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Ordered Mesoporous Silicas with 2,5-Dimercapto-1,3,4-Thiadiazole Ligand: High Capacity Adsorbents for Mercury Ions

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Abstract. This work reports two-step synthesis of novel ordered mesoporous silicas (OMS), which contain mercury-specific multifunctional ligand and have high surface area and well-developed porosity. One pot co-condensation synthesis was employed to introduce chloropropyl functionality on the mesopore walls of hexagonally ordered silica. In the next step, 2,5-dimercapto-1,3,4-thiadiazole was reacted with chloropropyl groups during template-displacement process, which resulted in high affinity adsorbent towards mercury ions. The maximum adsorption capacity of this adsorbent for mercury ions from aqueous solutions was as high as 1.7 g/g, which is about three times higher than the concentration of surface ligand. This study shows that the surface properties of OMS can be tailored by proper choice of chemical modification method, which affects the ligand bonding density and determines the adsorbent capacity and affinity towards heavy metal ions. Three methods, one-pot synthesis, template-displacement and post-synthesis modification, were used for the introduction of surface ligands into MCM41 and SBA15 mesostructures to prepare mercury-specific adsorbents. In addition, adsorption properties of these adsorbents as well as their effectiveness for mercury removal from aqueous solutions were comparatively studied.

Keywords: MCM-41, SBA-15, mercury ion adsorption, 2,5-Dimercapto-1,3,4-Thiadiazole ligand, co-condensation synthesis of organosilicas, template displacement synthesis, post-synthesis modification of mesoporous silicas

Introduction

Monitoring and clean-up of toxic chemicals are key issues in environmental protection. Toxic persistent pollutants such as heavy metal ions are extremely hazardous for environment and living organisms, and therefore they are subject to rigorous EPA regulations. In growing environmental pollution there is a strong demand to develop novel adsorbents of higher efficiency than those commercially available for mercury ions removal from aqueous media (Matlock et al., 2002). Today, material chemistry offers almost unlimited possibilities to design novel adsorbents with tailorable structural and chemical properties at the nanoscale level. Ordered mesoporous materials, especially ordered mesoporous silicas (OMS), were already recognized for their unique features and tremendous potential applications, among which environmentally related issues are of great importance. Chemically modified OMS of different structures as MCM41, MCM48 (Kresge et al., 1992), and SBA15 (Zhao et al., 1998) were reported as promising highly effective and selective adsorbents with unprecedented adsorption capacity and high regeneration ability. These properties are readily achievable due to the high surface area, large porosity, rich framework and surface chemistry that assure effective grafting of the OMS surface with functional groups of high affinity towards heavy

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metal ions (Feng et al., 1997; Mercier and Pinnavaia, 1998; Nooney et al., 2001; Liu et al., 1998, 2000; Kang et al., 2004; Yantasee et al., 2003a, 2003b; Venkatesan et al., 2003; Mattigod et al., 1999; Kang et al., 2004).

Organic-inorganic ordered nanostructured materials found applications in removal of toxic gases and other toxins from the environment (Hudson et al., 2004; Yoshitake et al., 2002). Along with post-synthesis chemical grafting, one-pot co-condensation synthesis allows one to incorporate desired functionality into mesoporous materials. This approach is advantageous to design adsorbents for heavy metal ions because it eliminates some synthesis steps and facilitates control of their morphology and metal-specific functionality (Bibby and Mercier, 2002; Im et al., 2004; Bois et al., 2003; Corriu et al., 2004; Zhang et al., 2003; Lu and Yan, 2004).

Our previous works on the development of OMS-based adsorbents for heavy metal ions indicate huge benefits of using multifunctional groups in surface modification. This type of ligands can bear more than one active sites of high affinity towards mercury ions such as sulfur, nitrogen and oxygen that assure selective mercury pre-concentration as suggests Pearson soft acid-soft base theory (Antochshuk and Jaroniec, 2002; Antochshuk et al., 2003; Olkhovyk et al., 2004). These active sites mimic naturally occurring targets in living organisms and cells that are undergoing malfunction upon binding to heavy metal ions. Synthesis, calcination and two-step post-synthesis modification, conventionally used for introduction of multifunctional ligands onto mesopore walls of OMS often afford adsorbents with reduced surface area and limited accessibility to the metal-chelating groups. This work presents an attempt to prepare effective adsorbents for mercury ions with multifunctional ligands via two-step synthesis involving co-condensation and template-displacement processes (Antochshuk and Jaroniec, 1999) for the introduction of metal-chelating entities into OMS without calcination and template extraction. The high adsorption capacity of these adsorbents was achieved by attaching multifunctionl ligand, 2,5-dimercapto-1,3,4-thiadiazole (DMT), capable for mercury complexation via at least three active sites. Among complexes with heterocyclic thione donors, thiadiazoline thione-metal complexes have a well-established stoichiometry and coordination affinity to various metal ions (Raper, 1985). Different characterization techniques were already used to recognize unique and interesting properties of the DMT ligand in relation to its chelating ability (Ortega et al., 1996). Since each site of the DMT ligand is potentially active for metal-ligand bond formation (Zaidi and Islam, 1977; Samkaeva et al., 1977), one DMT ligand is capable to attract more than one metal ion (Zaidi et al., 1977) and, consequently, increase adsorption capacity of DMT-modified adsorbent. Mercury-DMT complexes were reported having primary and secondary bonds through two N atoms and two S atoms (Castano et al., 1992). The high affinity of DMT towards some heavy metal ions was already utilized for their pre-concentration by DMT-modified conventional silicas (Lessi et al., 1996; Padilha et al., 1999; Roman et al., 1996).

