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"Solvent-washable polymer templated synthesis of mesoporous materials and solic-acid nanocatalysts in one-pot", Richard E. Mishler II, Ankush V. Biradar, Cole T. Duncan, Eric A. Schiff, and Tewodros Asefa, *Chem. Comm.* 6201-6203 (2009).

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Solvent-washable polymer templated synthesis of mesoporous materials and solid-acid nanocatalysts in one-pot†

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Received (in Berkeley, CA, USA) 1st July 2009, Accepted 1st September 2009

First published as an Advance Article on the web 18th September 2009

DOI: 10.1039/b913035g

We report a new and simple one-pot synthetic method to produce mesoporous silica and nanoporous solid acid catalyst capable of catalyzing pinacole-pinacolone rearrangement and esterification reactions, by preparing a solvent washable phosphonated triblock copolymer template and self-assembling it in the presence of alkoxy silane.

In the early 1990's, a family of mesoporous silicas (MCM41, MCM48 and MCM50) were discovered that had a broad range of uses including sensor applications, catalysis, drug delivery, and use in solar cells.¹ Depending upon the inorganic material, surfactant template, and synthetic conditions employed, mesoporous materials with widely varying composition, structure and pore sizes can be synthesized. The first report in 1998 on the synthesis of SBA15 mesoporous silica with very large pore diameter by using triblock copolymer templates was also a significant advance in the field of mesoporous materials chemistry.² The SBA15 material allows the immobilization *via* "host-guest" inclusion processes of larger molecules that are unable to diffuse in the MCM41 mesoporous material.³

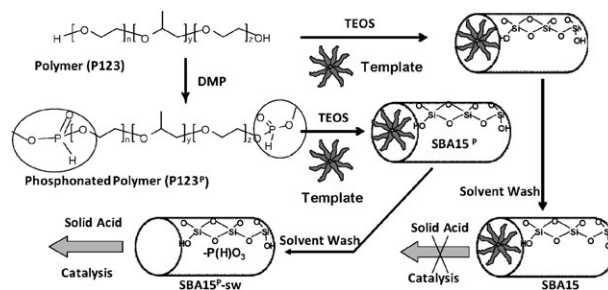
The synthesis of well-ordered mesoporous structures requires an extraction step to remove the templating agent. The most common method is calcination, which involves heating the material to a temperature sufficient to oxidize the organic or polymer template. Calcination is widely used in SBA15-type materials.^{1,2} Although extraction of polymer templates by calcination can completely remove the template, the fairly high temperature is known to promote condensation of surface hydroxyl (–OH) groups on the mesoporous framework, reducing the number of hydroxyl groups utilized for further organic functionalization of the material *via* grafting and post-modification. Calcination also modifies the framework, typically by shrinkage, and of course the template, which could be potentially recycled, is lost.

The second method is solvent-extraction,⁴ which is often able to remove ionic template molecules, but has been shown to be less successful in removing non-ionic templates such as

triblock copolymers that are hydrogen-bonded to and occluded within micropores of the framework.⁵ Other methods include Soxhlet extraction,⁶ stirring in supercritical fluids⁷ and stirring under reflux conditions.⁸ Here we report the synthesis of SBA15-type mesoporous material and solid acid nanostructures by using phosphonated pluronics P123 (designated P123^P), as a solvent-extractable template (Scheme 1).

Acid cleavable, phosphonated triblock copolymer (P123^P) template containing terminal phosphate ester groups was synthesized by converting the terminal hydroxyl groups of the PEG blocks of Pluronic P123 or poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer with dimethylphosphite (DMP) using a similar method as reported by Gitsov and co-workers for synthesis of block-copolymers *via* phosphorylation.⁹ The resulting P123^P polymer was then self-assembled with tetraethoxysilane (TEOS) in aqueous solution to produce mesostructured silica, SBA15^P, under conditions similar to those reported for making SBA15 with P123 (see ESI for details of the synthesis and characterization†).

