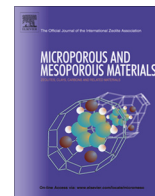




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Cobalt hydroquinolate-modified periodic mesoporous silicas

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ABSTRACT

A cobalt(II) silylamide complex was successfully grafted onto large-pore hexagonal and cubic periodic mesoporous silicas (PMSs) SBA-15 and KIT-6, respectively, to afford hybrid materials $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})@(\text{SBA}-15/\text{KIT}-6)$ with well-defined surface species $(=\text{SiO})_2\text{Co}(\text{thf})$, $=\text{SiOCo}[\text{N}(\text{SiMe}_3)_2](\text{thf})$, and $=\text{SiOSiMe}_3$. Surface silylamido/1,4-benzenediol ligand exchange gave hybrid materials with main moieties $=\text{SiOCoL}(\text{thf})$ and $(=\text{SiO})_2\text{Co}(\text{Me}_3\text{SiL})$ ($\text{L}=\text{O}(\text{C}_6\text{H}_4)\text{OSiMe}_3$), revealing *in situ* ligand silylation as a side reaction and the formation of a donor ligand. Consecutive grafting of $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ and surface ligand exchange (also termed as layer-by-layer-grafting) led to the alteration of the pore structure (shape and size) due to the formation of cobalt–hydroquinolate-frameworks via weak interactions between Co(II) centers and the donor oxygen atoms of the silylated group ($-\text{C}_6\text{H}_4\text{OSiMe}_3$) located in proximity to the pore walls. All featured surface species were confirmed by Diffuse Reflectance Infrared Fourier-Transform spectroscopy and elemental analysis. Pore parameters of hybrid materials were monitored by nitrogen physisorption. Preservation of the long-range ordered mesopore structures and the appearance of microcrystalline structures were proven by powder X-ray diffraction and transmission electron microscopy.

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1. Introduction

Periodic mesoporous silicas (PMSs) and organosilicas (PMOs) have attracted extensive attention due to long-range ordered arrays of the pore structure and high specific surface areas [1–8]. Routinely employed symmetrical PMS materials include 2D-hexagonal MCM-41/SBA-15, 3D-caged hexagonal SBA-2, 3D-cubic SBA-1/KIT-5/FDU-1 with an interconnected cage-like pore configuration, and 3D-cubic MCM-48/KIT-6 with channel-shaped pore structures. Such ordered porous materials are utilized as supports or nano-reactors or nanocontainers to fabricate inorganic–organic hybrid materials by molecular grafting, encapsulation, and covalent linkage [9–21]. Derivatization of PMS materials with organometallic complexes or functional organic compounds provides surface-modified PMS hybrid materials that can be used as heterogeneous catalysts, adsorbents, and sensing materials [22–36]. Notably, while such post-synthesis treatment markedly affects the surface physical and chemical properties (e.g., surface polarity and reactivity) of the hybrid materials, the long-range ordering of the inorganic silica framework intrinsically preserves [37–39].

Previously, MCM-41 and SBA-1 were reacted with chorosilanes, alkoxysilanes, and silazanes to form thermodynamically stable O–SiR₃ surface moieties, implying a transformation from a hydrophilic to a hydrophobic surface. In this case, the population of surface silyl species O–SiR₃ could be controlled by the amount of used silanes and the reaction time [40]. Long-chain alkyl dimethylaminosilanes with appropriate size were found to engage in pore-size engineering of mesoporous silicas such as SBA-1, SBA-2 and SBA-16 for the design of size-selective mesoporous catalysts [41]. Moreover, homoleptic metal (silyl)amides, $\text{M}(\text{NR}_2)_x$ (R = Me, Et, SiHMe₂, SiMe₃) were immobilized on PMSs to afford well-defined surface metal species, revealing the effect of surface attachment [39], and displaying promising catalytic performance in Danishefsky Diels–Alder reactions, methyl methacrylate (MMA) polymerization and Meerwein–Ponndorf–Verley (MPV) reduction of *tert*-butylcyclohexanone as well as the intramolecular hydroamination/cyclization of aminoalkenes [42–47]. Importantly, surface metal ligand moieties do engage in ligand exchange, and hence promote a rich surface coordination chemistry on PMSs [39,48–51]. More interestingly, the extent of grafted surface species located at internal (intrapore) or external surface sites not only depends on the PMSs pore size but also on the steric demand of the organometallic precursor or functional group [52,53]. Generally, pore size effects do apply when pore sizes of PMSs are found less than 3 nm.

