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Synthesis and Characterization of Organic−Inorganic Hybrid Mesoporous Anion-Exchange Resins for Perrhenate (ReO$_4^-$) Anion Adsorption

Byunghwan Lee,[†] Li−Li Bao,[†] Hee-Jung Im,[†] Sheng Dai,*[,†]
Edward W. Hagaman,[†] and J. S. Lin[‡]

Chemical Sciences and Condensed Matter Sciences Divisions, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Organic−inorganic hybrid mesoporous anion-exchange resins based on either pure silica or organosilica support materials were prepared and tested for the adsorption of perrhenate (ReO$_4^-$) anions in aqueous solutions. The prepared samples were characterized using nitrogen adsorption−desorption measurements, Fourier transform infrared spectroscopy, Raman spectroscopy, small-angle X-ray scattering, ^{29}Si cross-polarization/magic-angle-spinning nuclear magnetic resonance, and scanning transmission electron microscopy. Among the prepared samples, the hybrid mesoporous anion-exchange resins functionalized with *N*-((trimethoxysilyl)propyl)-*N,N,N*-tri-*n*-butylammonium ions showed higher affinities for perrhenate ions than did the resins functionalized with *N*-((trimethoxysilyl)propyl)-*N,N,N*-trimethylammonium ions. The enhancement by the bulky ammonium functional ligand is consistent with Hofmeister selectivity.

Introduction

Organic polymer anion-exchange resins are widely used to recover anions from various process waste streams. Among the various organic anion-exchange resins, quaternary ammonium resins are one of the most popular and effective in these applications.[1] However, drawbacks are associated with all organic anion-exchange resins: (1) instability in harsh chemical environments such as organic solvents and oxidizing agents, (2) limited surface areas, (3) hydrophobicity of polymer backbones, (4) thermal instability, and (5) swelling and deformation in contact with solvents.[2,3] For these reasons, organic−inorganic hybrid resins have been developed as sorbents for anionic copper cyanide complexes,[4] potentiometric sensors for anions,[3,5] and chemosensors for anions.[6] Mesoporous silica materials functionalized with Cu-chelated complexes[7] and amine ligands[8] have also been prepared for the adsorption of arsenate and chromate in aqueous solution. We have reported the synthesis of the new organic−inorganic

hybrid mesoporous anion-exchange resins based on the MCM-type hosts for the adsorption of anionic thorium nitrate complexes in nitric acid solutions.[2] As a further extension of the above research, we describe herein the preparation of several new organic−inorganic hybrid mesoporous anion-exchange resins by a cosynthesis method for the adsorption of perrhenate anions in aqueous solutions using either pure mesoporous silica or organo-silica materials[9−11] as support hosts. Perrhenate anions have adsorption characteristics similar to those of per-chlorate and pertechnate anions and can serve as sur-rogates for them. Both perchlorate and pertechnate anions are contaminants that cause major environmental con-cerns.[12] The development of sorbents for these anions is important for their effective removal from the contami-nated sites.

Although there are indications in the literature that the adsorption capacity of bulky anions may also depend on the hydrophobicity of the matrix (secondary environ-ments),[1] no systematic investigations have been reported.

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Our new hybrid sorbents synthesized with different hydrophobic matrixes should provide ideal model systems for such studies. The pure mesoporous silica supports used in our investigation include HMS[13] and SBA-15.[14] An entirely new class of organic−inorganic hybrid mesoporous materials based on organosilica (bridged polysilsesquioxane) has recently been successfully developed.[9−11,15] Several new sorbents for the adsorption of metal ions and organic pollutants (e.g., phenols) have been synthesized based on the incorporation of the functional ligands into these new periodic mesoporous organosilica (PMO) materials or the use of the intrinsic functionality of the bridged polysilsesquioxane.[9d,16−18] However, no anion-exchange resins have been prepared using these PMO materials as support hosts. These PMO materials are intrinsically amphiphilic, a feature that is attributed to the hydrophilic inorganic groups and the hydrophobic organic bridge groups inside the mesostructures. Accordingly, their adsorption performances for the hydrophobic anions such as perrhenate ions in aqueous solutions may be better than those of the pure mesoporous silica hosts such as HMS or SBA-15. At the same time, the new materials have better compatibilities with aqueous environments than those of organic polymer resins.

Experimental Section

(A) Preparation of Mesoporous Silica Materials. The mesoporous silica materials of HMS, SBA-15, and PMO were prepared following procedures described in the literature.[9−11,13,14]

(1) Synthesis of HMS. Briefly, the mole ratio of 1-hexadecylamine (99%, Aldrich)/tetramethyl orthosilicate (TMOS; 98%, Aldrich)/deionized water/ethyl alcohol (99.5%, Aldrich) was 1:4:200:50 for the preparation of HMS. This mixture was stirred for 20 h at room temperature, filtered, and then vacuum-dried overnight at room temperature. The dried sample was refluxed with ethanol three times to remove the surfactant and then vacuum-dried for 6 h at 80 °C.

