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Adsorption Characterization of Ordered Mesoporous Silicas with Mercury-Specific Immobilized Ligands

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Abstract. Nitrogen adsorption was employed to study the surface properties of organically modified ordered mesoporous silicas (OMS) of different structures as potential adsorbents for environmental applications. MCM41, MCM48, and SBA15 materials were functionalized via post-synthesis, one-pot synthesis and template-displacement synthesis with organic ligands containing mono- or multiple binding sites for heavy metal ions adsorption. Nitrogen adsorption isotherms at 77 K were used to evaluate the specific surface area, pore volume, pore size and pore accessibility of OMS after surface modification. It is shown that the adsorption and structural properties of OMS can be tailored by introducing multifunctional ligands of desired affinity towards mercury ions.

Keywords: adsorption, mercury removal, ordered mesoporous organosilica, surface modification

1. Introduction

Detection, separation and clean-up technologies for persistent pollutants are main issues in environmental chemistry. Mercury, cadmium and lead ions are the most harmful contaminants among heavy metal ions. They severely affect living cells; intoxicate their metabolic functions via bonding to important biomolecules such as glutathione, cysteine and homocysteine (Hultberg, 1998).

Lower detection limits, larger adsorption capacities, proper sensing properties and greater affinities to heavy metal ions were already recognized as important properties of hydrothermally stable, non-swelling ordered mesoporous silicas (OMS) for design of novel adsorbents. OMS of high surface area, large and accessible pores, which were reported in 1992 by Mobil Company (Kresge et al., 1992), are good candidates for creation of adsorbents of tailored surface properties for environmental applications.

Various conventional synthetic routes are not only useful for the preparation of nanoporous materials with tailored properties but also provide possibility to incorporate functional groups capable for further derivatization. Tailoring surface properties of OMS can be achieved by modification with suitable organosilanes. In this work a comparative adsorption study of OMS with incorporated ligands containing one or more sulfur atoms is presented. A special emphasis is given to OMS with mercaptopropyl, 1-allyl-3-propylthiourea, 1-benzoyl-3-propylthiourea and 2,5-dimercapto-1,3,4-thiadiazole functionalities. The soft acid-soft base approach (Pearson, 1963) implies that the functional groups containing “soft base” atoms (such as sulfur) would be able to retain “soft acid” atoms (such as mercury, cadmium, lead) without interference of “hard acids” such as magnesium, calcium, and so on in remediation processes. In comparison to the OMS with monofunctional groups such as mercaptopropyl ligands (Feng et al., 1997; Mercier et al., 1998; Nooney et al., 2001), introduction of multifunctional ligands containing more binding sites towards mercury ions allows one to increase significantly adsorption capacity and to regenerate such adsorbents under mild conditions. This approach was shown to be attractive for designing high-capacity and highly selective adsorbents for heavy metal ions (Antochshuk et al., 2002, 2003; Olkhovyk et al., 2004). The effectiveness of this approach can

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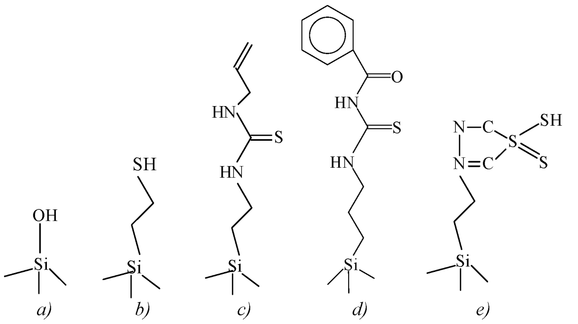

Figure 1. Chemical structures of various ligands showing affinity towards mercury ions (a) unmodified silica surface, (b) mercaptopropyl (SH), (c) allyl-thiourea (ATU), (d) benzoyl-thiourea (BTU), and (e) 2,5-dimercapto-1,3,4-thiadiazole (DMT) ligands. In the case of two-step modification method aminopropyl or chloropropyl groups (not shown), which were used in the first modification step and did not react in the second step, may be present on the silica surface.

be significantly increased by replacing conventional post-synthesis incorporation of multifunctional ligands by so-called template displacement synthesis (Antochshuk and Jaroniec, 1999) or one-pot synthesis reported in this work. The observed decrease in the surface area and ligand bonding density upon surface modification could be fully compensated by multifunctional nature of the introduced ligands (see Fig. 1). A special attention in this work is placed on a multifunctional ligand, 2,5-dimercapto-1,3,4-thiadiazole, which was used for surface modification of conventional silicas (Castano et al., 1992; Padilha et al., 1999; Lessi et al., 1996).

