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Effect of Framework and Textural Porosities of Functionalized Mesoporous Silica on Metal Ion Adsorption Capacities

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ABSTRACT

The effects of the framework and/or textural porosities and functional group densities of the functionalized HMS on the metal adsorption capacities were examined. Mercapto concentration was weakly correlated with pore size and the surface area of the supports, but was strongly dependent on the framework pore volume. In case of adsorbents with a well-developed framework porosity, the uptake of mercury ions increased with an increase in mercapto concentration, while adsorbents with a well-developed textural porosity show a slight increase with mercapto concentration. The characteristics of lead ions showed a similar absorption trend to that of mercury ions. The results showed that the amounts of metal ion

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uptake of SBA having long range 2-D pore channels were less than those of HMS having short range interconnected 3-D pore channels.

Key Words: Adsorption; Framework porosity; Heavy metal ion; Mesoporous silica; Textural porosity.

1. INTRODUCTION

The preparation of better adsorbents that are capable of removing heavy metal ions from aqueous environments has attracted a great deal of interest in wastewater treatment.[1–14] Mesoporous silica with a uniform and large pore structure would be expected to have high adsorption capacities.[4–14] A number of reports have appeared regarding highly effective heavy metal ion adsorbents that have functional group (e.g., thiol, amine, etc.) grafted to the mesoporous silica pores (M41S, HMS, SBA). Liu and Feng et al.[7] reported on a heavy metal ion adsorbent (FMMS) based on mercaptopropylsilyl functionalization of a calcined form of MCM-41. A high ligand concentration was functionalized via the grafting process, which involved repeated surface hydrolysis and silylation cycles. The mercury capacity of FMMS in an aqueous solution was high (2.5 mmol g^{-1}). Mercier et al.[8–11] used a neutral surfactant as a template. The synthesized adsorbent (MP-HMS-C12) had a large pore size, a high mercury loading capacity (1.5 mmol g^{-1}), and a high selectivity for mercury ions.

However, only a few studies on the effects of framework and/or the textural porosity of mesoporous silica have been reported in terms of the metal adsorption capacities. Mercier et al.[9] reported that in a amorphous silica gel to which ligands had been grafted the narrow pore channels were blocked, thus creating a bottleneck. In contrast, the uniform pore morphology of a mesoporous molecular sieve leads to a grafted material with unrestricted access of ions to all the functional sites. Gomez et al.[15] reported 2-D Monte Carlo simulations for a Langmuir type adsorption process on simple columnar profiles. For irregular micropores, the adsorption was strongly affected by a geometry effect of the surface, which induced a slit effect at the micropore entrance, a plugged bottleneck inside the micropores and a steric effect, such as tortuosity at the pores.

In this paper, the effect of framework and/or textural porosities of functionalized mesoporous silica on metal uptake capacities were investigated. HMS type mesoporous silica was prepared using a previously reported hydrogen-bonding pathway.[16,17] In addition, SBA type mesoporous silica was prepared using triblock copolymers, such as P-123, P-103, and P-65 as

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templates,[18] and the effect of porosity on metal uptake by SBA was then compared with that of HMS.

2. EXPERIMENTAL

2.1. Materials

Two different types of neutral surfactants, dodecylamine (Aldrich, Germany) and hexadecylamine (Fluka, Switzerland), were used as templates for preparing the mesoporous silica supports with various pore sizes. Trimethylbenzene (TMB, Fluka) was used as a swelling agent, to expand the inner micelle space. Tetraethoxysilane (TEOS, Fluka) was used as a silica precursor, and ethanol was used as a co-solvent. 3-Mercaptopropyltrimethoxsilane (MPTMS, Aldrich) was used as a chelating agent. The following metal nitrate salts were used to prepare the aqueous metal solutions: mercury(II) nitrate n-hydrate ($Hg(NO_3)_2 \cdot nH_2O$, Junsei), cadmium(II) nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$, Junsei), copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, Junsei), and lead(II) nitrate ($Pb(NO_3)_2$, Junsei).

