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Zeolite Microspheres with Hierarchical Structures: Formation, Mechanism and Catalytic Performance

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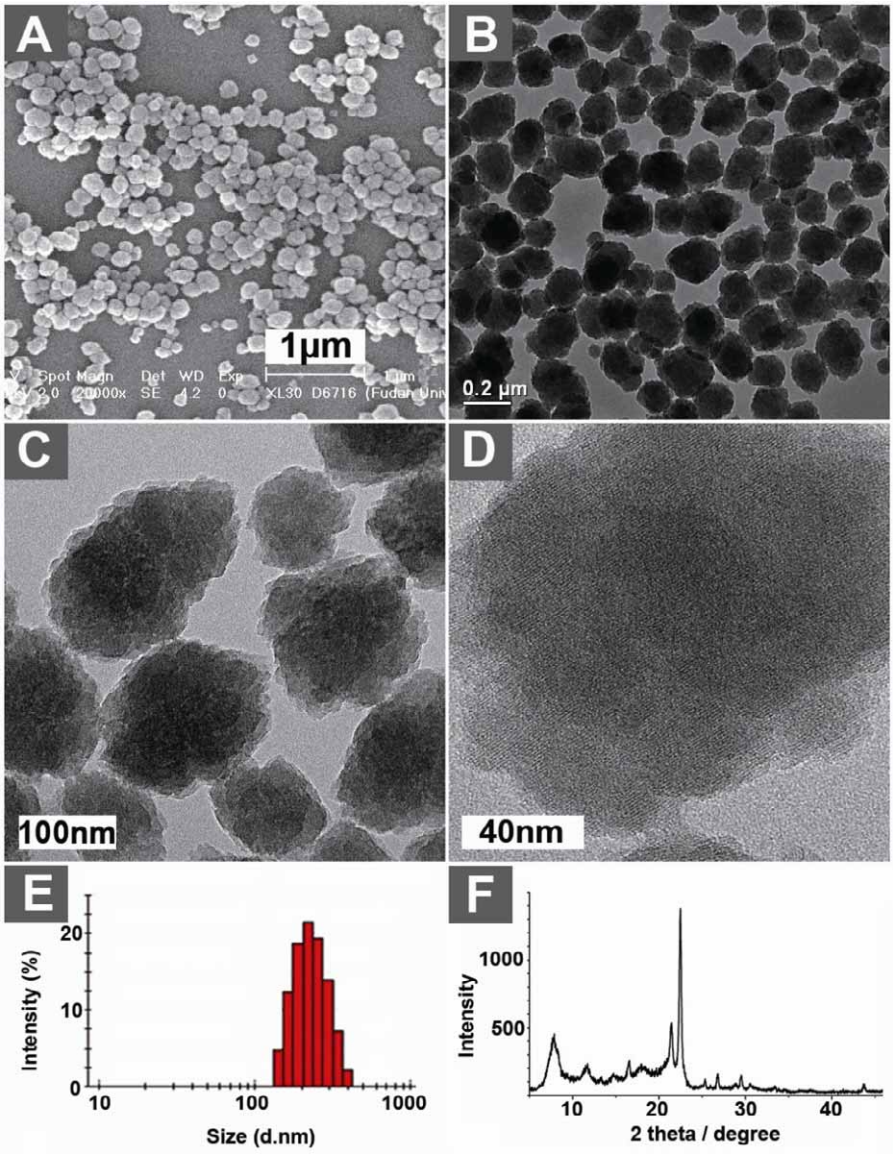

Fig. S1 SEM image (A), TEM images (B, C and D), particle size distribution (E), XRD pattern (F) of nanozeolite β.

