Bifunctional Catalysis

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Mesoporous Organosilicas with Acidic Frameworks and Basic Sites in the Pores: An Approach to Cooperative Catalytic Reactions**

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Recently there has been significant progress in mimicking nature's multistep reaction cascades for the synthesis of structurally complex organic molecules.[1] Well-controlled multifunctionalization of solid supports can be an efficient strategy for the design of cooperative catalytic systems.[2] This approach requires that the relative concentrations and the proper spatial arrangement of all functional groups are controlled. Biocatalysts such as enzymes immobilize mutually incompatible functional groups without destruction and allow these functional groups to act independently or in a cooperative manner.[3] To mimic such multistep reaction sequences in one-pot reactions will be effective in terms of waste and cost reduction.

Periodic mesoporous organosilicas (PMOs) derived from organosilanes of the type $(RO)_3Si\text{-}X\text{-}Si(OR)_3$ are a unique class of materials, as various organic functionalities can be integrated into the stable inorganic frameworks in a well-directed manner.[4] Development of these species has opened up a wide area for the chemical design of novel nanoporous materials. For instance, bifunctional mesoporous organosilica materials in which one functional group is located in the pore and the other in the framework were first reported by the groups of Ozin and Markowitz.[5] Ozin and co-workers described the formation of materials having both bridging ethylene groups in the framework and terminal vinyl groups in the channel pores, whereas the Markowitz group reported organosilica materials having bridging ethylene groups in the framework and a variety of other functional groups in the channel pores, obtained by a one-step co-condensation method. Thereafter, porous organosilica materials with bifunctional character were considerably refined by integration of multiple functional groups into a single material.[6]

Among the class of organosilica materials, PMOs with phenylene bridges (derived from $(RO)_3Si\text{-}C_6H_4\text{-}Si(OR)_3$) are important owing to their quasi-crystalline pore walls, in which hydrophobic benzene layers alternate with hydrophilic silica layers with a periodicity of 7.6 Å.[7] An important aspect of the PMO synthesis is that the channel pores as well as the framework can be functionalized, thus allowing the design of bifunctional materials with distinguishable locations of the functional groups.[2a] Recently, a few reports highlighted this approach and described the immobilization of incompatible acids and bases for one-pot acid–base reactions. For instance, the combination of weak and strong acids such as silanol groups, urea derivatives, or sulfonic acids with various organic bases on solid supports was investigated, and synergistic catalytic enhancements were observed.[8] However, the efficiency and selectivity of these catalysts are relatively poor owing to the lack of a continuous range of acidic and basic catalytic sites. Besides, acidic and basic functions with sufficient strength were necessary for the successful promotion of both acid- and base-catalyzed reactions. Hence, innovative synthetic efforts for the synthesis of heterogeneous multifunctional catalysts have to be worked out, which maintain and control the independent functionalities and give high concentrations of acidic and basic sites.

Herein we report a synthetic procedure to generate a successful cohabitation of two antagonistic functional groups in a periodic mesoporous organosilica: the acidic groups should be located in the framework walls and the basic groups directed into the channel pores. To achieve this aim, 1,4-bis(triethoxysilyl)benzene and 3-aminopropyltrimethoxysilane were hydrolyzed in the presence of cetyltrimethylammonium bromide (CTAB), resulting in the amine-functionalized mesoporous phenylene-bridged silica material **PMO-NH_2**. In the next step, the amino groups were protected using di-*tert*-butyl-dicarbonate, a strategy commonly used for amino group protection.[9] This procedure yielded **PMO-NHBoC**, which could be sulfonated at the bridging phenylene units by simple treatment with chlorosulfonic acid, giving **PMO-SO_3H-NHBoC**.[10] Deprotection of the amino groups by thermal treatment gave the bifunctional mesoporous catalyst **PMO-SO_3H-NH_2**, in which the sulfonic acid groups are located on the hydrophobic phenylene layers and the propylamine groups are attached to the hydrophilic silica layers (Scheme 1). Therefore the catalytically active sites are separated and give rise to an organosilica sample containing the two antagonistic functional groups.

The intermediates and the final bifunctional **PMO-SO_3H-NH_2** catalysts were characterized systematically by ^{13}C CP-MAS NMR, ^{29}Si CP-MAS NMR, X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (PXRD), and N_2 adsorption–desorption measurements.