The template extraction was performed under various conditions with special attention to solvent extraction with the expectation that the P123^P template would be easily removed through a low temperature solvent washing by undergoing hydrolysis at its terminal phosphate ester groups. For comparison purposes, a material templated with as-received P123 was also synthesized and subjected to similar extraction conditions. The samples were then characterized with transmission electron microscopy (TEM), gas adsorption, small angle X-ray scattering (SAXS), powder X-ray diffraction (XRD), elemental analysis, thermogravimetric analysis and solid-state NMR and FT-IR spectroscopy (FTIR).



Scheme 1 Synthesis of hexagonal mesoporous material and solid acid catalyst with solvent extractable phosphonated pluronics template, P123^P.

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† Electronic supplementary information (ESI) available: Synthesis, experimental details, catalysis results, and solution NMR and FT-IR spectra. See DOI: 10.1039/b913035g

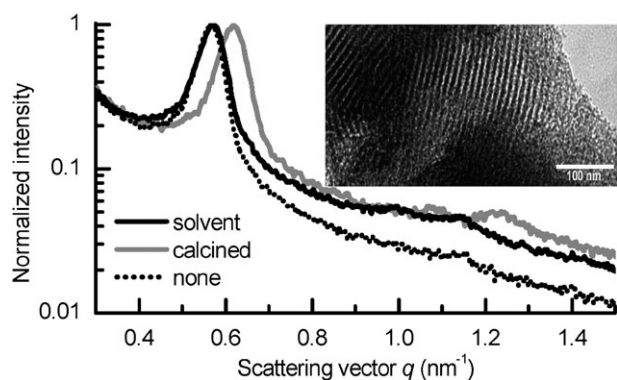


Fig. 1 Small angle X-ray scattering (SAXS) of mesoporous silica as synthesized from phosphonated template, P123^P (SBA15^P) and following solvent washing (SBA15^P-sw) and calcination (SBA15^P-cal). Inset: transmission electron micrograph of SBA15^P-sw.

Fig. 1 shows SAXS for material made with P123^P in its as-synthesized state (SBA15^P), after solvent washing (SBA15^P-sw), and after calcination (SBA15^P-cal). All three samples yield a peak near 0.6 nm⁻¹; higher order peaks are also discernible. The scattering for sample SBA15^P-sw is similar to that of SBA15^P, which supports the idea that the gentler approach of solvent extraction will not change the mesostructure. SBA15^P-cal showed slight unit cell shrinkage indicating that high temperature calcination reduced the unit cell of the material. The XRD patterns also exhibited that the materials have ordered mesostructures with unit cell dimensions of 11.5, 11.5, and 10.3 nm for SBA15^P, SBA15^P-sw, and SBA15^P-cal, respectively. The TEM images are consistent with an hexagonally ordered mesostructure (Fig. 1).

Fig. 2 illustrates nitrogen gas adsorption/desorption isotherms for several template-extracted samples; they all have type IV isotherms, which is indicative of the presence of mesoporous structures in the materials. Compared with SBA-15, the samples prepared from P123^P showed two desorption steps indicating that they have bottle-neck shaped pores or pore clogging.¹⁰ This may be due to the presence of residual phosphate ester groups on the walls of the materials after solvent washing or possible residues of phosphorus oxides from oxidation of phosphate esters inside the mesopores upon calcination.¹¹ The pore size distribution in Fig. S7 (ESI[†]) that was calculated from the isotherms revealed that sample SBA15^P-sw, SBA15^P-cal and SBA15^P have major pore diameters of 8.5, 8.5, and 8.0 nm, respectively. It is worth noting that SBA-15 has insignificant complementary or interconnecting small pores with only 0.09 cc/g pore volume, while samples synthesized with P123^P have significant amounts of such pores with an average size of 2.3 nm and with >0.2 cc/g pore volume (Table S1 and Fig. S7, ESI[†]).