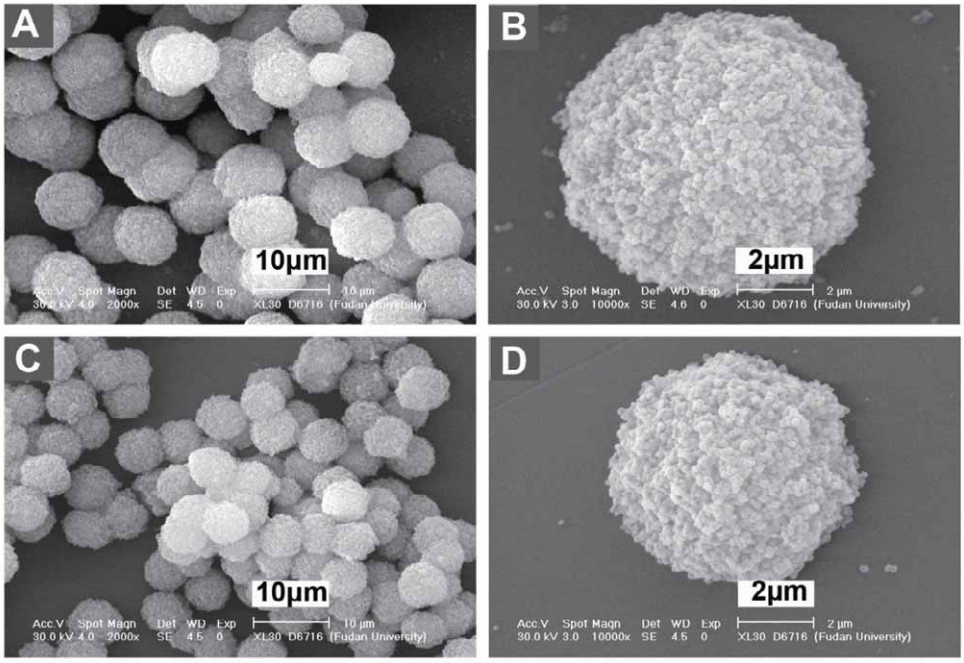

Fig. S2 SEM images of β/UF-ZMSs (A-B) and β-ZMSs (C-D) prepared at n_{HCl} : $w_{nanozeolite}$ of 4.5 mmol g^{-1}.

