



Sustainable, green protocols for heterogenized organocatalysts: *N*-Phenylthiazolium salts heterogenized on organic–inorganic hybrid mesoporous supports

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ABSTRACT

A heterogenized organocatalyst was synthesized by the covalent anchoring of *N*-phenyl-thiazolium salts over mesoporous organosilica (phenylene–silica, ethane–silica) and mesoporous silica (MCM-41) supports. Powder X-ray diffraction patterns as well as nitrogen physisorption analysis confirmed the retention of mesoporous structure after the grafting reactions. Solid-state NMR analysis (¹³C CP-MAS NMR, ²⁹Si MAS NMR) certified the integrity of organocatalyst residing inside the pore channels of the mesoporous supports. Catalytic evaluation in the benzoin condensation reaction as well as in the cross-coupling of aldehydes with acyl imines indicated that the organocatalyst heterogenized on mesoporous phenylene organosilica exhibited higher catalytic activity, stability and reusability than the analogous mesoporous silica support. The better activity and stability of the phenylene–silica support was attributed to the enhanced hydrophobic properties arising from the frame wall organic groups.

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1. Introduction

Metal free methods for the synthesis of organic molecules termed under organocatalysis have recently attracted widespread attention [1]. A wide variety of reactions has been investigated in this area of research, among them C–C couplings using azole type catalysts are widely explored [2]. Interestingly, the mechanisms behind these reactions often resemble those of biological processes and hence a better mechanistic understanding of organocatalytic reactions can alternatively improve our understanding of the basic biocatalytic transformations [2]. However, in contrast to transition metal based catalytic reactions, organocatalytic reactions are mainly homogeneous in nature [3]. Thus although organocatalytic transformations can be considered as green processes, catalyst separation and reuse of the active components still have to be worked out in detail. A simple solution relates to the heterogenization of organocatalysts on high surface area solid supports [4]. Since the unique textural features of (meso)porous materials allow high catalyst loadings and maintain a uniform dispersion of active sites, the protocols of

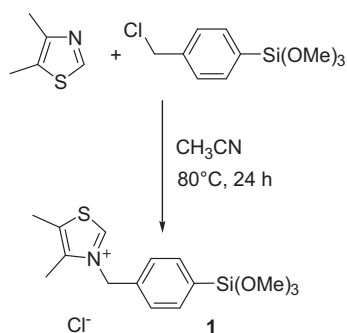
organocatalysis can be made more greener by using heterogenized systems.

The thiazolium motif usually found in thiamine (Vitamin B₁) is involved as a co-enzyme in a variety of enzymatically catalyzed reactions, such as C–C couplings in the fatty acid and carbohydrate metabolism [5]. In organocatalytic reactions, thiazolium salts turned out to catalyze a number of nucleophilic acylation reactions such as the benzoin condensation and the Stetter reaction by generating an acyl anion equivalent from an aldehyde [6]. Recently, we reported the first protocol for the heterogenization of a *N*-phenylthiazolium organocatalyst on mesoporous MCM-41 [7]. Therein we noted that hydrophilic support is not really preferable for recycling of this catalyst, since its activity decreases drastically already after the first run. However, we could prove that by removing residual silanol groups and thereby alternating the surface properties from hydrophilic to more hydrophobic, the catalytic activity and the stability of the heterogenized catalyst systems can be improved. These results prompted us to investigate the application of hydrophobic periodic mesoporous organosilicas (PMOs) as supports for thiazolium catalyzed reactions. Recently, it is well accepted that hydrophobic surfaces can improve the catalytic activity and stability of certain active sites in inclusion chemistry [8,9].

PMOs are organic–inorganic hybrid materials having organic moieties as bridging motifs in the frame wall positions. They are

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Scheme 1. Synthesis of the thiazolium precursor **1**.

obtained by a template directed condensation of bifunctional precursors of the type $(\text{RO})_3\text{Si}-\text{X}-\text{Si}(\text{OR})_3$ and have a homogeneous distribution of organic fragments and silica moieties in the framework [10]. Due to these organic moieties, they possess hydrophobic surfaces which consequently improve their hydrothermal stability compared to mesoporous materials derived from neat silica and their applicability in various catalytic transformations. For this purpose, hydrophobic PMOs possessing phenylene ($-\text{C}_6\text{H}_4-$) and ethylene ($-\text{CH}_2\text{CH}_2-$) bridges were prepared by a templating method using cetyltrimethylammonium bromide as the structure directing agent [8c]. An outstanding feature of the phenylene derivative is its molecular organization of the pore walls wherein hydrophobic arene and hydrophilic silica layers are alternatively arranged with a periodicity of 7.6 \AA [10]. The thiazolium precursor **1** was prepared by the synthetic procedure shown in Scheme 1.

