# In Situ Hydrothermal Grown Silicalite-1 Coating for Solid-Phase Microextraction

Heyun Fu and Dongqiang Zhu*

State Key Laboratory of Pollution Control and Resource Reuse/School of the Environment, Nanjing University, Jiangsu 210093, China

Ⓢ *Supporting Information*

ABSTRACT: A novel fiber coated with silicalite-1 for solid-phase microextraction (SPME) was prepared by in situ hydrothermal growth method. Six substituted benzenes (nitrobenzene, *p*-dichlorobenzene, *m*-dichlorobenzene, 1,3,5-trichlorobenzene, *p*-chloronitrobenzene, and *m*-chloronitrobenzene) were employed as model analytes. The fiber exhibited high thermal stability (little weight loss up to 600 °C) and high chemical stability (no loss of function after sequential immersion in 0.1 M HCl, 0.01 M NaOH, methanol, and *n*-hexane each for at least 4 h). Compared with commercial fibers, 3−6 times higher extraction efficiencies were shown on the fiber for mono- and *p*-substituted benzenes. Under the preoptimized conditions, the fiber afforded satisfactory enhancement factors (517−1292), wide linear ranges (more than 2 orders of magnitude), low limits of detection (0.001−0.130 µg/L), and acceptable repeatability (<9.6%) and reproducibility (<8.8%). Furthermore, the fiber offered distinct shape-selectivity attributed to the uniform molecular-scale pore structure of silicalite-1. The ratios of extraction were approximately 70 between *p*-dichlorobenzene and 1,3,5-trichlorobenzene, 30 between *p*-chloronitrobenzene and *m*-chloronitrobenzene, and 3 between *p*-dichlorobenzene and *m*-dichlorobenzene. After pore narrowing by surface modification with SiCl₄, the selectivity for *p*-dichlorobenzene over *m*-dichlorobenzene was further enhanced by another 10 times. Finally, the fiber was successfully applied to analysis of a real water sample.
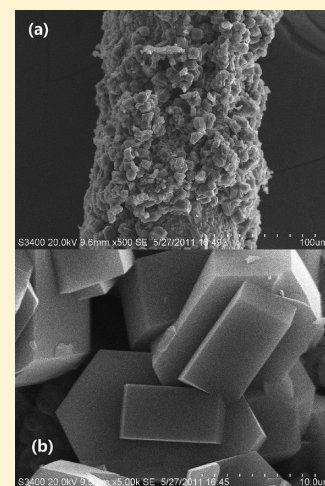
Solid-phase microextraction (SPME) has been commonly used in analysis of trace organic contaminants since first introduced by Pawliszyn and co-workers in 1990s.[1] Compared with other conventional techniques such as liquid−liquid extraction (LLE) and solid-phase extraction (SPE), SPME is organic solvent-free and easily incorporated into chromatographic analyses by integrating sampling, isolation, enrichment, and injection into one step.[2−6] Acting as the sorbing/desorbing agent of the analyte, fiber coating is considered the most important part of SPME.[7−9] Only a few coatings are commercially available for SPME nowadays, including polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB), carboxen (CAR), carbowax (CW), and their copolymers.[10,11] However, these coating materials generally present some disadvantages such as thermal and/or chemical instability, insufficient selectivity, and limited reuse times, which restrict the wider application of SPME.[11,12] Thus, it is always in high demand to develop more stable and more efficient SPME coatings having high selectivity for target compounds.

Recently, new coating materials such as polyaniline,[13] carbon nanotubes,[7,14] ZnO nanorods,[15] and graphene[16] were developed for SPME. These coating materials generally exhibit high extraction efficiency and good stability but inconspicuous selectivity. In contrast, owing to the well-defined pore structures, metal−organic framework (MOF) SPME coatings were found to have pronounced shape-selectivity for target analytes.[17]

Zeolites possess uniform, molecular-scale pore structure and are widely used as catalysts, sorbents, and ion-exchange materials.[18,19]

Silicalite-1 is a typical Mobil Fifth (MFI)-type zeolite and consists of unique three-dimensional microporous channels that are only accessible for molecules within 0.6 nm in diameter.[20] A number of studies reported the selective adsorption of benzene and *p*-substituted benzenes over *o*- and *m*-substituted benzenes on MFI-type zeolites including silicalite-1.[21−25] As a pure silica zeolite, silicalite-1 displays high thermal and chemical stability, as well as relatively high surface hydrophobicity,[26−28] primarily due to the absence of permanent charge. Furthermore, silicalite-1 is easy to grow on the surfaces of various substrates such as alumina and stainless steel.[29−32] All the characteristics mentioned above indicate that silicalite-1 is an ideal coating material for SPME. However, to the best of our knowledge, thus far, no reports published have employed silicalite-1 as SPME coatings.

In the present study, a novel SPME fiber coated with silicalite-1 was prepared by an in situ hydrothermal growth method. The analytical performance of the silicalite-1-based SPME/gas chromatographic-electron caption detection (GC-ECD) method was investigated under the preoptimized conditions for mono- and *p*-substituted benzenes. The extraction efficiency of three couples of substituted benzenes slightly differing in molecular dimension was also compared to test the shape-selectivity of the coating material. The pore size of silicalite-1 was further narrowed
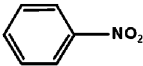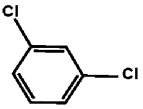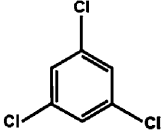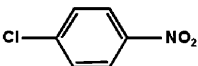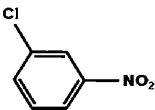
Table 1. Chemical Structures, Air−Water Partition Coefficients (K_{AW}), n-Octanol−Water Partition Coefficients (K_{OW}), and Dynamic Diameters of Analytes

Analyte	Chemical structure	Log K_{AW}[a] (mol/L)	Log K_{OW}[a] (L/L)	Dynamic diameter[b] (nm)
NB		-3.12	1.85	0.58
p-DCB		-1.04	3.45	0.58
m-DCB		-0.86	3.47	0.65
1,3,5-TCB		-0.36	4.19	0.77
p-CNB		-3.03	2.50	0.58
m-CNB		-3.39	2.48	0.69

[a]From Schwarzenbach et al.[54] [b]Calculated on the basis of the molecular structures at the energy minimum state using MM2 method by Chem 3D Ultra 8.0.

by a surface modification technique to enhance the selectivity. Finally, a real water sample was analyzed under the optimized conditions.

