFE Acrodisc filter prior to analysis via inductively coupled plasma (ICP). Copper ion concentration analyses were performed with a Thermo IRIS Intrepid II XSP inductively coupled plasma spectrometer. Each measurement was repeated four times with deviation less than 2%. The reported value for each concentration is an average of these measurements.

Results and Discussion

Table 1 shows the physiochemical properties of the pure BENZ- and EDA-bridged PMOs and the 90:10 BENZ/EDA, 80:20 BENZ/EDA, and 85:10:5 BENZ/EDA/DEB PMO copolymers. The molar ratios reflect the relative proportions of each organosilane added during synthesis. Nitrogen sorption measurements performed on the PMO copolymers displayed type IV isotherms with large nitrogen adsorption capacities of 0.48−1.05 cm³/g and sharp Barrett−Joyner−Halenda (BJH) pore size distributions (Figure S1, Supporting Information). The isotherms displayed a large step in the mesoporous region and then flatten out to indicate a lack of any macropores. The powder X-ray diffraction patterns of the copolymers are shown in Figure 1, with the (100) reflection clearly visible. All copolymers exhibit a high degree of pore ordering. The 90:10 BENZ/EDA also shows a weak (200) peak and a smaller spacing than the
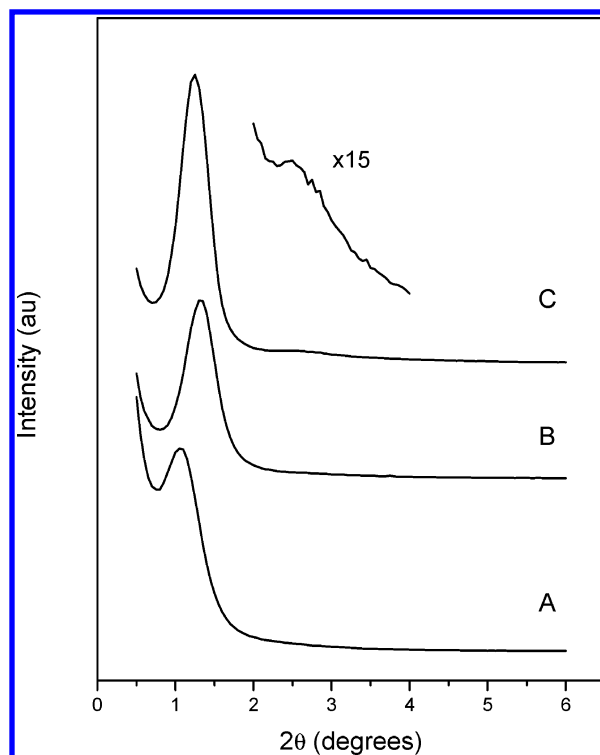

Figure 1. XRD spectra of PMO copolymers. (A) 80:20 BENZ/EDA bridged, (B) 85:10:5 BENZ/EDA/DEB bridged, (C) 90:10 BENZ/EDA bridged. Inset shows the enhanced (200) peak for 90:10 BENZ/EDA bridged copolymer.
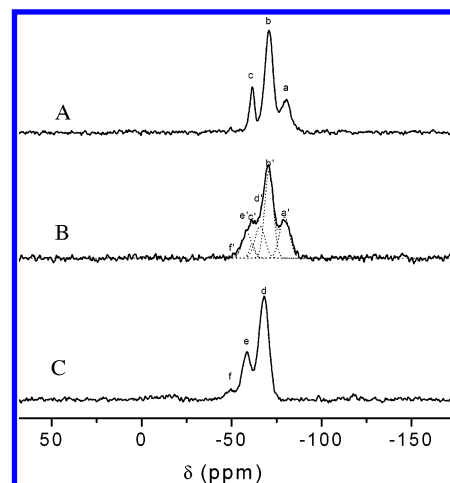

Figure 2. ^{29}Si CP MAS NMR spectra of the PMOs. (A) 100% BENZ bridged, (B) 80:20 BENZ/EDA bridged copolymer, (C) 100% EDA bridged PMO; a, b, c, and d, e, f are the −RSi(OSi)$_n$(OH)$_{3-n}$ or T$_n$ units where $n = 3$, 2, and 1, respectively, for BENZ- and EDA-bridged PMOs and the prime letters are the respective units in the copolymer.

