

Fuctionalization of SBA-16 Mesoporous Materials with Cobalt(III) Cage Amine Complex

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Surface modification of tridimensional cubic mesoporous silica, SBA-16, was investigated with pendant arm functionalized cobalt diaminosarcophagine (diAMsar) cage complex which covalently grafted onto the silica surface through the silication with sylanol group. The spectroscopic results showed that the mesoporous structure was preserved under the $[\text{Co}(\text{diAMsar})]^{3+}$ grafting reaction condition. Successful grafting prevented the cobalt diAMsar cage from leaching out from the SBA-16 support.

Key Words : SBA-16, Grafting, Cobalt, Diaminosarcophagine, Confinement effect

Introduction

Mesoporous materials, such as M41s and SBA families, are of great interest in catalysis because they possess uniformly large pore sizes (between 2.0 and 50.0 nm which are larger than microporous cavities (6-13 Å) of conventional zeolites) and extremely high surface areas (up to 1200 m²/g). Both pore sizes and surface areas make them excellent supports for new generation of heterogeneous catalysis and potential hosts for the inclusion of bulky organic and inorganic species.

Mesoporous materials with three-dimensional cubic structures are of particular interest for the applications to catalysis, chemical sensing or separation because their pores are more accessible than those of other anisotropic structures.^{1,2} Among the reported cubic mesoporous silica materials SBA-16 appears to be one of the best candidates for catalytic support or absorbent applications because of the good thermal stability of the thick wall, economical synthesis with inexpensive silica sources, and three dimensional large pores.^{2,3}

Modification of mesoporous silicates permits precise control over the surface property and pore size for specific applications, while at the same time stabilizing the materials towards hydrolysis. Mesoporous solid have been functionalized at specific sites, and were demonstrated to exhibit improved activity, selectivity, and stability in a large number of catalytic reaction and sorption processes.⁴ Thus, it is important to develop methods for the controlled, chemical modification of surfaces with introduction of precisely defined inorganic species.

Herein, we report surface modification of tridimensional cubic mesoporous silica, SBA-16, with cobalt diaminosarcophagine (diAMsar) cage complex which covalently grafted onto the silica surface. Mesoporous SBA-16 material was synthesized under microwave irradiation as we already reported.³ The cobalt diAMsar cage complex can be made cheaply and in high yield at room temperature in one step as reported by Sargeson and Harrowfield.⁵ The synthesis is

stereospecific and produces only one of the possible 16 isomers from one configuration of the chiral tris-ethylene-diamine template. The inert nature of complexes formed by diAMsar cage hexamine ligands should facilitate various applications of the complexes dependent upon the specific properties of the bound metal ion. One of these potential applications is cobalt cage complexes as electron transfer agents in, for example, photochemical conversion of solar energy.⁶ The high chemical stability of the cobalt cages allows the Co(II)–Co(III) redox states to be cycled repeatedly without decomposition. To our knowledge, no literature report about grafting cobalt diAMsar cage complex on surface of mesoporous materials has yet been published.

Experimental Section

Silylation of $[\text{Co}\{(\text{NH}_2)_2\text{sar}\}]^{3+}$: $[\text{Co}\{(\text{NH}_2)_2\text{sar}\}]\text{Cl}_5\cdot\text{H}_2\text{O}$ was prepared as described previously.⁵ The analogous acetate salt was obtained by passing a solution of $[\text{Co}\{(\text{NH}_2)_2\text{sar}\}]\text{Cl}_5\cdot\text{H}_2\text{O}$ (5.70 g, 10 mmol) in water (500 mL) through a column containing a tenfold excess of acetate-form Dowex 1×8 anion exchange resin. The complex was washed from the column with water, the eluate was concentrated to a viscous, orange oil under reduced pressure, the residue was almost dried by twofold co-evaporation of ethanol, and finally it was crystallized from ethanol by the addition of diethyl ether. The acetate salt of cobalt diAMsar complex was then suspended into 200 mL of MeCN and following by 4.25 g (40 mmol) of Na₂CO₃ and 4.82 g (20 mmol) of 3-chloropropyltrimethoxysilane. The mixture was then heated under reflux for 24 hours under nitrogen atmosphere. The precipitate was filtered off while hot and washed with MeCN (2 × 30 mL). Evaporation of the combined filtrate gave 8.63 g of $[\text{Co}\{(\text{Si}(\text{OMe})_3(\text{CH}_2)_3\text{NH}_2)_2\text{sar}\}]^{3+}$.