EXPERIMENTAL SECTION

Reagents and Chemicals. The six analytes were nitrobenzene (NB, 99.5%, Fluka, Switzerland), p-dichlorobenzene (p-DCB, 99.5%, Fluka), m-dichlorobenzene (m-DCB, 98%, Sigma Aldrich, USA), 1,3,5-trichlorobenzene (1,3,5-TCB, 99%, Supelco, USA), p-chloronitrobenzene (p-CNB, 100%, Accu-Standard, USA), and m-chloronitrobenzene (m-CNB, 99%, Sigma Aldrich). Their chemical structures, air−water partition coefficients (K_{AW}), n-octanol−water partition coefficients (K_{OW}), and dynamic diameters are listed in Table 1.

Tetrapropylammonium bromide (TPABr, 98%, Tokyo Chemical Industry, Japan), tetraethyl orthosilicate (TEOS, analytical grade, Sinopharm Chemical Reagent, China), and sodium hydroxide (NaOH, analytical grade, Nanjing Chemical Reagent, China) were used for the synthesis of silicalite-1. Silicon tetrachloride ($SiCl_4$, 98%, Tokyo Chemical Industry) was employed to modify the surface of silicalite-1 coating. Sodium chloride (NaCl, 98%, Sigma) was used to adjust sample ionic strength. High-performance liquid chromatography (HPLC) grade methanol and n-hexane were purchased from Tedia (USA). Purified water was obtained from a Milli-Q nanopure water system (Millipore, USA). Surface water (0−0.5 m depth) sample was collected from the Meiliang Bay, Taihu Lake in Jiangsu Province, China. The sample was stored in a 1 L brown glass bottle (with screw cap), which was transported to the laboratory in an ice bag. Upon arrival, the sample was analyzed immediately without any further pretreatment.

The total organic carbon (TOC) content of the sample was measured to be 16.4 mg/L.

Individual stock solutions of the six analytes (1000 mg/L) were prepared in methanol. Stock solutions of two or three desired substituted benzenes mixed in proper proportions were also prepared in methanol. All stock solutions were stored in the dark at 4 °C until use.
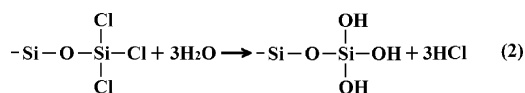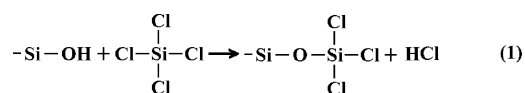
Instrumentation. A gas chromatography (GC, 6890N, Agilent, USA) equipped with an electron-capture detector was employed for all analyses. A narrow inlet liner (1.0 mm i.d.) was used to improve the chromatographic peak shape.[33] An HP-5 capillary column (30 m × 0.32 mm i.d. × 0.25 μm) (Agilent) was used for the analysis of NB, p-DCB, p-CNB, and 1,3,5-TCB. High purity nitrogen was used as carrier gas at a flow rate of 1.6 mL/min. The injector and detector temperatures were set at 270 and 280 °C, respectively. The oven temperature was initially set at 120 °C, then raised to 200 °C at a ramping rate of 10 °C/min and to 250 °C at a ramping rate of 30 °C/min, and held for 5 min. A DB-WAX capillary column (30 m × 0.32 mm i.d. × 0.25 μm) (Agilent) was used for the separation of the isomers (p- and m-CNBs, p- and m-DCBs). The oven temperature was programmed as follows: initially at 50 °C and held for 2 min, raised to 170 °C at 5 °C/min, and then raised to 240 °C at 30 °C/min and held for 5 min.

Commercial SPME fibers (100 μm PDMS, 65 μm PDMS/DVB, and 85 μm PA) and fiber holder were purchased from Supelco. Prior to use, all fibers were conditioned following the guidelines provided by the manufacturer. An HJ-3 stirring hot plate (Guangzhou GuoHua Electric Appliance, China) was used to control the temperature and stirring rate during the extraction process.

Scanning electron microscopy (SEM) images of the silicalite-1 coated fiber were collected on an S-3400N II (Hitachi, Japan). The X-ray diffraction (XRD) pattern of silicalite-1 was recorded with a D/max-RA powder diffraction meter (Rigaku, Japan) using Cu Kα radiation within a range of 3−30°. The thermal stability of silicalite-1 was examined using a Pyric 1 DSC thermogravimetric analyzer (PerkinElmer, USA).

