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Selective functionalization of the mesopores of SBA-15

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ABSTRACT

A method has been developed that permits the highly selective functionalization of the interior and exterior surfaces of the ubiquitous mesoporous material, SBA-15. The key step is reloading the as-synthesized material with structure-directing agent, Pluronic® P123, prior to selective functionalization of the external surface with a silylating agent. This new approach represents a significant improvement over literature procedures. Results from physisorption analyses as well as solid-state NMR permit a detailed, quantitative assessment of functionalized SBA-15. This work also provides insight into the stability of the silyl layer during extraction procedures – an issue often neglected in other studies but of significant importance as decomposition of this layer could result in the introduction of new silanols and reduce the effectiveness of any selective grafting procedure.

1. Introduction

Following their development in the 1990s [1–5], mesoporous silicas have become an important class of ordered materials that are easily prepared and functionalized [6–8]. While much effort has been put towards studying the properties and applications of their functional derivatives [9–11], the issue of controlling functional group distribution on the surface of these silicas has received much less attention. Functional group distribution is important since there are always at least two unique surface domains accessible to functionalization: the internal mesopore surface, which is more abundant but less accessible, and the external surface, which typically represents a small amount of the total surface area [12], but is inherently more accessible. The external-to-internal surface area ratio changes depending on the synthetic method, and for the case of mesoporous nanoparticles, depending on size, the external surface area can be significantly larger.

The ability to preferentially localize functionality onto specific surface domains is important for a variety of applications [13]. For instance, some drug delivery [14–16] methods depend on interactions with the particle external surface for recognition of a specific tissue type [17], while others exploit interactions at the internal surface (i.e., within the pores) to enable the controlled release of an active pharmaceutical ingredient [18]. Selective functionalization of the interior of pores can also be important for catalysis and nanoparticle synthesis [19–25,26–28], whereas pore-mouth functionalization has been a critical part of the design of molecular gates [29–32].

Two approaches are typically employed for the selective functionalization of the interior and exterior of mesoporous silicas: diffusion control and pore protection (Scheme 1) [13,33–35]. Diffusion-controlled selective functionalization (Scheme 1A) assumes that the silanols on the external surface are more reactive to post-synthesis grafting than those within the mesopores [33,36].

However, in seminal work by Brühwiler, it was demonstrated that this approach is largely ineffective, even for small-pore (2–3 nm) MCM-41-type materials [37]. Only when specially designed bulky siloxanes were employed along with pore-blocking approaches was selective grafting conclusively demonstrated [37].

In the pore-protection approach for selective functionalization (Scheme 1B), the mesopores are blocked with an agent that can be removed after the external surface is functionalized. Reports employing the use of the surfactant template (i.e., P123 or CTAB) in this role have appeared [24,38–40], although detailed evidence supporting their effectiveness is lacking. Indeed, the ability of alkoxy or chloro silanes to displace surfactant in as-synthesized

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materials has been described [41–45], which would seem to be contraindicated with this approach.

Schüth demonstrated that the pore-protection approach was ineffective with P123 and, in order to completely block the pores of SBA-15, polymerization of methyl methacrylate (PMMA) within the pores was necessary [39]. This novel approach permitted the selective blocking of the interior surface, and was highly effective for the preparation of SBA-15 with an exterior decorated with Co nanoparticles [39]. However, since calcination was required to remove the PMMA, this method is not designed for the introduction of organic groups. Thus, it is clear that additional methods for the selective functionalization of the two surfaces of mesoporous materials are needed.

Presented herein is the development and validation of the first pore-protection methodology that permits the selective grafting of functional groups within the mesopores of SBA-15 using commonly available reagents under mild conditions. The key step in this procedure is a reloading of the interior surface in the as-synthesized materials by treatment with additional surfactant (P123). This simple and easily performed reloading step is shown to be critical for effective blocking of the pores. Subsequently, passivation of the external surface can be accomplished with a commonly available silylating agent. After external passivation, the structure-directing agent is readily removed by extraction, and the accessible silanols in the mesopore domain are available for further functionalization. Solid-state (SS) NMR and physisorption analyses demonstrated that this is a highly effective, general strategy for pore-protection, which yields fully silylated and chemically stable surface domains.

2. Experimental section

2.1. Sample synthesis and preparation

The key synthetic procedures used in this study are detailed below. The full list of samples is given in Table 1.