The use of OMS instead of conventional silica allowed us to prepare mercury-specific adsorbents with much better adsorption characteristics due to the high surface area and well-developed porous structure of the former. In this work two-step modification of two OMS, MCM41 and SBA15, was studied to introduce 2,5-dimercapto-1,3,4-thiadiazole ligand. This modification was done by introducing chloropropyl functionality on the siliceous surface of ordered mesopores in the first step of synthesis (these samples are denoted by X-Cl, where X stands for the OMS-type) followed by chemical reaction of chloropropyl groups with 2,5-dimercapto-1,3,4-thiadiazole in the second step. This modification afforded adsorbent with mercury-specific ligand covalently bonded through alkyl-spacer to the insoluble silica surface (in our case OMS support), which was confirmed by spectroscopic studies (Lessi et al., 1996; Padilha et al., 1999; Roman et al., 1996). Our comparative study shows that the two-step post-synthesis modification (PSM) afforded materials with much lower surface area and several times lower ligand coverage. In contrast, one-pot synthesis (OPS) followed by either template displacement synthesis (TDS) or one-step post-synthesis modification (PSM) afforded materials with large surface area, open porosity and high concentration of multifunctional ligands showing high affinity towards mercury ions. The materials with chloropropyl functionality reported in this paper, which were obtained via one-pot synthesis, are denoted by volume percentage of organic (either 10 or 15%) used in co-condensation with primary silica source, tetraethylorthosilicate. Three synthesis methods and two types of ordered mesoporous materials are discussed and compared in relation to their adsorption and structural properties, which make the adsorbents studied highly effective for pre-concentration of mercury ions from aqueous media.

Experimental

Synthesis of Ordered Mesoporous Silica for Post-Synthesis Modification

The synthesis details and characteristics of the MCM41 material that was used for post-synthesis modification were described elsewhere (Kruk et al., 2000). SBA15 was synthesized by using P123 triblock-copolymer as reported by Zhao et al. (1998) except post-synthesis thermal treatment, which was done at 100°C for 48 h. The polymeric template was removed by calcination at 540°C. Post-synthesis modification with chloropropyltrimetoxysilane was done with pyridine as described previously (Ryoo et al., 2000).

The chloropropyl-grafted MCM41 and SBA15 materials were functionalized in the second step of synthesis with 2,5-dimercapto-1,3,4-thiadiazole (DMT) from dimethylformamide solvent according to the procedure reported by Lessi et al. (1996). The resulting samples were denoted as SBA15-DMT PSM and MCM41-DMT PSM, where PSM stands for post-synthesis modification.

One-Pot Co-Condensation Synthesis of Chloropropyl-Functionalized Materials

One-pot synthesis of SBA15 with chloropropyl ligand was carried out to incorporate 10 and 15% of chloropropyl moiety into mesopores via co-condensation reaction of organic ligand with tetraethylorthosilicate as primary silica source. In normal synthesis the molar composition of the materials with 10 volume percent of chloropropyltrimethoxysilane was: 0.017 M Pluronic123: 210 M H_2O: 6.5 M HCl: 1 M TEOS: 0.13 M chloropropyltrimetoxysilane, and for the synthesis of materials with 15 volume percent of chloropropyl was: 0.017 M Pluronic123: 210 M H_2O: 6.5 M HCl: 1 M TEOS: 0.21 M chloropropyltrimetoxysilane. The as-synthesized samples were divided into two parts. One part was extracted with 2.4% wt hydrochloric acid (or 48% wt sulfuric acid)/ethanol solution and reacted with DMT in dimethylformamide to give 2,5-dimercapto-1,3,4-thiadiazole-modified SBA15. The resulting samples were denoted as SBA15-10%Cl (or 15%Cl)-DMT PSM, where PSM stands for post-synthesis modification. The other, un-extracted part of the as-synthesized sample, was subjected to the template-displacement synthesis, during which as-synthesized chloropropyl-incorporated SBA15 sample was reacted with 2,5-dimercapto-1,3,4-thiadiazole in dimethylformamide. The resulting sample was denoted as SBA15-10%Cl (or 15%Cl)-DMT TDS, where TDS stands for template displacement synthesis.

