Electronic Supplementary Material (ESI) for RSC Advances

Supporting information

Direct synthesis of hierarchical zeolites with oriented nanocrystals without adding extra templates

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I. Synthesis

A typical crystallization condition of hierarchically nanosized zeolite beta was heated at 413K for 60 hours. Other precursors with different H_2O/SiO_2 could be obtained by controlling the time of dryness, and the crystallization condition was the same as before.

A typical synthesis of hierarchically nanosized zeolite ZSM-5 was as follows: the precursor solution was prepared by mixing 0.26g of aluminum isopropoxide (AIP, A.R., Sinopharm Chemical Reagent Co., Ltd, China), 8g of tetraethyl orthosilicate (TEOS, A.R., Beijing Chemical Works) and 12.22g of tetrapropylammonium hydroxide (TPAOH, 25 wt.% solution in water, Shanghai Nuotai Chemical Co., Ltd, China) together, then stirring for 12h at room temperature was necessary in order to remove alcohols, the initial molar composition was $0.017Al_2O_3:1SiO_2:0.4TPAOH:13.6H_2O$. The quasi-solid phase precursor could be obtained by drying at 348K using water bath, the final molar composition was $0.017Al_2O_3:1SiO_2:0.4TPAOH:2.1H_2O$. Next, the quasi-solid phase precursor was transferred into a 100ml Teflon liner, which was place into a suitable steel reactor, heated at 413K for 60 hours. Template removal was carried out at 823K for 4h.

Finally, we got the hierarchical zeolite H-ZSM-5.

II. Characterization

Scanning electron microscopy (SEM) was performed with Hitachi S-4700. High resolution transmission electron microscopy (HRTEM) images were obtained on JEOL JEM-3010. X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance series with Cu Kα (λ=0.1541nm). The nitrogen adsorption–desorption isotherms were conducted using Micromeritics TriStar II 3020, the specific surface area was estimated by using Brunauer-Emmett-Teller (BET) model, the total pore volume was calculated at P/P_0=0.99, the micropore size distribution was calculated by Horvath–Kawazoe (HK) model and the mesopore size distribution was calculated by Barrett-Joyner-Halenda (BJH) model using desorption isotherm, the micropore volume and external surface area were evaluated by t-plot method. The mercury intrusion porosimetry was carried out using Micromeritics AutoPore IV 9510. NH_3-temperature programmed desorption (NH_3-TPD) was determined by Thermo TPDRO1100 Series with temperature ranging from 400K to 800K at a rate of 10K/min.

III. Catalytic Reaction

The catalytic tests for the alkylation of benzene with propylene were carried out in a fixed-bed reactor at 443K under the pressure of 3.0MPa. The molar ratio of benzene to propylene was 4:1, and the weight hourly space velocity(WHSV) of propylene was $5h^{-1}$, the final products were analyzed by Varian GC 3900 Gas Chromatography equipped with VF-1ms capillary column (60m×0.25mm×0.25μm).