2.2. Preparation of Functionalized Mesoporous Silicas

The mesoporous silicas (MSd and MSh) were synthesized via a self-assembly process using amine surfactants, such as dodecylamine (for MSd) and hexadecylamine (for MSh). A 5.1 g of dodecylamine or 6.6 g of hexadecylamine was dissolved in 46 mL of ethanol, and sufficient water was then added to obtain a fine emulsion. This was followed by adding 22.3 mL of TEOS with vigorous stirring. TMB was added to the mixture, followed by stirring for 20 hr. The product was filtered, air-dried, and the surfactant was removed by solvent extraction. The molar ratio of the reagents was 1.0 TEOS : 0.27 $C_nH_{2n+1}NH_2$: 7.93 EtOH : 29.4 H_2O : m TMB, where n is 12 and 16; m is 0, 0.14, 0.27, and 0.41. Mesoporous silica synthesized using TMB is referred to as as MSd-Txx, where xx denotes the TMB to amine ratio, namely 0 : 1 for MSh-T00, 0.5 : 1 for MSh-T05, and so on.

The mercapto functionalized mesoporous silica was prepared as follows: A 1 g sample of the template removed mesoporous silica was heated under reflux in 25 mL of toluene containing 1 g of MPTMS for 24 hr. The products were recovered by filtration and washed with toluene, methyl chloride, acetone, and ethanol. The products are herein referred to as MP-MSh-Txx etc.

Representative hexagonal mesostructures, namely, the SBA family,[19] were also prepared and the metal adsorption tendency determined which was then compared with the metal adsorption of HMS.

2.3. Adsorption of Heavy Metal Ions

A batch experiment was performed to measure the metal ion adsorption capacities for each adsorbent (MP-MS family). Metal ion (Hg^{2+}, Pb^{2+}, Cu^{2+}, and Cd^{2+}) loading capacities were measured for five samples. A buffer solution of pH 4 was prepared using 50 mL of 0.1 M potassium hydrogen phthalate, 0.1 mL of 0.1 M hydrochloric acid, and 49.9 mL of deionized water,[20] and was used to prevent precipitating the metal ions during the adsorption experiment. Then 0.1 g (0.01 g for Hg^{2+}, 0.05 g for Pb^{2+}) of the adsorbents were added to 50 mL (100 mL for Hg^{2+}) of the metal(II) nitrate solutions of 0.5 mmol L^{-1} (0.2 mmol L^{-1} for Hg^{2+}), followed by stirring and shaking at room temperature for 12 hr. The samples were isolated by filtration and the adsorption capacities were calculated from the difference between the initial and the final concentration.

2.4. Characterization

Powder x-ray diffraction (XRD, M18XHF-SRA, MAC/Science, Japan) using CuK_{α} radiation at 50 kV and 100 mA was used to determine the crystallinity of the prepared samples. ^{29}Si MAS NMR spectra were measured using a Bruker DSK spectrometer (400 MHz) with 2.5 mm CP/MAS probe (^{13}C-^{31}P/^{1}H, 12 kHz, 300 K). To examine the pore structure, the samples were degassed at 150°C for 2 hr, and the N_2 adsorption–desorption isotherms were examined at 77 K using a Micromeritics ASAP-2010 sorptometer. Fourier transform infrared spectroscopy (FTIR, Jasco) was used to identify the functional groups in the samples. A CHNS corder (MT-2, Yanaco, Japan) was used to measure the number of functional groups in the samples. The adsorption capacities were measured by atomic absorption (AAS, Perkin Elmer 3110).

3. RESULTS AND DISCUSSION

3.1. Pore Properties of Synthesized Mesoporous Silicas

Mesoporous silica was prepared using dodecylamine and hexadecylamine as templates. Table 1 shows a summary of the pore properties of the synthesized mesoporous silica. Both the pore size and pore volume of the MSh silica was larger than those of the MSd due to the longer carbon chain of the surfactant, hexadecyamine. The results also showed that the pore size of the MSh-Txx samples increased with increasing TMB/surfactant ratios,

Table 1. Pore properties of synthesized and functionalized mesoporous silica, HMS type.