The thermogravimetric analysis (TGA) traces (Fig. 3) for the mesoporous samples show two regions of major weight loss. In the first ~25–100 °C, a distinct drop in weight is observed which is attributed to evaporation of physisorbed water. In the second drop between ~200 °C–600 °C, another distinct weight loss is observed due to the oxidation of the organic template. Upon comparing the graphs in Fig. 3A (mesoporous samples made using the new P123^P template)

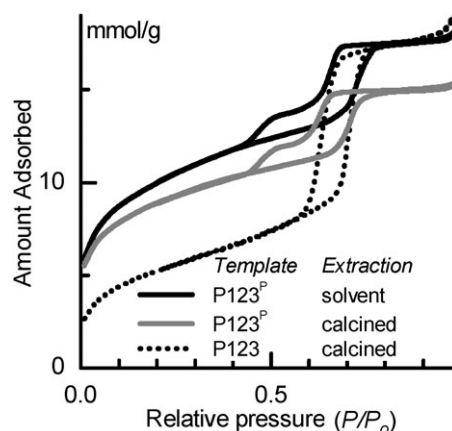


Fig. 2 Nitrogen gas adsorption/desorption isotherms of SBA15^P (from P123^P) and SBA15 (from P123) after template extraction with solvent washing and calcination.

to graphs in Fig. 3B (P123 template), a significant difference particularly between the two different solvent washes was observed. For the samples synthesized from P123^P, the calculated difference between the weight losses in the range of ~200 °C–600 °C for unextracted material and solvent washed for 24 h was 14%; when extracted for 48 h, an additional weight loss of 6% was observed (Fig. 3A). For the SBA15 sample synthesized from P123, the solvent washed sample lost only about 3% mass compared to the untreated sample. This clearly indicates that a simple solvent washing that is unable to remove P123 template does remove most of the mass of P123^P template. We attribute the latter to the hydrolytic cleavage of terminal phosphate ester groups of P123^P, facilitating bulk removal of the template leaving residual phosphate or phosphonic acid groups intact on the walls of the material. To confirm this, we characterized the sample with elemental analysis, FT-IR, which showed residual phosphorus after solvent washing (Fig. S10 and Table S2, ESI[†]). Because the content of phosphorus in the final samples is small (Table S2, ESI[†]), ³¹P solid-state NMR and X-ray photo-emission spectroscopy (XPS) did not show peaks corresponding to phosphorus. The low amount of residual phosphorus may

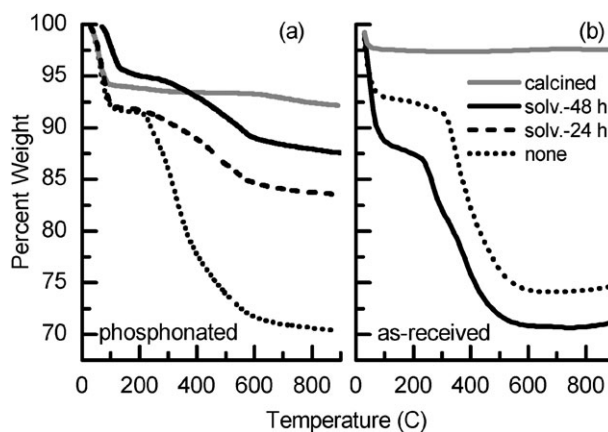
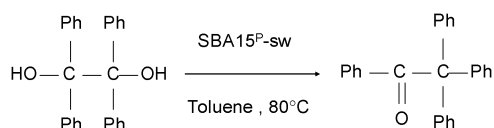


Fig. 3 Thermogravimetric traces before and after solvent washing of mesoporous materials made with (a) P123^P and (b) as-received P123.



Scheme 2 Catalytic transformation of benzopinacol to benzopinacolone using P123^P as a catalyst.

be a result of hydrolysis of phosphate esters over several minutes,^{9c} upon self-assembly at low pH.