Preparation and Modification of Silicalite-1 Coated Fiber. *Preparation.* Stainless steel wires (80 mm in length and 140 μm in diameter) (SUS304, Nantong Lili Steel Wire Factory, China) were chosen as the fiber core. The wire was first sonicated in 1.0 M HCl for 30 min to generate a rough surface (the diameter reduced to about 110 μm, see Supporting Information Figure S1) and then sonicated in methanol and in water,[34] followed by air-drying. Silicalite-1 coating was prepared by the in situ hydrothermal growth method according to the literature with slight modification.[29−31] The synthesis mixture consisting of 1.0 TEOS/0.8 TPABr/0.8 NaOH/180 H_2O (molar composition) was prepared and stirred at room temperature for 2 h and then was transferred to a Teflon-lined autoclave. The pretreated wire was placed into the autoclave and immersed in the mixture at a depth of 2.0 cm. The autoclave was then heated at 185 °C for 48 h. After cooling to room temperature, the coated wire and the excess product (material formed in the bulk phase) were washed repeatedly to neutrality with distilled water and dried at 100 °C overnight. To remove the organic template, the resulting materials were calcined in air at 500 °C at a ramping rate of 1 °C/min, held for 8 h, and then cooled to room temperature at a ramping rate of 1 °C/min. The coated part of the wire was cut into 1 cm in length.

Modification. The silicalite-1 coating was modified by $SiCl_4$ using a chemical liquid deposition method,[21,35] according to the following reactions:

$$-Si-OH + Cl-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Si}}-Cl \longrightarrow -Si-O-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Si}}-Cl + HCl \qquad (1)$$

$$-Si-O-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Si}}-Cl + 3H_2O \longrightarrow -Si-O-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-OH + 3HCl \qquad (2)$$

First, $SiCl_4$ condenses with the silanol groups on the silicalite-1 surface (eq 1); second, the newly formed Si−Cl bonds on the silicalte-1 surface hydrolyze to form silanol groups (eq 2), which could participate in the condensation reaction again. Because the molecular diameter (approximately 0.71 nm) of $SiCl_4$ is larger than the pore sizes (see below) of silicalite-1, the above reactions are deemed to occur only on the external surface and the pore mouth of silicalite-1.

To initiate the modification, the fiber coating was immersed in a 20 mL mixture of *n*-hexane and $SiCl_4$ at a volume ratio of 25:1, which was stirred at room temperature for 6 h. Then, the coated fiber was washed repeatedly with distilled water until neutral. The modification was implemented by repeating the above-described procedure two times.

Analysis Procedures. All extractions were carried out in 40 mL glass vials equipped with polytetrafluoroethylene-lined screw caps using the direct immersion technique (DI-SPME). Before each extraction, the silicalite-1 coated fiber was conditioned at 280 °C for 5 min. Working solutions were prepared 60 min before extraction by spiking the stock solution of target compound(s) into 30 mL of water. The methanol carrier was kept below 0.1% (v/v) to minimize possible cosolvent effects.[36]

It should be noted that a 10 mL headspace had negligible effects on extraction in the experimental setting, as estimated using Henry's Law constants of the three test analytes according to a previously developed method.[37,38] Egg-shaped Teflon stir bars were used, and the stirring rate was kept at 350 rpm. The extraction efficiency of NB, *p*-DCB, and *p*-CNB was compared between silicalite-1 coated fiber and commercial fibers under the same conditions attending to previous literature, extracted for 60 min at 30 °C in purified water and desorbed at 270 °C for 2 min.[39,40] The optimized operating parameters (including extraction and desorption times, extraction temperature, and ionic strength) of the silicalite-1 coated fiber were determined separately for NB (10 μg/L), *p*-DCB (50 μg/L), and *p*-CNB (0.45 μg/L). In experiments for estimation of the possible carryover effect (retention of analyte on the coating after desorption),[41,42] the fiber was kept in a commercial SPME vial (Supelco) and capped with a GC inlet septa (Agilent) to prevent the loss of analyte between the first and second desorption. Evaluation for the analytical performance of the silicalite-1-based SPME/GC-ECD method, as well as the analysis of real water sample, was conducted under the optimized conditions. To determine the concentrations of the substituted benzenes in real sample and spiked samples (for examination of recovery), calibration curves were prepared by extracting analytes from spiked pure water. The calibration curves included at least 12 standards and covered all test concentrations.

■ RESULTS AND DISCUSSION

Morphological and Structural Characterization of Silicalite-1 Coating. The SEM images of silicalite-1 coated fiber were presented in Figure 1. Regular-shaped crystals were observed, indicative of the successful growth of silicalite-1 on the wire. The coating was about 12 μm in thickness. The formation of silicalite-1 on the stainless steel wire likely commenced with crystal bonding.[43] Chemical bonding also presumably occurred due to abundance of O-containing groups on the surface of the acid-treated stainless steel wire.[44] Additionally, silicalite-1 might be physically anchored to the stainless steel wire because its surface was rough on a microscopic scale.[43,45] The XRD pattern of the synthesized material was presented in Supporting Information Figure S2. Diffraction peaks at 2θ = 7.92°, 8.76°, 23.06°, and 23.90° characteristic of the MFI structure were observed, providing further support to the development of silicalite-1.[20,29,31]