2.1.1. as-SBA, ex-SBA, and cal-SBA

The condensation procedure was adapted from Stucky et al. [46]. 4.0 g of P123 was weighed into a 500-mL glass jar equipped with a magnetic stirring bar, and 40 mL of distilled water and 5.0 mL of concentrated HCl were added. The resulting mixture was stirred at 40 °C in a sealed jar in an oil bath for approximately 4 h until the mixture became homogeneous. To this solution, tetraethyl orthosilicate (TEOS, 9.0 mL) was added via syringe over a period of 1 min, the jar was re-sealed and the mixture was stirred vigorously at 40 °C for another 24 h followed by 48 h at 80 °C. The as-synthesized material (as-SBA) was recovered by filtration without washing and dried on a vacuum funnel for 1 h. The surfactant of as-SBA was then either removed by Soxhlet extraction with ethanol for 48 h to produce ex-SBA or calcination in an oven at 550 °C using a 1 °C/min ramp from 25 °C to 550 °C, where the temperature was maintained for 6 h, followed by a 1.5 °C/min ramp down to 25 °C to produce cal-SBA. The recovered ex-SBA material was further dried under 2 mmHg at 80 °C in a flask overnight prior to analysis.

2.1.2. re-SBA

In a 250-mL glass jar, 20 g of P123 was dissolved in 70 mL of ethanol. The jar was sealed and the mixture vigorously stirred at 40 °C until P123 was dissolved. To the resulting solution was added 5.0 g of as-SBA and the suspension was stirred in the sealed jar for 24 h at room temperature. The material was recovered by vacuum filtration without washing, and was dried on a vacuum funnel for 1 h. The reloaded material (re-SBA) was further dried under 2 mmHg at 80 °C in a flask overnight prior to further modifications.

2.1.3. re-SBA-selTMS-ex

In a 250-mL round-bottomed flask equipped with a magnetic stirring bar, 5.0 g of re-SBA was added and the flask purged with argon. To the flask, 50 mL of hexamethyldisilazane (HMDS) was added and the resulting suspension was stirred at room temperature for 3 h. The material was recovered by vacuum filtration, washed with copious amounts of hexane, and dried on a vacuum funnel for 15 min. The surfactant was removed by Soxhlet extraction with ethanol for 48 h. The recovered material (re-SBA-selTMS-ex) was further dried under 2 mmHg at 80 °C in a flask overnight prior to any further modifications.

2.1.4. lit-SBA-selTMS-ex

The synthesis was adapted from Asefa et al. [24]. To a 50-mL round-bottomed flask fitted with a magnetic stir bar and septum was added as-SBA (250 mg) and toluene (18 mL). HMDS (1.8 mL) was added to the suspension via syringe and the flask was purged with Ar for 10 min prior to being sealed and stirred vigorously at room temperature for 18 h. The solution was filtered and the recovered powder washed with hexanes. The surfactant was removed using the ethanol Soxhlet extraction and heating procedure outlined above in Section 2.1.1. The procedure furnished 110 mg of lit-SBA-selTMS-ex.

2.1.5. ex-SBA-SH

In a 10-mL round-bottomed flask equipped with a magnetic stirring bar, 200 mg of ex-SBA was added and charged with argon followed by an addition of 2.0 mL of toluene. To the suspension, 0.2 mL of (3-mercaptopropyl)-trimethoxy-silane (MPTMS) was added and the resulting mixture was stirred at 100 °C in an oil bath for 24 h. After cooling the mixture to room temperature, the material was recovered by vacuum filtration, washed with copious amounts of toluene, ethanol, and acetone, and finally dried on a vacuum funnel for 15 min. The recovered material (ex-SBA-SH) was further dried under 2 mmHg at 80 °C in a flask overnight prior to use or analysis.

2.1.6. re-SBA-selTMS-ex-SH

In a 10-mL round-bottomed flask equipped with a magnetic stirring bar, 200 mg of re-SBA-selTMS-ex was added and the flask charged with argon followed by an addition of 2.0 mL of toluene. To the suspension, 0.2 mL of MPTMS was added and the resulting mixture was stirred at 100 °C in an oil bath for 24 h. After cooling the mixture to room temperature, the material was recovered by vacuum filtration, washed with copious amounts of toluene, ethanol, and acetone, and finally dried on a vacuum funnel for 15 min. The recovered material (re-SBA-selTMS-ex-SH) was further dried under 2 mmHg at 80 °C in a flask overnight prior to use or analysis.

2.1.7. ex- and cal-SBA-TMS

In a 250-mL round-bottomed flask equipped with a magnetic stirring bar, 1.0 g of ex- or cal-SBA was added and the flask was purged with argon. To the flask, 10 mL of HMDS was added and then the resulting suspension was stirred at room temperature for 3 h. The material was recovered by vacuum filtration, washed with copious amounts of hexane and then was dried on a vacuum funnel for 15 min. The recovered material was dispersed in 10 mL of acetone and the resulting suspension was stirred for 30 min at ambient temperature. The material was again recovered by vacuum filtration, washed with acetone, and dried on a vacuum funnel for 15 min. The recovered material was further dried under 2 mmHg at 80 °C in a flask overnight.