Besides its ease of extraction by hydrolytic cleavage, the use of the P123^P template allowed the placement of residual phosphate ester, which was converted to phosphonic acid groups on the mesoporous framework in one-pot, creating a solid acid nanocatalyst (see ESI for details[†]).[‡] We tested the solid acid catalytic properties of the material by first acidifying its phosphate esters with dilute HCl solution and then using the resulting material as a solid acid catalyst in the benzopinacol–benzopinacolone rearrangement^{12,13} (Scheme 2) as well as esterification reactions.¹⁴ The acidified SBA15^P material showed nearly a 100% conversion of benzopinacol with 100% selectivity towards benzopinacolone in 12 h at 120 °C (Table 1). Furthermore, the catalyst was recycled three times without loss of its catalytic activity. The product was confirmed by GC, GC-MS, FT-IR, and ¹H NMR spectroscopy. To perform the control reaction, we used an acidified SBA15 (see ESI[†]). This sample resulted in no reaction under the same conditions. It is also worth noting that this catalytic reaction is dependent on the reaction temperature, where higher temperatures favored this catalytic transformation (Table 1).

We also used this catalyst successfully for esterification reaction of acetic acid with ethanol. The catalyst produced 40% conversion with 100% selectivity to ethyl acetate at 75 °C in 24 h whereas in a control run with SBA15 only 25% conversion in the same time was observed. Also this catalyst was successfully recycled 5 times with only marginal loss in activity. This slight loss in activity was mainly due to handling losses of catalyst (see ESI[†]). These experiments suggest that we have generated an important catalyst with a systematic design and synthetic approach using easily extractable polymer template.

In conclusion, we have synthesized mesoporous silica by preparing and using a phosphonated template, P123^P, and

demonstrated its extraction by a simple solvent washing; the solvent washing procedure had little effect on material prepared using the P123 template. The residual phosphate ester groups could be converted into phosphonic acids, making the material a solid acid nanocatalyst; its catalytic activity was demonstrated by acid-catalyzed pinacol to pinacolone transformation.

We gratefully acknowledge the financial support by the Empire State Development Corporation through the Syracuse Center of Excellence in Environmental and Energy Systems. We thank Prof. I. Gitsov of SUNY-ESF, Prof. Mietek Jaroniec at Kent State University and Dr. Maura Weathers at Cornell University for valuable discussion.

Notes and references

[†] A solid acid catalyzed pinacol–pinacolone reaction was conducted by using the mesoporous material, SBA15^P-sw, as a catalyst. Typically, 0.1 g of benzopinacol was mixed and stirred with 0.1 g SBA15^P-sw catalyst and 10.0 mL of toluene at 80 °C. Samples were collected at 0, 6, 12 and 24 h after starting the reactions for three separate runs using the same catalyst to show recyclability. Three different temperatures (80, 100, and 120 °C) were also tried close the boiling point of solvent used (toluene ~ 110 °C) to determine the most efficient temperature for the transformation of benzopinacol into benzopinacolone. Control experiment using SBA15 as a catalyst was also conducted in the same way. The reaction mixture was taken with a filter syringe and characterized by ¹H NMR spectroscopy.

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Table 1 % Conversion data for benzopinacol to benzopinacolone transformation^a

Entry	Sample	t/h	T/°C	% Conversion
1	SBA15 ^P	6	80	33.0
2	SBA15 ^P	12	80	39.6
3	SBA15 ^P	24	100	66.3
4	SBA15 ^P -1 ^b	6	80	33.0
5	SBA15 ^P -1 ^b	12	80	47.6
6	SBA15 ^P -1 ^b	24	120	~100
7	SBA15 ^P -2 ^c	6	120	94.8
8	SBA15 ^P -2 ^c	12	120	98.3
9	SBA15 ^P -2 ^c	24	120	~100

^a % Conversion determined by ¹H NMR. ^b The catalyst after recycling once. ^c The catalyst after recycling twice.