ELECTRONIC SUPPLEMENTARY INFORMATION

Insights into Pore Surface Modification of Mesoporous Polymer-Silica Composites: Introduction of Reactive Amines

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Experimental Section

Synthesis of the mesoporous silica hosts. The syntheses of mesoporous silicas were performed in large batch at low acidic concentrations (0.3-0.5 M HCl)[1,2] In a typical SBA-15 synthesis, 55.4 g of Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Aldrich) was first dissolved overnight at room temperature in a 0.3 M HCl solution (989g H_20, 30.9 g HCl 37%, Fisher Scientific). The solution was then stirred at 35°C for 1h before addition of 89.3 g of tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich), which corresponds to a P123/TEOS molar ratio of 45. The reaction mixture was left at 35 °C under vigorous stirring for 24 h. The resulting powder was subsequently aged in its mother liquor at 100 °C for 48h, then filtered and dried at 100 °C for 24h. Removal of the structure-directing agent was performed by a brief extraction in an acidic ethanol solution, followed by calcination in air at 550 °C for 5h. To synthesize KIT-6,[2] 27.0 g of P123 was dissolved overnight at room temperature in a mixture of 976g H_2O, 52.3g HCl 37% and 27.0 g *n*-BuOH (99%, Sigma-Aldrich) under vigorous stirring. The solution was then transferred at 35 °C and stirred for 1h before addition of 58.05 g TEOS. The material was subsequently aged at 100 °C for 48h, filtered, and dried at 100 °C for 24h. The structure-directing agent was removed by extraction in acidic EtOH followed by calcination in air at 550 °C for 5h.

References:

1) M. Choi, W. Heo, F. Kleitz and R. Ryoo, *Chem. Commun*., 2003, 1340.

2) F. Kleitz, S. H. Choi and R. Ryoo, *Chem. Commun.*, 2003, 2136.

Table S1 Experimental conditions for the amination with EDA used during optimisation.

EDA molar excess	N content (mmol/g)
2	1.8
5	2.1
10	2.1
100	2.1

Table S2 Physicochemical characteristics derived from N_2 sorption measurements of the EDA-PCMS composites prepared with different polymer locations. * recalculated taking into account only the mass of silica.

Materials	BET surf. area	Total Pore vol.	Pore size $BJH_{ads.}$	Pore size $DFT_{des.}$	Pore size $DFT_{ads.}$
	m^2/g	cm^3/g	nm	nm	nm
Physical mix	623	0.85	8.4	8.1	7.8
*Recalculated**	*828*	*1.12*			
Random	363	0.48	6.4	5.1	6.9
*Recalculated**	*521*	*0.66*			
Coated	351	0.61	6.8	6.3	7.0
*Recalculated**	*607*	*0.92*			

Table S3 Recycling tests (Knoevenagel condensation).

Material	Use	Productivity[a] mol $mg_{cat.}^{-1}$ h^{-1}
EDA-PCMS(30)-SBA-15	1	38
	2	28
	3	14

[a] moles of product per mass of catalyst per hour.

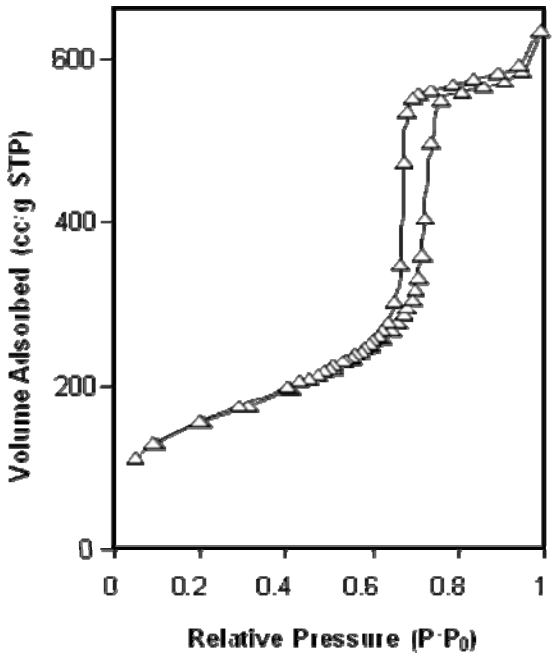

Figure S1 N_2 physisorption isotherm of EDA-PCMS(30)-KIT-6 measured at -196 °C.