Thermal and Chemical Stability of Silicalite-1 Coating. The high thermal stability of the silicalite-1 coating was evidenced by the little weight loss in TG analysis − 3.09% at 300 °C and 3.89% at 600 °C (Figure 2). Weight loss at lower temperatures was possibly due to evaporation of adsorbed water, while further weight loss at higher temperatures was possibly due to minor dehydroxylation of the silanol groups on silicalite-1.[46] To test the chemical stability of the silicalite-1 coating, the fiber was sequentially immersed into 0.1 M HCl (pH = 1) for 4 h, 0.01 M NaOH (pH = 12) for 4 h, methanol overnight, and *n*-hexane overnight. The extraction efficiency of the treated and untreated fibers was compared in Figure 3. The relative standard deviations (RSD) for extractions under the different pretreatments were 11.0% for *p*-DCB, 7.7% for NB, and 10.8% for *p*-CNB. The results indicated that the synthesized silicalite-1 coating was stable within a large pH range (1−12) and tolerant to both polar and nonpolar organic solvents. It is worth noting that the recommended extraction pH range for commercial coatings is 2−11, and those coatings are often made from
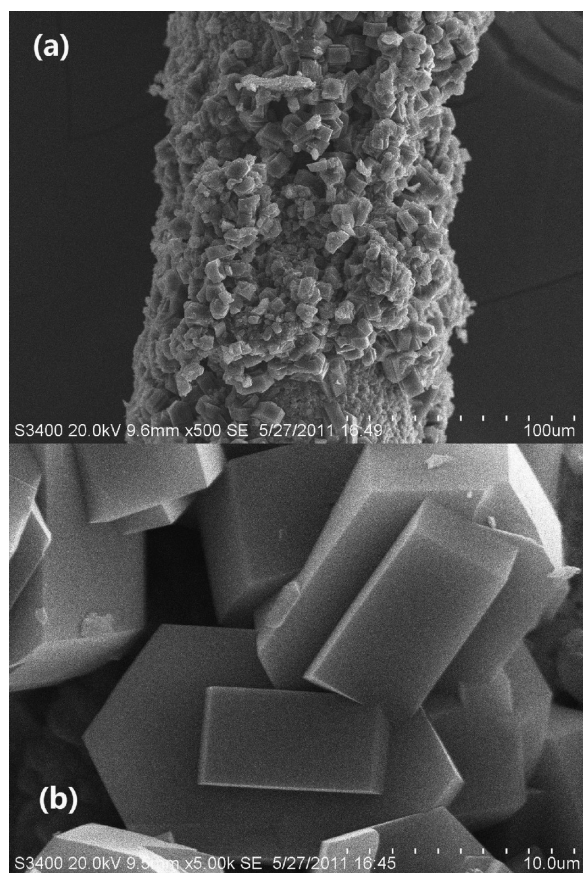
Figure 1. Scanning electron microscopy (SEM) images of the silicalite-1 coated fiber at a magnification of (a) 500 and (b) 5000.
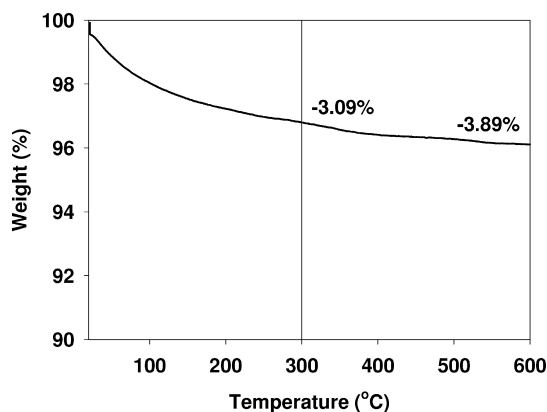

Figure 2. Thermal gravity (TG) analysis of silicalite-1.

organic polymers and copolymers and can easily swell in organic solvents and slip off the fiber core. Thus, the silicalite-1 coated fiber might help to expand the application of SPME, especially when coupled with liquid chromatography (LC) upon exposure to the extremely acidic/basic aqueous mixed or organic solvent mobile phase.[6,11] Additionally, the homemade fiber could be reused more than 110 times and then regenerated by calcining at 500 °C in air for 240 min to fully restore the extraction capability (see Supporting Information Figure S3). The combustion treatment expectedly removed the carbonized residues deposited on silicalite-1 completely. The regenerated fiber could be used for at least another 50 times without losing extraction efficiency. The commercial fibers could only be reused about 40 times under the experimental conditions.
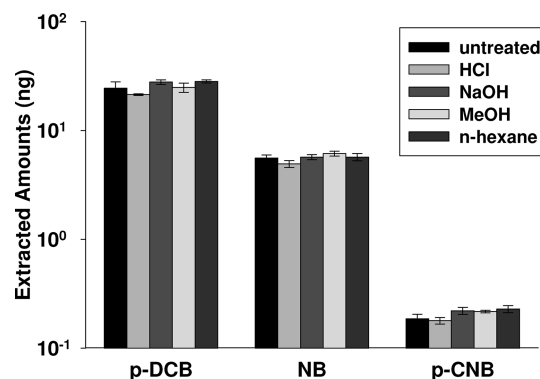
Figure 3. Extraction efficiencies of substituted benzenes in pure water by silicalite-1 coated fiber as originally made (untreated) and after each sequential immersion into 0.1 M HCl, 0.01 M NaOH, methanol (MeOH), and *n*-hexane. Analyte concentrations: 10 μg/L for NB, 50 μg/L for *p*-DCB, and 0.45 μg/L for *p*-CNB; extraction time: 60 min; desorption time: 2.0 min; extraction temperature: 30 °C. Error bars represent standard deviations calculated from triplicate extractions.

Comparison of Extraction Efficiency between Silicalite-1 Coated Fiber and Commercial Fibers. The extraction efficiency (as reflected by the extracted amount of analyte) of silicalite-1 coated fiber was compared with that of 100 μm PDMS, 65 μm PDMS/DVB, and 85 μm PA fibers (results presented in Figure 4). These commercial fibers are suitable for
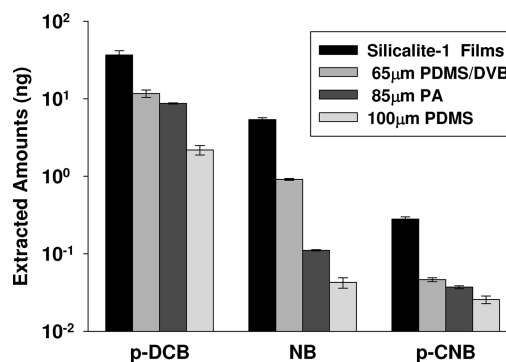
Figure 4. Comparison of extraction efficiency of substituted benzenes in pure water between silicalite-1 coated fiber and commercial fibers. Analyte concentrations: 10 μg/L for NB, 50 μg/L for *p*-DCB, and 0.45 μg/L for *p*-CNB; extraction time: 60 min; desorption time: 2.0 min; extraction temperature: 30 °C. Error bars represent standard deviations calculated from triplicate extractions.