(2) Synthesis of SBA-15. To prepare SBA-15, a 2 g of block copolymer Pluronic P-123 was dissolved in the mixture of distilled water (15 g) and 2 M hydrochloric acid solution (60 g). To this solution, 4.25 g of tetraethyl orthosilicate (TEOS; 98%, Aldrich) was added and then stirred for 20 h at 45 °C. The mixture was then aged at 85 °C for 12 h. The filtered silica materials were vacuum-dried overnight at room temperature, and then calcined for 6 h at 550 °C to remove the templates.

(3) Synthesis of PME. For the preparation of the PMO material with ethane bridges (PME), the molar ratio of bis-(trimethoxysilyl)ethane (BTMSE; Gelest)/cetyltrimethylammonium chloride (CTAC; 25 wt % in water)/sodium hydroxide (NaOH)/water was 1:0.12:1:230. This mixture was stirred for 24 h at room temperature. The surfactant was removed by refluxing 1 g of as-synthesized sample with a solution of 184 mL of ethanol and 20 g of aqueous HCl (37%) three times. The extracted sample was washed with copious amounts of water and ethanol and then vacuum-dried for 6 h at 80 °C.

(B) Preparation of Anion-Exchange Resins. The typical procedure for the preparation of mesoporous anion-exchange resins functionalized with quaternary ammonium ion involves mixing templates, silica precursors, quaternary ammonium ion precursors, solvents, and (if necessary) acid or base catalysts. The molar ratio of quaternary ammonium group to silica precursor was 0.15 in every sample. This process is shown schematically in Supporting Information (Figure S-1).

(1) Synthesis of HMM and HMB. The anion-exchange resins of HMS type were prepared using *N*-((trimethoxysilyl)propyl)-*N,N,N*-trimethylammonium chloride (TSPMC; 50% in methanol, Gelest) and *N*-((trimethoxysilyl)propyl)-*N,N,N*-tri-*n*-butylammonium chloride (TSPBC; 50% in methanol, Gelest) as quaternary ammonium ion precursors. The molar ratio of 1-hexadecylamine/TMOS/water/ethanol/TSPMC (or TSPBC) was 1:4:200:50:0.6 for the preparation of HMS functionalized with TSPMC (HMM) or HMS functionalized with TSPBC (HMB). This mixture was stirred for 20 h at room temperature, filtered, and then vacuum-dried overnight at room temperature. The dried sample was refluxed with ethanol three times to remove the surfactant and then vacuum-dried for 6 h at 80 °C.

(2) Synthesis of SBM and SBB. The anion-exchange resins based on the functionalization of SBA-15 (SBA-15 functionalized with TSPMC (SBM) and SBA-15 functionalized with TSPBC (SBB)) were prepared in a similar way. Briefly, Pluronic P-123 (2 g) was dissolved in the mixture of water (15 g) and 2 M hydrochloric acid solution (60 g). To this solution, 4.25 g of TEOS and 3 mmol of TSPMC (or TSPBC) were added. The mixture was stirred for 20 h at 45 °C and then aged at 85 °C for 12 h. The filtered materials were refluxed with ethanol three times to remove the template. The materials were then filtered again and vacuum-dried for 6 h at 80 °C.

(3) Synthesis of MEM and MEB. The molar ratio of BTMSE/CTAC/NaOH/water/TSPMC (or TSPBC) was 1:0.12:1:230:0.15 for the preparation of the mesoporous organosilica anion-exchange resins functionalized with TSPMC (MEM) or TSPBC (MEB). This mixture was stirred for 24 h at room temperature. The subsequent process is similar to that for the preparation of PME.

(4) Synthesis of NMEB. A similar mesoporous organosilica anion-exchange resin labeled as NMEB was prepared using a neutral surfactant (hexadecylamine) instead of CTAC as a template and TSPBC as a quaternary ammonium precursor. The molar ratio of 1-hexadecylamine/bis(triethoxysilyl)ethane (BTESE; Gelest)/water/ethanol/TSPBC was 1:4:200:50:0.6 for the preparation of NMEB. The mixture was stirred for 24 h at room temperature, filtered, and then vacuum-dried overnight at room temperature. The dried sample was refluxed with ethanol three times to remove the surfactant and then vacuum dried for 6 h at 80 °C.

(5) Synthesis of MNMEB. To further increase the hydrophobicity of the surface of the anion-exchange resin and thereby increase the adsorption capacity for hydrophobic anions such as perrhenate, a surface-functionalized NMEB anion-exchange resin (MNMEB) was prepared by refluxing 1 g of NMEB with 100 mL of toluene and 1 mL of trimethylchlorosilane (99+%, Gelest) for 6 h. The filtered materials were washed with copious amounts of ethanol and then vacuum dried for 6 h at 80 °C.