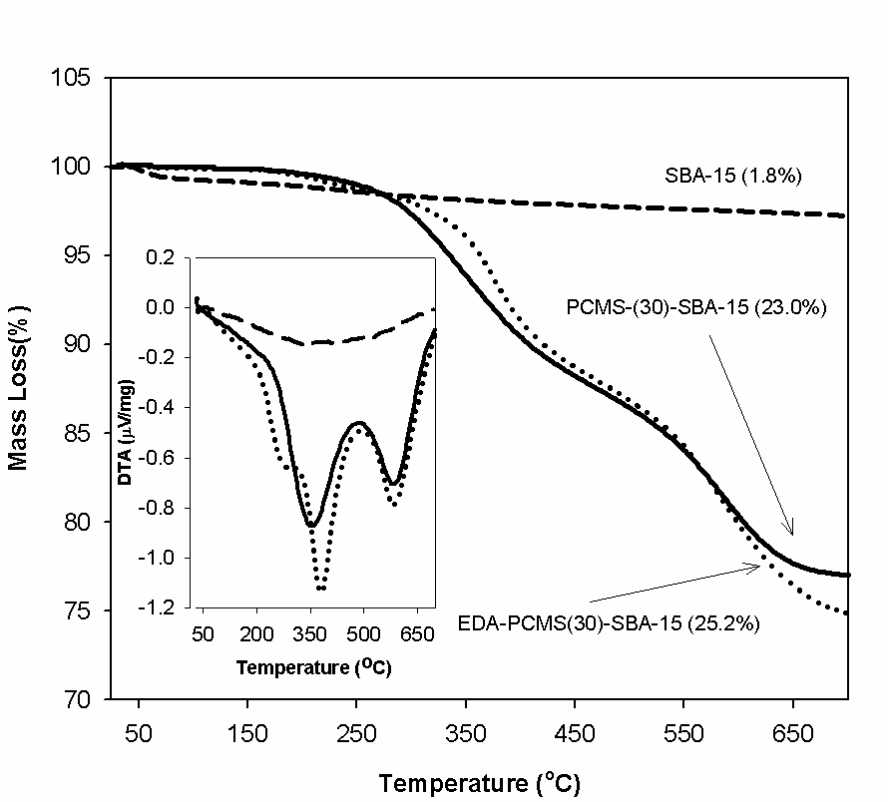

Figure S2 TGA curves of the PCMS(30)-SBA-15 composite before and after treatment with EDA. Inset: DTA analysis (pure SBA-15 is shown as a reference).