Nitrogen Adsorption Measurements

Nitrogen adsorption isotherms were measured on Micromeritics model ASAP 2010 adsorption analyzer (Norcross, GA) using nitrogen of 99.998% purity. Measurements were performed in the pressure range from 10^{-6} to 0.995 at −196°C. The samples were degassed for 2 h at 110°C under vacuum.

Mercury Adsorption Measurements

Mercury adsorption was tested on all materials from aqueous solutions. The mercury solutions were prepared by dilution of the proper amount of mercury (II) nitrate volumetric standard, 0.145 N aqueous solution, to the total volume of 10 ml. In a typical experiment, 0.05 g of the sample was equilibrated for 40 min with 10 ml aqueous solution of mercury of known concentration. A series of experiments for Hg^{2+}: ligand ratios of 3:1 and 6:1 was conducted.

Determination of the Adsorbent Capacity

Mercury (II) concentration in the filtrate after adsorption was measured spectrophotometrically with dithizone (diphenylthiocarbazone) as a complexing agent (Svehla, 1975). Mercury photometric determinations (Herrich, 1990) were performed on a Shimadzu-1601 spectrometer in 1 cm quartz photocell (volume ca. 5 ml). The amount of mercury was determined from the calibration curve that was prepared for the mercury concentration range from zero to 50 μg with desirable correlation to the complexing agent concentration. The background correction was performed against pure chloroform. Each sample was analyzed at 490 nm.

Elemental Analysis

Quantitative estimation of ligand coverage was done by CHNS analysis. The content of carbon, nitrogen and sulfur in all samples was determined using a LECO elemental analyzer (Model CHNS-932) from St. Joseph, MI.

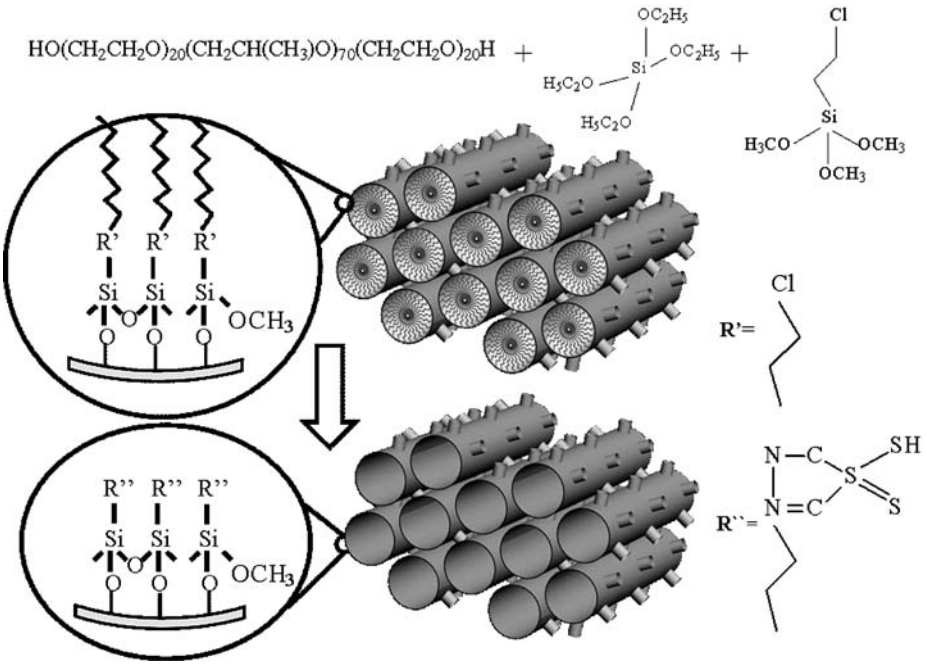
Thermogravimetric Measurements

The unmodified and modified samples were subjected to high-resolution thermogravimetric analysis HR TGA. All measurements were done in nitrogen atmosphere using a TA Instruments Inc. (New Castle, DE, USA) model TGA 2950 high-resolution thermogravimetric analyzer. The weight change (TG) curves were recorded over a temperature range from 25°C to 1000°C. The instrument was equipped with an open platinum pan and an automatically programmed temperature controller. The high-resolution mode was used to record the TG data. The maximum heating rate was 5°C per minute and this rate was adjusted automatically during measurement to achieve the best resolution. The resolution and sensitivity parameters were 4 and 6, respectively. The flow rate of the nitrogen gas in the system was 100 cm^3 and 50 cm^3 per minute on the furnace and balance, respectively.