(6) Synthesis of NMBB. The molar ratio of hexadecylamine/1,4-bis(triethoxysilyl)benzene (BTESB)/TSPBC/water/ethanol was 1:4:0.6:200:50 for the preparation of the mesoporous benzene-bridged organosilica anion-exchange resin functionalized with TSPBC (NMBB). This mixture was stirred for 24 h at room temperature. The rest of the procedure is similar to that for PME. The host precursor (BTESB) was synthesized according to the method described in the literature.[19]

(C) Characterization. The prepared samples were characterized using nitrogen adsorption−desorption measurement (Autosorb-1, Quantachrome) to examine surface areas and pore structures. Fourier transform infrared (FTIR; Excalibur, Bio-Rad) spectroscopy and Raman spectroscopy (System 1000, Renishaw) were used to examine the existence of organic groups and quaternary ammonium ions in the prepared samples. Small-angle X-ray scattering (SAXS; RU-200RV, Rigaku) was employed to determine the ordered structures of the mesopores. Scanning transmission electron microscopy (STEM; HD-2000, Hitachi) was used to characterize both morphology and pore structure of the anion-exchange resins. 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

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Table 1. Properties of the Prepared Anion-Exchange Resins: Surface Area, Pore Volume, Pore Diameter, d Spacing (d_{100}), the Repeat Distance (a_0) between Pore Centers, and Wall Thickness

	surface area[a]/$m^2 \cdot g^{-1}$	total pore volume/$cm^3 \cdot g^{-1}$	pore diameter[b]/nm	d_{100}/nm	a_0[c]/nm	wall thickness[d]/nm
HMS	954	1.02	3.0	4.2	4.8	1.8
HMM	208	0.61				
HMB	303	0.41				
SBA-15	885	1.27	9.0	10.2	11.8	2.8
SBM	513	0.43				
SBB	321	0.33				
PME	677	0.58		3.6		
MEM	863	0.59		3.9		
MEB	808	0.59		4.2		
NMEB	745	0.76				
MNMEB	550	0.55				
NMBB	299	0.18				

[a] BET surface area. [b] Pore diameter in which BJH adsorption isotherm shows maximum adsorbed volume. [c] Repeat distance, $a_0 = 2d_{100}/\sqrt{3}$. [d] Wall thickness = repeat distance (a_0) − pore diameter.
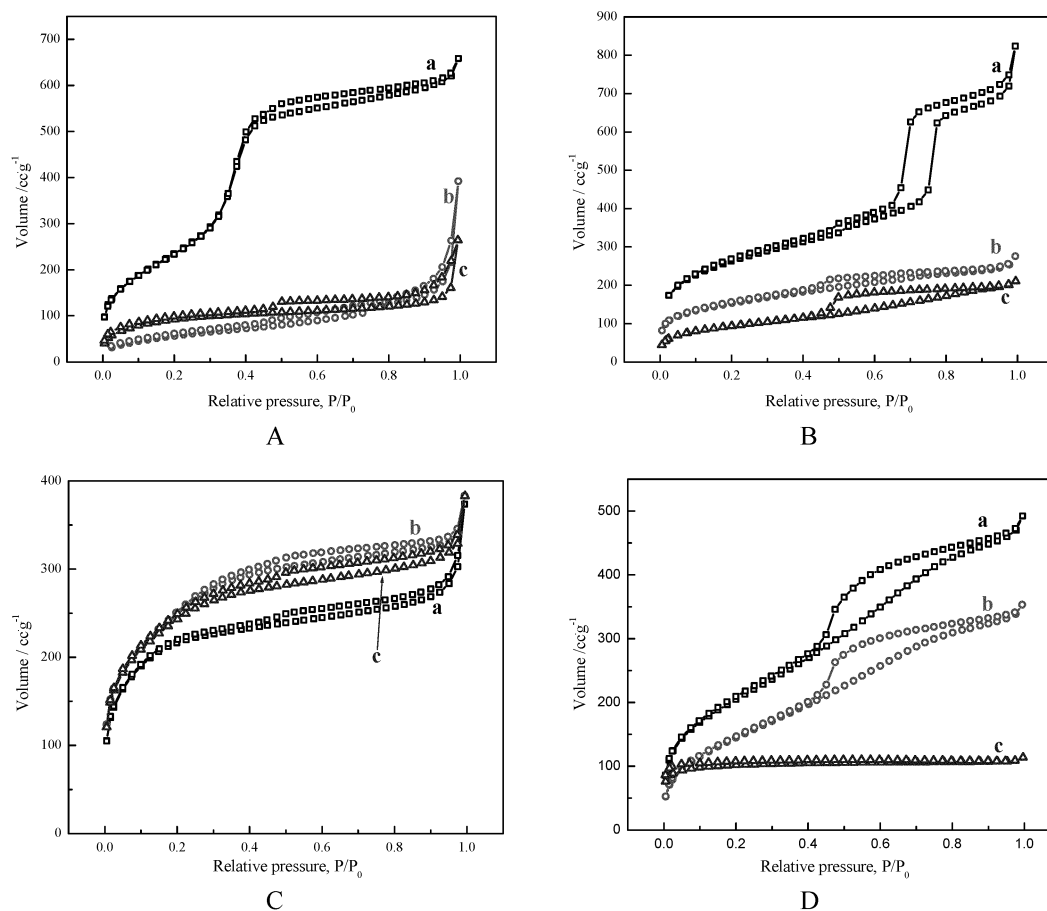
Figure 1. Nitrogen adsorption−desorption isotherms: (A) a, HMS; b, HMM; and c, HMB. (B) a, SBA-15; b, SBM; and c, SBB. (C) a, PME; b, MEM; and c, MEB. (D) a, NMEB; b, MNMEB; and c, NMBB.

