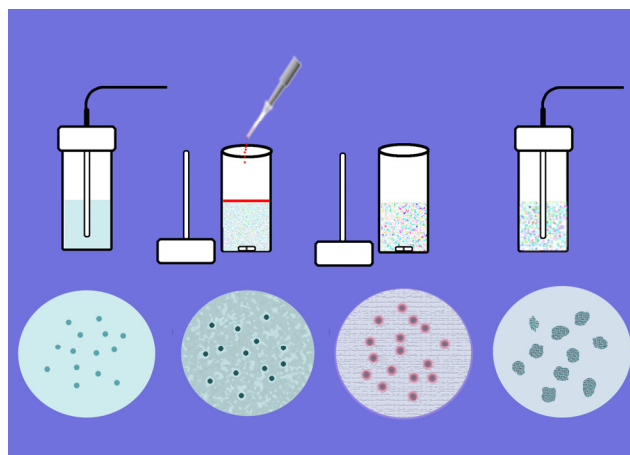


One-step hydrothermal synthesis of surface organosilanized nanozeolite under microwave irradiation

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Scheme 1 Synthesis procedure of surface organosilanized zeolite ZSM-5 nanocrystals.

HCl titration process: A typical titration method under non-aqueous condition was employed to detect the coverage density of amino group on the surface of nanozeolites by using HCl ethanol standard solution. [1] The concentration of standard HCl solution was titrated by Na_2CO_3 standard solution. Tymol-blue was used as indicator in the titration, where the referred HCl was used to quantify the amount of amino groups on the nanozeolites ZSM-5- NH_2 dispersed in the ethanol. By this titration process, the coverage density of $-\text{NH}_2$ group on the nanozeolites ZSM-5- NH_2 surface is about $135.2 \mu\text{mol/g}$, which is an average of more than 4 times of titration.

[1] D. Li, X. Xu, S. Zhang, Z. Wu, Z. Zhang, *J. Anal. Sci.*, 2007, **23**, 323.

Table S1 Chemical compositions of as-prepared samples detected by XPS and EDS

Sample	XPS		EDS	
	N/Si	S/Si	C/Si	S/Si
ZSM-5-none	—	0	2.060	0
ZSM-5- NH_2	0.064	—	—	—
ZSM-5-SH	—	0.020	—	0.017
ZSM-5- $\text{CH}_2\text{-CH=CH}_2$	—	—	2.511	—
LTA-SH	—	0.014	—	0.013
Silicalite-1-SH	—	0.016	—	0.016

It is found from Table S1 that the contents of N, C and S elements in the surface modified nanozeolite ZSM-5 are clearly higher than those in ZSM-5-none.

Table S2 Chemical compositions and synthesis conditions of surface-modified zeolites silicalite-1 and LTA with mercapto-groups (silicalite-1-SH and LTA-SH) synthesized under microwave irradiation.

Zeolite Type	Sol aging time (h)	Gel composition			MW hydrothermal synthesis condition		Surface functional group	Si/Al of sample	Crystal size (nm)
					Stage 1	Stage 2			
		ROH /SiO ₂	SiO ₂ /Al ₂ O ₃	H ₂ O /SiO ₂	T ₁ (°C) / t ₁ (min)	T ₂ (°C) / t ₂ (min)			
silicalite-1-SH	24	0.39 ^a	-	19.60	80/90	120/60	-SH	-	100
LTA-SH	24	2.21 ^b	3	108.59	80/90	130/60	-SH	2.20	120

a: ROH of silicalite-1-SH is tetrapropylammonium (TPAOH);

b: ROH of LTA-SH is tetramethylammonium (TMAOH).

Table S3 The water contact angles of as-prepared samples.