analyzing non/less-polar, middle-polar, and polar compounds, respectively. Consistent with the results of previous studies,[39,40] given the same conditions, PDMS/DVB fiber showed the highest extraction efficiency for the test substituted benzenes among all three commercial fibers. The extracted amounts of the analytes by the silicalite-1 coated fiber were 3−6 times larger than that by the PDMS/DVB fiber, verifying the much higher extraction efficiency of the former. The combination of the large specific surface area (301 m²/g, determined by the Brunauer−Emmett−Teller N₂ adsorption method) and the relatively hydrophobic surface of silicalite-1 led to very strong adsorption of analytes.[27,28,47] Moreover, the adsorption affinity of the substituted benzenes to silicalite-1 might be further facilitated by micropore filling due to the closeness of the adsorbate molecular size and the adsorbent pore size to cause additive adsorption energy.[48] In line with this hypothesis, the pore sizes of the

Table 2. Linearity, Limit of Detection (LOD), Repeatability, Reproducibility, and Enhancement Factor (EF) of the Developed SPME-GC/ECD Method

analyte	linear range (μg/L)	correlation coefficient (R^2)	LOD (μg/L)	repeatability[a] (%, n = 6)	fiber-to-fiber reproducibility[a] (%, n = 3)	EF
NB	0.08−45.00	0.994	0.010	8.3	8.1	1272
p-DCB	0.50−96.00	0.995	0.130	9.6	8.8	517
p-CNB	0.02−4.50	0.995	0.001	4.6	6.9	1292

[a]The repeatability of one unique fiber and reproducibility between fibers were determined at 10 μg/L for NB, 50 μg/L for p-DCB, and 0.45 μg/L for p-CNB.

zigzag and straight channels of silicalite-1 are 0.51 × 0.55 and 0.53 × 0.56 nm (see schematic structure of silicalite-1 in Supporting Information Figure S4), respectively, which are exactly matched with the dynamic diameters of the test mono- and p-substituted benzenes (approximately 0.58 nm; see Table 1). Such micropore-filling mechanism was proposed previously to explain the enhanced adsorption of organic compounds to zeolites and other microporous adsorbents such as activated carbon.[20,49] On the other hand, extraction by organic polymer-based commercial coatings was mainly driven by hydrophobic partition with low excess molar free energy.

Optimization of Extraction Conditions for Silicalite-1 Coated Fiber. Effects of extraction and desorption times, extraction temperature, and ionic strength on the extraction efficiency of the homemade fiber were examined to determine the optimized conditions for NB, p-DCB, and p-CNB.

Extraction Time. The effect of extraction time was presented in Supporting Information Figure S5. The extraction efficiency of the three analytes increased remarkably from 10 to 60 min and reached the maximum at approximately 80 min. Note that SPME is a nonexhaustive approach, and absolute extraction equilibrium is thus not necessary.[50,51] Taking into account both extraction efficiency and analysis speed, 60 min was chosen as the operating extraction time (more than 80% of the maximum yield).

Desorption Time and Carryover. The desorption time profiles ranging from 0.1 to 2.0 min were displayed in Supporting Information Figure S6. Most of the analytes could be desorbed off the fiber coating in 0.25 min. To further quantify the amounts of retained analytes (carryover) on the coating after desorption, a 5 min second desorption was applied. The percent of carryover was calculated by dividing the peak area from the second desorption by the peak area from the first desorption.[3] As displayed in Supporting Information Figure S7, with 0.25 min desorption, the carryover was 1.7% for p-DCB, 7.5% for NB, and 2.7% for p-CNB, while with 1.0 min desorption, the carryover was less than 1.0% for all three analytes. To minimize the carryover effect, a 1.0 min desorption time was then chosen.

Extraction Temperature. Temperature is an important factor affecting SPME performance. In general, increasing the extraction temperature increases the extraction rate but decreases the distribution constant.[2,5,6] As illustrated in Supporting Information Figure S8, the highest extraction efficiency was observed at approximately 50 °C for the three analytes. Therefore, 50 °C was set as the operating extraction temperature.

Ionic Strength. The effect of ionic strength (0%−30% of NaCl, w/v) on the extraction efficiency was presented in Supporting Information Figure S9. For all three test analytes, the extraction efficiency increased slightly but consistently with the ionic strength up to 10% of NaCl. A further increase of the ionic strength to 30% moderately suppressed the extraction of p-DCB but markedly facilitated the extraction of NB and p-CNB. The different responses to high ionic strength (>10% NaCl)

between the three analytes were likely due to the dual-influence of "salting out" on DI-SPME: (1) enhanced extraction by facilitating the sorption of analytes to the fiber coating; (2) suppressed extraction by facilitating the mass transfer of analytes to air. Due to the much higher volatility (as reflected by K_{AW} values, shown in Table 1), p-DCB would suffer more from the extraction suppression when compared with the two polar nitroaromatic compounds[52] and, therefore, demonstrated a distinct pattern of ionic strength effect. After comprehensive consideration of the ionic strength effects of the three test analytes, 30% of NaCl was added to the working solutions.