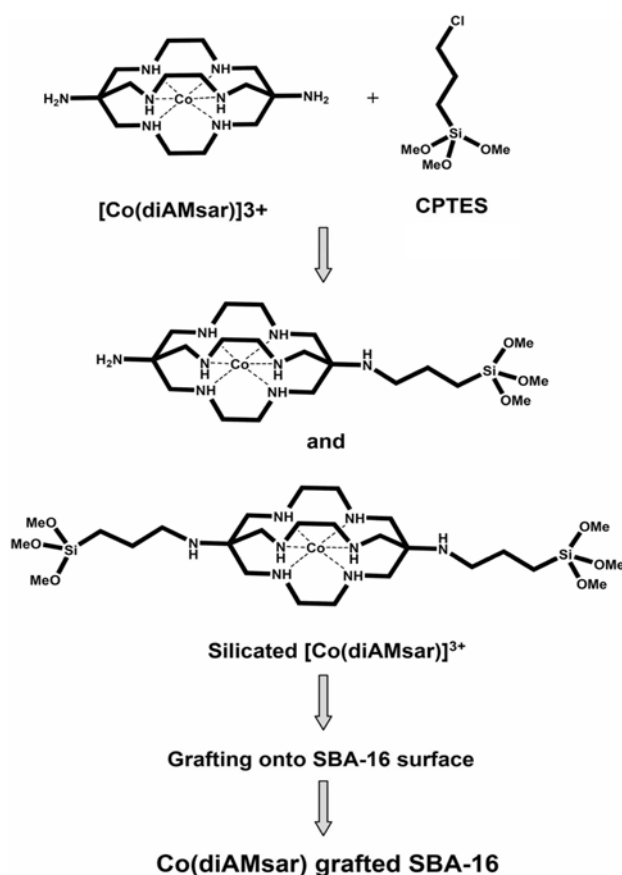
$[\text{Co}(\text{diAMsar})]$ -SBA-16: $[\text{Co}\{(\text{Si}(\text{OMe})_3(\text{CH}_2)_3\text{NH}_2)_2\text{sar}\}]^{3+}$ was added to a vigorous-stirred toluene suspension (200 mL) of 10 g SBA-16. The mixture was then heated under reflux for 24 hours under nitrogen atmosphere. The

$[\text{Co}(\text{diAMsar})]^{3+}$ grafted SBA-16 was filtered and the non grafted $[\text{Co}\{(\text{Si}(\text{OMe})_3(\text{CH}_2)_3\text{NH}_2)_2\text{sar}\}]^{3+}$ was removed by Soxhlet-extraction for 24 hours with ethanol. The resulting solid was dried under vacuum. Based on different weight before and after grafting reaction, we found that the loading of $\text{Co}(\text{diAMsar})$ complex was 0.8 mmol/gram.

Characterization. The prepared samples were characterized by several instrumental analysis techniques. The crystallinity of the samples was measured using powder X-ray diffraction (XRD) patterns which were obtained on a Rigaku diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 0.1547$ nm). BET measurements including surface areas and pore volumes were performed using a Micromeritics porosimeter (model ASAP-2400). The samples were degassed at 300 °C for 3 h. Scanning electron microscopic (SEM) images were collected with a JEOL 630-F microscope. The FT-IR spectra were recorded at room temperature, using a Nicolet Impact 410 spectrometer over the range of 400-4000 cm^{-1} . UV-Vis-NIR diffuse reflectance spectra (DRUV) were measured with a Solidspec 3700 UV-Vis-NIR spectroscopy.