80:20 sample. This is consistent with previous results which showed a well ordered, hexagonally packed $p6mm$ structure for 100% BENZ.[16] No peaks were resolved in the diffraction pattern of the 100% EDA material.

Figures 2 and 3 show the ^{29}Si CP/MAS NMR and ^{13}C−CP/MAS NMR spectra of the pure BENZ- and EDA-bridged PMOs and the 80:20 BENZ/EDA copolymer revealing the nature of the Si−C and Si−O bonds and their stability during processing. A single major region of ^{29}Si peaks centered around −75 ppm for the BENZ-bridged silica, −63 ppm for the EDA bridged silica and −70 ppm for the copolymer, was observed.

These regions represent the −RSi(OSi)$_n$(OH)$_{3-n}$ or T$_n$ units of the individual PMOs, where R is either a BENZ (−C₆H₄−)
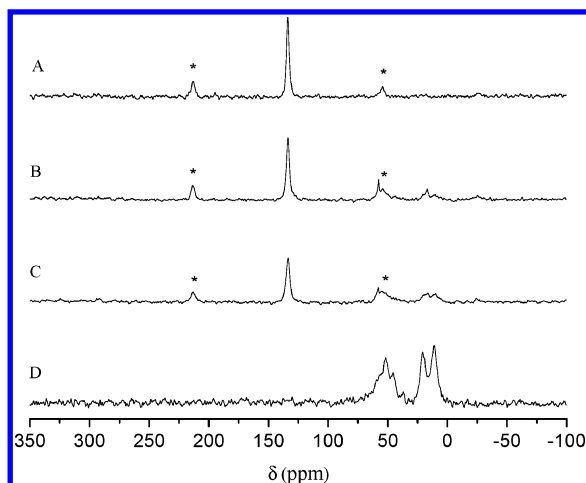
Figure 3. ^{13}C CP MAS NMR spectra of the PMOs. (A) 100% BENZ bridged, (B) 90:10 BENZ/EDA bridged copolymer, (C) 80:20 BENZ/EDA bridged copolymer, (D) 100% EDA bridged PMO.

or an EDA ($-CH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2CH_2-$) moiety. The BENZ-bridged silica spectrum (Figure 2A) displays three resolved peaks at -80, -70, and -61 ppm, which can be assigned to the T_n structural units within the silica matrix where $n = 3$, 2, and 1 respectively (peaks a, b, and c). The EDA-bridged silica spectrum (Figure 2C) displays the T_n structural unit peaks at -68, -58, and -49 ppm for $n = 3$, 2, and 1, respectively, (peaks d, e, and f). Qualitatively, a shift of intensity from the T_2 peak to the T_3 peak is observed in the EDA bridged silicate when compared to the BENZ-bridged silicate, indicating a high degree of condensation or an increase in the number of Si$-$O$-$Si groups in the EDA bridged PMO. The relative peak patterns extracted from the deconvoluted silica spectrum of the 80:20 BENZ/EDA bridged copolymer (Figure 2B) displays six resolved peaks which can be assigned to the T_n structural units of the two equivalent R groups of the individual polymers within the silica matrix of the copolymer. The copolymerized PMO did not show any significant changes in the chemical shifts or the line half widths of the T_n signals equivalent to the individual PMOs of BENZ- and EDA-bridged materials. The equivalent T_n structural peaks in the copolymer corresponding to the individual organic moieties are labeled as a′, b′, and c′ for R = $-C_6H_4-$ and d′, e′, and f′ for R = $-CH_2CH_2-NH-CH_2CH_2-NH-CH_2CH_2-$ when $n = 3$, 2, and 1 respectively (Figure 2B). The absence of any signals centered around -105 ppm, where the characteristic $Si(OSi)_n(OH)_{4-n}$ units generally appear, confirms that the C$-$Si bonds of the precursors did not cleave during the synthesis and/or the subsequent extraction process of the Brij 76 surfactant in the individual polymers as well as in the copolymers.