Sample	ZSM-5-none	ZSM-5-NH ₂	ZSM-5-SH	ZSM-5-CH ₂ CH=CH ₂
Contact Angle (°)	< 5.0	0	0	10.7

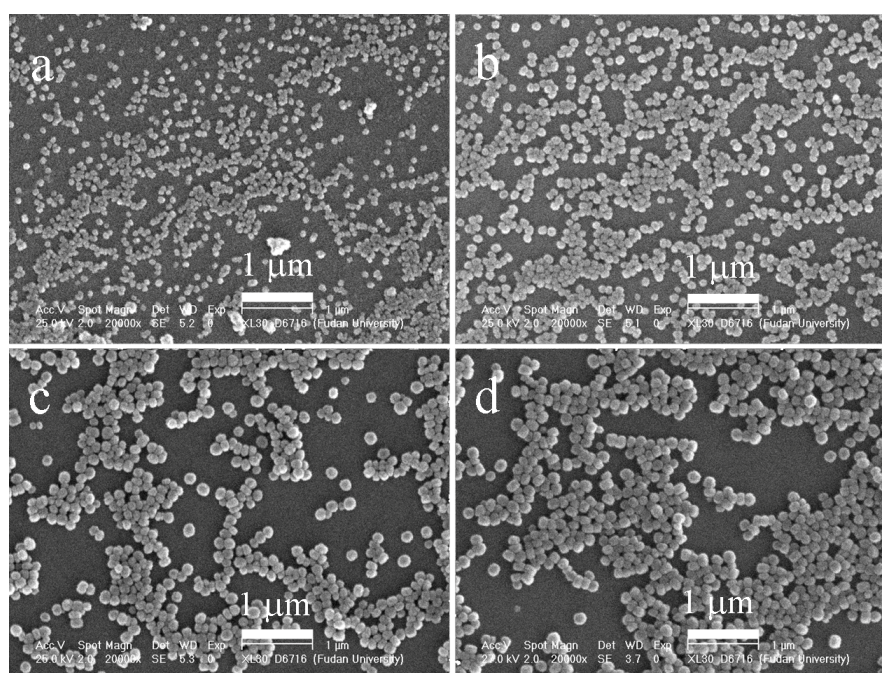


Fig. S1 SEM images of ZSM-5-NH₂ (a), ZSM-5-SH (b), ZSM-5-CH₂-CH=CH₂ (c) and ZSM-5-none (d) synthesized at 120 °C for 90 min.