MHz; ^{29}Si, 19.883 MHz; ^{1}H rf amplitude, 64 kHz (3.9 μs 90E 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 dodecamethylcyclohexasilane as secondary standard (δ = −41.9 ppm).

(D) Anion Adsorption Test. In a typical run, 0.1 g of a sorbent was added to a 1×10^{-4} M NaReO$_4$ solution (10 mL). The solution was then sonicated for 1 h. The adsorption equilibrium can be reached in less than 30 min. 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). To examine the effect of the pH of the aqueous solution on the perrhenate

adsorption, different concentrations of acid solutions were used for the preparation of NaReO$_4$ solutions: 1 N HCl, 0.1 N HCl, and distilled water solutions.

Results and Discussion

Table 1 lists the surface areas and pore volumes of the prepared organic−inorganic hybrid anion-exchange resins. The nitrogen adsorption−desorption isotherms of the prepared resins are shown in Figure 1. When the quaternary ammonium ion ligands were used to functionalize mesoporous silica materials, both the surface areas and the pore volumes drastically decreased, compared with the values for the corresponding pure mesoporous silica materials (HMS and SBA-15). This finding is consistent with the general observation that the surface

areas of the mesoporous hybrid silica materials prepared by the surfactant template decrease with the content of the hybrid ligands.[2,20,21] The anion-exchange resins of HMS and SBA-15 types showed surface areas and pore volumes similar to those of the MCM type of the anion-exchange resin.[2] However, a different trend was noted in the preparation of the mesoporous organosilica anion-exchange resins. When the quaternary ammonium ion ligand was introduced to the process for the preparation of mesoporous organosilica anion-exchange resin, the surface areas of the corresponding anion-exchange resins (MEM and MEB) were larger than that of PME, and the pore volumes of MEM and MEB were similar to that of PME.

For the preparation of MEM and MEB, CTAC was used as a surfactant. To extract CTAC from these anion-exchange resins, a solution of 184 mL of ethanol and 20 g of aqueous HCl (37%) was used for 1 g of sample. During this process, a large quantity of chloride ions can be attached to anion-exchange sites and protonated silanols. Even after the anion-exchange resins are washed with water and ethanol, chloride ions can be still retained inside the resins. This retention may hinder the adsorption of the target anion, perrhenate. To prevent high chloride content in the resins, an anion-exchange resin (NMEB) was prepared using hexadecylamine instead of CTAC as a template. The neutral template was extracted with pure ethanol instead of acidic ethanol solution. The surface area and the pore volume of NMEB (745 m^2/g and 0.76 cm^3/g, respectively) were larger than those of PME (677 m^2/g and 0.58 cm^3/g, respectively).

To test the dependence of the adsorption capacity on the hydrophobicity of the NMEB surface, NMEB was functionalized with trimethylsilyl chloride. By this functionalization, hydrophobic trimethylsilyl groups were bound to the unreacted hydroxyl groups on the surface of the resin. The trimethylsilyl-functionalized anion-exchange resin (MNMEB) showed decreased surface area and pore volume (550 m^2/g and 0.55 cm^3/g, respectively). The corresponding adsorption−desorption isotherm was shifted downward (Figure 1D). This shift indicates that trimethyl groups are successfully functionalized on the surface of NMEB.

To further increase the matrix hydrophobicity, a mesoporous anion-exchange resin with a benzene-bridged organosilica network (NMBB) was prepared using BTESB as an organosilica precursor. BTESB was synthesized according to the procedure suggested by Shea et al.[19] The spacer bridge of NMBB is benzene, which is bulkier and more hydrophobic than the ethane bridge. The surface area and pore volume of NMBB (299 m^2/g and 0.18 cm^3/g, respectively) were smaller than those of other mesoporous organosilica anion-exchange resins.