Results and Discussion

The preparation of surface functionalized SBA-16 mesoporous material by post-grafting method is represented in Scheme 1. The “externally” amine functionalized sarcophagine, 1,8-diaminosarcophagine (diAMsar), seems to be a



Scheme 1. Synthesis of $\text{Co}(\text{diAMsar})$ grafted SBA-16.

useful starting material for further functionalization.^{7,8} In fact, it has already been used as the source for a number of cage amine derivatives. In this work we introduced propyl-trimethoxysilane entities as functional groups by using modification of procedure which has been widely and successfully applied to macromonocyclic polyamines.⁹ The generally inert nature of complexes formed by cage hexamine ligands should facilitate functionalized of the complexes only on the external primary amine. However, the presence of Co^{3+} ion inside the cage complex may cause the “external” amine sites such as the 1,8-amino groups of a diaminosarcophagine metal ion complex considerably weaker nucleophiles than those in the free base. As reported previously, nucleophilic substitution by this ‘external’ amine pendants could happen on both site and only one site,⁷ however both mono-functionalized and bis-functionalized $\text{Co}(\text{diAMsar})$ can be grafted on SBA-16 surface. Since grafting through two spacer groups can yield more stable and robust material, we attempted to maximize the chloropropyl bis-functionalized $\text{Co}(\text{diAMsar})$ by elongation of reaction time and the use of large excess chloropropyl trimethoxysilane alkylating agent.

This functionalization provided pendent arms useful for grafting the cage complex onto silica surface. The silylated cobalt cage complex (functionalized $[\text{Co}(\text{diAMsar})]^{3+}$) was then anchored on SBA-16 surface by reacting it with SBA-16 in toluene through silylation reaction between surface silanol group of the SBA-16 and methoxy group of the complex (see experimental section). The successful grafting of the cobalt diAMsar complex was visually confirmed by its resistance to leaching in strong acidic medium (2 M HCl solution), by using UV-Vis spectroscopy we observed that after stirring in 2 M HCl medium for 24 hour there was no $\text{Co}(\text{diAMsar})$ complex leaching out from mesoporous material. Near infrared, infrared and UV-Vis spectroscopy were used to identify the presence of cobalt cage complex which is grafted on the surface of SBA-16. Figure 3. shows NIR spectra of pure SBA-16 and $\text{Co}(\text{diAMsar})$ grafted SBA-16 mesoporous materials. The appearance of peaks between 6000 to 5500 cm^{-1} and peak at 6460 cm^{-1} , which were assigned to aliphatic CH_2 first overtone stretching vibration and amine NH stretching respectively, confirmed the existence of $\text{Co}(\text{diAMsar})$ in the SBA-16 mesopore. Two sharp peaks on IR spectra of neat cobalt diAMsar complex at 3070 cm^{-1} and 2871 cm^{-1} which can be identified as the primary C-H stretching were observed with small blue shift (3094 cm^{-1} and 2881 cm^{-1} respectively) on IR spectra of $\text{Co}(\text{diAMsar})$ grafted SBA-16. Small blue shifts are also observed on 1463 cm^{-1} and 1403 cm^{-1} peaks of C-N stretching (1446 and 1315 cm^{-1} respectively on neat $\text{Co}(\text{diAMsar})$ IR spectra). $\text{Co}(\text{diAMsar})$ grafted SBA-16 showed three typical ${}^1\text{T}_{1g} \leftarrow {}^1\text{A}_{1g}$, ${}^1\text{T}_{2g} \leftarrow {}^1\text{A}_{1g}$ and metal to ligand charge transfer (MLCT) electronic transition peaks at UV-Vis region for Cobalt hexamine complexes. The transitions ${}^1\text{T}_{1g} \leftarrow {}^1\text{A}_{1g}$ and ${}^1\text{T}_{2g} \leftarrow {}^1\text{A}_{1g}$ occur at the same energies level to neat $\text{Co}(\text{diAMsar})$ complex.⁵

The calcined parent SBA-16 mesoporous material has

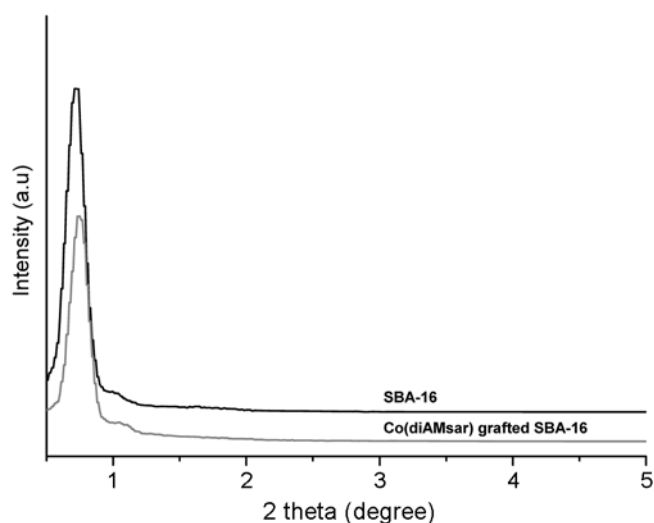


Figure 1. Powder XRD patterns of SBA-16 and Co(diAMsar) grafted SBA-16.