Nitrogen adsorption study of different types of OMS modified with mercaptopropyl, 1-allyl-3-propylthiourea, 1-benzoyl-3-propylthiourea and 2,5-dimercapto-1,3,4-thiadiazole ligands via post-synthesis and template displacement methods is presented. Also, mercury adsorption capacities for those materials are compared.

2. Materials and Methods

2.1. Synthesis of Ordered Mesoporous Silica

MCM41 and MCM48 with mercaptopropyl, 1-allyl-3-propylthiourea, and 1-benzoyl-3-propylthiourea were studied in our previous works (Antochshuk et al., 2002, 2003; Olkhovyk et al., 2004). SBA15 type of materials 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 hours. The polymeric template was removed by calcination at 540°C. MCM41 and SBA15 materials were functionalized with 2,5-dimercapto-1,3,4-thiadiazole according to the recipe reported by Lessi et al. (1996). The resulting samples were denoted as SBA15-DMTp and MCM41-DMTp, where *p* stands for post-synthesis modification. Also, one-pot synthesis of SBA15 with chloropropyl ligand was carried out to incorporate 15% of chloropropyl moiety into mesopores via co-condensation with tetraethylorthosilicate as primary silica source. This sample was divided into two parts. One was extracted with ethanol/ hydrochloric acid (or sulfuric acid) solution and reacted to give 2,5-dimercapto-1,3,4-thiadiazole-modified SBA15(denoted SBA15-DMTe, where e stands for extraction). The other part 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 (denoted as SBA15-DMTd sample).

2.2. 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 hours at 110°C under vacuum.

2.3. Mercury Adsorption Measurements

Mercury adsorption data presented here were obtained for all materials from aqueous solutions. The desired solutions of Hg^{2+} were prepared by dilution of the proper amount of mercury (II) nitrate volumetric standard, 0.145N 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 3:1 and 6:1 were conducted.

2.4. 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.

2.5. *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).

3. Results

The BET specific surface area (Brunauer et al., 1938) for OMS modified with organic ligands 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 estimated from the amount adsorbed at a relative pressure of about 0.99. The pore size distribution (PSD) was calculated from adsorption branches of nitrogen isotherms using the BJH method (Barrett et al., 1951) improved by Kruk et al. (1997). Adsorption parameters for OMS modified with organic ligands are listed in Tables 1 and 2.

4. Discussion

4.1. *Adsorption Properties of MCM41, MCM48, and SBA15 Materials with Mercury-Specific Mono- and Multifunctional Ligands*

The multifunctional ligands incorporated into mesoporous MCM41 and MCM48 afforded materials with much higher mercury adsorption capacity in comparison to that obtained for simple thiol-functionalized mesostructures (Fryxell et al., 1997; Mercier et al., 1998; Nooney et al., 2001), which were reported to

Table 1. Adsorption characteristics of the modified OMS (MCM41, MCM48, and SBA15) with mercaptopropyl (SH), allyl-thiourea (ATU), benzoyl-thiourea (BTU), and 2,5-dimercapto-1,3,4-thiadiazole (DMT).

Sample	S_{BET} (m^2/g)	d_{BJH} (nm)	V_{tot} (cm^3/g)	C_{lig} (mmol/g)	Hg^{2+} adsorbed (g/g*)	Maximum adsorption capacity (gHg^{2+}/g)
MCM41-SH	535	3.7	0.53	2.8	–	–
MCM41-ATU	320	3.2	0.24	1.7	0.3	0.3
MCM41-BTU	380	3.0	0.45	1.5	0.6	1.0
MCM48-BTU	505	2.8	0.47	1.6	0.6	1.3
SBA15-DMTd	582	4.6	0.43	2.7	–	1.7

S_{BET}—BET specific surface area; d_{BJH}—primary mesopore diameter; V_{tot}—total pore volume; C_{lig}—surface coverage of bonded ligands.*-adsorption of Hg^{2+} ions tested for mercury:ligand ratio 3:1. Maximum adsorption capacity examined for mercury:ligand ratio equal to 6:1.

Table 2. Parameters of the modified with 2,5-dimercapto-1,3,4-thiadiazole (DMT) samples.