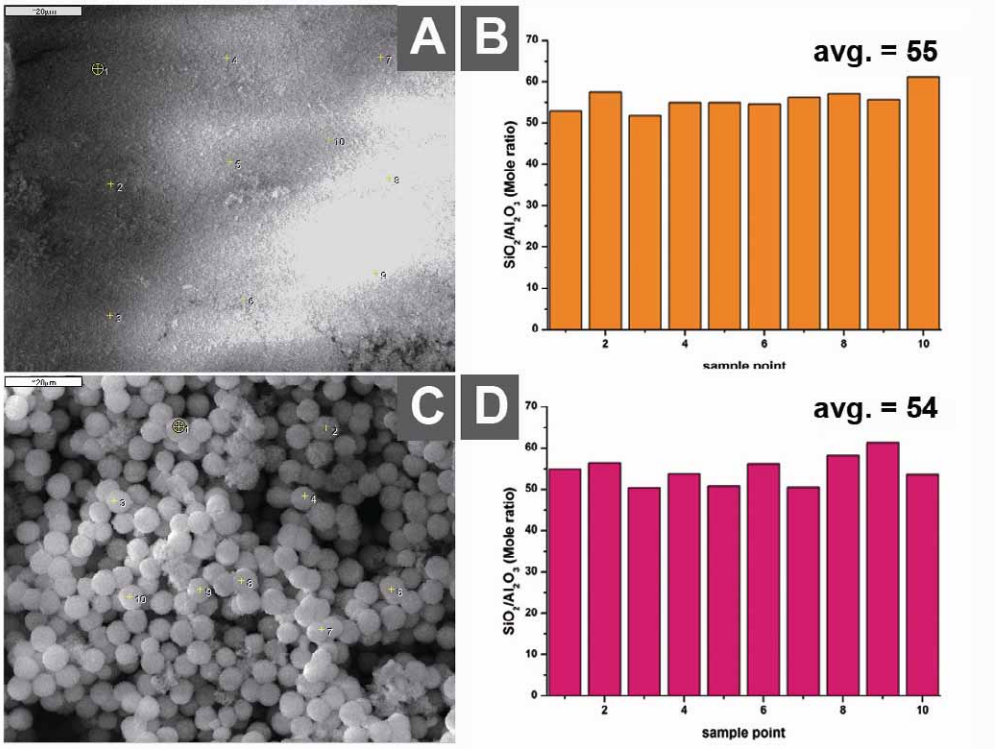

Fig. S3 EDS analysis of nanozeolite β (A, B) and β-ZMSs (C, D) prepared at n_{HCl}:$w_{nanozeolite}$ of 4.5 mmol g^{-1}

Table S1. Textural Properties of C-β and β-ZMS

zeolite type	$V_{secondary\ mesopore}$ [a] (cm^3/g)	$A_{micropore}$ [b] (m^2/g)	$A_{external\ surface}$ [b] (m^2/g)	$V_{micropore}$ [c] (cm^3/g)	$D_{secondary\ mesopore}$ [d] (nm)
C-β	0.11	366	93	0.17	-
β-ZMS	0.52	347	133	0.16	31

[a] Secondary mesopore volumes of C-β and β-ZMS obtained by desorption data using BJH model between 1.7 and 300 nm width. [b] Micropore area and external surface area of C-β and β-ZMS calculated by t-plot method. [c] Micropore volumes of C-β and β-ZMS obtained by t-plot method. [d] Most probable diameter of the secondary mesopore in C-β and β-ZMS.

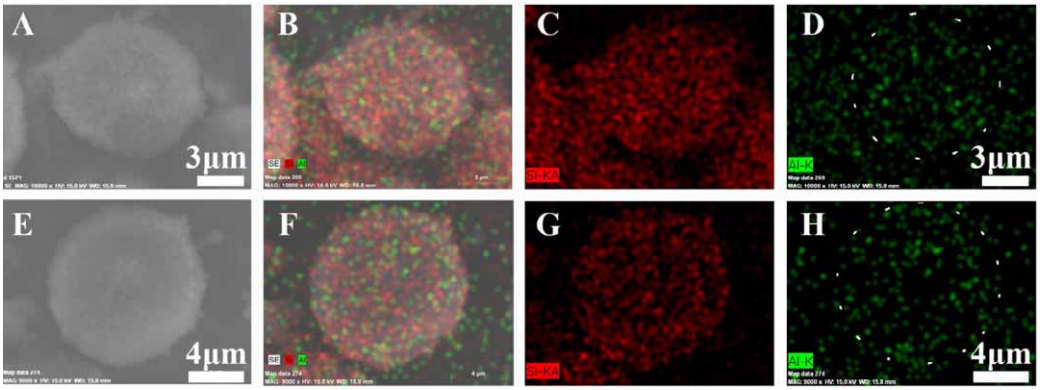

Fig. S4 Element distribution of β/UF-ZMS as synthesized with adding HCl at n_{HCl}:$w_{nanozeolite}$ of 4.5 mmol g^{-1} (A-D，region II) and 23.25 mmol g^{-1} (E-H, region III), respectively.