Results and Discussion

The BET specific surface area (Brunauer et al., 1938) for unmodified and modified with organic ligands OMS was evaluated using adsorption data in the relative pressure range from 0.04 to 0.2 (Sing et al., 1985). The total pore volume was calculated from the amount adsorbed at a relative pressure of about 0.99. The pore size distribution (PSD) was estimated from adsorption branches of nitrogen isotherms using the BJH method (Barrett et al., 1951) with corrections for cylindrical pores introduced by (Kruk et al., 1997). Scheme 1 illustrates the template-displacement procedure used in materials synthesis. The co-condensation mechanism involves self-assembly of Pluronic123 triblock co-polymer with subsequent co-hydrolysis of chloropropyltrimethoxysilane and tetraethylorthosilicate as silica source. The as-synthesized sample was thermally treated in dimethylformamide as solvent with 2,5-dimercapto-1,3,4-thiadiazole. During this treatment the polymeric template was displaced by 2,5-dimercapto-1,3,4-thiadiazole, which reacted with surface chloropropyl groups. The modified OMS samples obtained via template displacement synthesis are compared with those prepared by using conventional post-synthesis modification of calcined OMS. Adsorption parameters for the modified OMS samples are listed in Table 1.

Hexagonally ordered MCM41 material after post-synthesis modification was examined by nitrogen adsorption to monitor the attachment of chloropropyl functionality onto the mesopore surface in the first step



Scheme 1. The polymer-templated synthesis route for introduction of multifunctional ligand (R''): one-pot co-condensation of TEOS and organosilane followed by template displacement procedure.

Table 1. Parameters for modified OMS with chloropropyl and 2,5-dimercapto-1,3,4-thiadiazole (DMT) groups.

Sample	S_{BET}, (m^2/g)	d_{KJS}, (nm)	V_{tot}, (cm^3/g)	C_{lig}, (mmol/g)	Maximum adsorption capacity, (gHg^{2+}/g)
MCM41-Cl PSM	112	3.3	0.2	4.5	–
MCM41-Cl PSM 2D WASH	196	3.4	0.3	–	–
MCM41-Cl PSM 3D WASH	185	3.5	0.3	–	–
MCM41-DMT PSM	56	2.9	0.1	0.25	0.015
SBA15-10%Cl OPS HCl extr	668	6.9	1.0	–	–
SBA15-10%Cl OPS H_2SO_4 extr	728	7.6	1.1	–	–
SBA15-10% DMT TDS	511	5.4	0.6	1.3	–
SBA15-15% Cl OPS HCl extr	726	6.0	0.9	3.0	–
SBA15-15% DMT PSM	684	5.7	0.8	2.0	0.97
SBA15-15% DMT TDS	556	4.9	0.5	2.7	1.7
SBA15-DMT PSM	192	8.3	0.4	0.5	0.03

S_{BET}, BET specific surface area; d_{KJS}, primary mesopore diameter; V_{tot}, total pore volume; C_{lig}, surface coverage of bonded ligands.

of grafting. The adsorption isotherm curve in Fig. 1 (open circles) shows that the post-synthesis modification of OMS reduces significantly nitrogen adsorption. The adsorption isotherms with open triangles and squares in this figure indicate the change in the adsorption behavior of the initial chloropropyl-modified material after its subsequent washing, which was done with solvent after post-synthesis treatment. Such big difference in the volume adsorbed of the unwashed and twice-washed materials suggests that extensive washing with polar and nonpolar solvents is required to remove residual modifier and products of hydrolysis from the mesopores. As can be seen in Fig. 1 the extensive washing caused a significant increase in the surface area from 112 to 185 m^2/g. Also, subsequent washing increased the pore width for about 0.2 nm and the total pore volume for about 0.1 cm^3/g (Table 1, Fig. 2). However, the introduction of

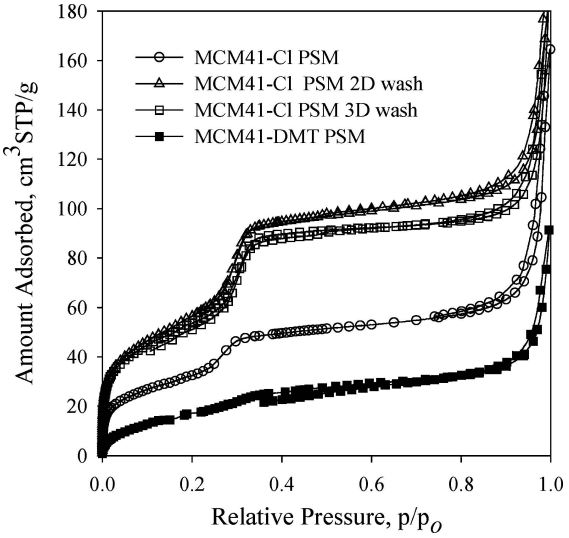


Figure 1. Nitrogen adsorption isotherms for MCM41 with chloropropyl functionality grafted via post-synthesis modification (PSM) (open circle); the same material after second washing (open triangles); the same material after third washing (open squares); the same material with 2,5-dimercapto-1,3,4-thiadiazole (DMT) ligand obtained via post-synthesis modification (filled squares).