The successful cohabitation of the acidic framework walls and basic pore channels in **PMO-SO_3H-NH_2** was confirmed

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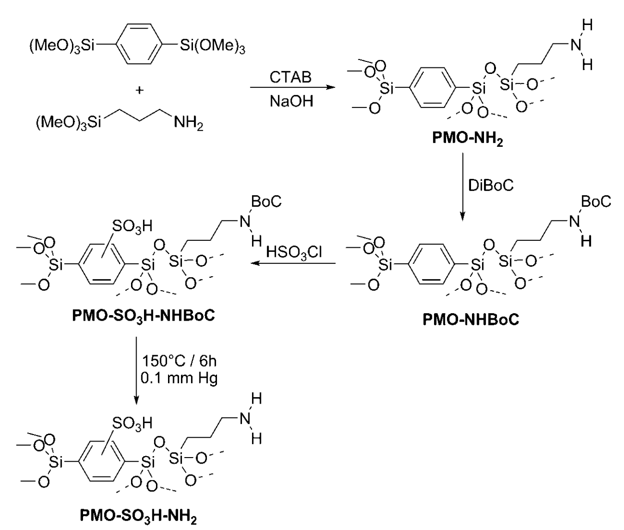


Scheme 1. Synthesis of the bifunctional **PMO-SO_3H-NH_2** material.

by NMR spectroscopy. The ^{13}C CP-MAS NMR spectrum of **PMO-NH_2** shows the signals of both the phenylene units ($\delta =$ 134 ppm) and the aminopropyl chains (CH_2N $\delta = 43.0$, CH_2 $\delta = 23.7$, CH_2Si $\delta = 10.3$ ppm, Figure 1). In addition to these signals, the ^{13}C NMR spectrum of **PMO-NHBoC** depicts sharp resonances at $\delta = 28.0$ (*tert*-butyl), 78.6 (C–O), and 157.1 ppm (C=O), which confirm the BoC protection of the amine groups. In the ^{13}C-CP-MAS NMR spectrum of **PMO-SO_3H-NH_2**, the resonances associated with the BoC protection have disappeared, while the resonances associated with the propyl spacers are still present. Furthermore, the phenylene signal at $\delta = 134$ ppm becomes broadened, and a weak shoulder at $\delta = 141.3$ ppm occurs, which, according to the literature,[11] can be assigned to the C–SO_3H carbon atom. The presence of the sulfonic acid groups was also confirmed by XPS analysis (see the Supporting Information, Figure S1). The solid-state ^{29}Si CP-MAS NMR spectra show three signals at $\delta = -80.6$, -70.5, and -61.0 ppm. They can be assigned to T^2 and T^3 species for silicon attached to phenylene ($\delta = -80.6$ and -70.5) and to the propyl chain ($\delta = -70.5$ and -61.0), respectively (see the Supporting Information, Figure S2).[12] The absence of quaternary Q^n sites indicates that the C–Si bonds remain untouched during the gelation process, the sulfonation reaction, and the thermal treatments, which we anticipated would give a more hydrophobic nature and a pseudo-crystalline structure to the phenylene silica PMO.

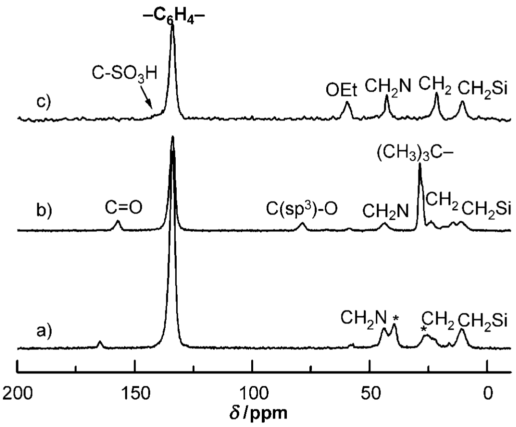


Figure 1. ^{13}C CP-MAS NMR spectra of a) **PMO-NH_2**, b) **PMO-NHBoC**, and c) **PMO-SO_3H-NH_2**. * in (a) denotes residual peaks of CTAB, which disappear after the sulfonation reaction (c).