Samples	D_{BJH}[a] (nm)	S_{BET} ($m^2\,g^{-1}$)	V_t[b] ($cm^3\,g^{-1}$)	V_f[c] ($cm^3\,g^{-1}$)	V_{tx}[d] ($cm^3\,g^{-1}$)	V_{tx}/V_f	d_{100} (Å)
MSd-T00	2.0	825	0.54	0.47	0.07	0.15	39
MSh-T00	2.8	812	0.89	0.75	0.14	0.19	46
MSh-T05	3.0	825	1.03	0.54	0.49	0.91	47
MSh-T10	3.1	839	1.04	0.70	0.34	0.49	53
MSh-T15	3.1	939	1.08	0.96	0.12	0.13	42
MP-MSd-T00	1.1[e]	618	0.32	0.27	0.05	0.19	38
MP-MSh-T00	1.8	738	0.45	0.36	0.09	0.25	45
MP-MSh-T05	2.3	651	0.68	0.36	0.32	0.89	45
MP-MSh-T10	2.4	622	0.55	0.38	0.17	0.45	51
MP-MSh-T15	2.5	846	0.84	0.73	0.11	0.15	40

[a] Pore size obtained from the adsorption isotherm branch using the BJH model.
[b] Total pore volume obtained from the volume of N_2 adsorbed at 0.99 P/P_0.
[c] Framework pore volume obtained from the volume of N_2 adsorbed at 0.60 P/P_0.
[d] Textural pore volume obtained from the difference ($V_t - V_f$).
[e] Pore size ($D = a_0 - e - 2f$) obtained from the XRD data; a_0 is the cell parameter; e is the wall thickness; f is the deposition thickness of the functional group.

while the pore uniformity decreased. This might be due to the collapse of the cylindrical micelle structure as a result of the heterogeneous mixture when the ratio is further increased. Full width at half maximum (FWHM) of PSD was increased with increasing TMB addition (0.65 nm for MSh-T00, 0.74 nm for MSh-T15, and 1.16 nm MSh-T20). For the TMB/surfactant ratio of above 1, hydrophobic part of micelles expanded and then reduced the regularity of pore size. The peak intensity of MSh-T15 was decreased in powder XRD, and thus structural change occurred when the molar ratio of TMB/surfactant becomes larger than 1. Silica prepared with the excess of TMB has meso celluar foam (MCF) structure.[21] Based on these results, it was concluded that MSh-T15 or MSh-T20 has a different structural feature with other MSh-Txx.

The porosity of the mesoporous silica varied according to the synthesis conditions. As shown in Fig. 1, the N_2 adsorption/desorption isotherm was typical for a mesoporous silica, with hysteresis loops near the relative pressure of 0.5 and/or 0.9. Tanev et al.[14] defined and classified those loops in terms of framework porosity and textural porosity. The framework porosity represents the porosity contained by the uniform channels of the templated framework, while the textural porosity represents the porosity arising from non-crystalline intra-aggregate voids and spaces formed by the interparticle contacts. The

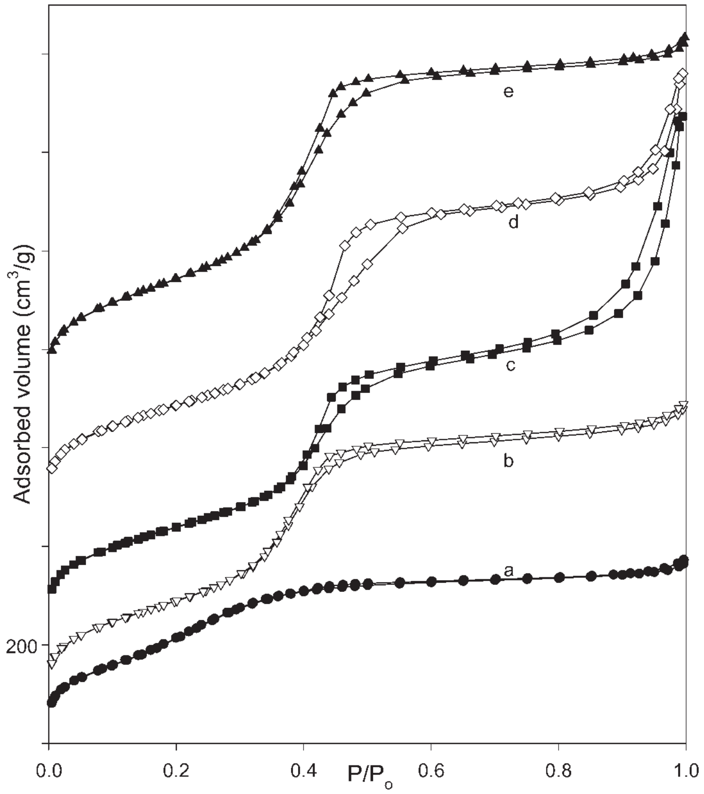

Figure 1. N_2 adsorption/desorption isotherms of (a) MSd-T00, (b) MSh-T00, (c) MSh-T05, (d) MSh-T10, and (e) MSh-T15.