The SAXS curve of HMS shows a broad reflectance at *d* spacing of 4.2 nm, which is characteristic of HMS materials (see Figure S-2 in the Supporting Information).[13] The scattering curve of SBA-15 shows typical d_{100} and d_{110} peaks.[14] However, the corresponding anion-exchange resins containing quaternary ammonium ions do not show distinct X-ray diffraction peaks assigned to microstructures or mesostructures, indicating these anion-exchange resins (HMM, HMB, SBM, and SBB) have disordered structures. Broad scattering peaks were observed in the SAXS measurement of PME, MEM, and MEB. The *d* spacing values were 3.6, 3.9, and 4.2 nm for PME, MEM,
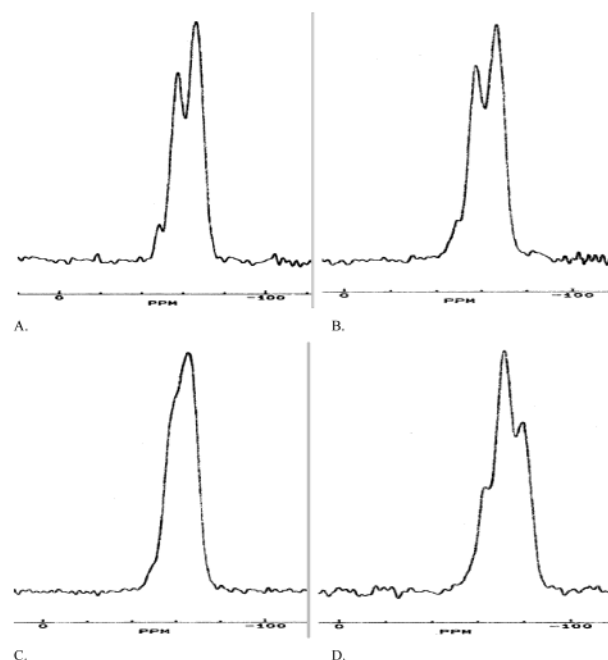

Figure 2. ^{29}Si CP/MAS NMR spectra of prepared mesoporous organosilica anion-exchange resins: A, MEM; B, MEB; C, NMEB; and D, NMBB. Three T resonances are found in each spectrum, assigned to T^1, T^2, and T^3 sites, from low to high field (left to right), respectively. The superscript designates the degree of condensation, i.e., the number of siloxane bonds to a silicon atom. Numerical assignments are given in Table 2.

Table 2. Chemical Shifts and Integrals in ^{29}Si CP/MAS NMR Measurements of Anion-Exchange Resins

assignment	MEM	MEB	NMEB	NMBB
T^1/ppm (integral %)	−48.4 (5)	−48.4 (6)	−49.5(2)	−63.1 (16)
T^2/ppm (integral %)	−57.9 (37)	−57.9 (41)	−59.5 (32)	−71.7 (54)
T^3/ppm (integral %)	−67.3 (57)	−66.8 (53)	−65.5 (66)	−79.6 (30)

and MEB, respectively. These findings imply that PME, MEM, and MEB samples have wormhole structures with regular mesopores. The PMO anion-exchange resins synthesized with the neutral surfactants (NMEB, MN-MEB, and NMBB) did not show clear scattering patterns in the SAXS measurements, indicating highly disordered mesoporous and microporous structures.

In STEM measurements of the anion-exchange resins, the typical wormhole pore structure was observed for HMS, while SBA-15 shows a one-dimensional hexagonal structure (see Figure S-3 in the Supporting Information). When the anion-exchange resin was prepared using quaternary ammonium ion, the prepared resin had a very small mesoscopically ordered domain size, which is consistent with the result of SAXS. While mesoporous organosilica anion-exchange resins with an ethane bridge had spherical morphology when prepared using CTAC as a surfactant, no specific morphology was shown when these resins were prepared using hexadecylamine as a surfactant. Both resins showed disordered pore structures.

