Supplementary Information

Hybrid mesoporous organosilicas with molecularly imprinted cavities: towards extended exposure of active amino groups in the framework wall

Hang Huo^a, Xianzhu Xu^a, Tingting Zhao^a, Yudong Li^a, Yanqiu Jiang^{*a} and Kaifeng Lin^{*a,b}

^a School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, Heilongjiang, 150001, P. R. China

^b Key laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin, 300071, P. R. China.

*Corresponding authors' Email: jiangyanqiu@hit.edu.cn; linkaifeng@hit.edu.cn.

Experimental section

The APTES functionalized material SBA-15-APTES was synthesized according to a previously reported procedure¹. Specifically, 1.0 g P123 was dissolved with 7.5 mL deionized water at 35°C with vigorously stirring, followed by adding 15.0 g of 2 M HCl solution and dropwise addition of the mixture of 1.87 g TEOS and 0.35 g APTES (The molar ratio of TEOS and APTES is 85:15). The mixture was allowed to stir at 35°C for 24 h before transferring into a Teflon bottle sealed in an autoclave, which was then heated to 100°C for 2 days in an oven. The solid was filtered off, washed three times with deionized water for three times. Removal of surfactant P123 was conducted by using ethanol extraction at 80°C for 24 h. The solid product was filtered out, washed with ethanol, and dried at 60°C under vacuum condition.

Mesoporous material SBA-15 was synthesized according to a reported paper². In a typical synthesis, Pluronic P123 (2.0 g) was dissolved in a mixture of deionized water (15 g) and 2M HCl (60 g) at temperature of 40°C. Then, TEOS (4.25 g) was added with vigorous stirring. The solution was stirred at 40°C for 24 h and then crystalized in oven at temperature of 100°C for 72 h. The final gel was calcined at 500°C for 6 h at a heating rate of 0.75°C/min to remove the template, and the sample was named as SBA-15.

The material of SBA-15-APTES-grafted was synthesized by adding 0.54 g APTES into the solvent of absolute toluene containing 0.3 g SBA-15. The mixture was refluxed at inert atmosphere for 12 h. The powder SBA-15-APTES-grafted was obtained by filtration and washing by absolute ethanol for three times, then dried in oven at temperature of 60°C.

The XRD and N₂ adsorption-desorption characterizations were conducted. The graphs are displayed in Fig. S6 & Fig. S7. The powder XRD patterns of SBA-15-APTES and SBA-15-APTES-grafted show three well-resolved Bragg diffraction peaks in region of $2\theta = 0.5 \sim 2^{\circ}$ after removal of the surfactant P123, which can be indexed as [100], [110], [200] reflections. These reflections are typical for a well-ordered 2D-hexagonal (p6mm) mesostructure. The adsorption-desorption isotherms of SBA-15-APTES and SBA-15-APTES grafted display type IV curves with H2-type

hysteresis loop at relative high pressure region, which is the typical characteristic of ordered mesoporous materials. The BET surface area of SBA-15-APTES and SBA-15-APTES-grafted is 513 m²g⁻¹ and 288 m²g⁻¹, and pore volume is 0.64 cm³g⁻¹ and 0.39 cm³g⁻¹, respectively.

	MIMS-	MIMS-	MIMS-	MIMS-	MIMS-	MIMS-	MIMS-	MIMS-
	NHQ (7)	HQ (7)	NHQ (10)	HQ (10)	NHQ (14)	HQ (14)	NBPA (14)	BPA (14)
CO ₂ chemisorption ^a (mg g ⁻¹)	38.38	64.52	31.68	40.82	39.87	75.31	69.49	80.43

Table S1 CO₂ chemisorption test of the hybrid mesoporous materials

[a] Calculated from the desorption branch of CO₂-TPD analysis.

Table S2 Catalytic performance with different catalysts and substrates in Knoevenagel reaction^a

Entry	Substrate	Product	Catalyst	Conversion ^b (%)	TOF ^c
1	<i>С</i> рсно	NC CO	MIMS-BPA (14)	60.1	78.9
2	Сно		MIMS-BPA (14)	54.9	72.1
3	СНО		MIMS-BPA (14)	51.5	67.5

[a] 1mmol aldehyde and 1 mmol cyanoacetate were dispersed in 2 mL of toluene with 40 mg of catalyst and the reactions were proceeded at 110oC for 10 minutes.

[b] The conversion of aldehyde was calculated by GC analysis with n-butanol as internal standard substrate.

[c] The number of TOF was calculated depending on N content of the catalyst with the result at the reaction time of 10 minutes.

Characterization



Fig. S1 ¹H NMR spectrums for organosilica precursors of HQP (A) and BPAP (B)



Fig. S2 ²⁹Si NMR spectra of hybrid materials MIMS-HQ (14) (left) and MIMS-BPA (14) (right).



Fig. S3 TG profiles of hybrid mesoporous materials MIMS-NHQ/MIMS-HQ (left) and MIMS-NBPA/MIMS-BPA (right).



Fig. S4 SEM images of hybrid mesoporous materials of a) MIMS-NHQ (7), b) MIMS-HQ (7), c) MIMS-NHQ (10), d) MIMS-HQ (10), e) MIMS-NHQ (14), f) MIMS-HQ (14), g) MIMS-NBPA (14), h) MIMS-BPA (14)



Fig. S5 The SEM images of a) MIMS-NHQ (14), b) MIMS-HQ (14), c) MIMS-NBPA (14), d) MIMS-BPA (14) and the corresponding EDS-Mapping of element Si (green), O (blue) and N (purple).



Fig. S6 Powder SAXRD patterns of the APTES functionalized materials of SBA-15-APTES (black) and SBA-15-APTES-grafted (red)



Fig. S7. N₂ adsorption and desorption isotherms and pore size distribution (inset) for materials SBA-15-APTES (black) and SBA-15-APTES-grafted (red)



Fig. S8 FT-IR spectrums of MIMS-HQ (14) (black) and MIMS-HQ (14)-recycled (red) with calcination after six times cycling



Scheme S1 The react procedure during the formation of imprinted molecularly cavities.

Reference

- 1. A. S. M. Chong and X. S. Zhao, J. Phy. Chem. B, 2003, 107, 12650-12657.
- 2. D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *SCIENCE*, 1998, **279**, 548-552.