ratios of textural pore volume to framework pore volume are shown in Table 1. The framework pore volume was obtained from the volume of the N_2 adsorption isotherm branch at 0.6 P/P_o, and the textural pore volume was calculated from the difference between the total pore volume and the framework pore volume. MSh-T05 and MSh-T10 have a well-developed textural porosity and much lower framework porosity.

Pauly et al.[22] investigated the factors that affect the textural mesoporosity in HMS. The particle size and associated textural porosity were correlated with the solubility of the surfactant in water–alcohol solvents. Polar solvents containing a relatively low volume fraction of alcohol yielded a heterogeneous surfactant emulsion in which the intergrown aggregates of small primary particles with a high textural pore volume were assembled, while three-dimensional

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interconnected particles with little or no textural porosity were formed when homogeneous surfactant solutions in lower polarity co-solvents were used. Therefore, MSh-T05 and MSh-T10 would be producted to have a well-developed textural porosity due to heterogeneous mixing with TMB, as listed in Table 1.

All the mesoporous silica samples exhibited a single peak in the powder XRD patterns, and showed an intense d_{100} scattering peak around 40–50 Å (Table 1). The absence of higher angle peaks suggests that the inorganic walls of these materials are amorphous. Although a single XRD peak is indicative of a lack of long-range order, the presence of a disordered hexagonal or wormhole-like pore structure is indicated.[8]

3.2. Pore Properties of Functionalized Mesoporous Silicas

The pore properties of the mercapto functionalized mesoporous silica are shown in Table 1. The pore size, surface area, and pore volume of these samples were reduced as the result of grafting MPTMS on their surface. As organosilane moieties are incorporated into the meostructures, the d_{100} peaks of the materials become shifted to higher diffraction angles, indicating progressive contractions of the lattice d-spacings upon functional group loading. In addition, the intensities of the (1 0 0) peaks for the functionalized materials were reduced compared to their respective parent mesostructures.[23]

Both the framework and textural pore volume of all adsorbents were lower than those of the supports. However, the ratio of the textural to the framework pore volume changed according to the type of material employed. The pore volume ratio (V_{tx}/V_f) of the adsorbents with a well-developed framework porosity such as MP-MSd-T00, MP-MSh-T00, and MP-MSh-T15 was relatively low, while that of adsorbents with a well-developed textural porosity such as MP-MSh-T05 and MP-MSh-T10 was high. A possible explanation for this is that the functional groups bound more readily to the surface in the framework pores compared with those in textural pores.

3.3. Identification of Functional Groups

The functional groups of the samples were characterized by FTIR (Fig. 2). O–H stretching bands assigned to silanol groups were observed at 3200–3600 cm^{-1}. A very weak S–H stretching peak was observed at 2560–2580 cm^{-1} for samples that had been modified with mercaptopropyl groups.

^{29}Si MAS NMR data and peak assignments for MSh-T10 and MP-MSh-T10 are shown in Fig. 3. Non-functionalized HMS shows mainly two peaks of Q^4 (−111 ppm) and Q^3 (−101 ppm), while MP-HMS represents the large decrease in the intensity of the Q^3 signal and the small increase of the Q^2

