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Green synthesis of mesoporous molecular sieve incorporated monoliths using room temperature ionic liquid and deep eutectic solvents

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ABSTRACT

A hybrid monolith incorporated with mesoporous molecular sieve MCM-41 of uniform pore structure and high surface area was prepared with binary green porogens in the first time. With a mixture of room temperature ionic liquids and deep eutectic solvents as porogens, MCM-41 was modified with 3-(trimethoxysilyl) propyl methacrylate (γ-MPS) and the resulting MCM-41-MPS was incorporated into poly (BMA-co-EDMA) monoliths covalently. Because of good dispersibility of MCM-41-MPS in the green solvent-based polymerization system, high permeability and homogeneity for the resultant hybrid monolithic columns was achieved. The MCM-41-MPS grafted monolith was characterized by scanning electron microscopy, energy dispersive spectrometer area scanning, transmission electron microscopy, FT-IR spectra and nitrogen adsorption tests. Chromatographic performance of MCM-41-MPS grafted monolith was characterized by separating small molecules in capillary electrochromatography, including phenol series, naphthyl substitutes, aniline series and alkyl benzenes. The maximum column efficiency of MCM-41-MPS grafted monolith reached 209,000 plates/m, which was twice higher than the corresponding MCM-41-MPS free monolith. Moreover, successful separation of non-steroidal anti-inflammatory drugs and polycyclic aromatic hydrocarbons demonstrated the capacity in broad-spectrum application of the MCM-41-MPS incorporated monolith. The results indicated that green synthesis using room temperature ionic liquid and deep eutectic solvents is an effective method to prepare molecular sieve-incorporated monolithic column.

1. Introduction

Polymer monolithic column prepared by in situ polymerization have been developed as a method for efficient separation owing to excellent properties of high resolution, long service life, excellent permeability, inexpensive expenditure and fast transfer kinetics [1,2]. The large through-pores in polymer monolith permit high flow rates at low backpressures and the enhancement of mass transfer rate. It has been widely adopted in high performance liquid chromatography (HPLC), capillary electrochromatography (CEC), capillary liquid chromatography (CLC) and solid-phase microextraction (SPME) [3–6]. However, neat polymer monoliths usually suffer from poor column efficiency by virtue of smaller surface area, lack of sufficient interaction sites and mesopores [7]. Recently, the fabrication of polymer monolith incorporated with functional nanoparticles has been considered as a powerful solution to improve column efficiency [8]. Multifunctional polymer nanocomposites simultaneously equipped great thermal stability, large electrical conductivity, high strength and novel optical responses have turned into popular research topic [9,10]. To data, inorganic and organic hybrid monolith, including grapheme oxide (GO) [11], carbon nanotubes (CNT) [12], metal-organic frameworks [13], hydroxyapatite [14], metals [15], and metal oxides [16], have been developed with commendable characteristic structure and selectively tailored surface chemistry for a number of separation.

Mesoporous material MCM-41, one member of silicate/aluminosilicate mesoporous molecular sieves, has demonstrated potential capacity in various fields for its high surface area and uniform pore system [17]. As reported, applications of MCM-41 include catalysis, sensing, optics, adsorption, electronics, separation and drug delivery [18–23]. A significant promotion of chromatographic performance of stationary phase containing MCM-41 spheres as sorbent in HPLC was observed [22]. Coated and packed capillary column with MCM-41 mesoporous material as a composition of stationary phase was also reported in GC [24,25]. However, the application of mesoporous MCM-41 as inorganic particles in hybrid stationary phase for CEC was not found.

Recently, interest in room temperature ionic liquids (RTILs) as green solvent for application is ever-increasing [26]. As a type of species constituted entirely of ions that exist in the molten state at

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room temperature, RTILs have important feature: virtually no vapor pressure, wide range of solubility, miscibility, and high viscosity. Thus, they provide a solvent environment that is quite unlike any other available at room temperature. For example, some research revealed that RTILs were capable of affording a feasible and promising way for nanoparticles suspension since the inherent quality of strong viscosity [27]. Thus, homogeneous monolith matrix could be obtained after polymerization. To overcome the potential toxicity of RTILs, deep eutectic solvents (DESs) are developed as alternative RTILs [28], which are consisted of hydrogen bond acceptors (e.g., quaternary ammonium salts) and hydrogen bond donors. Compared with traditional RTILs, DESs could be prepared conveniently and were comparatively cheap with optional constituents and properties. Similar to RTILs, DESs was demonstrated to have sufficient suspending properties of functional nanoparticles in pre-polymerization solution as well [29]. The combination of RTILs and DESs as reaction medium has displayed advantage in preparing inorganic and organic hybrid monolith [12].

Herein, we reported a feasible method for preparation of MCM-41 incorporated hybrid monolith with binary green porogen system of RTILs and DESs. By our knowledge, it was the first time to prepare monolith grafted with molecular sieve. In the suitable type and proportion mixture of RTILs and DESs, MCM-41 was well-suspended in the polymerization system. The MCM-41 incorporated monolith was characterized by scanning electron microscopy, energy dispersive spectrometer area scanning, transmission electron microscopy, FT-IR spectra and nitrogen adsorption tests. The separation ability and column efficiency of the newly designed MCM-41 hybrid monolith were evaluated in CEC.

