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SBA-15 mesoporous silica coated with macrocyclic calix[4]arene derivatives: Solid extraction phases for heavy transition metal ions

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ABSTRACT

A layer of macrocyclic calix[4]arene derivatives has been grafted on the internal surface of the mesochannels of the ordered mesoporous SBA-15 to develop highly efficient trap for heavy transition metal (HTM) ions. To ensure the successful anchoring of calix[4]arene derivatives on the surface of SBA-15, two different types of calix[4]arene derivatives, one with one trimethoxysilane functional group and another with two trimethoxysilane functional groups have been explored. XRD, N_2 adsorption and TEM results provide strong evidence that the mesoporous structure of the supporting materials retain their long range ordering throughout the grafting process. Solid-state NMR, TG and FT-IR spectroscopy indicate that both types of calix[4]arene derivatives can be well-anchored on the surface of the wall of SBA-15. Calix[4]arene derivative with only one trimethoxysilane functional group showed high grafting efficiency compared to that with two trimethoxysilane functional groups due to the intramolecular and intermolecular polycondensation between two trimethoxysilane functional groups. The HTM ions extraction capacity in aqueous solution of macrocycle functionalized SBA-15 nanohybrides for a series of HTM ions has been studied. The obtained materials demonstrated very high HTM ions extraction capacity up to 96% for Pb^{2+} in aqueous solution.

1. Introduction

The synthesis of porous silica-organic hybrid materials has become a fascinating area of research with great promise in catalysis, separation and sensor design as well as adsorption because of the high surface areas and large pore volume of inorganic matrix and the choice of versatile organic functional groups [1–4]. Depending on the lengths of alkyl chains, these organically modified silica porous materials normally exhibit hydrophobic properties and have the flexibility to be further modified for a variety of applications [5–16]. Many researches have focused on the preparation of organic-functionalized mesoporous silicas by the direct incorporation of organic functional groups through co-condensation, or covalent versus non-covalent linkage, or post-synthetic grafting of the organic groups onto the surface of the mesoporous silica [7–9]. Grafting method consists of reaction of a suitable organosilane with surface silanol groups using an appropriate solvent under reflux conditions [7], where its most apparent advantage is to well preserve the mesostructure after post-modification [9,10]. Actually, many of these investigations have utilized periodic mesoporous silicas, including HMS, MCM-41, MCM-48, SBA-15 or CMI-1 as the inorganic matrix [7,11–27]. Among them, SBA-15 materials show attractive properties due to its large pore size (from 10 nm to over 30 nm) and improved thermal and hydrothermal stability.

Since their discovery as by-products in the phenol–formaldehyde condensation to prepare bakelites [28,29], the calixarenes have gained much attention for their application as both surfactants and chemoreceptors. Calixarenes are characterized by a wide upper rim and a narrow lower rim and a central annulus. Their rigid cup-like hydrophobic three-dimensional cavities enables calixarenes to act as host molecules. By functionally modifying either the upper and/or lower rims, it is possible to prepare various derivatives with different selectivity for various guest ions and small molecules [30–32]. Calixarenes are efficient sodium ionophores used in commercial applications as sodium selective electrodes for the measurement of sodium levels in blood. With the right

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chemistry these molecules exhibit great selectivity towards other cations. Calixarenes can form complexes with cadmium, lead, lanthanides and actinides [30]. Calixarenes or calixarene-derivatives have also been used to prepare the ion-selective electrode (ISE) and bulk optode sensing devices. However, till now, there have little reports on the calixarene-based derives grafted on the surface of mesoporous silica for environmental remediation to eliminate selectively the mercury (II) ions [33] and other metal ions.

Therefore, our synthetic strategy is to use the periodically mesoporous SBA-15 with large pore diameter and also huge surface area as a host for immobilizing the calix[*n*]arene derivatives as a potential highly specific HTM ions extraction. There exists a series of calix[*n*]arenes with $n = 4, 6, 8, \ldots$ while calix[4]arene presents significant advantages over its analogs since calix[*n*]arene derivatives with *n* higher than 4, i.e. 6, 8, 10, ... have different conformations and all benzene rings cannot be in the same direction, giving a deformed macro cycle. Calix[4]arenes have a very good rigidity and the internal volume around 10 nm^3. In the present work, the calix[4]arene derivatives containing one or two organosiloxane groups have been grafted on the surface of mesoporous SBA-15-type materials through a one-step incipient-wetness impregnation process at elevated temperature, which are performed by refluxing freshly activated mesoporous SBA-15 in dry toluene containing calix[4]arene derivatives. This system can decrease the limitation concerning relatively slow diffusion of the analyte in the matrix owing to the highly periodic mesoporosity in SBA-15. The multiple characterization techniques, such as XRD, nitrogen adsorption, TEM, FT-IR and solid-state ^{29}Si NMR, as well as TG, indicate that the calix[4]arene derivatives have been well-anchored on the surface of SBA-15 to generate a new class of hybrid calix[4]arene derivatives-based mesoporous silica materials possessing uniform framework mesoporosity. Furthermore, the functionalized mesoporous SBA-15 with calix[4]arene derivatives have demonstrated their high affinity and strong trap capacity for metal ions, including Hg^{2+}, Pb^{2+} and Cd^{2+}, etc., which may develop HTM ions extraction phase for environmental protection applications.