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The layer-by-layer technique is an advanced approach for the preparation of thickness-controlled thin membranes [54–56]. We extended this method, comprising consecutive molecular grafting of organometallic precursors and surface ligand exchange (also termed layer-by-layer grafting), to PMSs in order to fabricate crystalline single-component metal or multiple-component heterometal oxide layers located at the intrapore and at the external surface of PMSs [50,57]. Such consecutive molecular grafting was also applied for the preparation of titanium phosphate@SBA-15 by Dai et al. [58].

Our previous investigations [39] involved the reactions of $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ -modified large-pore hexagonal SBA-15 and cubic KIT-6 with a difunctional carboxylic acid or hydroquinone (HQ) yielding $\text{N}(\text{SiMe}_3)_2/\text{R}(\text{C}_6\text{H}_4)\text{R}$ surface ligand exchange ($\text{R} = \text{COOH}$ or OH) and *in situ* silylation of the terminal functional group of the exchanged ligand. This finding seemed to terminate the surface modification of such hybrid silicas. However, the present study revealed that weak interactions between cobalt and silylated moieties of type $\equiv\text{SiO}-\text{CoO}(\text{C}_6\text{H}_4)\text{OSiMe}_3$ may offer a new avenue to fabricate metal–organic frameworks onto the surface of periodic mesoporous silicas. Subsequent $\text{N}(\text{SiMe}_3)_2/\text{HO}(\text{C}_6\text{H}_4)\text{OH}$ (hydroquinone) surface ligand exchange and consecutive layer-by-layer grafting involving grafting of the cobalt precursor and ligand exchange were primarily monitored by elemental analysis, N_2 physisorption, and electron microscopy. Interactions between cobalt(II) centers and the PMSs surface, as well as the cobalt(II) centers and the silylated hydroquinone, which form cobalt–hydroquinolate-incorporated PMS materials, were investigated in detail.

2. Experimental section

2.1. Chemicals and materials

Hydroquinone (or 1,4-dihydroxybenzene, 99.5%) was purchased from ACROS Organics. The solvents hexane and tetrahydrofuran (thf) were purified by using Grubbs columns (MBraun SPS, solvent purification system) before use. $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ [59–61] as well as large-pore hexagonal SBA-15 and cubic KIT-6 were synthesized according to slightly modified literature procedures [39,62].

Surfactant-free SBA-15 and KIT-6 were dehydrated at 270 °C for 8 h in high vacuum (1×10^{-4} Torr) and stored in a glovebox under an argon atmosphere. The synthesis and grafting of the organometallics and corresponding posttreatments were operated in a glovebox with rigorous exclusion of air and moisture (MB Braun MB150B-G-II; <1 ppm O_2 , <1 ppm H_2O , argon atmosphere).

2.2. Synthesis of large-pore hexagonal SBA-15 and cubic KIT-6

Long-range ordered hexagonal or cubic PMSs were synthesized by using a mixture of poly-(alkylene oxide)-based triblock copolymer Pluronic P123 as a structure-directing agent, *n*-butanol as a co-solvent, and tetraethylorthosilicate (TEOS) as a silica source under acidic conditions. Detailed synthesis procedures are found in previous literature [39,62]. The calcined SBA-15 and KIT-6 were activated at 270 °C for 8 h under high-vacuum conditions. The DRIFT spectra of the dehydrated SBA-15 (1) and KIT-6 (2) are quite similar: $\nu_{\text{max}}/\text{cm}^{-1}$: 3747 vs ($\nu_{\text{Si-O-H}}$), 1000–1200s, 810m and 570w ($\nu_{\text{Si-O-Si}}$), 463m and 437m ($\nu_{\text{s,O-Si-O}}$). Elemental analyses (wt%) are listed in Table 1.

2.3. Preparation of $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ -grafted SBA-15/KIT-6 and surface ligand exchange (consecutive layer-by-layer grafting)

$\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ @SBA-15/KIT-6 and $[\text{HO}(\text{C}_6\text{H}_4)\text{OH}]$ -@ $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ @SBA-15/KIT-6 hybrid materials were prepared according to a previously reported method [39]. Detailed synthesis procedures are as follows.