Sample	S_{BET} (m^2/g)	d_{BJH} (nm)	V_{tot} (cm^3/g)	C_{lig} (mmol/g)	Hg^{2+} adsorbed (g/g*)
MCM41-DMTp	270	3.1	0.2	0.6	0.20
SBA15-DMTp	201	8.2	0.3	0.5	0.04
SBA15-DMTd	514	4.7	0.4	2.4	0.83
SBA15-DMTe	714	5.5	0.7	2.0	0.97

S_{BET}—BET specific surface area; d_{BJH}—primary mesopore diameter; V_{tot}—total pore volume; C_{lig}—surface coverage of bonded ligands, *-adsorption of Hg^{2+} ions tested for mercury:ligand ratio 3:1. The SBA15-DMTd samples listed in Tables 1 and 2 denote different batches.

have a very high ligand coverage and almost 1:1 mercury: ligand capacity. In contrast, OMS with multifunctional ligands are capable to adsorb more mercury ions per one ligand, which may increase several times their adsorption capacity depending on the number of mercury-specific sites per ligand. Therefore, high adsorption capacity for MCM41 and MCM48 with immobilized multifunctional ligands was achieved despite a significant reduction in their BET surface area and pore volume (Table 1). The BET specific surface area of the materials with hexagonal arrangement of mesopores, MCM41, varies from 535 m^2/g for the sample with mercaptopropyl surface groups to 380 m^2/g for the sample with 1-benzoyl-3-propylthiourea. In contrast to MCM41, the decrease in the specific surface area upon surface modification was smaller for the materials with cubic arrangement of mesopores such as MCM48, e.g., the resulting surface area of MCM-48 with 1-benzoyl-3-propylthiourea ligand was equal to 505 m^2/g instead of 380 m^2/g observed for MCM-41 modified with the same functionality (Fig. 2). The SBA15 material that was synthesized via block-copolymer templating mechanism assures larger pores suitable for accommodation bulk multifunctional ligands without significant decrease in the surface area. Introduction of 2,5-dimercapto-1,3,4-thiadiazole ligand into the SBA15 mesostructure via one-pot synthesis reduced the number of synthesis steps allowing to obtain materials with a large surface area (up to 714 m^2/g) and the pore size of about 5.5nm. This one-pot synthesis afforded material with high ligand coverage (~2.7 mmol/g calculated from sulfur content obtained by elemental analysis) and high mercury adsorption capacity.

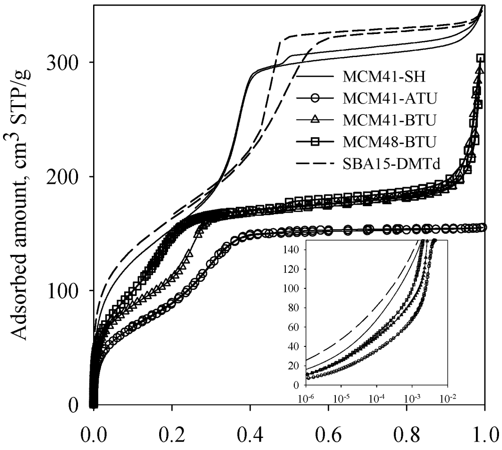

Figure 2. Nitrogen adsorption isotherms for OMS modified with mercaptopropyl (SH), allyl-thiourea (ATU), benzoyl-thiourea (BTU), and 2,5-dimercapto-1,3,4-thiadiazole (DMT) ligands. Inset shows the low pressure parts of adsorption isotherms in semi-logarithmic scale.

4.2. *Adsorption and Thermal Properties of MCM41 and SBA15 Materials with DMT Ligand Immobilized via Different Synthetic Routes*

Study of different synthesis methods for incorporation of high affinity ligands towards mercury ions into ordered mesopores allowed us to obtain materials with tailored adsorption properties. The MCM41 and SBA15 materials functionalized by 2,5-dimercapto-1,3,4-thiadiazole via post-synthesis modification exhibit low adsorption capacity. Adsorption branches of the isotherms indicate huge difference in the pore size of these materials after surface modification and confirm the preservation of two-dimensional hexagonal and three-dimensional cubic mesostructures in these two materials, respectively. Due to the significant reduction of the adsorption capacity upon post-synthesis modification, this modification leads to the SBA15 and MCM41 materials with low mercury ions uptake (0.04 and 0.2 g/g, respectively). In contrast, the recipe that involves one-pot synthesis of chloropropyl-modified SBA15 intermediate, afforded much better control of adsorption properties of the resulting material. Figure 3 shows nitrogen adsorption isotherms for SBA15 with 2,5-dimercapto-1,3,4-thiadiazole ligands introduced via template-displacement procedure (filed circles) and via chemical reaction of 2,5-dimercapto-1,3,4-thiadiazole agent with the chloropropylsilyl-modified SBA15 material obtained by extraction of the polymeric template with sulfuric acid/ethanol solution for 24 hours at 60°C (empty circles). These procedures allowed us to obtain materials with high surface area (500–700 m^2/g), large pores (*ca.* 5 nm), and relatively large pore volume (0.4–0.7 cm^3/g). Thermogravimetric study of those materials (Fig. 4) showed that they are thermally stable up to 200°C. In addition, thermogravimetry was used to monitor the degree of functionalization and the effectiveness of extraction process.