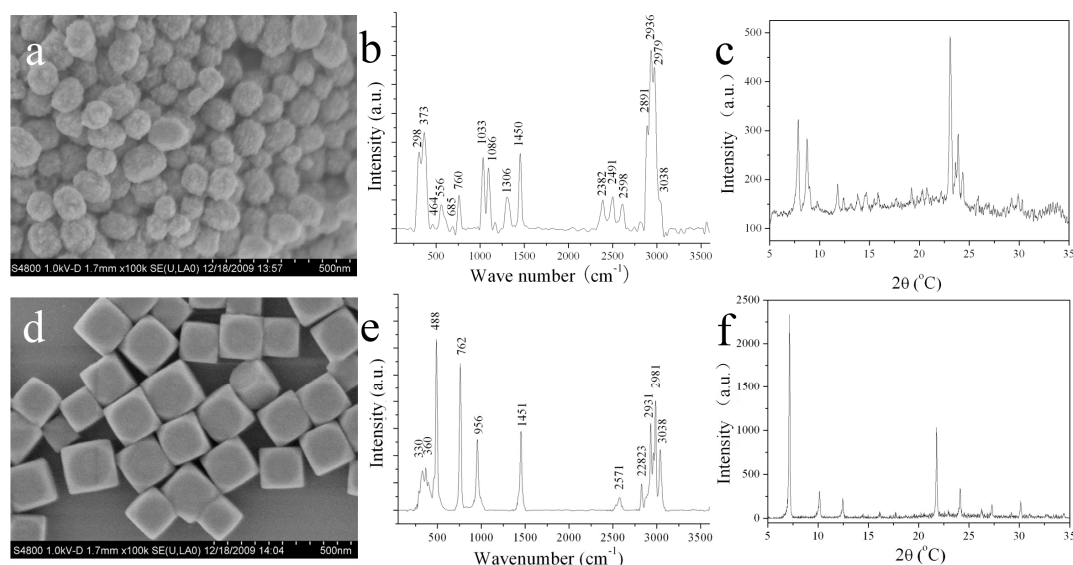


Fig. S2 SEM images (a, d), Raman spectra (b, e) and XRD patterns(c, f) of nanozeolites silicalite-1 and LTA modified with mercapto-groups (silicalite-1-SH and LTA-SH), respectively. In Fig. S1b, the bands at 373, 298 and 464 cm^{-1} are assigned to bending mode of 5-, 6- and 4-membered rings in MFI structure, respectively. The bands at 1033 and 1086 cm^{-1} are assigned to the asymmetric stretching vibrations of Si-O-Si bonds. The bands at 2382~2598 cm^{-1} are assigned to stretching mode of S-H. In Fig. S1e, the bands at 488 and 330 cm^{-1} are assigned to the bending mode of 4- and 6-membered Si-O-Al ring in zeolite LTA structure. The band at 956 cm^{-1} is ascribed to asymmetric T-O stretching motion. The band at 2571 cm^{-1} is assigned to stretching mode of S-H. The bands at 1450 and 2820~3038 cm^{-1} in Figs. S1b and S1e belong to distortion bending modes of CH_2 and CH_3 which are the parts of structure directing agent in the micropore and organosilane grafted on the surface.

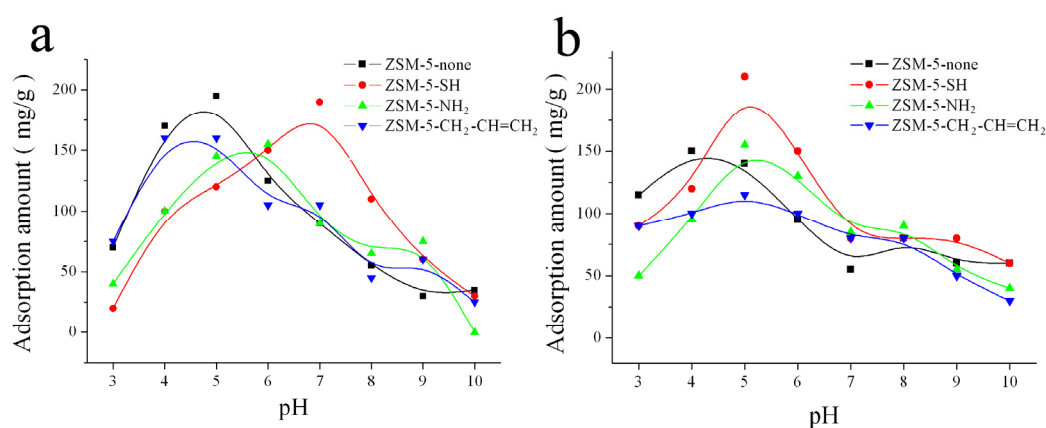


Fig. S3 Protein (a: transferrin and b: bovine serum albumin) adsorption behaviors of as-prepared nanozeolites ZSM-5 with different surface groups at the pH range from 3 to 10.

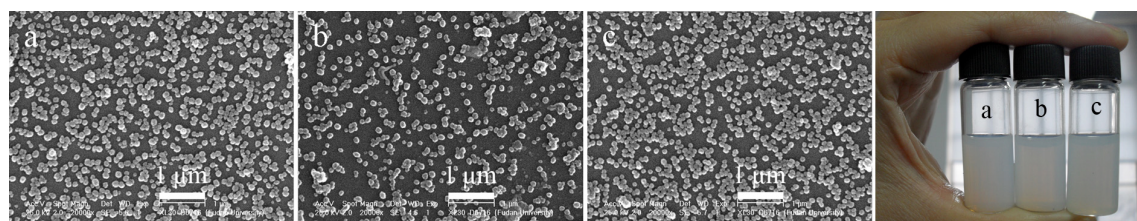


Fig. S4 SEM images of the re-dispersed nanozeolites ZSM-5-NH₂ (a) ZSM-5-SH (b), and ZSM-5-CH₂-CH=CH₂ (c) after calcination at 550 °C for 300 min in air; and optical photograph (right) of colloidal solutions obtained by re-dispersing the calcined samples in water.