2. Experimental

2.1. Synthetic procedures

2.1.1. Synthesis of 4,5-dimethyl-3-(4-trimethoxysilylphenylmethyl)thiazolium chloride (**1**)

1.13 g (10 mmol) of 4,5-dimethylthiazole and 2.47 g (10 mmol) of (*p*-chloromethyl) phenyltrimethoxysilane were dissolved in 5 mL of dry CH_3CN and the mixture was refluxed for 24 h under inert conditions. All volatiles were removed in vacuum, leaving **1** as a yellow powder in quantitative yield.

2.1.2. Synthesis of the heterogenized catalysts

1.0 g of the desired mesoporous support was degassed at 150°C for 2 h and then suspended in 100 mL of dry toluene. To this suspension, 1 mmol of **1** was added and the mixture was heated to reflux for 24 h. The solid was filtered, washed with ethanol and subsequently extracted with ethanol in a Soxhlet extractor for additional 12 h. The solid materials were then dried under vacuum.

2.1.3. Synthesis of silylated supported catalyst (Sil-MCM-OC)

1.0 g of organocatalyst heterogenized MCM-41 support (MCM-41-OC) suspended in 30 mL of toluene was treated with 1.0 g (9.2 mmol) of Me_3SiCl at room temperature under continuous stirring for 24 h. The solid was then filtered, washed with ethanol and dichloromethane and dried in vacuum.

2.2. Characterization

Powder X-ray diffraction patterns were obtained on a Siemens D5005 diffractometer with $\text{Cu K}\alpha$ radiation (30 kV, 30 mA). Nitrogen adsorption-desorption isotherms were measured at 77 K on a Sorptomatic 1990 analyzer after evacuation of the samples at 413 K overnight. The specific surface areas were calculated using the BET method and pore size distributions were evaluated from

the desorption branches of nitrogen isotherms using the BJH model. Solid-state ^{13}C and ^{29}Si CP-MAS NMR spectra were recorded at 100.6 and 79.49 MHz, respectively, using a Bruker AVANCE 400 spectrometer.

2.3. Catalytic reactions

2.3.1. Benzoin condensation

Benzaldehyde was distilled in vacuum and triethylamine was distilled under ambient pressure before use. The heterogenized organocatalyst was suspended in the solvent under an atmosphere of nitrogen and benzaldehyde was added followed by the dropwise addition of Et_3N . The reactions were performed in refluxing solvents under stirring. After the reaction, the mixture was filtered under an atmosphere of N_2 and the yield of benzoin was determined by GC-MS analysis.

2.3.2. Cross-coupling reaction for the synthesis of α -amido ketones

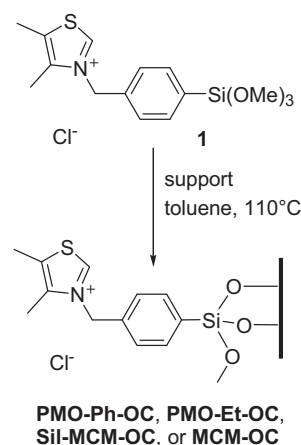
N-[(4-Ethylphenyl sulfonyl)(phenyl)methyl]cyclohexanecarboxamide was prepared according to a literature procedure [11]. The reactions were carried out in a 25 mL flask under nitrogen atmosphere. Typically, 0.55 g (1.5 mmol) of the carboxamide and 300 mg of the heterogenized catalyst were set under vacuum at 35°C for 1 h. Then 15 mL of the appropriate solvent was added followed by the addition of 0.17 g (1.6 mmol) 4-pyridinecarbaldehyde. An appropriate amount of distilled triethylamine was added in one portion *via* a syringe to initiate the reaction. After the reaction, the catalyst was filtered off and the product was isolated by flash chromatography over silica (70% EtOAc and 30% hexane).