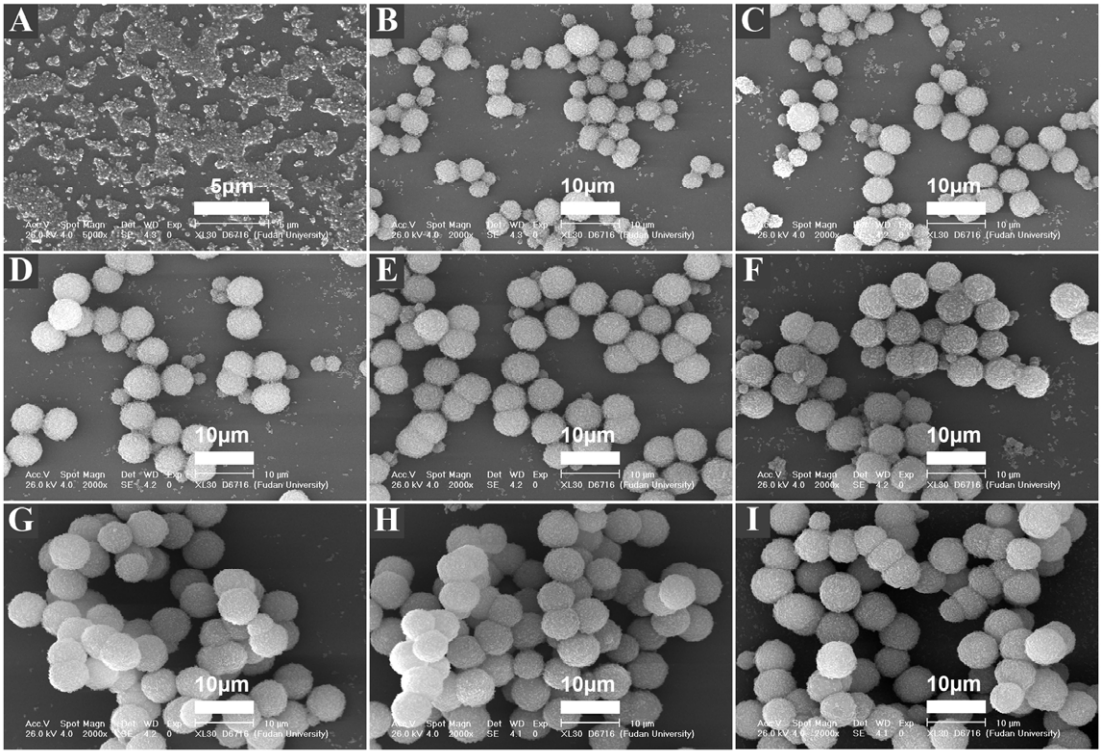

Fig. S5 SEM images of β/UF-ZMSs directly collected from the reaction mixture at different time of 0 (A), 0.5 (B), 1 (C), 1.5 (D), 2 (E), 2.5 (F), 5 (G), 10 (H), 720 (I) min at n_{HCl}:$w_{nanozeolite}$ of 12 mmol g^{-1}.