Fig. S1 Picture of hierarchical zeolite H-beta with a honeycomb-like monolith

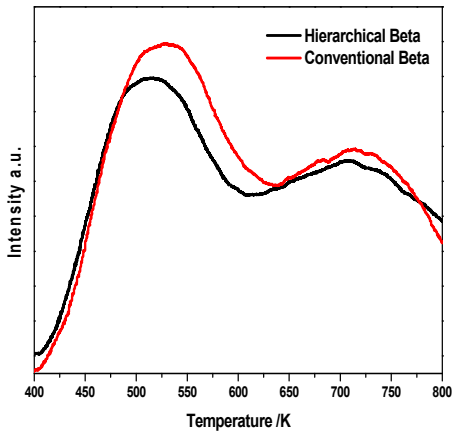

Fig. S2 NH_3-TPD of hierarchical beta and conventional beta

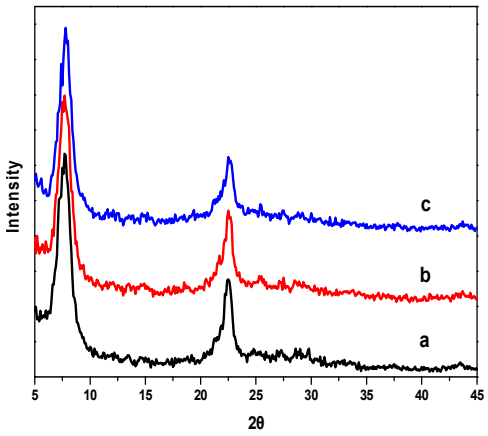

Fig.S3 XRD patterns of (**a**) hierarchical zeolite beta calcined at 823K for 4h (parent); (**b**) the steam treatment of hierarchical zeolite beta at 873K for 2h; (**c**) hierarchical zeolite beta calcined at 1073K for 6h;

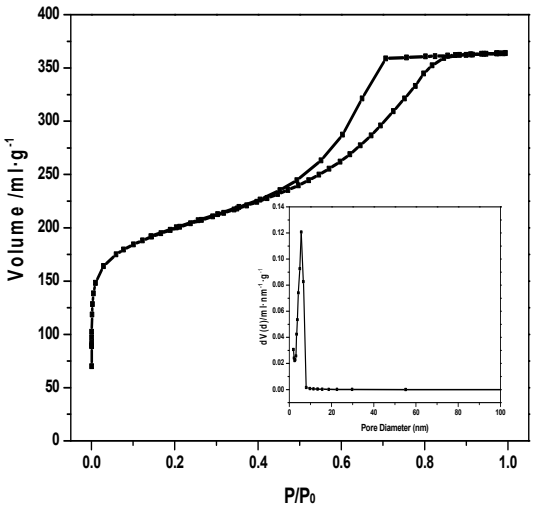

Fig. S4 N_2 adsorption–desorption isotherm and BJH pore size distribution (insert) of hierarchical zeolite beta scaled up for 18 times

Table S1 N_2 adsorption–desorption date

	S_{BET}	V_{total}	V_{mic}	S_{ext}
	$m^2 \cdot g^{-1}$	$ml \cdot g^{-1}$	$ml \cdot g^{-1}$	$m^2 \cdot g^{-1}$
Hierarchical Beta-18[a]	684	0.563	0.180	295

[a] scaled up for 18 times

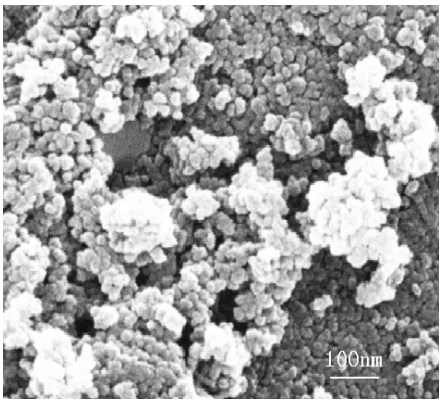

Fig. S5 SEM image of hierarchical zeolite beta scaled up for 18 times

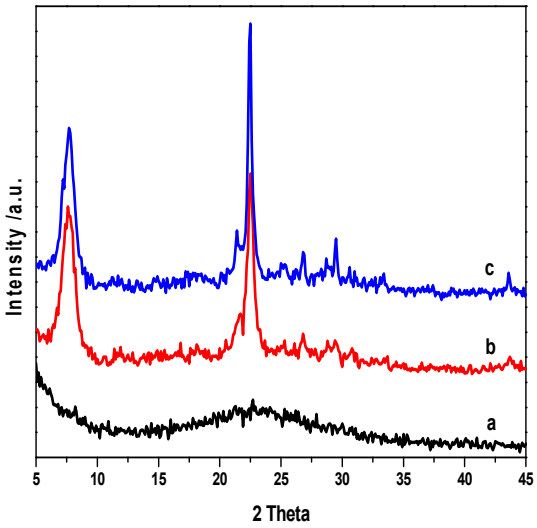

Fig. S6 XRD patterns of samples synthesized by different water content (a) H_2O/SiO_2=0.9; (b) H_2O/SiO_2=1.7; (c) H_2O/SiO_2=5.1