Figure 2 and Table 2 show the ^{29}Si CP/MAS NMR spectra of selected mesoporous organosilica anion-exchange resins. As expected, only T peaks are observed for these resins as all silicon precursors contain trialkoxysilylorganyl moieties.[22] From the integrals of the partially resolved T^1, T^2, and T^3 peaks, MEM and MEB show similar degrees of condensation to siloxane linkages, with T^3 sites dominant (Table 2), in agreement with the literature for

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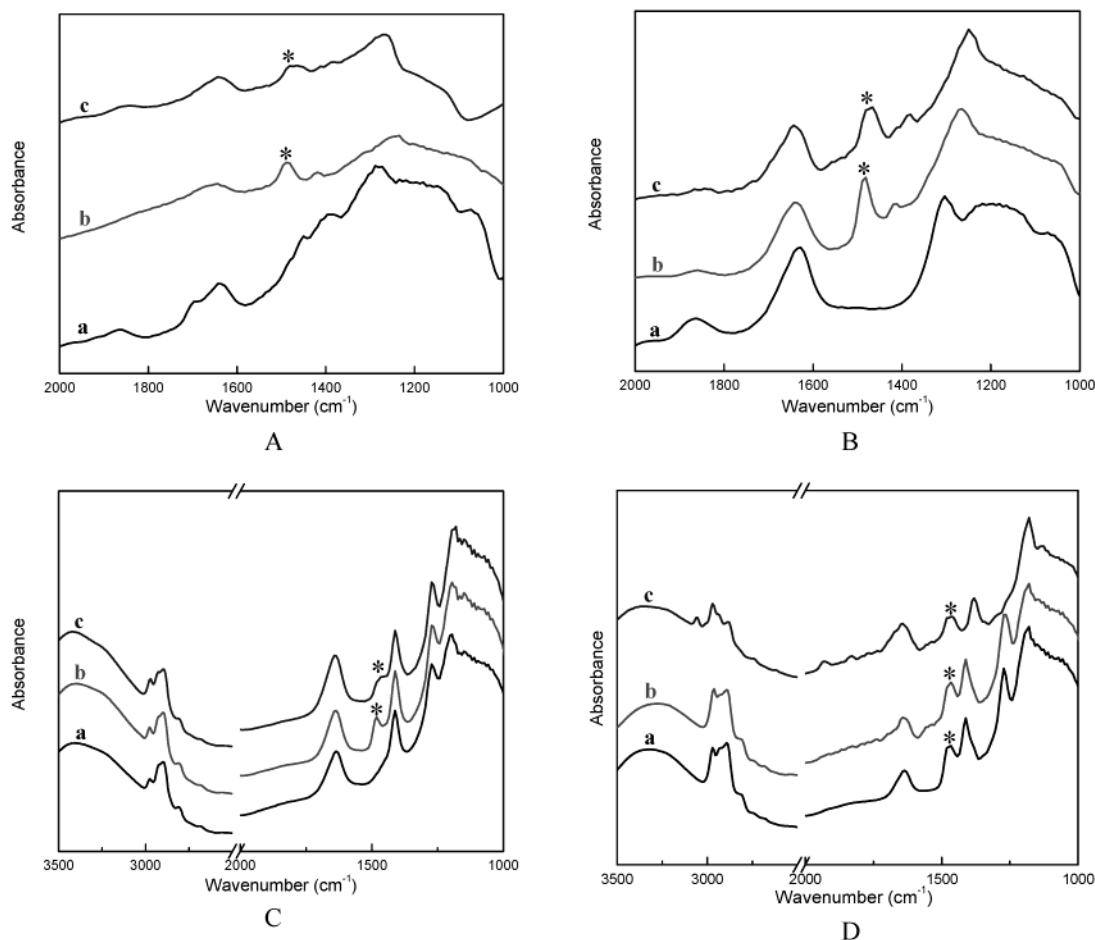
Figure 3. Diffuse reflectance FTIR spectra of prepared organic−inorganic anion-exchange resins: (A) a, HMS; b, HMM; and c, HMB. (B) a, SBA-15; b, SBM; and c, SBB. (C) a, PME; b, MEM; and c, MEB. (D) a, NMEB; b, MNMEB; and c, NMBB. While HMS, SBA-15, and PME show no band from 1488 to 1463 cm^{-1}, anion-exchange resins containing quaternary ammonium ions have an extra band (∗) at this range, which shows the presence of −N$^+$(CH$_3$)$_3$ or −N$^+$(C$_4$H$_9$)$_3$ functional group in the samples.

base-catalyzed condensations using BTMSE.[22] Similarly, the resin made using the charge-neutral template hexa-decylamine in lieu of CTAC has T^3 sites dominant (Figure 2C). In contrast to the BTMSE-based resins, that made with the BTESB reveals a much lower degree of conden-sation under our reaction conditions. T^1 sites constitute 16% of the linkages and T^2 sites are dominant (54%).

Figure 3 shows the diffuse reflectance FTIR spectra of prepared anion-exchange resins. While HMS, SBA-15, and PME show no band from 1488 to 1463 cm^{-1}, anion-exchange resins containing quaternary ammonium ions have an extra band at this range, which shows the presence of −N$^+$(CH$_3$)$_3$ or −N$^+$(C$_4$H$_9$)$_3$ functional group in the samples (e.g., N−CH$_3$ bending at 1494 cm^{-1}).[3] Figure 4 shows the results of Raman spectroscopy measurement. Mesoporous organosilica materials including PME, MEM, MEB, and NMEB showed a −CH$_2$ band at the region from 2912 to 2894 cm^{-1}. These spectral results indicate the successful extraction of templating surfactants.