The amount of sulfonic acid was quantitatively determined by titration. The acid content of **PMO-SO_3H-NH_2** was estimated to be 0.81 $mmol\,g^{-1}$, which is almost equivalent to the acid content in **PMO-SO_3H-NHBoC** (0.92 $mmol\,g^{-1}$). This finding shows that the deprotection of the amino groups had only a minor impact on the acid character of the SO_3H groups. Besides, it is noteworthy that the N/S ratio obtained from the elemental analysis does not change after thermal treatment. **PMO-SO_3H-NH_2** contains about 1.79 $mmol\,g^{-1}$ amine and 1.10 $mmol\,g^{-1}$ sulfonic acid. The low rate of conversion of phenylene groups into sulfonated species in the phenylene silica PMO may be related to a low reactivity of the covalently bound phenylene groups in the siloxane network.[7]

Powder X-ray diffraction (PXRD) patterns showed the characteristic reflections at low diffraction angles assigned to the mesoporous structure of the material (see the Supporting Information, Figure S3). Moreover, the PXRD patterns at $10° < 2\theta < 40°$ display peaks with *d* spacings of 7.6, 3.8, and 2.5 Å (Figure 2), which can be assigned to the molecular-scale periodicity in the pore walls with a spacing of 7.6 Å. Evidently, the structural integrity of the materials is maintained during the functionalization process.[12]

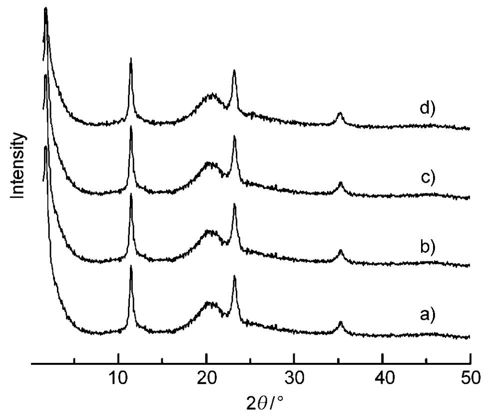


Figure 2. Powder X-ray diffraction patterns of a) **PMO**, b) **PMO-NH_2**, c) **PMO-NHBoC**, and d) **PMO-SO_3H-NH_2**.

Nitrogen adsorption/desorption isotherms show type IV behavior (Figure 3). The BJH method yields pore size distributions typical for slightly disordered materials (see the Supporting Information, Figure S4). The **PMO-NH_2** sample shows a BET surface area, total pore volume, and pore size of 905 m^2g^{-1}, 0.962 cm^3g^{-1}, and 25.7 Å, whereas **PMO-NHBoC** and **PMO-SO_3H-NH_2** had corresponding values of 794 m^2g^{-1}, 0.735 cm^3g^{-1}, 25.1 Å and 768 m^2g^{-1}, 0.676 cm^3g^{-1}, 24.2 Å, respectively. As evidenced by these investigations, the structure of the crystal-like pore walls is

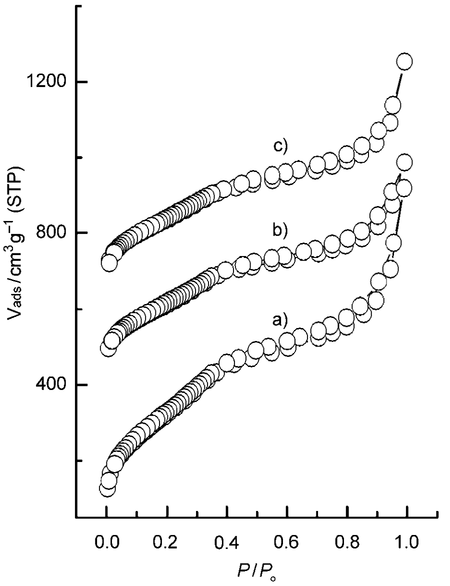


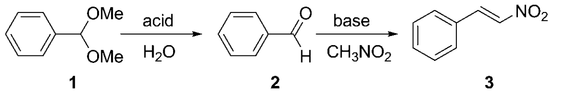
Figure 3. Nitrogen adsorption–desorption isotherms of a) **PMO-NH$_2$**, b) **PMO-NHBoC**, and c) **PMO-SO$_3$H-NH$_2$**.

retained, and the C–Si bonds of the phenylene silica PMO survive the functionalization reactions.