3. Results and discussion

3.1. Structural characterization

Nucleophilic substitution at (*p*-chloromethyl)phenyltrimethoxysilane using 4,5-dimethyl thiazole produces the ionic precursor **1** in quantitative yields. The mesoporous supports were developed according to literature protocols [7,8c]. Treatment of phenylene (**PMO-Ph**) and ethylene bridged PMO (**PMO-Et**) as well as silylated mesoporous MCM-41 (**Sil-MCM**) and MCM-41 (**MCM**) with compound **1** in dry toluene gives the desired heterogenized catalysts **PMO-Ph-OC**, **PMO-Et-OC**, **Sil-MCM-OC** and **MCM-OC** (Scheme 2).

The success of these syntheses can be demonstrated by means of solid-state NMR spectroscopy. The ^{13}C CP-MAS NMR spectra



Scheme 2. Synthesis of the mesoporous supported organocatalysts.

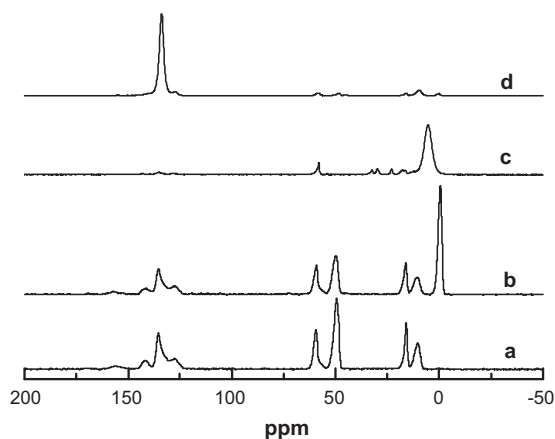


Fig. 1. Solid-state ^{13}C MAS NMR of (a) **MCM-OC**, (b) **Sil-MCM-OC**, (c) **PMO-Et-OC** and (d) **PMO-Ph-OC**.

of **PMO-Ph-OC** (**PMO-Et-OC**) show sharp peaks at δ ca. 133.7 (5.3) ppm, corresponding to the $-\text{Si}-\text{C}_6\text{H}_4-\text{Si}-$ ($-\text{Si}-\text{CH}_2\text{CH}_2-\text{Si}-$) groups in the framework walls (Fig. 1). All heterogenized samples additionally exhibit resonances in their ^{13}C CP-MAS NMR spectra similar to those of the thiazolium precursor **1**, but with decreased intensities for the methoxy groups which are cleaved off during the condensation process. In **PMO-Ph-OC**, the shoulder peak centering at δ ca. 127 ppm can be assigned to the aromatic carbon atoms of the benzyl group of the thiazolium salt, demonstrating the successful support modification. Resonances at δ 58, 49, and 12 ppm give additional evidence for the presence of thiazolium sites covalently bound to the mesoporous solid supports. Remnant ethanol from the extracting process produces resonances at δ 60 and 16 ppm and the $-\text{OSiMe}_3$ groups on the surface of **Sil-MCM-OC** give a very sharp resonance at -0.56 ppm confirming the surface silylation of the mesoporous solid.

The ^{29}Si MAS NMR spectrum of **PMO-Ph-OC** displays three signals (Fig. 2), which can be assigned to T^2 and T^3 silicon centres bound to phenylene moieties (-81.2 and -71.4 ppm) and to the linker unit of the thiazolium motif (-71.4 and -63.3 ppm) [12]. **PMO-Et-OC** shows two peaks: one at -58 (T^2 : $\text{C}(\text{OH})\text{Si}(\text{OSi})_2$) and the another at -67 ppm (T^3 : $\text{CSi}(\text{OSi})_3$). There are no resonances typical for Q^n species ($\text{Q}^n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$, $n = 2-4$), which means that no silicon-carbon bond cleavage occurred during the synthesis of the supports and the subsequent high temperature grafting process. As expected, the ^{29}Si MAS NMR spectrum of **MCM-OC** shows

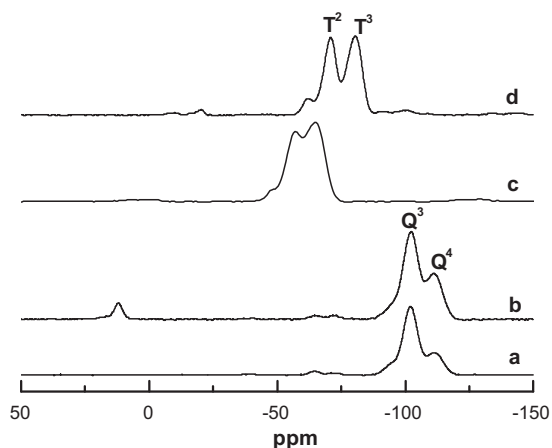


Fig. 2. Solid-state ^{29}Si MAS NMR of (a) **MCM-OC**, (b) **Sil-MCM-OC**, (c) **PMO-Et-OC** and (d) **PMO-Ph-OC**.