2.3.1. $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ @SBA-15 (1-co)

To a suspension of dehydrated SBA-15 (1, 1.107 g, 2.23 mmol OH) in 5 mL of hexane, green $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ (1.007 g, 2.23 mmol) in 5 mL of hexane was added quickly. This mixture was stirred at ambient temperature for 24 h. The resulting solid was collected by centrifugation, washed with hexane (3×3 mL) and dried in vacuum until constant weight to yield 1.58 g of a greyish green powder. The supernatant was filtered and dried in vacuum to give 0.352 g of unreacted cobalt precursor. DRIFT ($\nu_{\text{max}}/\text{cm}^{-1}$): 2952m and 2898w ($\nu_{\text{C-H}}$), 1458w, 1407w and 1384w ($\delta_{\text{C-H}}$),

Table 1
Elemental analysis and pore parameters of parent materials and hydroquinone(HQ)–cobalt-modified PMSs (molecular layer-by-layer grafting).

Materials	C (wt%)	H (wt%)	N (wt%)	Co (wt%)	a_s^a ($\text{m}^2 \text{g}^{-1}$)	a_{exter}^b ($\text{m}^2 \text{g}^{-1}$)	$d_{\text{ads,p}}^c$ (nm)	V_{sp}^d ($\text{cm}^3 \text{g}^{-1}$)
SBA-15 (1)	0.15	0.16	0.13		713	564	7.7	0.95
$\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ @SBA-15 (1-co)	11.14	2.28	1.37	7.3	354	345	5.9	0.45
$[\text{HO}(\text{C}_6\text{H}_4)\text{OH}]$ @ $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ @SBA-15 (1-co-HQ)	11.64	1.55	0.47	7.2	441	436	5.8	0.52
$\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ @ $[\text{HO}(\text{C}_6\text{H}_4)\text{OH}]$ @ $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ @SBA-15 (1-co-HQ-co)	14.49	2.19	1.07	8.5	238	313	4.7	0.29
$\{[\text{HO}(\text{C}_6\text{H}_4)\text{OH}]$ @ $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})\}_2$ @SBA-15; (1-co-HQ) ₂	15.31	1.86	0.47	8.3	379	377	4.8	0.35
$\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ @ $\{[\text{HO}(\text{C}_6\text{H}_4)\text{OH}]$ @ $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})\}_2$ -@SBA-15 (1-co-HQ) ₂ -co)	16.29	2.17	0.86	8.9	285	270	4.3	0.23
$\{[\text{HO}(\text{C}_6\text{H}_4)\text{OH}]$ @ $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})\}_3$ @SBA-15; (1-co-HQ) ₃	17.63	2.01	0.43	8.5	356	354	4.0	0.27
KIT-6 (2)	0.12	0.20	0.07		684	600	10.8	1.61
$\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ @KIT-6 (2-co)	10.88	2.29	1.26	7.9	376	454	8.0	0.76
$[\text{HO}(\text{C}_6\text{H}_4)\text{OH}]$ @ $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ @KIT-6 (2-co-HQ)	13.06	1.83	0.33	7.6	437	497	7.7	0.74
$\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ @ $[\text{HO}(\text{C}_6\text{H}_4)\text{OH}]$ @ $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ @KIT-6 (2-co-HQ-co)	14.39	2.49	1.11	9.2	351	438	6.6	0.57
$\{[\text{HO}(\text{C}_6\text{H}_4)\text{OH}]$ @ $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})\}_2$ @KIT-6; (2-co-HQ) ₂	16.55	1.79	0.55	8.8	445	533	5.8	0.60
$\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})$ @ $\{[\text{HO}(\text{C}_6\text{H}_4)\text{OH}]$ @ $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})\}_2$ -@KIT-6 (2-co-HQ) ₂ -co)	18.62	2.41	1.15	9.1	366	441	5.6	0.45
$\{[\text{HO}(\text{C}_6\text{H}_4)\text{OH}]$ @ $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})\}_3$ @KIT-6. (2-co-HQ) ₃	20.97	1.94	0.43	8.9	468	554	4.5	0.45

^a Specific BET surface area.

^b External surface area from *t*-plot report.

^c Pore diameter according to the maximum of the BJH pore size distribution calculated from the adsorption branch of the isotherm.

^d Single point adsorption total pore volume of pores taken at relative pressure $p/p_0 = 0.99$; Samples were pretreated at 250 °C (parent), and 25 °C (organometallic-grafted and surface ligand exchanged) in vacuo until the pressure was $<10^{-3}$ Torr.

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