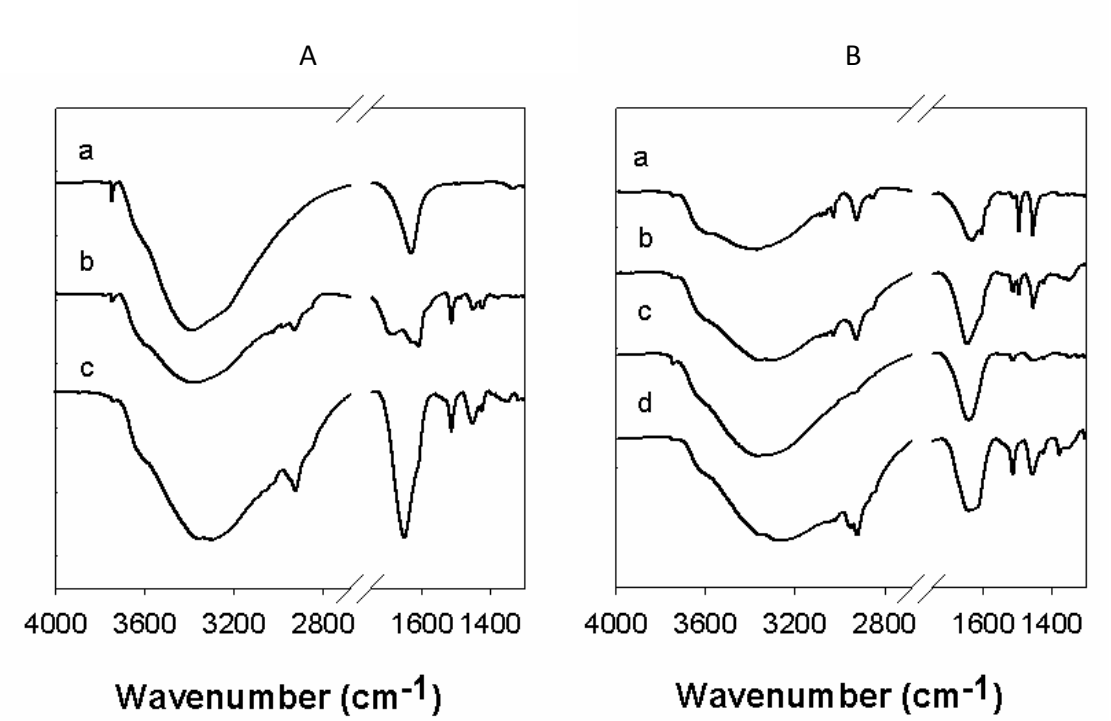

Figure S3 ATR-FTIR spectra of A: a) KIT-6; b) PCMS(30)-KIT-6; and c) EDA-PCMS(30)-KIT-6, and B) a) EDA-PCMS(0.1; 30)-SBA-15; b) EDA-PCMS(0.5; 30)-SBA-15; c) EDA-PCMS(10)-SBA-15 and d) EDA-PCMS(30)-SBA-15.

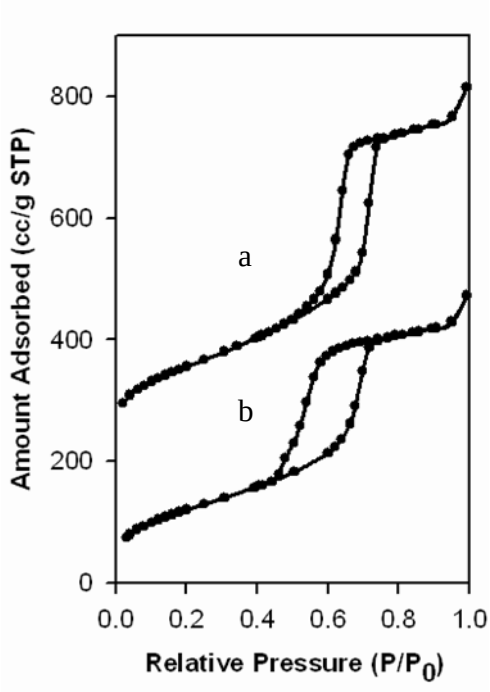

Figure S4 N_2 sorption isotherms of EDA-PCMS:PS composites, a) PCMS(0.1; 30)-SBA-15 (offset is 250 cm^3g^{-1}); b) PCMS(0.5; 30)-SBA-15.

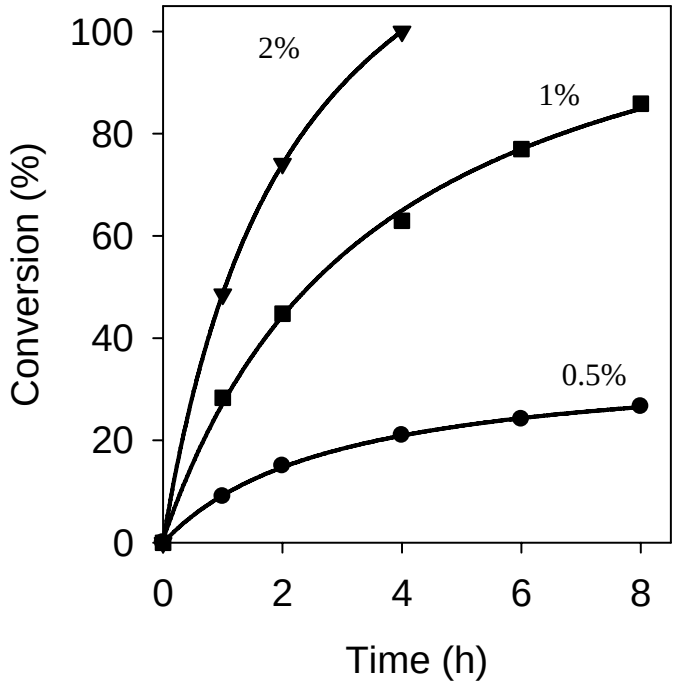

Figure S5 Time-course of the Knoevenagel condensation of benzaldehyde with ethylcyanoacetate catalyzed by amino-functionalized mesoporous polymer-silica composite with different amine-to-reagents ratios, as indicated. Reaction was carried out with 5mmol of benzaldehyde and ethyl cyanoacetate in 35mL toluene at 80 ^{o}C, with the mass of the catalyst (EDA-PCMS(30)-SBA-15) adjusted to correspond either to 2, 1 or 0.5% ratio.