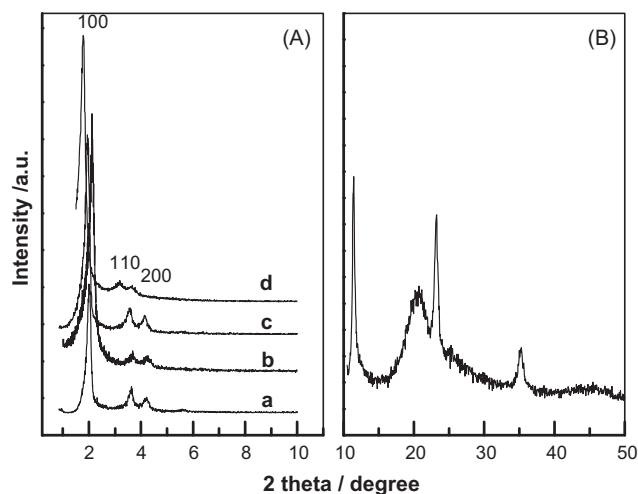


Fig. 3. (A) Small angle XRD patterns of (a) **MCM-OC**, (b) **Sil-MCM-OC**, (c) **PMO-Et-OC**, (d) **PMO-Ph-OC** and (B) wide angle XRD patterns of **PMO-Ph-OC** showing the crystalline nature of the pore walls.

signals between -110 and -90 ppm (Q sites) typical for the silica frame work and weak resonances between -75 and -65 ppm (T sites) originating from the heterogenized thiazolium precursor **1**. The silylated **Sil-MCM-OC** sample shows an additional resonance at 12 ppm for the $-\text{SiOMe}_3$ groups.

Powder XRD patterns of the samples with heterogenized thiazolium sites exhibit characteristic peaks at low angles related to the hexagonal mesoporous structure (Fig. 3). Additional peaks appear for **PMO-Ph-OC** in the range of $10^\circ < 2\theta < 50^\circ$ which can be assigned to a periodicity with a spacing of 7.6 \AA in the frame walls [12].

N_2 adsorption/desorption experiments produced type IV isotherms typical for mesoporous materials having a uniform pore structure (Fig. 4). Compared to the pristine mesoporous supports, the modified materials showed a decrease in surface area, pore size, and pore volume due to the presence of bulky organic groups inside the pore channels. The measured BET surface areas and BJH pore sizes of all thiazolium heterogenized mesoporous solids are collected in Table 1. Furthermore, the catalyst loading of all mesoporous materials was found to be $0.34-0.48 \text{ mmol g}^{-1}$ (calculated from the elemental analysis), corresponding to ~ 10 wt% of organic moieties in the materials (Table 1).

Thermogravimetric data were recorded in air for the surfactant free phenylene-silica **PMO-Ph** and thiazolium modified **PMO-Ph-OC** material (Fig. 5). The TG-DTG curve of neat **PMO-Ph** exhibits a

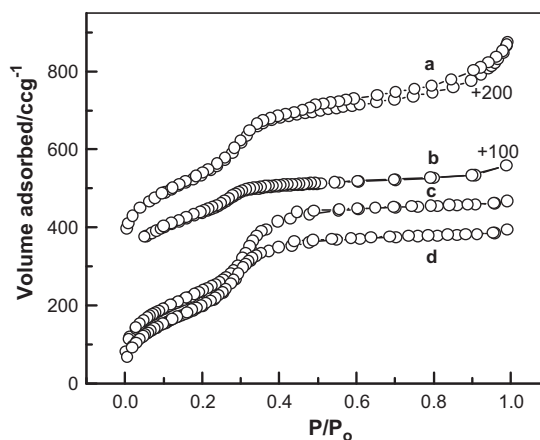


Fig. 4. Nitrogen adsorption-desorption isotherms of (a) **PMO-Ph-OC**, (b) **PMO-Et-OC**, (c) **MCM-OC** and (d) **Sil-MCM-OC**.