uniform morphology as shown in scanning electron microscopy (SEM) picture, large surface of 1016 m²/g, and an average pore size of 5 nm, as determined using the nitrogen adsorption technique. The X-ray powder diffraction pattern shows a very intense peak and additional high order peaks with lower intensities, indicating a significant degree of long range ordering of the structure and well organized cubic pore arrays of the sample. The XRD data show that the mesoporous structure was preserved under the [Co(diAMsar)]³⁺ grafting reaction condition (Fig. 1). [Co(diAMsar)]³⁺ grafted SBA-16 shows lower intensity peaks and small shift of 2 theta to higher degree (0.01 degree). The specific area and the pore diameter of SBA-16 were decreased. Those changes were due to the surface modification by the grafting reaction onto the surface of mesoporous support.

Figure 2 illustrates the N₂ adsorption/desorption isotherms of both SBA-16 and Co(diAMsar)-grafted SBA-16. These

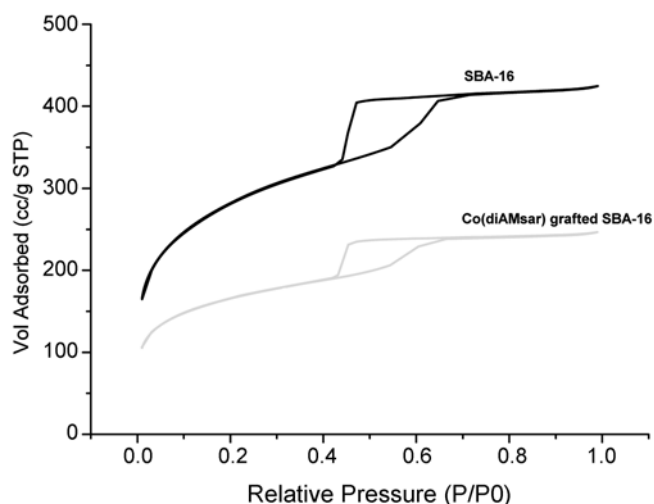


Figure 2. N₂ adsorption-desorption full isotherm for SBA-16 and Co(diAMsar) grafted SBA-16.

Table 1. Physicochemical Characteristics of SBA-16 and Co(diAMsar) Grafted SBA-16

Sample	S _A BET (m ² /g)	TPV (cc/g)	Meso PV (cc/g)	MicroPV (cc/g)	D _p (nm)
SBA-16	1019	0.65	0.53	0.12	5.40
Co(diAMsar)-SBA-16	693	0.38	0.28	0.10	4.77

S_ABET: BET surface area; TPV: total pore volume; Meso PV: mesopore volume; Micro PV: micropore volume; D_p: pore diameter

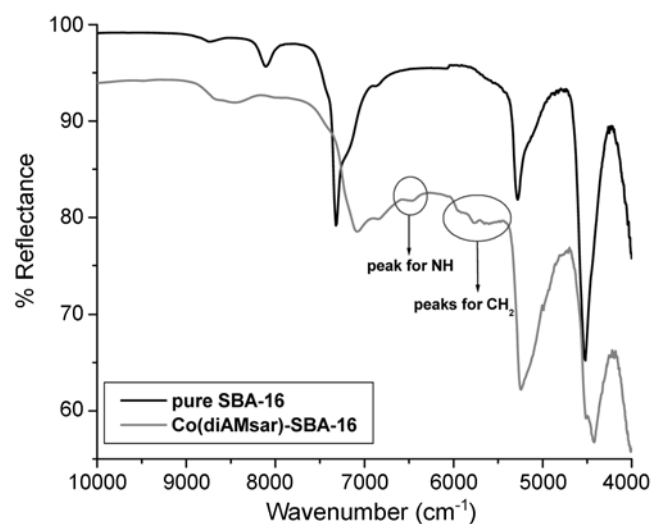


Figure 3. Near Infrared spectra for pure SBA-16 (black) and Co(diAMsar)-SBA-16 (gray).