Solid-state $^{13}C-CP/MAS$ NMR spectra of the individual and copolymer samples of the PMOs also show that the BENZ and EDA moieties were intact and were stable during synthesis (Figure 3). The absence of any Brij 76 surfactant peaks in the $^{13}C-CP/MAS$ NMR spectra (ca. 72.9, 70.9, 61.7, 32.7, 30.5, 26.9 ppm) also indicates the successful surface extraction of the surfactant. The ^{13}C chemical shifts of the BENZ-bridged sample shows a single peak centered around 134 ppm (Figure 3A). The $^{13}C-CP/MAS$ NMR spectrum of the EDA bridged sample (Figure 3D) shows signals at 10.8, 20.6, 45.5, and 51.8 ppm corresponding to C_1, C_2, C_4+C_5, and C_3 respectively of the $\equiv SiCH_2(1)CH_2(2)CH_2(3)NHCH_2(4)CH_2(5)NHCH_2(3′)-CH_2(2′)CH_2(1′)Si\equiv$ group. The downfield shifted C_1 signal at 10.8 ppm from the 6.9 ppm signal of a cleaved C_1 carbon further confirms the stability of the C$-$Si bond at the C_1 carbon.
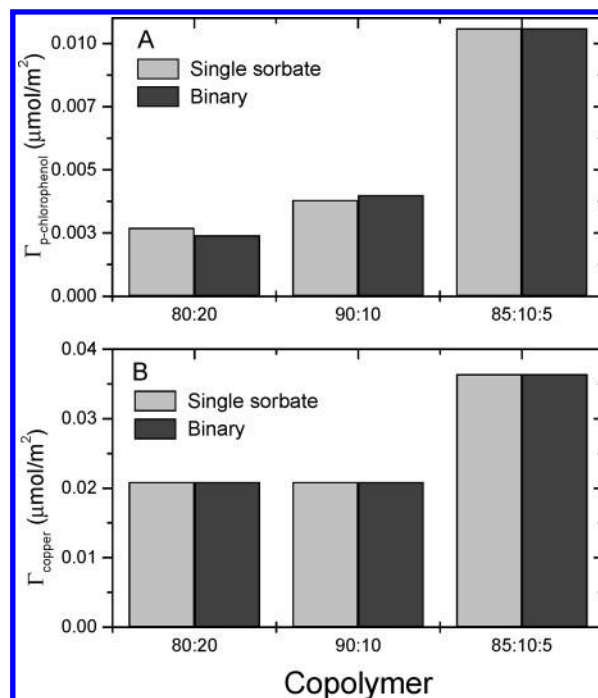

Figure 4. Single sorbate and binary solution (*p*-chlorophenol-copper) adsorption of (A) *p*-chlorophenol onto various copolymers, and (B) copper onto various copolymers.

Resonances associated with trace amounts of ethanol ($\sim$16 ppm and $\sim$58 ppm), used in the extraction of the surfactant, were observed in the EDA bridged PMO and the copolymer samples. The ^{13}C chemical shifts of the copolymers show peaks assigned to the EDA and BENZ groups covalently linked to Si. This shows that the carbon moieties and the C$-$Si bonds were stable during the synthesis of the pure polymers and copolymers of the PMOs. The ^{13}C MAS NMR resonances associated with the methoxy groups in the BENZ bridged PMO precursors were undetectable indicating that a high degree of hydrolysis was achieved during synthesis of these sorbents.