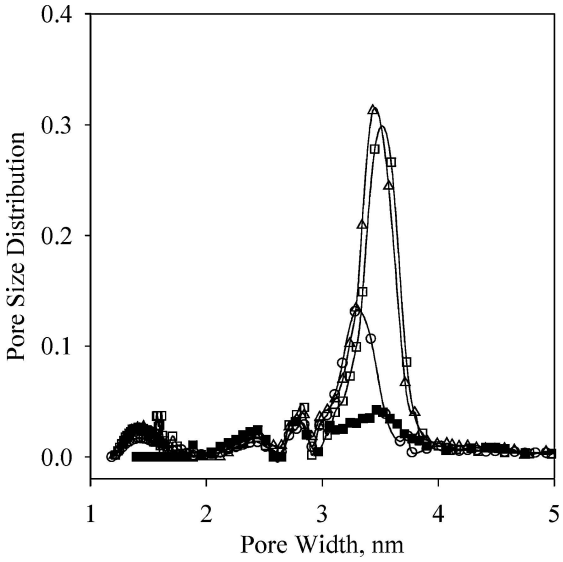


Figure 2. Pore size distributions ($cm^3\ g^{-1}\ nm^{-1}$) for MCM41 with chloropropyl functionality grafted via post-synthesis modification (PSM) (open circle); the same material after second washing (open triangles); the same material after third washing (open squares); the same material with 2,5-dimercapto-1,3,4-thiadiazole (DMT) ligand obtained via post-synthesis modification (filled squares).

2,5-dimercapto-1,3,4-thiadiazole (DMT) ligand inside mesopores of MCM41-Cl material in the second post-synthesis step caused a substantial decrease in the total pore volume and surface area of the resulting material. Structural constrains and limited number of available reactive chloropropyl groups resulted in the small ligand coverage (0.45 mmol/g) of the DMT-modified material, which was a primary reason of very low mercury adsorption capacity, about 0.015 gHg^{2+}/g.

Taking advantage of one-pot co-condensation synthesis that allowed us to incorporate chloropropyl functionality into OMS, a series of chloropropyl-functionalized materials was synthesized. Figure 3 shows the adsorption isotherms for the samples with 10% of chloropropyltrimethoxysilane used in one-pot synthesis. Comparison of the two methods used for polymer extraction from as-synthesized materials suggests that the sulfuric acid/ethanol method is more effective than that employing HCl/ethanol. The former extraction procedure gave materials with the surface area higher about 60 m^2/g and the pore widths wider about 0.7 nm in comparison to the samples obtained by hydrochloric acid/ethanol extraction method (Figs. 3 and 4). The use of template-displacement procedure for incorporation of the DMT ligand into the OMS material with 10% of chloropropyl groups allowed us to obtain the modified OMS with pore size of 5.4 nm, and ligand coverage of 1.3 mmol/g (calculated from sulfur content, obtained by elemental analysis). Thermogravimetric (TG) weight change curves recorded for modified materials allowed us to perform the qualitative

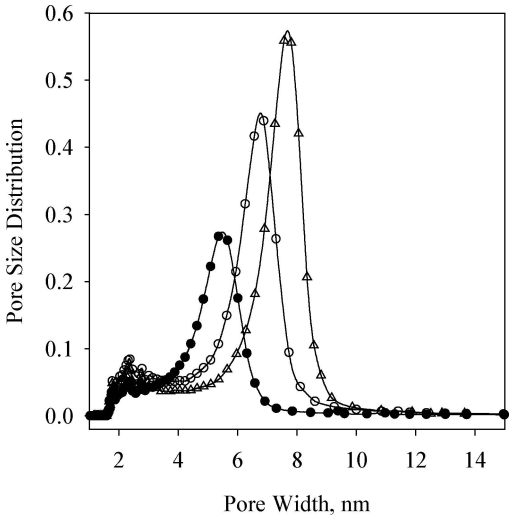


Figure 4. Pore size distributions ($cm^3\ g^{-1}\ nm^{-1}$) for SBA15 material obtained via one-pot synthesis (OPS) with 10% chloropropyltrimethoxysilane used in co-condensation, after extraction with hydrochloric acid/ethanol solution (open circles); after extraction with sulfuric acid/ethanol solution (open triangles); modified with 2,5-dimercapto-1,3,4-thiadiazole (DMT) via template-displacement process (filled circles).