2. Experimental section

2.1. Preparation

2.1.1. Inorganic synthesis of the mesoporous silica SBA-15

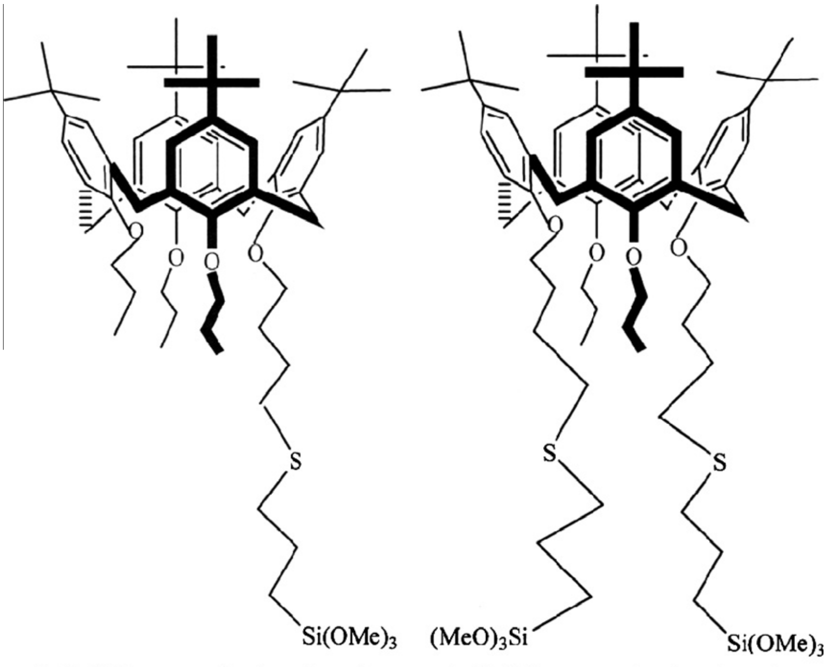
The synthesis of pure siliceous SBA-15-typed matrix was adapted from the procedure reported by Zhao et al. [34] using Pluronic P123 triblock copolymers (Aldrich, $EO_{20}PO_{70}EO_{20}$ as templates. Typically, 4.0 g of $EO_{20}PO_{70}EO_{20}$ was stirred with 30 mL of deionized water at 35 °C until fully dissolved, followed by adding 120 g of 2 M HCl aqueous solution and then dropwise addition of 8.5 g of TEOS. The mixture was stirred for further 24 h at 35 °C before transferring into a Teflon bottle sealed in an autoclave and aging at 100 °C for 2 days in an electronic oven. The white precipitate was filtered off, washed several times with deionized water and dried at 60 °C. The copolymer P123 was removed by calcination under air at 500 °C for 4 h.

2.1.2. Synthesis of the calix[4]arene derivatives

To study the efficiency of the grafting of calyx[4]arene derivatives on the surface of SBA-15 mesoporous silica, two types of calyx[4]arene derivatives with one trimethoxysilane group, labeled calix[4]arene derivative-1 (Scheme 1), or two trimethoxysilane groups, labeled as calix[4]arene derivative-2 (Scheme 1) have been used. The synthesis procedure and characterization of intermediate and final products by a series of instruments are detailed in supporting information.

2.1.3. Grafting of the calix[4]arene derivatives on SBA-15

Mesoporous silica SBA-15 powders (0.5 g) were dried under vacuum for 12 h at 100 °C and then introduced into dried toluene (10 mL) under an argon atmosphere. After stirring for 30 min, dried toluene containing around 0.5 mmol calix[4]arene derivative-1 (0.31 g) or calix[4]arene derivative-2 (0.37 g) was quickly added into the above suspension. The reaction mixture was stirred at room temperature for 2 h and then refluxed at 150 °C for 24 h.



Scheme 1. Molecular structures of calix[4]arene-derivative-1 and 2.