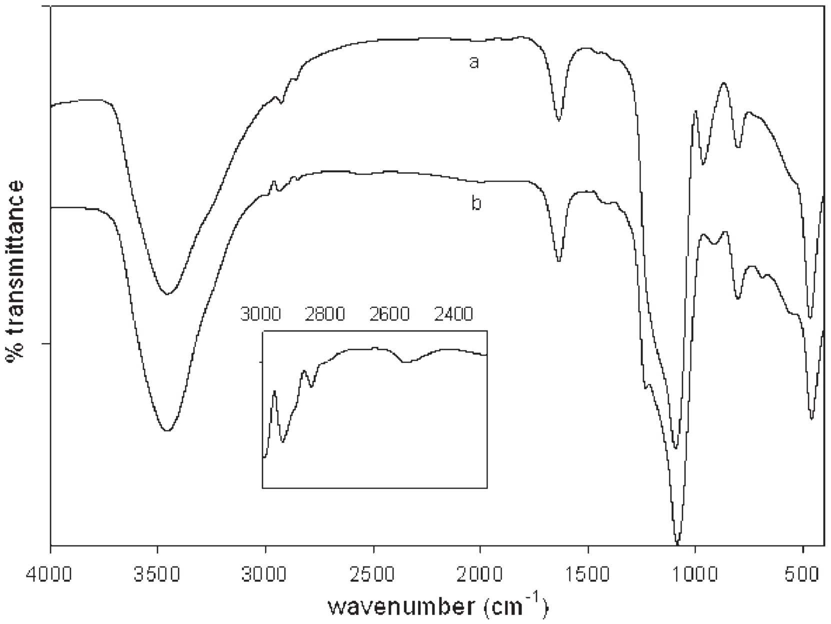

Figure 2. FTIR spectra of (a) MSh-T10 and (b) MP-MSh-T10 [inset: mercapto spectrum band of (b)].

(−95 ppm), which verified the anchoring of the functional groups to Si–OH (Q^3). The grafted materials showed a small or no Q^3 signal, compared with the Q^2 and Q^4 signals. This shows that the isolated hydroxyl groups of Q^3 siloxanes were used to graft the mercapto groups on the surface of the mesoporous silica. A new peak appearing at the range of −50 to −80 ppm was assigned to the silicon centers of the grafted functional group. The peak at −111 ppm is from the silica support, and three additional peaks from −50 to −80 ppm are observed, corresponding to isolated (T^1), terminal (T^2), and cross-linked (T^3) conformation.[13] Integration of those deconvoluted peaks revealed a $Q^4:Q^3:Q^2:T^x$ ($x = 1$, 2, and 3) of 0.65 : 0.29 : 0.06 : 0.00 and 0.66 : 0.02 : 0.07 : 0.25, respectively.

The C, H, N, and S content of adsorbents was analyzed by an element analyzer, which was used to calculate the quantity of mercapto moieties grafted to the framework channels (Table 2). The surfactant could be completely removed by Soxhlet extraction, and no N was detected in the synthesized mesoporous silica. The mercapto density on the pore walls of the adsorbents was calculated on the basis of the S concentration and the BET surface area of

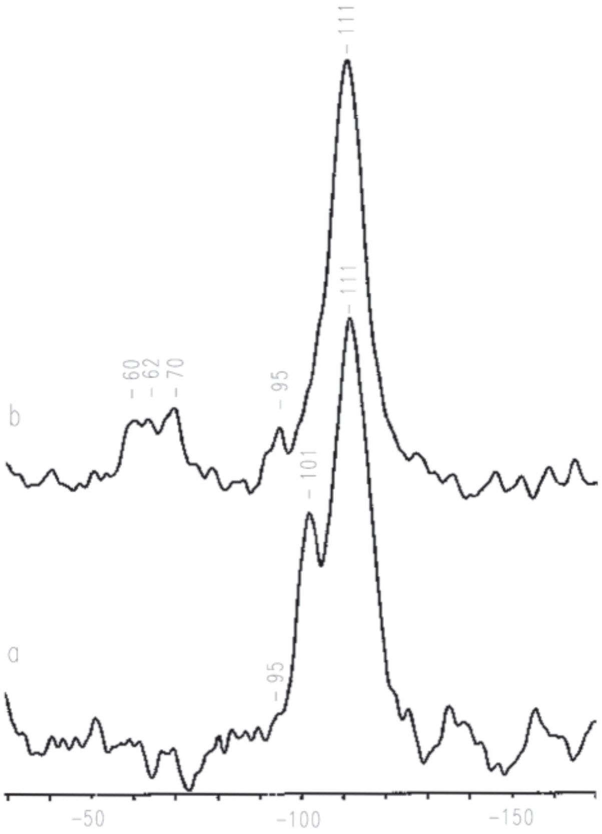

Figure 3. ^{29}Si NMR spectra of (a) MSh-T10 and (b) MP-MSh-T10.

the synthesized mesoporous silica. The mercapto concentration was linearly proportional to the mercapto density.