The accessibility of the free amino and sulfonic acid groups in **PMO-SO$_3$H-NH$_2$** was evaluated in a tandem reaction, the catalytic conversion of benzaldehyde dimethyl acetal (**1**) into 2-nitrovinyl benzene (**3**). This reaction sequence involves two separate steps: an acid-catalyzed deprotection to give the intermediate benzaldehyde (**2**) and the subsequent base-catalyzed nitroaldol (Henry) reaction to yield 2-nitrovinyl benzene (**3**, Table 1).[8u]

Remarkably, the bifunctionalized **PMO-SO$_3$H-NH$_2$** sample converts **1** into **3** in almost quantitative yields after 20 h. This result demonstrates that the reactivity of the aminopropyl groups is not affected by the presence of sulfonic acid groups in the sample. In the absence of amine groups (in **PMO-SO$_3$H-NHBoC**), benzaldehyde (**2**) is the only product, while formation of a negligible amount of **3** was noted with **PMO-NH$_2$**. Thus, each catalyst (acid and base) on its own is unable to promote the conversion **1**→**2**→**3** in quantitative yields, which indicates the cooperative behavior of the bifunctionalized catalyst **PMO-SO$_3$H-NH$_2$**. Addition of equivalent amounts of structurally similar free acid (*p*-toluenesulfonic acid) or base (*tert*-butylamine) to solid **PMO-SO$_3$H-NH$_2$** stops the activity, as these homogeneous species diffuse into the pore channels and destroy the catalytic sites, presumably by formation of ion pairs. Thus the formation of the nitroaldol product **3** was anticipated to take place by a sulfonic acid catalyzed deacetalization reaction and a subsequent nitroaldol reaction of nitromethane with benzaldehyde. These results confirm that a well-designed localization of acid and base functionalities in mesoporous solids will lead to an effective catalyst for one-pot reaction cascades.

Table 1: One pot deacetalization-nitroaldol reaction cascade.[a]



Entry	Catalyst	Conv. of **1** [%]	Yield of **2** [%]	Yield of **3** [%]
1	**PMO-SO$_3$H-NH$_2$**	100	2.5	97.5
2	**PMO-SO$_3$H-NHBoC**	100	100	0
3	**PMO-NH$_2$**	trace	trace	trace
4	**PMO-SO$_3$H-NH$_2$** + *tert*-butyl amine	trace	trace	trace
5	**PMO-SO$_3$H-NH$_2$** + *p*-toluene-sulfonic acid	100	100	trace

[a] Reaction conditions: benzaldehyde dimethyl acetal (1 mmol), CH_3NO_2 (5 mL), 90 °C, 20 h.

The recyclability of the bifunctional catalyst **PMO-SO$_3$H-NH$_2$** was examined by isolating it from the reaction mixture (centrifugation, washing with ethanol and dichloromethane, and drying). Owing to the tight covalent anchoring and the spatial separation of the organic functional groups, the catalyst showed almost no loss in activity in the third run. Furthermore, the ^{1}H NMR spectroscopic analysis of the reaction filtrate gave no hint of leaching of the immobilized organic groups, and the elemental analysis of the recovered catalyst confirmed the retention of the organic content on the mesoporous surface.

In summary, bifunctional mesoporous organosilicas possessing organic amines and sulfonic acid groups were successfully generated and used in a cooperative catalytic transformation. Compared to earlier reports, the current methodology benefits from a precise location and concentration of the active functional groups in a mesoporous phenylene silica with crystalline pore walls, in which the acidic groups reside mainly on hydrophobic benzene layers and the basic amino groups on hydrophilic silica layers for cooperative effects. Further investigation is currently underway regarding enhancement of the acid–base properties of the materials, additional catalytic enhancements, and advanced applications.

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[1] a) J. C. Wasilke, S. J. Obrey, R. T. Baker, G. C. Bazan, *Chem. Rev.* **2005**, *105*, 1001; b) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115; c) A. N. Thadani, V. H. Rawal, *Org. Lett.* **2002**, *4*, 4321; d) K. Motokura, N. Fujia, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *Tetrahedron Lett.* **2005**, *46*, 5507; e) K. Motokura, N. Fujita, K. Mori, T. Muzugaki, K. Ebitani, K. Htsukawa, K. Kaneda, *Chem. Eur. J.* **2006**, *12*, 8228; f) J. Louie, C. W. Bielawski, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 11312; g) K. Mori, Y. Kondo, S. Morimoto, H. Yamashita, *Chem. Lett.* **2007**, *36*, 1068; h) K. M. Koeller, C. H. Wong, *Chem. Rev.* **2000**, *100*, 4465.