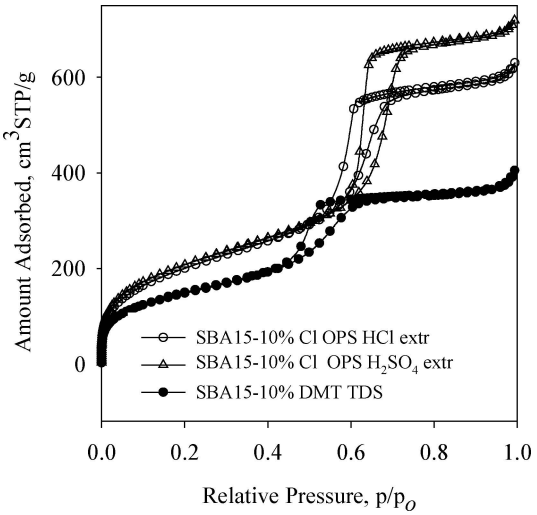


Figure 3. Nitrogen adsorption isotherms for SBA15 material obtained via one-pot synthesis (OPS) with 10% chloropropyltrimethoxysilane used in co-condensation, after extraction with hydrochloric acid/ethanol solution (open circles); after extraction with sulfuric acid/ethanol solution (open triangles); modified with 2,5-dimercapto-1,3,4-thiadiazole (DMT) via template-displacement process (filled circles).

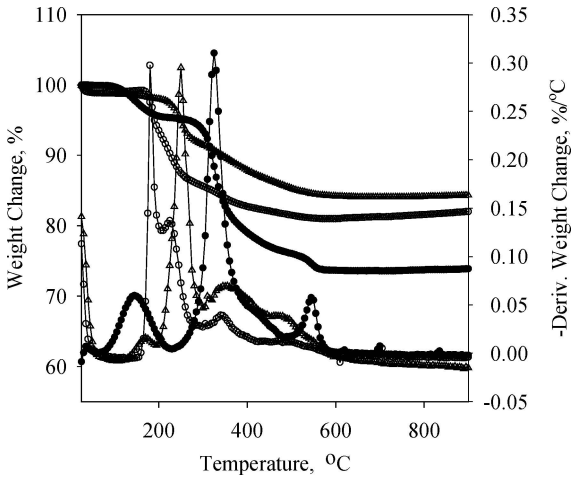


Figure 5. High-resolution TG and DTG curves for SBA15 material obtained via one-pot synthesis (OPS) with 10% chloropropyltrimethoxysilane used in co-condensation, after extraction with hydrochloric acid/ethanol solution (open circles); after extraction with sulfuric acid/ethanol solution (open triangles); modified with 2,5-dimercapto-1,3,4-thiadiazole (DMT) via template-displacement process (filled circles).

estimation of the ligand coverage and to monitor the effectiveness of the template-extraction procedure used in the materials synthesis (Fig. 5). High efficiency of sulfuric acid/ethanol extraction is evident from the difference in the TG curves, which is manifested by about 5% lower weight loss for the extracted sample with sulfuric acid/ethanol. The differential TG curve (DTG) shows that the DMT-modified sample is thermally stable up to 220°C. A distinct shift in the DTG curve for the DMT-modified material to higher temperatures indicates strong anchoring of the ligand to the surface. Over 10% difference in the weight change for chloropropyl modified and DMT-modified samples indicates that the attachment of DMT ligand in the second step of modification was successful.

An increase in the amount of incorporated chloropropyl groups for about 5% in one-pot co-condensation synthesis was performed to obtain greater amount of reactive functionality on the mesopore surface for subsequent modification with multifunctional ligand under study. The sample extracted with hydrochloric acid/ethanol solution (open circles in Fig. 6) possesses high surface area of 726 m^2/g. A sharp vertical condensation step on the adsorption isotherm at relative pressure about 0.5 indicates the presence of large and uniform mesopores (with widths about 7.6 nm) in the resulting material. Two different methods of chemical modification were performed to graft the material's surface with multifunctional DMT ligand. The post-synthesis modification of the extracted sample and template displacement treatment of the as-synthesized samples allowed us to obtain high concentration of ligand on the surface without structure deterioration. The sample obtained by post-synthesis modification with DMT ligand reveals a decrease in the surface area from 726 m^2/g to 684 m^2/g and in the pore width from 6.0 to 5.7 nm. The template displacement synthesis afforded materials with almost 2.7 mmoles of the DMT ligand per gram of OMS. Nitrogen adsorption isotherms and pore size distributions indicate clearly that the modification used was successful because the capillary condensation step is shifted to smaller relative pressures and the pore volume decreased by about 0.4 cm^3/g (Figs. 6 and 7). The HR TG curves recorded for the samples after each synthesis step clearly show the difference in the DTG weight change for chloropropyl-modified material and subsequently modified samples with DMT (Fig. 8). A broad DTG peak observed for chloropropyl-modified sample that underwent thermal decomposition in the temperature range between 220 and 400°C is transformed into one well-defined DTG peak for the DMT-modified SBA15 showing the