3.4. Removal of Heavy Metal Ions from Aqueous Solution

Heavy metal ion adsorption studies were carried out using the mercapto functionalized mesoporous silica for the purpose of evaluating the importance of SH density and pore properties, such as pore size, surface area, and framework, and/or textural porosities. Heavy metal ions included Hg^{2+}, Pb^{2+}, Cu^{2+}, and Cd^{2+} were used as targets. In order to compare changes in heavy metal ion uptake for the support types, three different SBAs were prepared

Table 2. Elemental analysis and mercapto density of adsorbents.

Materials	Contents ($\mathrm{mmol\,g^{-1}}$) C	H	S	SH groups per $\mathrm{nm}^{2\,a}$	Ratio of Hg/S
MP-MSd-T00	7.93	20.54	1.78	1.30	0.51
MP-MSh-T00	8.45	20.38	2.39	1.77	0.49
MP-MSh-T05	7.60	19.74	1.37	0.99	0.72
MP-MSh-T10	9.60	23.70	2.45	1.55	0.41
MP-MSh-T15	6.40	18.39	0.77	0.49	1.03

[a] SH density = S contents × N_A × (surface area of unfunctionalized silica)$^{-1}$.

using triblock copolymers, i.e., Pluronic P123 ($EO_{20}PO_{70}EO_{20}$), P103 ($EO_{17}PO_{56}EO_{17}$), and P65 ($EO_{20}PO_{30}EO_{20}$) as templates.[18] The procedure used to graft the mercapto groups on the synthesized SBA was identical to that used for HMS. For the synthesis of SBA-15, surfactants (P123, P103, and P65) are removed by the Soxhlet extraction using ethanol for 4 days, and thus re-hydration procedure such as HCl treatment is not required. Their pore properties were summarized in Table 3. The morphological features of surface (SEM) and pore channel (TEM) have been reported elsewhere.[19] Mesoporous silicas of SBA-15 type show the characteristics of less textural pores with much more of micropores than those of HMS type. The pore size of the SBA was determined to be 6.3–7.5 nm, and both the pore volume and surface area were similar to that of HMS. However, the SH concentration of the thiol-functionalize SBA series (MP-SBA) was very small compared with those of the thiol-functionalize HMS series. The SH contents (densities) of the MP-SBA-123, MP-SBA-103, and MP-SBA-65 were $0.20\,\mathrm{mmol\,g^{-1}}$ ($0.14\,\mathrm{nm^{-2}}$), $0.24\,\mathrm{mmol\,g^{-1}}$ ($0.18\,\mathrm{nm^{-2}}$), and $0.30\,\mathrm{mmol\,g^{-1}}$ ($0.22\,\mathrm{nm^{-2}}$), respectively. HMS with interconnected pore structure is a better support for the grafting of functional group on inner pore channel than SBA. Therefore, metal loading content of HMS is larger than that of SBA.

Table 3. Pore properties of synthesized and functionalized mesoporous silica, SBA-15 type.

Samples	D_{BJH} (nm)	S_{BET} ($\mathrm{m^2\,g^{-1}}$)	V_t ($\mathrm{cm^3\,g^{-1}}$)	Samples	D_{BJH} (nm)	S_{BET} ($\mathrm{m^2\,g^{-1}}$)	V_t ($\mathrm{cm^3\,g^{-1}}$)
SBA-65	6.3	829	0.70	MP-SBA-65	5.5	631	0.50
SBA-103	6.5	800	0.79	MP-SBA-103	5.6	639	0.61
SBA-123	7.6	877	0.96	MP-SBA-123	5.8	677	0.72

When adsorbents with a variety of mercapto concentrations were exposed to heavy metal ions, the amount of heavy metal adsorbed varied over a range of 0 and 2.45 mmol g^{-1}, in terms of the SH concentration (Fig. 4). The metal uptake capacities for mercury and lead ions increased with increasing SH concentration, while those for cadmium and copper ions increased only slightly. The distribution coefficients (K_d mL^{-1} g^{-1}) for the MP-MSh-T10 were 5400 for Cu^{2+}, 4000 for Cd^{2+}, 12,000 for Pb^{2+}, and 143,000 for Hg^{2+}. The K_d of the metal ions in aqueous solution was defined as the ratio of the concentration of metal ions in the adsorbent (mmol g^{-1}) to that in the aqueous solution (mmol g^{-1}). The metal adsorption selectivity (1) of the adsorbents, $k_{Hg/Me}$, represents the adsorption selectivity for mercury ion to the others, such as Pb^{2+}, Cu^{2+}, and Cd^{2+}.