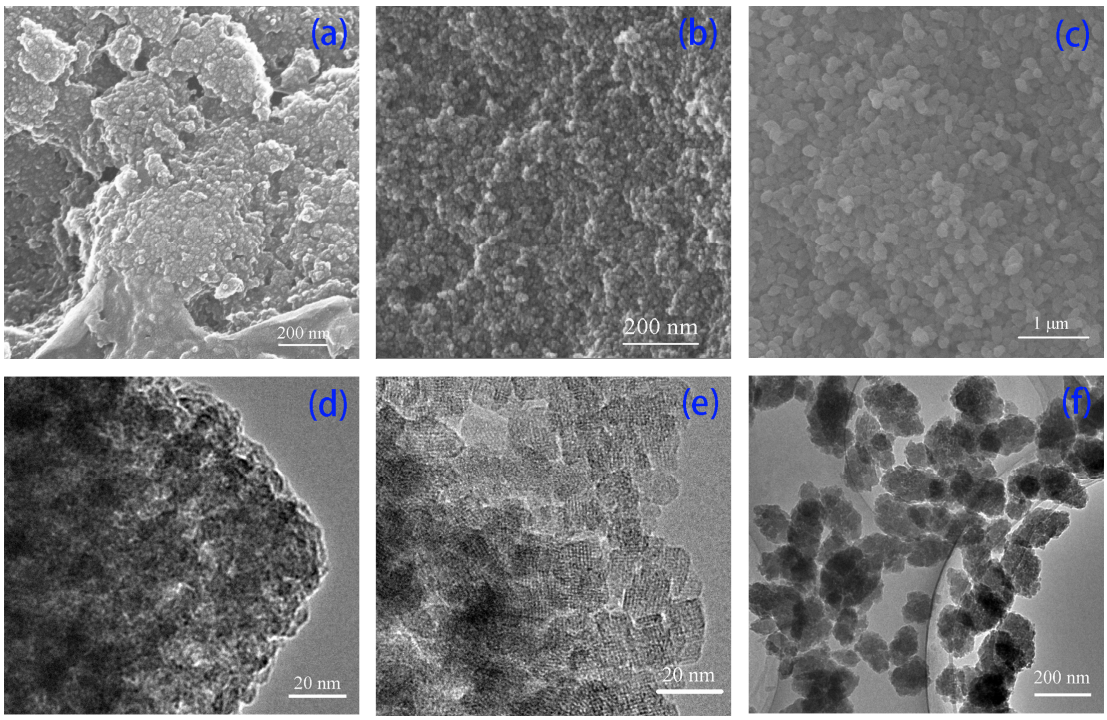

Fig. S7 SEM images of samples synthesized by different water content (a) H_2O/SiO_2=0.9; (b) H_2O/SiO_2=1.7; (c) H_2O/SiO_2=5.1

HRTEM images of samples synthesized by different water content (d) H_2O/SiO_2=0.9; (e) H_2O/SiO_2=1.7; (f) H_2O/SiO_2=5.1