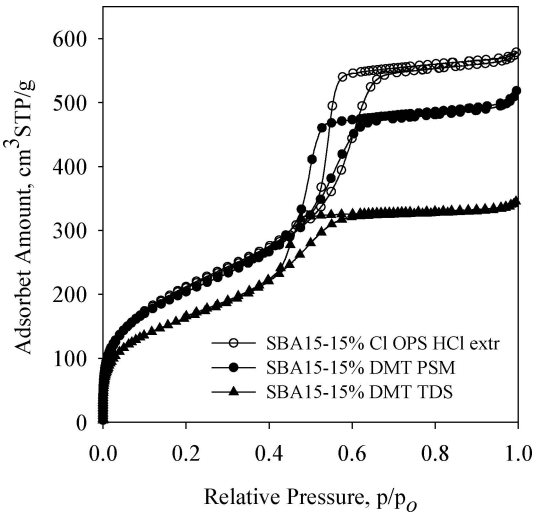


Figure 6. Nitrogen adsorption isotherms for SBA15 material obtained via one-pot synthesis (OPS) with 15% chloropropyltrimethoxysilane used in co-condensation, after extraction with hydrochloric acid/ethanol solution (open circles); extracted materials modified with 2,5-dimercapto-1,3,4-thiadiazole (DMT) via post-synthesis modification (filled circles) and template-displacement synthesis (filled triangles), respectively.

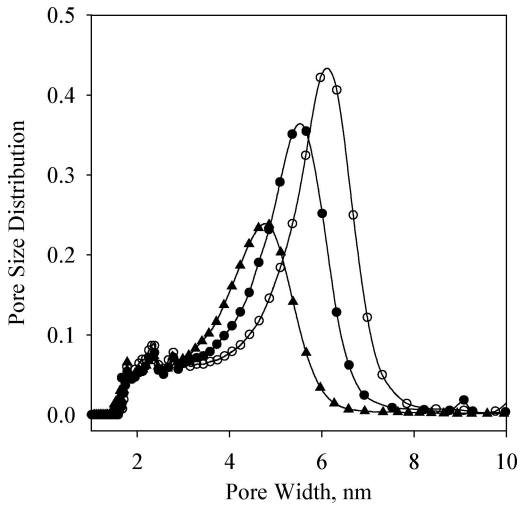


Figure 7. Pore size distributions ($cm^3\ g^{-1}\ nm^{-1}$) for SBA15 material obtained via one-pot synthesis (OPS) with 15% chloropropyltrimethoxysilane used in co-condensation, after extraction with hydrochloric acid/ethanol solution (open circles); extracted materials modified with 2,5-dimercapto-1,3,4-thiadiazole (DMT) via post-synthesis modification (filled circles) and template-displacement synthesis (filled triangles), respectively.

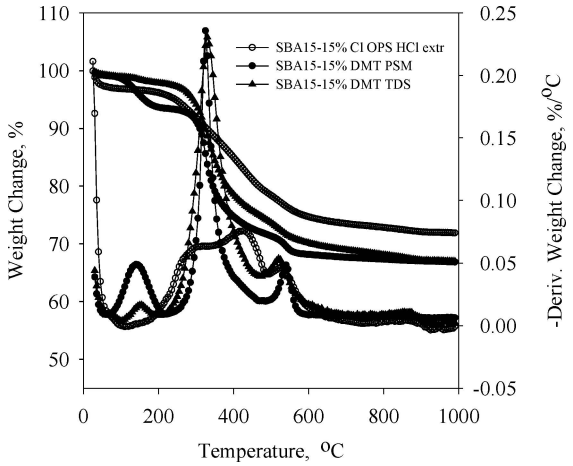


Figure 8. High-resolution TG and DTG curves for SBA15 material obtained via one-pot synthesis (OPS) with 15% chloropropyltrimethoxysilane used in co-condensation, after extraction with hydrochloric acid/ethanol solution (open circles); extracted materials modified with 2,5-dimercapto-1,3,4-thiadiazole (DMT) via post-synthesis modification (filled circles) and template-displacement synthesis (filled triangles), respectively.

stability of that material up to 220°C and confirming the removal of polymeric template during second synthesis step. In comparison to the post-synthesis modification the difference in the ligand coverage by about 0.7 mmol/g for SBA15-15% DMT TDS resulted in much higher mercury adsorption capacity of this sample. The maximum mercury adsorption capacity measured for these materials was obtained for mercury: ligand ratio of 6:1 and was as high as 1.7 gHg^{2+}/g. The high binding affinity of the DMT ligand to Hg^{2+} ions can be also illustrated by high value of distribution coefficient, $K_d = 1.11 \times 10^8$, defined as the amount of adsorbed metal (μg) per gram of the adsorbent divided by metal concentration (μg/ml) remaining in the effluent after adsorption test. The high maximum adsorption capacity of ~8.5 mmoles of mercury versus ligand coverage of ~2.7 mmol/g suggests that in the attached ligand 3 out of 4 active sites participate in the mercury coordination. In comparison to the adsorption capacity of the same ligand grafted onto the surface of conventional silica (Padilha et al., 1999), our material has ~20 times higher maximum adsorption capacity. This finding shows distinctly the benefit of using functionalized ordered mesoporous materials for heavy metal ions adsorption because they have much higher surface area, non-swelling and hydrothermally stable matrix as well as accessible mesopores with specific ligands and desired width that could prevent adsorption of bulk organics from waste waters. Regeneration of loaded samples with mercury was done under mild conditions using the method reported elsewhere (Antochshuk et al., 2003). The adsorption capacity of the DMT-modified SBA15 materials retained after regeneration was about 70%. The lowest regeneration ability of some samples was 30% of the initial adsorption capacity, which could result from insufficient regeneration.