isotherms with characteristic “hysteresis loop” resembled the type IV isotherm, typical for mesoporous materials. BET surface areas measured from these isotherms were 1019 and 693 m²/g for SBA-16 and Co(diAMsar)-grafted SBA-16, respectively. The presence of Co(diAMsar) grafting on SBA-16 wall caused significantly decrease of the surface area and systematical decrease in mesopore volume,

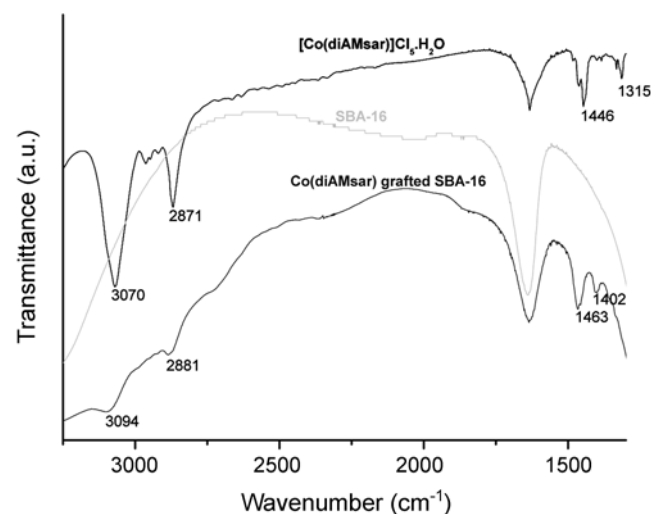


Figure 4. FTIR spectra of Co[(diAMsar)]Cl₃·H₂O, SBA-16 and Co(diAMsar) grafted SBA-16.

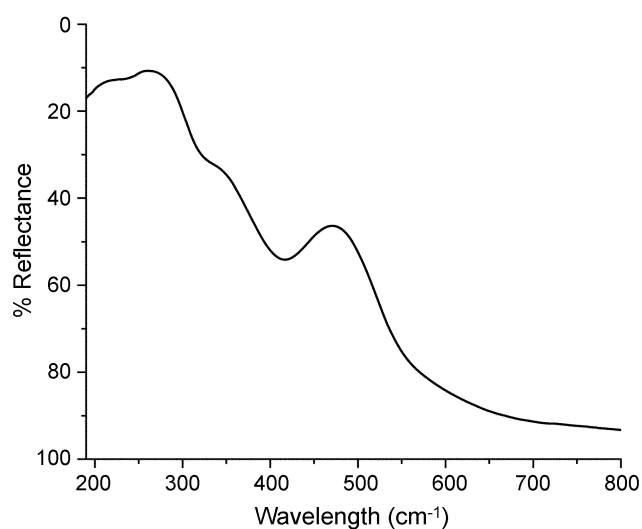


Figure 5. UV-Visible spectra of Co(diAMsar)-SBA-16.

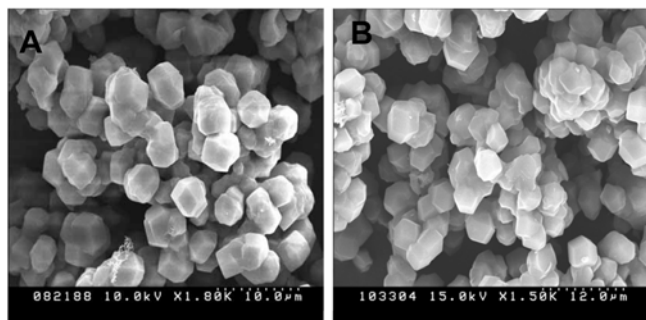


Figure 6. SEM pictures of (A) SBA-16 and (B) Co(diAMsar) grafted SBA-16.

micropore and adsorption pore diameter as shown in Table 1.

Conclusion

Functionalization of Co(diAMsar) cage complex was

provided by the grafting the cage complex having pendent arms onto SBA-16 surface. The Co(diAMsar) grafted SBA-16 showed a preserved mesoporous structure, uniform morphology, and significant lower surface area comparing with its parent SBA-16.

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