Analytical Performance of Silicalite-1 Coated Fiber. Table 2 summarized the analytical figures of merit of the optimized SPME-GC/ECD method based on the silicalite-1 coated fiber. The enhancement factor (EF) of a given analyte was defined as the ratio of the peak area from fiber extraction to the peak area from direct injection of 1 μL of standard solution.[7] The silicalite-1 coated fiber had EFs from 517 (p-DCB) to 1292 (p-CNB). The obtained linearity was more than 2 orders of magnitude in range with a correlation coefficient (R^2) of at least 0.994. The limits of detection (LOD) were calculated as 0.13 μg/L for p-DCB, 0.01 μg/L for NB, and 0.001 μg/L for p-CNB. Repeatabilities from six replicate samples were in the range of 4.6−9.6%, and reproducibilities from three different fibers were in the range of 6.9−8.8%. For comparison, the analytical performance of several commercial and other homemade fibers (under optimized conditions) for the substituted benzenes reported in literature were surveyed and listed in Supporting Information Table S1. Overall, our proposed method worked better, in particular, when compared with the commercial fibers. Less analysis improvements were shown on p-DCB than on NB and p-CNB. This might be explained by the relatively low compatibility of the DI-SPME mode to the highly volatile p-DCB.

Shape-Selectivity of Silicalite-1 Coated Fiber. To test the shape-selectivity of silicalite-1 coated fiber, three couples of substituted benzenes (p-DCB and 1,3,5-TCB, p- and m-CNBs, and p- and m-DCBs) were extracted from their 1:1 mixed solutions (molar ratio). A commercial 65 μm PDMS/DVB fiber was chosen for comparison. The chromatograms were displayed in Supporting Information Figure S10. In contrast to the PDMS/DVB fiber, the silicalite-1 coated fiber consistently produced much larger peak areas for the p-substituted benzenes than for the tri- and m-substituted benzenes, indicative of preferential extraction for p-substituted benzenes.

To better illustrate the shape-selectivity of the homemade fiber, the relationships of extracted amounts (ng) vs extraction concentrations (μg/L) were plotted in Figure 5 for the different analyte/fiber combinations. The slopes (mL) and correlation coefficients (R^2) from the linear regression were presented in Supporting Information Table S2. The curves of each couple of substituted benzenes extracted by the PDMS/DVB fiber were nearly overlapping, indicating poor selectivity for the analytes.
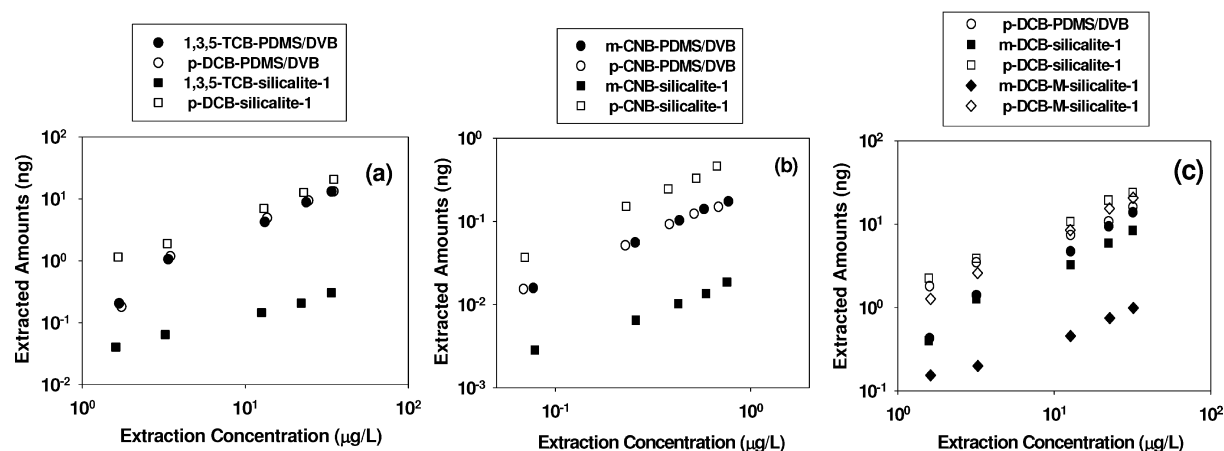
Figure 5. Relationships of extracted amounts (μg) vs extraction concentrations (μg/L) of substituted benzenes in pure water by 65 μm PDMS/DVB and silicalite-1 and modified silicalite-1 (M-silicalite-1) coated fibers. Extraction time: 60 min; desorption time: 2.0 min; extraction temperature: 30 °C. (a) p-DCB and 1,3,5-TCB. (b) p- and m-CNBs. (c) p- and m-DCBs.

However, the silicalite-1 coated fiber exhibited pronounced preferential extraction for the p-substituted benzenes. The extraction efficiency of p-DCB by the silicalite-1 coated fiber was about 70 times higher than that of 1,3,5-TCB. For the two couples of isomers, the ratios of extraction were approximately 30 between p-CNB and m-CNB, and 3 between p-DCB and m-DCB. The remarkable high extraction efficiency for p-substituted benzenes by the homemade fiber can be well interpreted by the micropore-filling enhanced adsorption mentioned above. On the contrary, the tri- and m-substituted benzenes have dynamic diameters (see values in Table 1) slightly larger than the pore sizes of silicalite-1, giving rise to size-exclusion effect in adsorption and in turn suppressed extraction.[20−25]

Compared with the isomers of p- and m-CNBs, the silicalite-1 coated fiber presented lower shape-selectivity for the isomers of p- and m-DCBs due to the smaller difference in dynamic diameter. Consistent results were reported in previous adsorption studies.[21] To improve the shape-selectivity for p-DCB, the silicalite-1 coating of the same fiber was modified with SiCl$_4$ to narrow the pore entrance without significant effects on the specific surface area and pore volume.[21,35] The extraction efficiency of the modified fiber (referred to as M-silicalite-1) was almost unchanged for p-DCB but reduced prominently (about 10 times) for m-DCB (see Figure 5c and Supporting Information Table S2). The suppressed extraction of m-DCB by M-silicalite-1 was primarily caused by the reinforced size-exclusion effect due to the narrowed pore entrance. Such unique shape-selectivity of the coating material would largely simplify the analysis of real samples by effectively suppressing the extraction of undesired compounds with larger molecular sizes. Recently, similar shape-based adsorption selectivity of MOFs was successfully applied in the analysis of complex petroleum-derived fuels and in the enrichment of peptides in biological samples.[17,53]