[2] a) J. Alauzun, A. Mehdi, C. Reye, R. J. P. Corriu, *J. Am. Chem. Soc.* **2006**, *128*, 8718; b) M. Jaroniec, *Nature* **2006**, *442*, 638; c) F. Gelman, J. Blum, D. Anvir, *Angew. Chem.* **2001**, *113*, 3759;

Angew. Chem. Int. Ed. **2001**, *40*, 3647; d) B. J. Cohen, M. A. Kraus, A. Patchornik, *J. Am. Chem. Soc.* **1977**, *99*, 4165; e) M. W. McKittrick, C. W. Jones, *J. Am. Chem. Soc.* **2004**, *126*, 3052; f) J. M. Notestein, A. Katz, *Chem. Eur. J.* **2006**, *12*, 3954; g) B. M. Choudary, N. S. Chowdari, S. Madhi, M. L. Kantam, *J. Org. Chem.* **2003**, *68*, 1736; h) K. C. Nicolaou, T. Montagnon, S. A. Snyder, *Chem. Commun.* **2003**, 551; i) R. Voss, A. Thomas, M. Antonietti, G. A. Ozin, *J. Mater. Chem.* **2005**, *15*, 4010; j) M. Kanai, N. Kato, E. Ichikawa, M. Shibasaki, *Synlett* **2005**, 1491; k) T. Okino, Y. Hoashi, T. Furukawa, X. N. Xu, Y. Takamoto, *J. Am. Chem. Soc.* **2005**, *127*, 119; l) N. T. S. Phan, C. S. Gill, J. V. Nguyen, Z. J. Zhang, C. W. Jones, *Angew. Chem.* **2006**, *118*, 2267; *Angew. Chem. Int. Ed.* **2006**, *45*, 2209.

[3] a) E. L. Margelefsky, R. K. Zeidan, M. E. Davis, *Chem. Soc. Rev.* **2008**, *37*, 1118; b) S. Saito, H. Yamamoto, *Acc. Chem. Res.* **2004**, *37*, 570.

[4] a) S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* **1999**, *121*, 9611; b) T. Asefa, M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* **1999**, *402*, 867; c) B. J. Melde, B. T. Holland, C. F. Blanford, A. Stein, *Chem. Mater.* **1999**, *11*, 3302.

[5] a) T. Asefa, M. Kruk, M. J. MacLachlan, N. Coombs, H. Grondey, M. Jaroniec, G. A. Ozin, *J. Am. Chem. Soc.* **2001**, *123*, 8520; b) M. C. Burleigh, M. A. Markowitz, M. S. Spector, B. P. Gaber, *Chem. Mater.* **2001**, *13*, 4760; c) M. C. Burleigh, M. A. Markowitz, M. S. Spector, B. P. Gaber, *J. Phys. Chem. B* **2001**, *105*, 9935.

[6] a) O. Olkhovyk, S. Pikus, M. Jaroniec, *J. Mater. Chem.* **2005**, *15*, 4285; b) O. Olkhovyk, M. Jaroniec, *Ind. Eng. Chem. Res.* **2007**, *46*, 1745; c) Y. Yang, A. Sayari, *Chem. Mater.* **2007**, *19*, 4117; d) S. Huh, J. W. Wiench, B. G. Trewyn, S. Song, M. Pruski, V. S.-Y. Lin, *Chem. Commun.* **2003**, 2364; e) R. J. P. Corriu, A. Mehdi, C. Reye, *J. Mater. Chem.* **2005**, *15*, 1517; f) C. Baleizão, B. Gigante, D. Das, M. Alvaro, H. Garcia, A. Corma, *J. Catal.* **2004**, *223*, 106; g) W. J. Hunks, G. A. Ozin, *Adv. Funct. Mater.* **2005**, *15*, 259; h) M. A. Wahab, I. Imae, Y. Kawakami, C.-S. Ha, *Chem. Mater.* **2005**, *17*, 2165; i) B. E. Grabicka, M. Jaroniec, *Microporous Mesoporous Mater.* **2009**, *119*, 144.