Figure 9 depicts the difference in the chemically modified SBA15 samples with 2,5-dimercapto-1,3,4-thiadiazole ligand. By choosing proper modification method for design of mercury-specific adsorbents it is possible to tailor not only structural properties at nanoscale level but also design and tailor chemistry of pore walls. The dashed line in Fig. 9 represents adsorption isotherm for the calcined SBA15 material after post-synthesis modification with DMT. Two other adsorption isotherms in this figure refer to the samples obtained by one-pot co-condensation synthesis followed either by extraction and post-synthesis modification (empty circles) or template-displacement synthesis (filled circles). It is evident that the use of different chemical modification procedures to incorporate the same functionality into the particular type of

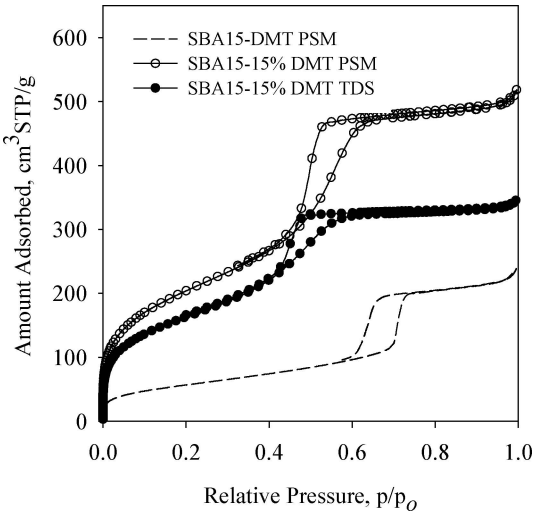


Figure 9. Nitrogen adsorption isotherms for SBA15 materials with 2,5-dimercapto-1,3,4-thiadiazole (DMT) ligand obtained by: post-synthesis modification of calcined SBA15 (dashed line); one-pot synthesis (OPS) of the SBA15 material with 15% chloropropyl functionality followed by post-synthesis modification with DMT (empty circles); one-pot synthesis (OPS) of the SBA15 material with 15% chloropropyl functionality followed by template-displacement with DMT (filled circles).

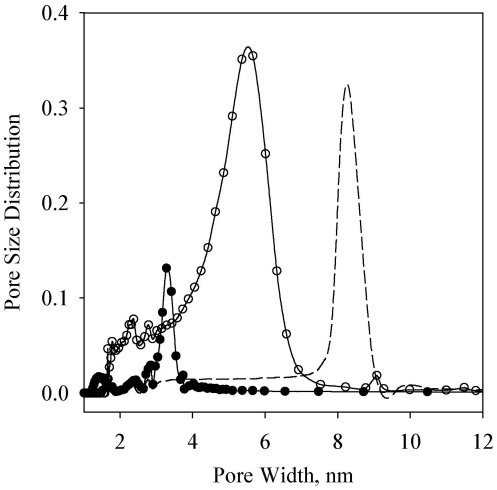


Figure 10. Pore size distributions ($cm^3\ g^{-1}\ nm^{-1}$) for SBA15 materials with 2,5-dimercapto-1,3,4-thiadiazole (DMT) ligand obtained by: post-synthesis modification of calcined SBA15 (dashed line); one-pot synthesis (OPS) of the SBA15 material with 15% chloropropyl functionality followed by post-synthesis modification with DMT (empty circles); one-pot synthesis (OPS) of the SBA15 material with 15% chloropropyl functionality followed by template-displacement with DMT (filled circles).

polymeric-templated SBA15 OMS affords materials with different properties (Fig. 10), which is manifested by significant difference in their mercury adsorption capacity.

Conclusions

Comparative studies of different routes of chemical modification of ordered mesoporous materials are reported. It is shown that the modification procedure is essential for designing effective heavy metal ions adsorbents, especially those with multifunctional ligands. This study shows that the template displacement procedure and one-pot co-condensation synthesis are effective to tailor the surface properties of OMS and to obtain adsorbents with surface area up to $730\ m^2/g$, open mesopores with widths about 5–6 nm and high ligand coverage, about 2.7 mmol/g as evidenced by nitrogen adsorption analysis, high resolution TGA measurements and elemental analysis. The use of 2,5-dimercapto-1,3,4-thiadiazole for the modification of OMS was extremely beneficial in design of high capacity adsorbents for mercury ions because this modifier was shown to be capable to coordinate more than 3 metal ions per attached ligand giving the mercury adsorption capacity as high as 1.7 g Hg^{2+}/g.

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