Real Water Sample Analysis by Silicalite-1 Coated Fiber. The silicalite-1 coated fiber was applied to the analysis of a water sample collected from the Meiliang Bay in Taihu Lake. Chromatograms for the standard mixture of substituted benzenes (NB, p-DCB, and p-CNB) and the sample were shown in Supporting Information Figure S11. The analytic results were summarized in Table 3, along with the recoveries of the standards. A concentration of 0.14 μg/L was detected for NB,

Table 3. Analytical Results of the Determination of Substituted Benzenes in Water Sample from Taihu Lake

analyte	measured concentration (μg/L, n = 3)	spiked concentration (μg/L)	recovery (%, n = 3)
NB	0.14 ± 0.01	0.1	86 ± 9.4
		1.0	102 ± 8.5
		10.0	82 ± 4.8
p-DCB	nd[a]	0.5	105 ± 9.2
		5.0	89 ± 11.2
		50.0	96 ± 9.0
p-CNB	nd[a]	0.0045	106 ± 7.5
		0.045	92 ± 10.2
		0.45	92 ± 6.9

[a]Not detected.

comparable with the water quality monitoring data reported earlier.[13] The concentrations of p-DCB and p-CNB were below the LODs in the experimental setting. Notably, the presence of natural organic matter (TOC = 16.4 mg/L) in the water sample appeared to have little effect on the analysis. The uniform molecular-scale pore structure of silicalite-1 could completely prevent adsorption of large-size dissolved humic substances and thus possible interference on extraction of the analyte. A separate set of experiments verified negligible adsorption of humic acids on silicalite-1 (data not shown).

■ CONCLUSIONS

We introduced the first in situ hydrothermal grown silicalite-1 coating for SPME. The homemade fiber afforded excellent thermal and chemical stability and high extraction efficiency (3−6 times larger than commercial fibers), as well as great capability for reuse and regeneration. Additionally, the fiber displayed pronounced shape-selectivity for mono- and p-substituted benzenes. After pore narrowing by surface modification with SiCl$_4$, the extraction selectivity was further enhanced substantially. At last, the silicalite-1-based SPME-GC/ECD method was successfully used in analyzing a real water sample. The results highlight the great potential of in situ hydrothermal grown silicalite-1 coating for SPME, especially when coupled with LC due to the superior tolerance to highly acidic/basic aqueous solutions and organic solvents. It is noteworthy that zeolite is a large group of framework materials having a wide

range of uniform pore sizes (0.3−20 nm),[19] which can be further fine-tuned by surface modification to enhance the adsorption selectivity specific to target compounds. Such unique shape-based adsorption selectivity of zeolite provides extra benefit for SPME when the analyte of interest is present in a complex suite together with many other organic compounds and natural organic matter components.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel/Fax: +86 025-8968-0372. E-mail: zhud@nju.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Arthur, C. L.; Pawliszyn, J. *Anal. Chem.* **1990**, *62*, 2145−2148.

(2) Arthur, C. L.; Killam, L. M.; Buchholz, K. D.; Pawliszyn, J. *Anal. Chem.* **1992**, *64*, 1960−1966.

(3) Buchholz, K. D.; Pawliszyn, J. *Environ. Sci. Technol.* **1993**, *27*, 2844−2848.

(4) Buchholz, K. D.; Pawliszyn, J. *Anal. Chem.* **1994**, *66*, 160−167.

(5) Kataoka, H.; Lord, H. L.; Pawliszyn, J. *J. Chromatogr., A* **2000**, *880*, 35−62.

(6) Lord, H.; Pawliszyn, J. *J. Chromatogr., A* **2000**, *885*, 153−193.

(7) Wang, J.; Jiang, D.; Gu, Z.; Yan, X. *J. Chromatogr., A* **2006**, *1137*, 8−14.

(8) Hu, X.; Pan, J.; Hu, Y.; Huo, Y.; Li, G. *J. Chromatogr., A* **2008**, *1188*, 97−107.

(9) Cui, X.; Gu, Z.; Jiang, D.; Li, Y.; Wang, H.; Yan, X. *Anal. Chem.* **2009**, *81*, 9771−9777.

(10) Dietz, C.; Sanz, J.; Cámara, C. *J. Chromatogr., A* **2006**, *1103*, 183−192.

(11) Ouyang, G.; Pawliszyn, J. *Anal. Bioanal. Chem.* **2006**, *386*, 1059−1073.

(12) Prosen, H.; Zupančič-Kralj, L. *Trends Anal. Chem.* **1999**, *18*, 272−282.

(13) Li, X.; Chen, J.; Du, L. *J. Chromatogr., A* **2007**, *1140*, 21−28.

(14) Li, Q.; Wang, X.; Yuan, D. *J. Chromatogr., A* **2009**, *1216*, 1305−1311.

(15) Alizadeh, R.; Najafi, N. M.; Kharrazi, S. *Anal. Chim. Acta* **2011**, *689*, 117−121.

(16) Zhang, S.; Du, Z.; Li, G. *Anal. Chem.* **2011**, *83*, 7531−7541.

(17) Chang, N.; Gu, Z.; Wang, H.; Yan, X. *Anal. Chem.* **2011**, *83*, 7094−7101.