Table 1
Textural and compositional details of the mesoporous solids functionalized with the thiazolium organocatalyst.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{pore} ($\text{cm}^3 \text{g}^{-1}$)	D_{pore} (nm)	TOG (mmol g^{-1}) ^a	Wt. loss (%) ^b
PMO-Ph-OC	882	0.87	2.57	0.34 (0.33)	9.9
PMO-Et-OC	735	0.81	2.51	0.39	–
Sil-MCM-OC	766	0.64	2.52	0.34	10.7
MCM-OC	897	0.71	2.69	0.48 (0.18)	9.4

^a Total amount of organic moieties, determined by elemental analysis.

^b Weight loss between 200 and 500 °C (from TG data). Values in parenthesis show the results of the second run.

small weight loss below 100 °C with an endothermic peak, corresponding to the desorption of physisorbed water. No weight loss for the decomposition of remnant surfactant in the range of 100–300 °C was noted, confirming the complete removal of the surfactant by solvent extraction. A main weight loss occurs from 500 to 650 °C with a strong exothermic peak corresponding to the combustion and release of organic fragments from the pore walls [13]. For **PMO-Ph-OC**, a weight loss with an exothermic peak can be observed from 200 to 350 °C, which can be assigned to the partial decomposition of the thiazolium salt since this feature is absent in the decomposition curve of **PMO-Ph**. These results also confirm the successful introduction of the organocatalyst into the mesoporous organosilica support.

3.2. Catalytic activity evaluation

The activity of the heterogenized thiazolium catalysts was investigated for the benzoin condensation (Scheme 3) as well as for the cross-coupling of aldehydes with acyl imines (Scheme 4), which are typical test reactions for thiazolium based organocatalytic transformations. Optimization of the solvent and the amount of external base provided that methanol as the solvent and an Et_3N concentration of 0.22 mol/L gave the highest productivity for the benzoin condensation (Table 2). Under identical conditions, **PMO-Ph-OC** showed the best activity among all supported catalysts. The organocatalyst loading was almost similar for all mesoporous materials evaluated.

For practical applications of heterogeneous catalysts the stability and reusability are important factors. The recyclability of

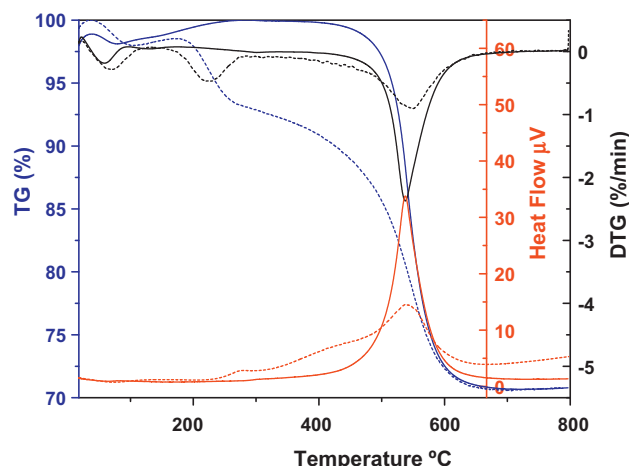
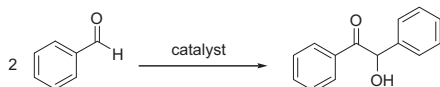


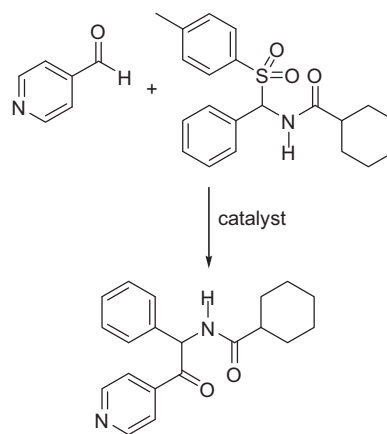
Fig. 5. Thermogravimetric (TG) and differential thermogravimetric (TG-DTG) analyses of pristine phenylene silica **PMO-Ph** (solid lines) and **PMO-Ph-OC** (dash lines).