[7] a) S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, *Nature* **2002**, *416*, 304; b) S. Fujita, S. Inagaki, *Chem. Mater.* **2008**, *20*, 891; c) F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem.* **2006**, *118*, 3290; *Angew. Chem. Int. Ed.* **2006**, *45*, 3216.

[8] a) B. Voit, *Angew. Chem.* **2006**, *118*, 4344; *Angew. Chem. Int. Ed.* **2006**, *45*, 4238; b) H. Gröger, *Chem. Eur. J.* **2001**, *7*, 5246; c) S. Huh, H.-T. Chen, J. W. Weinch, M. Pruski, V. S-Y. Lin, *Angew. Chem.* **2005**, *117*, 1860; *Angew. Chem. Int. Ed.* **2005**, *44*, 1826; d) J. D. Bass, A. Solovyov, A. J. Pascal, A. Katz, *J. Am. Chem. Soc.* **2006**, *128*, 3737; e) M. J. Climent, A. Corma, V. Fornes, R. Guil-Lopez, S. Ibora, *Adv. Synth. Catal.* **2002**, *344*, 1090; f) Y. Huang, B. G. Trewyn, H.-T. Chen, V. S.-Y. Lin, *New J. Chem.* **2008**, *32*, 1311; g) F. Gelman, J. Blum, A. Anvir, *J. Am. Chem. Soc.* **2000**, *122*, 11999; h) J. D. Bass, S. L. Anderson, A. Katz, *Angew. Chem.* **2003**, *115*, 5377; *Angew. Chem. Int. Ed.* **2003**, *42*, 5219; i) K. Motokura, N. Fujita, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2005**, *127*, 9674; j) K. Motokura, M. Tada, Y. Iwasawa, *J. Am. Chem. Soc.* **2007**, *129*, 9540; k) K. Motokura, M. Tomita, M. Tada, Y. Iwasawa, *Chem. Eur. J.* **2008**, *14*, 4017; l) S-J. Huang, S. Huh, P. S. Lu, S. H. Liu, V. S.-Y. Lin, S.-B. Liu, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3080; m) R. K. Zeidan, S.-J. Hwang, M. E. Davis, *Angew. Chem.* **2006**, *118*, 6480; *Angew. Chem. Int. Ed.* **2006**, *45*, 6332; n) R. K. Zeidan, M. E. Davis, *J. Catal.* **2007**, *247*, 379; o) J. D. Bass, A. Katz, *Chem. Mater.* **2006**, *18*, 1611; p) K. K. Sharma, T. Asefa, *Angew. Chem.* **2007**, *119*, 2937; *Angew. Chem. Int. Ed.* **2007**, *46*, 2879; q) K. K. Sharma, A. Anan, R. P. Buckley, W. Quellette, T. Asefa, *J. Am. Chem. Soc.* **2008**, *130*, 218; r) K. Motokura, M. Tada, Y. Iwasawa, *J. Am. Chem. Soc.* **2009**, *131*, 7944; s) S. Huh, H. T. Chen, J. W. Wiench, M. Pruski, V. S.-Y. Lin, *J. Am. Chem. Soc.* **2004**, *126*, 1010; t) A. Anan, K. K. Sharma, T. Asefa, *J. Mol. Catal. A* **2008**, *288*, 1; u) S. Shylesh, A. Wagener, A. Seifert, S. Ernst, W. R. Thiel, *Chem. Eur. J.* **2009**, *15*, 7052–7062.

[9] a) A. Mehdi, C. Reye, S. Brandes, R. Guilard, R. J. P. Corriu, *New J. Chem.* **2005**, *29*, 965; b) A. Katz, M. E. Davis, *Nature* **2000**, *403*, 286.

[10] Chemical modification of phenylene groups with amino groups was reported earlier, for example: M. Ohashi, M. P. Kapoor, S. Inagaki, *Chem. Commun.* **2008**, 841.

[11] a) C. Li, J. Yang, X. Shi, J. Liu, Q. Yang, *Microporous Mesoporous Mater.* **2007**, *98*, 220; b) K. Nakajima, I. Tomita, M. Hara, S. Hayashi, K. Domen, J. N. Kondo, *Adv. Mater.* **2005**, *17*, 1839.

[12] Q. Yang, M. P. Kapoor, S. Inagaki, *J. Am. Chem. Soc.* **2002**, *124*, 9694.