(18) Tassel, P. R. V.; Phillips, J. C.; Davis, H. T.; McCormick, A. V. *J. Mol. Graphics* **1993**, *11*, 180−184.

(19) Cundy, C. S.; Cox, P. A. *Chem. Rev.* **2003**, *103*, 663−701.

(20) Flanigen, E. M.; Bennett, J. M.; Grose, R. W.; Cohen, J. P.; Patton, R. L.; Kirchner, R. M.; Smith, J. V. *Nature* **1978**, *271*, 512−516.

(21) Yue, Y.; Tang, Y.; Liu, Y.; Gao, Z. *Ind. Eng. Chem. Res.* **1996**, *35*, 430−433.

(22) Guo, G.; Chen, H.; Long, Y. *Microporous Mesoporous Mater.* **2000**, *39*, 149−161.

(23) Yuan, W.; Lin, Y. S.; Yang, W. *J. Am. Chem. Soc.* **2004**, *126*, 4776−4777.

(24) Guo, Z.; Zheng, S.; Zheng, Z.; Jiang, F.; Hu, W.; Ni, L. *Water Res.* **2005**, *39*, 1174−1182.

(25) Guo, Z.; Zheng, S.; Zheng, Z. *Chem. Eng. J.* **2009**, *155*, 654−659.

(26) Deng, S. G.; Lin, Y. S. *Ind. Eng. Chem. Res.* **1995**, *34*, 4063−4070.

(27) Long, Y.; Jiang, H.; Zeng, H. *Langmuir* **1997**, *13*, 4094−4101.

(28) Khalid, M.; Joly, G.; Renaud, A.; Magnoux, P. *Ind. Eng. Chem. Res.* **2004**, *43*, 5275−5280.

(29) Mintova, S.; Valtchev, V.; Konstantinov, L. *Zeolites* **1996**, *17*, 462−465.

(30) Exter, M. J. D.; Bekkum, H. V.; Rijn, C. J. M.; Kapteijn, F.; Moulijn, J. A.; Schellevis, H.; Beenakker, C. I. N. *Zeolites* **1997**, *19*, 13−20.

(31) Mabande, G. T. P.; Pradhan, G.; Schwieger, W.; Hanebuth, M.; Dittmeyer, R.; Selvam, T.; Zampieri, A.; Baser, H.; Herrmann, R. *Microporous Mesoporous Mater.* **2004**, *75*, 209−220.

(32) Guo, H.; Zhu, G.; Li, H.; Zou, X.; Yin, X.; Yang, W.; Qiu, S.; Xu, R. *Angew. Chem.* **2006**, *118*, 7211−7214.

(33) Langenfeld, J. J.; Hawthorne, S. B.; Miller, D. J. *J. Chromatogr., A* **1996**, *740*, 139−145.

(34) Musteata, F. M.; Walles, M.; Pawliszyn, J. *Anal. Chim. Acta* **2005**, *537*, 231−237.

(35) Lee, K.; Tan, C. *Ind. Eng. Chem. Res.* **2000**, *39*, 1035−1038.

(36) Nkedl-Kizza, P.; Rao, P. S. C.; Hornsby, A. G. *Environ. Sci. Technol.* **1985**, *19*, 975−979.

(37) Górecki, T.; Pawliszyn, J. *Analyst* **1997**, *122*, 1079−1086.

(38) Górecki, T.; Khaled, A.; Pawliszyn, J. *Analyst* **1998**, *123*, 2819−2824.

(39) Furton, K. G.; Almirall, J. R.; Bi, M.; Wang, J.; Wu, L. *J. Chromatogr., A* **2000**, *885*, 419−432.

(40) Almeida, C. M. M.; Boas, L. V. *J. Environ. Monit.* **2004**, *6*, 80−88.

(41) Valor, I.; Moltó, J. C.; Apraiz, D.; Font, G. *J. Chromatogr., A* **1997**, *767*, 195−203.

(42) Hall, B. J.; Brodbelt, J. S. *J. Chromatogr., A* **1997**, *777*, 275−282.

(43) Koegler, J. H.; Bekkum, H.; Jansen, J. C. *Zeolites* **1997**, *19*, 262−269.

(44) Hang Chau, J. L.; Tellez, C.; Yeung, K. L.; Ho, K. *J. Membr. Sci.* **2000**, *164*, 257−275.

(45) Jansen, J. C.; Koegler, J. H.; Bekkum, H.; Calis, H. P. A; Bleek, C. M.; Kapteijun, F.; Moulijn, J. A.; Geus, E. R.; Puil, N. *Microporous Mesoporous Mater.* **1998**, *21*, 213−226.

(46) Sunseri, J. D.; Cooper, W. T.; Dorsey, J. G. *J. Chromatogr., A* **2003**, *1011*, 23−29.

(47) Shu, H.; Li, D.; Scala, A. A.; Ma, Y. *Sep. Purif. Technol.* **1997**, *11*, 27−36.

(48) Ismadji, S.; Bhatia, S. K. *Langmuir* **2001**, *17*, 1488−1498.

(49) Ji, L.; Liu, F.; Xu, Z.; Zheng, S.; Zhu, D. *Environ. Sci. Technol.* **2010**, *44*, 3116−3122.

(50) Ai, J. *Anal. Chem.* **1997**, *69*, 1230−1236.

(51) Pawliszyn, J. *Anal. Chem.* **2003**, *75*, 2543−2558.

(52) Xu, H.; Li, Y.; Jiang, D.; Yan, X. *Anal. Chem.* **2009**, *81*, 4971−4977.

(53) Gu, Z.; Chen, Y.; Jiang, J.; Yan, X. *Chem. Commun.* **2011**, *47*, 4787−4789.

(54) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2nd ed.; Wiley-Inter-Science: New York, 2003.