$$k_{Hg/Me} = \frac{K_{dHg}}{K_{dMe}} \qquad (1)$$

For the MP-MSh-T10 adsorbents, the k values for Pb^{2+}, Cu^{2+}, and Cd^{2+} were 11.9, 26.5, and 35.7, respectively. This indicates that mercapto

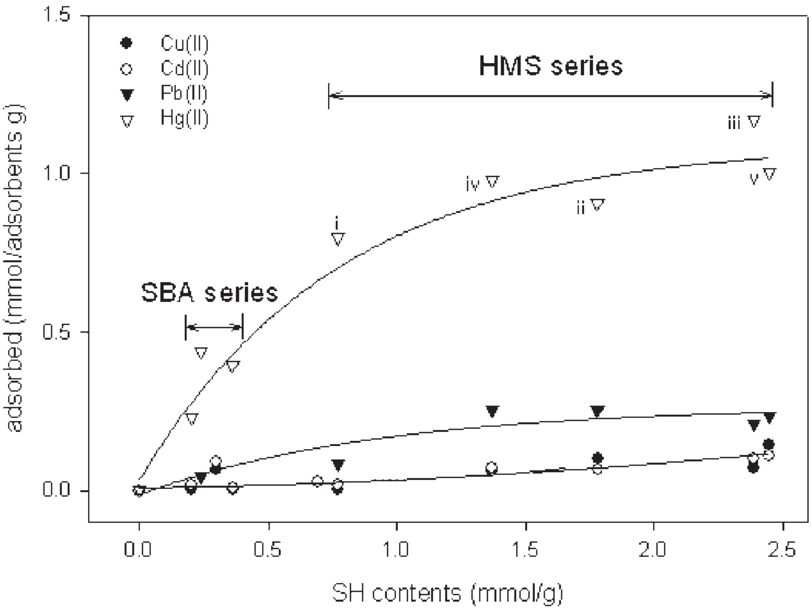

Figure 4. Adsorption test for a single heavy metal ion solution (i, MSh-T15; ii, MSd-T00; iii, MSh-T00; iv, MSh-T05; v, MSh-T10).

functionalized mesoporous silica has a high selectivity for mercury and lead, compared to cadmium and copper ions.[6,10,11]

In addition, the K_d values of MP-MSh-T10 and MP-SBA-T103 for mercury ions were 143,000 mL g^{-1} and 24,000 mL g^{-1}, respectively. This suggests that the adsorption of metal ions to the MP-HMS adsorbents was superior to that of MP-SBA. This may be due to the structural features of SBA, compared with HMS. SBA contains pore channels in a long and bundled form,[18] while HMS contains three-dimensional interconnected pore channels.[9] Therefore, the diffusion of functional groups into the sequestered internal pore channel might be limited, resulting in a relatively low number of grafted functional groups in SBA compared to HMS.

3.5. Mercapto Densities and Pore Properties

It is interesting to note no close correlation between the pore size of the supports and the mercapto concentration of the adsorbents was observed in this study (Tables 1 and 2). For example, SBA adsorbents with pore size larger than HMS had a low mercapto concentration. Since the pore channel of SBA is one directional and bundled form with less textural porosity, the functional group is hard to transport deeply into inside the pores during the preparation step. Thus, most of functional groups are mainly grafted onto the entrance of pore and/or external surface, and metal ions are easily adsorbed in these external surfaces (1 : 1 complexation). It is known that HMS with interconnected pore structure is a better support for the grafting of functional group on inner pore channel than SBA. Therefore HMS has more active site than SBA. Consequently, pore congestion is minimized at the expense of loading capacity and the meal ions can access most of the binding sites.[8] Although the pore size of MSh-T10 was similar to that of MSh-T15, the mercapto content of MP-MSh-T10 was not similar to that of MSh-T15. Therefore there is no close correlation between pore size and the contents of functional groups. In addition, both the surface area and total pore volume were not closely correlated with the SH concentration.