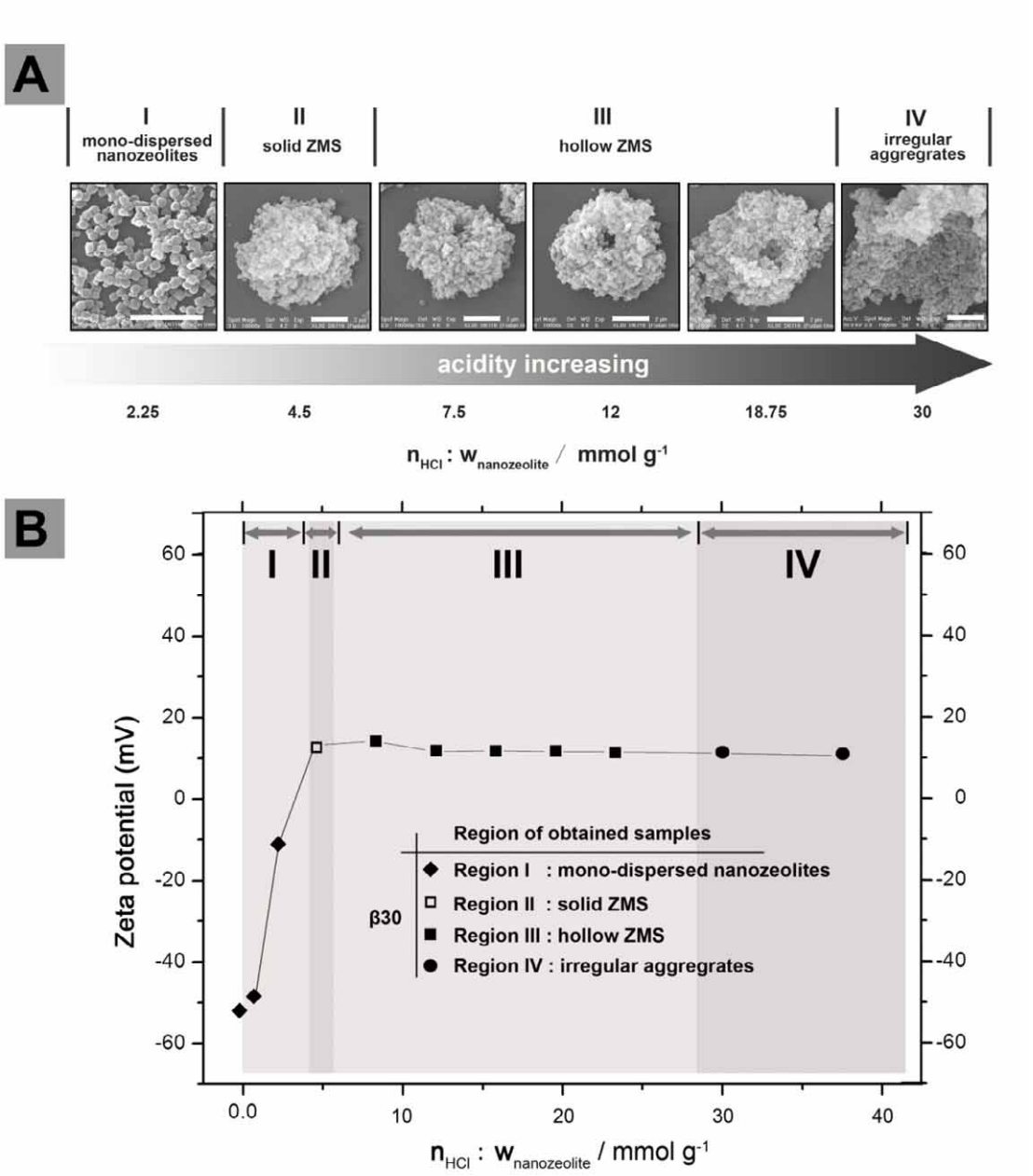

Fig. S6 (A) Morphological transformation of samples obtained at different n_{HCl}:$w_{nanozeolite}$ ratios in im-PICA process using nanozeolite β (SiO_2/Al_2O_3 = 30) colloidal solution. The scale bars in all images are 2 μm. (B) Zeta potential curve of nanozeolite β (SiO_2/Al_2O_3 = 30) with the variation of n_{HCl}:$w_{nanozeolite}$ ratios and the related structure oriented region division. The nanozeolite β with 30 of SiO_2/Al_2O_3 ratio was synthesized by the following procedure with a mole ratio of SiO_2:Al_2O_3:$(TEA)_2O$:H_2O = 1:0.033:0.135:6.8. Typically, 3.4 g of fumed silica was dissolved with 6.5 g of 25 wt % TEAOH aqueous solution and stirred for 12 h (Solution I). Then 0.101 g of aluminum foil was dissolved in 2.5 g of 25 wt % TEAOH, and the mixture was stirred and centrifugated to get the upper clear solution (Solution II). Then, Solution II was added into Solution I with violent stirring. After contineously stirring for another 1 day, the obtained mixture was transferred into a teflon-lined autoclave at 140 ºC for 14 days to get the colloidal solution of nanozeolite β. The colloidal solution of nanozeolite β was collected without any treatment.