2. Experimental

2.1. Chemicals and materials

Anthracene, acenaphthylene, chrysene, fluoranthene, fluorine, naphthalene, pyrene, benzo(a)anthracene, benzo(b)fluoranthene, acetanilide, 1-naphthylamine, 2-nitroanline, 4-fluoroaniline, 1-naphthol, 1-chloronaphthalele, 1-methylnaphthalene, 1-bromonaphthalene, m-cresol, resorcinol, 2,6-dichlorphenol, 2,6-dimethylphenol and choline chloride (ChCl, AR grade) were purchased from Aladdin (Shanghai, China). Acetophenone (AR grade) and butyl methacrylate (BMA, AR grade) were purchased from Bodi Chemical Reagent (Tianjin, China). Azobisisobutyronitrile (AIBN, AR grade) and 2, 5-dihydroxyacetophenone (98%) were obtained from J & K CHEMICA Co. Ltd. (Beijing, China). 2-Acrylamido-2-methyl-propanesulfonic acid (AMPS, 98%), 3-(trimethoxysilyl) propyl methacrylate (γ-MPS, 98%), butyrophenone (99%), ethylene glycol dimethacrylate (EDMA, 98%) and acetonitrile (ACN, HPLC grade) were supplied by Sigma-Aldrich (St. Louis, MO, USA). All the RTILs used were 98%, which were from Chengjie Chemical Co. Ltd. (Shanghai, China). Other reagents were at least analytical reagents and were purchased from Tianjin Chemical Reagent Co. Ltd. (Tianjin, China). Bare capillary (100 μm ID, 375 μm OD) was supplied by Xinnuo Optic Fiber Plant (Hebei, China). Mesoporous molecular sieve, MCM-41 (200 nm of particle diameter), was purchased from JCNANO Reagent Co. Ltd. (Nanjing, China).

2.2. Silanization of MCM-41

0.5 g of pristine MCM-41 was suspended with 50 mL toluene by ultrasonic dispersion 20 min in flask. 10 mL of silanization reagent γ-MPS was mixed with the MCM-41 suspension. After sonicating for 10 min, the mixture was degased with nitrogen for 5 min. The flask was sealed and placed into water bath at 55 °C with magnetic stirring of 500 r/min for 24 h. After silanization, the obtained suspension was recovered by successive centrifugation-resuspension cycling with toluene and methanol. The MCM-41-MPS was dried at 40 °C in vacuum to constant weight.

Table 1
Composition of MCM-41-MPS incorporated monoliths.

Column	[HMIM]BF$_4$ (μL)	ChCl-PG (μL)	MCM-41-MPS (wt/wt%)
1	216	144	10
2	144	216	10
3	180	180	10
4	252	108	10
5	288	72	10
6	216[a]	144	10
7	216[b]	144	10
8	216[c]	144	10
9	216[d]	144	10
10	216[e]	144	10
11	216[f]	144	10
12	216	144[g]	10
13	216	144[h]	10
14	216	144[i]	10
15	216	144[j]	10
16	216	144[k]	10
17	216	144[l]	10
18	216	144	5
19	216	144	15
20	216	144	20

[a] The amount of [BMIM]BF$_4$.
[b] The amount of [OMIM]BF$_4$.
[c] The amount of [DMIM]BF$_4$.
[d] The amount of [HMIM]HSO$_4$.
[e] The amount of [HMIM]PF$_6$.
[f] The amount of [HMIM]Br.
[g] The amount of DESs (choline chloride/ethylene glycol, 1/2, mol/mol).
[h] The amount of DESs (choline chloride/butylene glycol, 1/2, mol/mol).
[i] The amount of DESs (choline chloride/methyl alcohol, 1/2, mol/mol).
[j] The amount of DESs (choline chloride/ethyl alcohol, 1/2, mol/mol).
[k] The amount of DESs (choline chloride/butyl alcohol, 1/2, mol/mol).
[l] The amount of DESs (choline chloride/glycerol, 1/2, mol/mol).

2.3. Preparation of DESs

In this investigation, DESs were synthesized with ChCl and alcohols. All of reaction composition for DESs preparation was treated by vacuum drying at 60 °C for 24 h before use. ChCl was mixed with different type of alcohols (1:2, mol/mol). After the mixture was heated to melt at 100 °C in oil bath for 3–6 h, a homogeneous colorless solution was obtained. Synthesized DESs were stored in drier until use.

2.4. Preparation of MCM-41-MPS grafted capillary monolith

Bare capillary was continuously flushed by pumping NaOH solution (1 mol L^{-1}) and deionized water for 30 min, respectively. The capillary was then flushed with the solution of 0.4% γ-MPS/acetic acid (6 mmol L^{-1}) for 90 min. The capillary after derivatization was then rinsed with deionized water and dried with nitrogen before use.

Pre-polymerization mixture comprised of EDMA (0.075 mmol, cross-linking monomers), BMA (0.175 mmol, functional monomers), AMPS (1%, wt/wt%, electroosmotic flow provider), AIBN (1%, wt/wt%, initiator), MCM-41-MPS (10%, wt/wt%) and binary solvent, which was composed of RTILs and DESs (Table 1). The mixture above was sonicated for 10 min, degassed with nitrogen for 5 min then introduced into the derivative capillary with a syringe. Both inlet and outlet of capillary were plugged with rubber septum before the capillary was putted into a 65 °C thermostat water bath for 30 min. After reaction, unreacted reagents were removed by rinsing the packed capillary with acetonitrile. Detection window was generated by burning 2–3 mm segment of polyimide coating at distance of 10 cm from outlet end of the capillary monolith. The MCM-41-MPS free monolith was prepared with same way in absence of MCM-41-MPS.