While both BENZ- and DEB-bridged PMOs are capable of adsorbing aromatic phenols, there are important differences both in the adsorption behavior and structural characteristics of BENZ and DEB sorbents. Figure 4A shows the adsorption of *p*-chlorophenol onto various copolymers in single sorbate and binary *p*-chlorophenol-copper solutions. The amount of adsorbed *p*-chlorophenol increased as the proportion of the BENZ or DEB bridge in the copolymer increased. Yet, the overall performance of the highly ordered BENZ-bridged sorbent for *p*-chlorophenol was disappointing, removing only a small portion of the phenol from solution. In contrast, the DEB-bridged nanoporous organosilica has demonstrated a high capacity for aromatic phenol adsorption in par with activated carbon.[18] Our experiments examining the relative adsorption efficiency of BENZ and DEB mesoporous organosilicas demonstrated that the DEB material is an order of magnitude more efficient sorbent with a surface excess ($^{DEB}\Gamma_{NP}$) of 0.050 μmoles/m^2 as compared to $^{BENZ}\Gamma_{NP}$ = 0.005 μmoles/m^2 (Figure S2, Supporting Information). The BENZ group forms a relatively more rigid bridge between the siloxanes of the PMO, resulting in a material with an ordered porosity, high surface area, and high pore volume. In contrast, DEB is a more flexible bridging group, resulting in a material with amorphous pore ordering, lower surface area, and lower pore volume. A relatively higher decay of the ^{13}C spins in the BENZ-bridged PMO versus the DEB-bridged PMO in solid-state ^{13}C NMR dipolar dephasing experiments also indicates that the BENZ formed a more rigid bridge than DEB. Neverthe-

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less, what the DEB sorbent lacks in pore order and surface area, it more than makes up for in its high adsorption capacity. It seems a reasonable assumption that the differences in the structures of the BENZ and DEB bridging groups are the root of the observed differences in adsorption behavior. A definitive determination requires a very detailed direct analysis of the surface interactions. The effect of this difference in adsorption efficiency was examined with the 85:10:5 BENZ/EDA/DEB copolymer. Replacement of a small portion of the benzene bridge in the 90:10 BENZ/EDA copoloymer with diethylbenzene produced a copolymer 2.5-fold more efficient for *p*-chlorophenol adsorption. It is worth noting that although the surface area and pore volume of the BENZ/EDA/DEB copolymer 85:10:5 were smaller than those for the 90:10 BENZ/EDA copolymer, the BENZ/EDA/DEB still has reasonably high surface area and porosity. The plots of the *p*-chlorophenol adsorption from solutions containing copper ions mirrored those from the single sorbate solution, demonstrating that there is minimal competitive effect from copper on *p*-chlorophenol adsorption. Figure 4B shows the adsorption of copper onto various copolymers containing the metal chelating EDA bridge in single sorbate and binary *p*-chlorophenol-copper solutions. Similar to *p*-chlorophenol adsoption, the presence of *p*-chlorophenol in solution or adsorbed onto the copolymers did not interfere with copper adsorption, and a high removal rate was observed.

To determine how efficiently metal ions could be extracted from the copolymers, we modified a method previously used to demonstrate complete extraction of adsorbed phenols from the surfaces of an aromatic-bridged PMO.[18] The ICP analysis of the extracted supernatants revealed that greater than 98% of adsorbed copper was removed during this process. Furthermore, Figure S3 demonstrates that this extraction process can be repeated with no difference in copper adsorption after regeneration.

In conclusion, we have found that aromatic and metal chelating bridging groups can be incorporated into PMO copolymers while maintaining an ordered pore structure. Most importantly, the nature of the aromatic group is an important factor in the adsorption efficiency of the resulting nanoporous material. Replacement of a relatively small fraction of the benzene groups with diethylbenzene resulted in a much better sorbent for *p*-chlorophenol. In addition to the efficient removal

of phenols and copper ions by the PMO coplymers, they can also be easily regenerated. Further studies will be required to determine if these materials can be used as sorbents that remove multiple types of pollutants from waste streams.

Supporting Information Available: Detailed synthetic procedure nitrogen sorption measurements performed on the PMO copolymers, surface excess data for comparative adsorption of 4-nitrophenol by DEB and BENZ, and copolymer regeneration. This material is available free of charge via the Internet at http://pubs.acs.org.

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