Scheme 3. Benzoin condensation starting from benzaldehyde.

the catalysts was examined by isolating it from the reaction mixture (centrifugation, washing with ethanol and dichloromethane and drying). The catalytic activity of **PMO-Ph-OC** remains almost unchanged upon reuse for three consecutive runs, whereas **MCM-OC** showed very sharp decrease in activity already after the second run (Table 2). Ethylene bridged **PMO-Et-OC** and silylated **Sil-MCM-OC** showed almost comparable reactivity and stability. The pronounced decrease in activity of the **MCM-OC** probably relates to a structural degradation of the support by the basic and protic reaction medium, which results in a leaching of the active sites and in a collapse of the pore structure. The spent **MCM-OC** catalyst showed disordered mesoporous structure (from XRD patterns and N_2 physisorption), a loss of catalytic active sites (from elemental analysis) and thereby a decrease in catalytic activity. Such effects will be decreased by increasing the hydrophobicity and structural stability of the supports. The crystalline pore walls of **PMO-Ph-OC** may provide a special benefit in this context.

As a further proof of principle, the thiazolium catalyzed cross-coupling of aldehydes with acyl imines to α -amido ketones was investigated (Scheme 4) [11,14]. This reaction effectively produces biologically relevant α -amido ketones and the presence of Et_3N as the base assists in the conversion of tosylamides to the acyl imine as well as in the deprotonation of the thiazolium moiety. As expected, the coupling reaction between 4-pyridine carbaldehyde



Scheme 4. Cross-coupling of aldehydes with acyl imines to amido ketones.

Table 2
Catalytic activity in the benzoin condensation of benzaldehyde.^a

Entry	Catalyst	Solvent	[BA]:[Et_3N]	Yield (%) ^b
1	PMO-Ph-OC	CH_2Cl_2	3:1	55
2	PMO-Ph-OC	CHCl_3	3:1	42
3	PMO-Ph-OC	MeOH	3:1	85 (73)
4	PMO-Et-OC	MeOH	3:1	71 (48)
5	Sil-MCM-OC	MeOH	3:1	66 (36)
6	MCM-OC	MeOH	3:1	62 (18)

^a Reaction conditions: benzaldehyde (BA, 0.67 mol/L), Et_3N (0.22 mol/L), reflux temperatures, t : 24 h.

^b Determined by GC-MS, values in parenthesis show the results of the second run.

Table 3

Organocatalytic addition of 4-pyridine carbaldehyde to *N*-[(4-methylphenyl)sulfonyl](phenyl)methylcyclohexanecarboxamide.^a

Entry	Catalyst	Yield (%) ^b
1	PMO-Ph-OC	91 (86) ^c
2	PMO-Et-OC	89
3	Sil-MCM-OC	90 (79) ^d
4	MCM-OC	82 (71) ^d

^a Reaction conditions: *N*-[(4-methylphenyl)sulfonyl](phenyl)methylcyclohexanecarboxamide (1 equiv.), 4-pyridine carbaldehyde (1.1 equiv.), base (Et₃N, 5 equiv.), catalyst (7 mol%), *t*: 2 h, CH₂Cl₂ (15 mL), *T*: 35 °C.

^b Isolated yields after chromatography (EtOAc/hexane).

^c After 4 h.

^d After 24 h, values in parenthesis show the results in second run.

and a α -tosylated amide produced the desired α -amido ketone in presence of the heterogenized organocatalysts with excellent yields (Table 3). As for the benzoin condensation, a solvent effect was noticed: non-protic CH₂Cl₂ as the solvent and five equivalents of Et₃N as the base produced the best results. Again the hydrophobic **PMO-Ph-OC** catalyst performed over the conventional MCM-41 based catalyst systems in terms of catalytic activity, stability and reusability.

4. Conclusions

In summary, the present study demonstrates the first example for tuning the catalytic activity and stability of a heterogenized organocatalyst by the nature of the support. Compared to conventional MCM-41 and its surface silylated analogue, the hydrophobic mesoporous phenylene–silica material gives outstanding activities along with high stabilities for both organocatalytic reactions investigated. The results also highlight that the use of structurally well defined PMOs as supports allows the reuse of the catalysts without activity loss, which is of special importance for multi-step designed organocatalytic systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.08.022.

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