The mercapto concentration (or density) was strongly dependent on the framework and textural pore volume of the supports. With the exception of the MSh-T15 material, the functional group concentration was proportional to the framework pore volume of unfunctionalized mesoporous silicas (Tables 1 and 2). In the case of supports with a well-developed framework porosity, a large portion of the functional groups were grafted to the surface of the framework pore. Table 1 shows that the textural pore volumes of MP-MSd-T00, MP-MSh-T00, and MP-MSh-T15 were slightly smaller, compared with those of MP-MSh-T05 and MP-MSh-T10. This suggests that the functional group concentration increased with an increase in the degree of the framework porosity of the support.

The effect of framework and textural porosity on metal uptake capacities was also investigated. In the HMS series in Fig. 4, the feature of metal uptake was correlated with framework and/or textural porosity. The mercury ion uptake for adsorbents with a well-developed framework porosity increased with increasing mercapto concentration (MSh-T15, MSd-T00, and MSh-T00 of Fig. 4), while samples with a well-developed textural porosity increased only slightly with increasing mercapto concentration (MSh-T05, and MSh-T10 of Fig. 4). This indicates that a large portion of the grafted functional groups in the textural pore were not used as adsorption sites for metal ions. Textural pores form and intergrow at the surface of colloidal particles when a free surfactant in emulsion form is used.[22] Voids associated with textural porosity are larger than the framework porosity, but an irregular pore structure induces pore blockage. Amorphous Davisil$^{\text{TM}}$ (Aldrich) silica ($D_{\text{ave}} = 21\,\text{nm}$; $S_{\text{BET}} = 293\,\text{m}^2\,\text{g}^{-1}$; $V_{\text{P}} = 1.16\,\text{cm}^3\,\text{g}^{-1}$) also shows an irregular pore structure that is similar to a textural pore structure. The concentration of mercapto groups on the amorphous silica was determined to be $0.69\,\text{mmol}\,\text{g}^{-1}$. However, the metal adsorption capacities for Hg, Pb, Cu, and Cd ion are very low. The use of functional groups on the irregular pore channels and textural pores to achieve metal adsorption was limited due to steric hindrance and pore blockage. Functional groups contained by the uniform pore channel and framework pores showed no pore blockage by metal ions, and all the functional sites were available for metal ion adsorption.

This was clearly evidenced by the modeling data reported,[24] in that an adsorption coefficient for mesoporous materials with a pore size of 2 nm was two orders of magnitude higher than that for the irregularly (non)mesoporous materials. It is also reported that the uptake rate of mercury was noticeably slower for adsorbent with less textural porosity and a long-range hexagonal framework (MP-MCM-41 or MP-SBA-15) than for MP-HMS with large textural porosity.[8] HMS particles are loosely packed aggregates of mesoscale fundamental particles, while those of MCM-41 or SBA-15 are bulky and much more monolithic. Therefore, textural porosity of the adsorbents developed here can enhance the accessibility of a molecule to the active sites, and consequently facilitate the transport of the metal ions to the framework mesopores.[22]

4. CONCLUSIONS

Adsorbents with a variety of pore properties were prepared to remove heavy metal ions from aqueous solutions. The aim of this study was to deter-

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mine the effect of framework and/or textural porosities on metal uptake capacities. It is interesting to note that the mercapto concentration showed a low correlation with pore size and the surface area of the supports, but was strongly dependent on the framework pore volume. The concentration of grafted functional groups increased with increasing framework pore volume. Therefore, mesoporous silica, which has a well-developed framework porosity, was able to accomodate a larger concentration of functional groups on the adsorbents.

The mercury ion uptake capacity of adsorbents with only a framework porosity increased with increasing concentration of functional groups, while that with a large textural porosity remained constant with increasing functional group concentration. An irregular pore channel structure, such as amorphous silica, caused pore blockage. Therefore, a large proportion of the grafted functional groups in the textural pores appear to be underutilized. The metal ion uptake capacities of SBA having long range 2-D pore channels were small compared with those of HMS, with short range interconnected 3-D pore channels.

It is concluded that framework pores increased the loading of functional groups, while additional textural pore enhanced the accessibility of a molecule to the active sites.

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