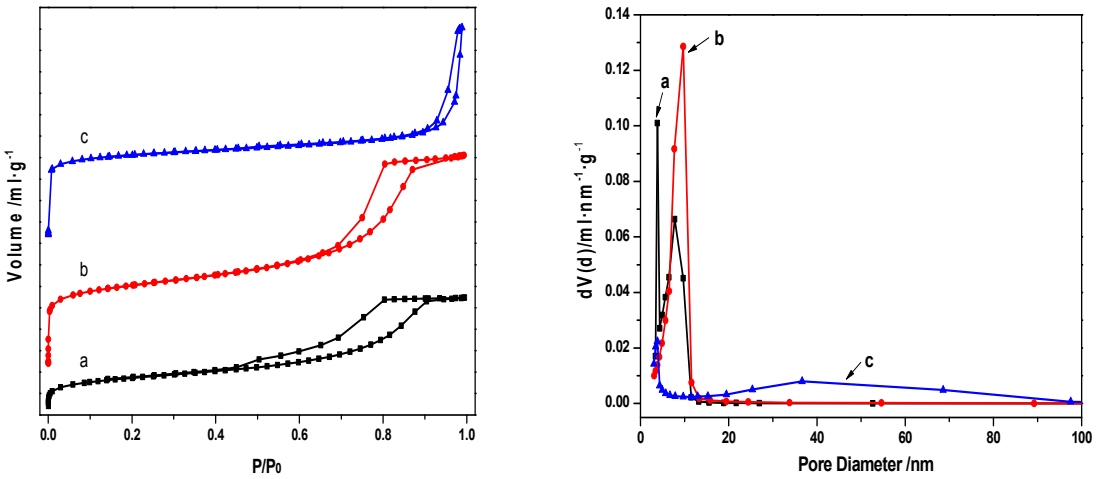

Fig. S8 N_2 adsorption–desorption isotherms and BJH pore size distribution of samples synthesized by different water content (a) H_2O/SiO_2=0.9; (b) H_2O/SiO_2=1.7; (c) H_2O/SiO_2=5.1

Table S2 N_2 adsorption–desorption date of samples synthesized by different water content

Sample	S_{BET}	V_{total}	V_{mic}	S_{ext}	Yield
	$m^2 \cdot g^{-1}$	$ml \cdot g^{-1}$	$ml \cdot g^{-1}$	$m^2 \cdot g^{-1}$	%
H_2O/SiO_2=0.9	301	0.418	0.047	194	-
H_2O/SiO_2=1.7	622	0.743	0.149	297	98
H_2O/SiO_2=5.1	624	0.739	0.203	187	84

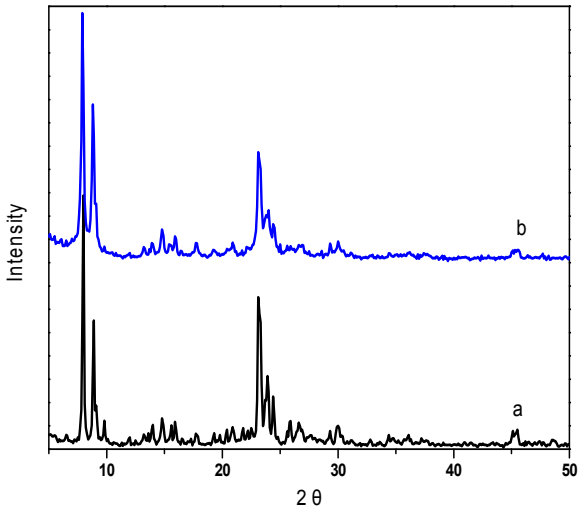

Fig.S9 XRD patterns of (a) conventional microporous zeolite ZSM-5; (b) hierarchically nanosized zeolite ZSM-5

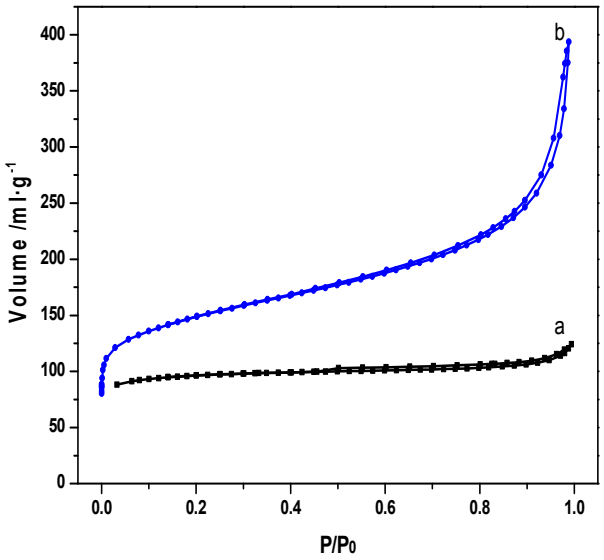

Fig. S10 N_2 adsorption–desorption isotherms of (a) conventional microporous zeolite ZSM-5; (b) hierarchically nanosized zeolite ZSM-5

Table S3 N_2 adsorption–desorption date

	S_{BET}	V_{total}	V_{mic}	S_{ext}	D_{mes}
	$m^2 \cdot g^{-1}$	$ml \cdot g^{-1}$	$ml \cdot g^{-1}$	$m^2 \cdot g^{-1}$	nm
Hierarchical ZSM-5	510	0.60	0.11	276	~3
Conventional ZSM-5	322	0.19	0.12	67	-