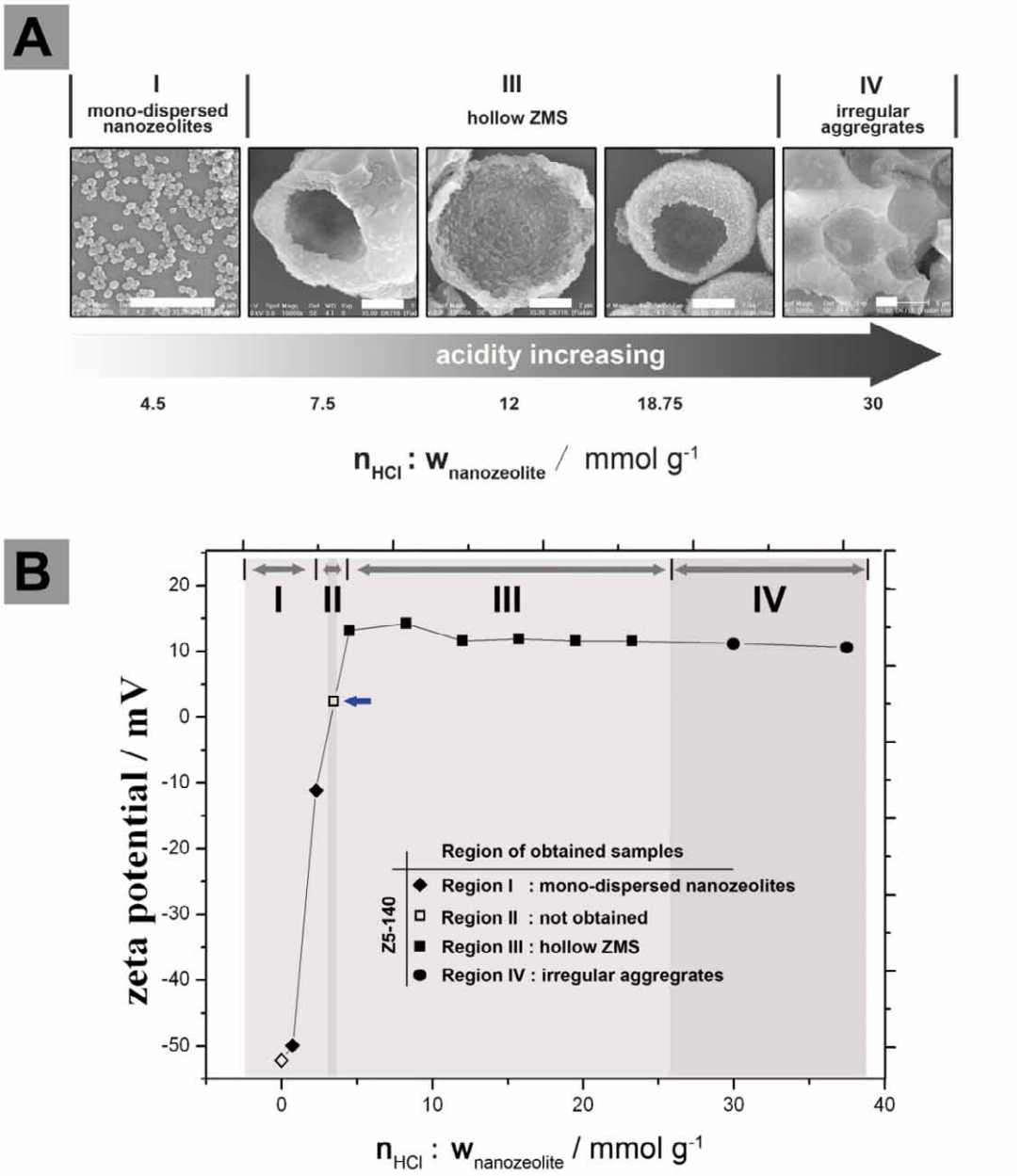

Fig. S7 (A) Morphological transformation of samples obtained at different n_{HCl}:$w_{nanozeolite}$ ratios in im-PICA process using nanozeolite ZSM-5 (SiO_2/Al_2O_3 = 140) colloidal solution. The scale bars in all images are 2 μm. (B) Zeta potential curve of nanozeolite ZSM-5 (SiO_2/Al_2O_3 = 140) with the variation of n_{HCl}:$w_{nanozeolite}$ ratios and the related structure oriented region division. There is a sharp increase at low acid adding amount. And at high HCl concentration, the flat platform means that saturation of proton in the electrical double layer. The reason why no solid Z5-ZMS obtained in im-PICA process is ascribed to the rather narrow region of zeta potential between 0 mV to 14 mV (stability of electrical double layer).

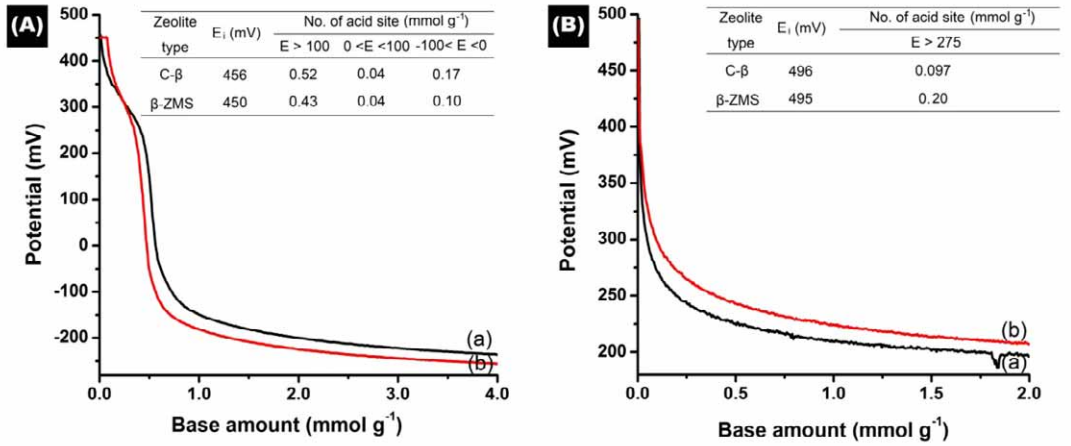

Fig. S8 The total (A) and external (B) acidity measurement of C-β (a) and β-ZMS (b) by potentiometric titration in acetonitrile using n-butylamine (A) and 2,6-di-tert-butylpyridine (B). The insets in Figures display the detailed total and external acidic properties of two catalysts, respectively. For the potentiometric titration with n-butylamine, it is suggested as a criterion that the initial electrode potential (E_i) indicates the maximum acid strength, and the value of mequiv amine g^{-1} solid at the beginning of plateau indicates the total acid amount.[S1] The acid strength of the sample could be classified according to the following scale[S1-S2]: the amount of n-butylamine titration at $E > 100$ mV is corresponding to very strong sites, that at $0 < E < 100$ mV corresponding to strong sites, that at $-100 < E < 0$ mV corresponding to weak sites, and that at $E < -100$ mV is very weak sites. For the potentiometric titration with 2,6-di-tert-butylpyridine, because 2,6-di-tert-butylpyridine (7.9 Å) is difficult to enter the micropore of zeolite, it can only interact with the acidic site on the external surface. The consumed amount of the organic base presents the number of acidic sites on the external surface of the catalysts.

[S1] K. N. Rao, K. M. Reddy, N. Lingaiah, I. Suryanarayana, and P. S. Sai Prasad, *Appl. Catal. A-Gen* 2006, **300**, 139-146.

[S2] A. S. Khder, E. A. EI-Sharkawy, S. A. El-Hakam, and A. I. Ahmed, *Catal. Commun.,* 2008, **9**, 769-777.