A single treatment of 0.0003 M mercury aqueous solution with 0.05 g of the DMT-modified SBA15 was sufficient to reduce mercury concentration to $5.7 * 10^{-5}$ M. For this case the K_d constant defined as the amount of adsorbed metal (μg) per gram of the

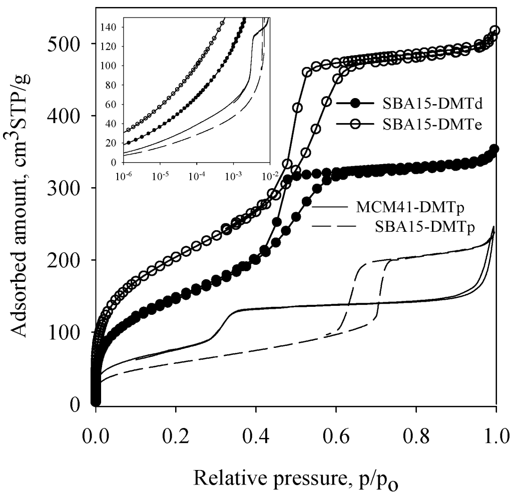

Figure 3. Nitrogen adsorption isotherms for OMS with 2,5-dimercapto-1,3,4-thiadiazole (DMT) ligands introduced via post-synthesis modification (p), modification of chloropropylsilyl-SBA15 (e), and template-displacement method (d). Inset shows the low pressure parts of the isotherms in semi-logarithmic scale.

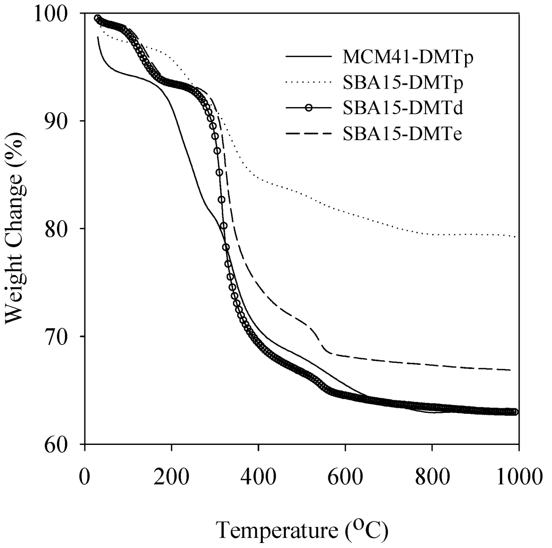

Figure 4. Thermogravimetric curves for OMS modified with 2,5-dimercapto-1,3,4-thiadiazole (DMT) via post-synthesis modification (p), modification of template-extracted chloropropylsilyl-SBA15 (e), and template-displacement procedure (d).

adsorbent divided by metal concentration (μg/ml) remaining in the eluent was equal to $1.11 * 10^8$.

5. Conclusions

The nitrogen adsorption at −196°C is a simple and very effective tool to characterize ordered mesoporous materials functionalized with mono- and multifunctional mercury-specific ligands. By choosing proper ligand and modification method ordered mesoporous silicas with mercaptopropyl, 1-allyl-3-propylthiourea, 1-benzoyl-3-propylthiourea and 2,5-dimercapto-1,3,4-thiadiazole were obtained with tailored pore size and surface area for mercury ions removal and related environmental applications. The post-synthesis modification, one-pot synthesis and template-displacement methods allow one to achieve not only the high surface coverage of multifunctional ligands but also to preserve the structural ordering of the resulting materials, and consequently, to obtain high-capacity adsorbents for removal of mercury ions and other heavy metal ions from water.

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