Perrhenate adsorption tests were performed using prepared anion-exchange resins. To investigate the roles played by the surfactants, the anion-exchange resins were also synthesized without using the surfactant templates. Their uptake capacities are less than those of the corresponding resins prepared using the surfactant tem-plates (see Table S-1 in the Supporting Information). Accordingly, the enhanced uptakes of the latter resins could be attributed to the template synthesis with surfactants. Table 3 summarizes the measured adsorption capacities for perrhenate ions of prepared organic−
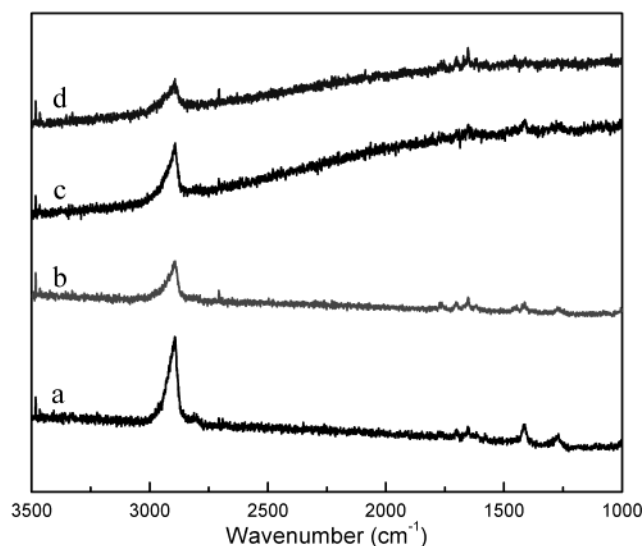

Figure 4. Raman spectra of prepared organic−inorganic anion-exchange resins: a, PME; b, MEM; c, MEB; and d, NMEB.

inorganic mesoporous anion-exchange resins at different pH conditions. As seen from the table, the adsorption capacities of the functionalized resins decrease with the reduction of pH by HCl. This reduction could be correlated to the increase of the concentration of competitive anions (Cl$^-$) in the corresponding solutions. This assertion was supported by the adsorption measurements of ReO$_4^-$ under

Table 3. Capacity for Perrhenate Ion Uptake of Prepared Mesoporous Anion-Exchange Resins in the Solution of 1 × 10^{-4} M NaReO$_4$ at Different pH Conditions

	1 N HCl (pH 0.2)			0.1 N HCl (pH 1.2)			distilled water (pH 6.4)		
	Re (% ads)	K_d	capacity (mg of Re/g)	Re (% ads)	K_d	capacity (mg of Re/g)	Re (% ads)	K_d	capacity (mg of Re/g)
HMS	0.0	0	0.00	0.0	0	0.00	3.2	3	0.06
HMM	10.0	11	0.19	43.1	76	0.80	27.3	37	0.51
HMB	63.5	174	1.18	93.5	1450	1.74	99.1	10 800	1.85
SBA-15	0.0	0	0.00	0.0	0	0.00	0.0	0	0.00
SBM	1.0	1	0.02	17.5	21	0.32	79.1	380	1.47
SBB	51.5	106	0.96	92.7	1260	1.73	99.1	11 000	1.85
PME	a			1.1	1	0.02	9.7	11	0.18
MEM	0.5	1	0.01	8.3	9	0.16	55.8	126	1.04
MEB	5.8	6	0.11	23.7	31	0.44	79.7	392	1.48
NMEB	67.8	210	1.26	95.3	2050	1.78	99.9	145 000	1.86
MNMEB	a			97.4	3750	1.81	99.9	160 000	1.86
NMBB	a			93.5	1450	1.74	99.8	41 900	1.86

a Not available.

high chloride concentrations through the addition of NaCl (see Table S-2 in the Supporting Information). The variation in the adsorption capacities for ReO$_4^-$ with pH is significantly reduced under the high concentration of NaCl.

Although pure HMS and SBA-15 did not adsorb any detectable perrhenate ions in acidic solutions, HMS showed 3.2% perrhenate uptake in distilled water. PME showed a relatively high uptake capacity (9.7%) for perrhenate ions in distilled water. This adsorption might be caused by the interaction between the hydrophobic organic groups inside the framework of PME and the hydrophobic anion, ReO$_4^-$. In aqueous solution, NaReO$_4$ is dissociated to Na$^+$ and ReO$_4^-$. The ReO$_4^-$ is more hydrophobic than common anions in water solution such as Cl$^-$ and NO$_3^-$. To evaluate the uptake capacity of prepared anion-exchange resins, the anion distribution constant (K_d) was calculated for each resin.

$$K_d = \{(C_i - C_f)/C_f\} \times \{\text{volume solution (mL)}\}/ \{\text{mass gel (g)}\} \quad (1)$$

Here, C_i is the initial solution concentration before the adsorption test and C_f is the final solution concentration after the adsorption test.[2] In every sample, anion-exchange resins functionalized with tri-*n*-butylammonium ions (HMB, SBB, MEB, NMEB, MNMEB, and NMBB) showed higher uptake capacity than those functionalized with trimethylammonium ions (HMM, SBM, and MEM). The molecular size of ReO$_4^-$ is larger than that of common anions such as Cl$^-$ and NO$_3^-$. Larger anions are generally more easily adsorbed on the larger cations, in agreement with the well-known principle of Hofmeister selectivity.[23]

Anion-exchange resins showed higher adsorption capacity in neutral distilled water than in acidic solutions, because chloride ions in acidic HCl solutions compete for adsorption sites. In the preparation of mesoporous organosilica anion-exchange resins, the cationic surfactant, CTAC, was extracted with 1 M hydrochloric ethanol solution. After the sample was washed using copious quantities of water and ethanol, the chloride ions used for extraction remained in the sample. For this reason, MEB showed relatively low adsorption capacity for perrhenate ions than pure silica anion-exchange resins, HMB and SBB, where the surfactant was removed by ethanol extraction instead of acidic ethanol extraction. To overcome this drawback, NMEB was prepared using neutral surfactant, hexadecylamine, which was removed by etha-

(23) Kavallieratos, K.; Moyer, B. A. *Chem. Commun.* **2001**, 1620–1621.

Table 4. Capacity for Perrhenate Ion Uptake of NMEB Resin in the Mixed Solution of 1 × 10^{-4} M NaReO$_4$ and Different Concentrations of Competitive Sulfate Ions

	1 N HCl		0.1 N HCl		distilled water	
concn of Na$_2$SO$_4$ [M]	Re (% ads)	K_d	Re (% ads)	K_d	Re (% ads)	K_d
0	67.8	210	95.3	2050	99.9	145 000
1 × 10^{-4}	51.1	104	92.5	1233	99.8	49 900
1 × 10^{-3}	57.8	137	93.2	1371	99.5	19 900

nol extraction. The anion-exchange resin, NMEB, showed higher adsorption capacity for perrhenate ions than did MEB, HMB, and SBB. This high capacity (99.9% removal) is ascribed to the prevention of retaining of chloride ions during the synthesis of anion-exchange resin, the synergetic effect of the hydrophobic support structure, and the large size of the quaternary ammonium ions.

To increase the hydrophobicity of the surface of the anion-exchange resin and thus increase the adsorption capacity for hydrophobic anions such as perrhenate, the trimethylsilyl group was used to remove SiOH functionality on the surface of NMEB. The functionalization decreased the surface area and pore volume of the prepared resin, MNMEB. However, the adsorption capacity increased by the introduction of this hydrophobic group (Table 3). Anion-exchange resin with benzene bridge, NMBB, showed a slight decrease in the adsorption capacity compared with the ethane bridge analogy, NMEB.

Table 4 shows the capacity for perrhenate ion uptake for NMEB in the mixed solution of 1 × 10^{-4} M NaReO$_4$ and different concentrations of competitive sulfate ions. In the presence of sulfate ions, NMEB exhibits a slightly decreased uptake capacity for perrhenate ions. Hence, this anion-exchange resin shows good potential for use in mixed anionic solutions.

Conclusions

Mesoporous organic−inorganic anion-exchange resins were prepared for the adsorption of perrhenate ions in aqueous solutions. Among the synthesized resins, NMEB and MNMEB, prepared by using a neutral surfactant and *N*-((trimethoxysilyl)propyl)-*N*,*N*,*N*-tri-*n*-butylammonium chloride (TSPBC) precursor showed the highest adsorption capacity. A small increase in adsorption capacity for MNMEB was realized by functionalizing the free silanols of the surface of NMEB with trimethylsilyl moieties and thereby increasing the hydrophobic character of the resins. These results provide the basis for the synthesis of new organic−inorganic hybrid anion-exchange resins.

Supporting Information Available: Protocols for preparation of anion-exchange resins without surfactant templates and table containing the corresponding adsorption tests, table containing the comparison of capacities of NMEB with and without 1 N NaCl under various pH values, table containing capacities normalized with respect to surface areas for perrhenate-ion uptakes, schematic diagram for general synthesis protocols, SAXS curves of prepared organic−inorganic anion-exchange resins, TEM images of SBA-15, SBB, MEB, and NMEB, and SEM images of MEB and NMEB. This material is available free of charge via the Internet at http://pubs.acs.org.

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