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Supporting information

The templating effect of an easily available cationic polymer with widely separated charge centers on the synthesis of hierarchical ZSM-5 zeolite

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Synthesis of Low-molecular-weight PCA (LPCA) and LPCA-ZSM-5

To a solution of 12 g of DMDAP in 6.04 g water, 9.82 g ECH was added with cooling. The mixture was held between 60 ^{o}C for 15 minutes. Dilution water (3.36 g) was added, and the mixture was reheated at 60 ^{o}C for 65 minutes. Additional 0.48 g ECH was added and further stirred for 2 hours.

The obtained polymer was recovered by precipitation with acetone and was then dried in vacuum over P_2O_5 at room temperature.

The procedure for synthesis of LPCA-ZSM-5 is similar to that of PCA-ZSM-5 and PCS-ZSM-5.

Synthesis of PCS-silica and PCA-silica composites

6 g TEOS and about 0.8 g PCS or PCA were mixed together in methanol and stirred at room temperature for 2 hours, followed by the addition of 3 g ammonia. The solution was stirred for 3 hours and turned into suspension. The suspension was dispersed in a dish for solvent evaporation under reduced pressure. It took 5-8 hours to evaporate the solvent at room temperature in the drafty closet. The obtained dry gel was used for TG analysis.

Synthesis of the mixture of severely decomposed PCA and silica (SDPCA-silica)

0.4 g PCA and 0.08 g $NaAlO_2$ were dissolved in a solution of 0.3 g NaOH in 13.6 g deionized water. Then 0.94 g fumed silica was added into the solution and stirred for 3 hours. The obtained gel was hydrothermally treated at 170 ^{o}C for 24 hours. The precipitate and mother liquor were directly stirred at 80 ^{o}C to evaporate the water. The obtained wet gel was further dried at 100 ^{o}C overnight to get a dry solid, which contains all the severely decomposed PCA (SDPCA) and is denoted as SDPCA-silica. The obtained solid was used for TG analysis.

Synthesis of zeolite ZSM-5 with pre-crystallized zeolite seeds (PCA-ZSM-5 (seeds))

0.19 g AIP was dissolved in 7.42 g TPAOH solution, followed by the addition of 14.96 g deionized water and 9.50 g TEOS. After stirring at room temperature for 5 hours, a clear solution with the following molar composition was obtained: AIP: TEOS: TPAOH: H_2O = 1: 50: 10: 1250. This solution was pre-crystallized under reflux with vigorous stirring 90 ^{o}C for 20 hours.

After cooling the precursor solution to room temperature, the still clear solution was mixed with an aqueous solution of 0.95 g PCA and stirred at 80 ^{o}C for 2 hours. At last, the obtained white suspension mixture was charged into Teflon-lined steel autoclaves for hydrothermal treatment at 150 ^{o}C for 48 hours. The products were washed, air-dried, and calcined at 550 ^{o}C for 6 hours to remove the SDA and polymer. The final product was then characterized by powder X-ray diffraction (XRD), N_2 adsorption-desorption measurement, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The obtained material is designated as PCA-ZSM-5 (seeds).

Table S1. Textural properties obtained by nitrogen physisorption experiments[a].

Sample	S_{BET} [m^2/g]	V_{total} [cm^3/g]	V_{micro} [cm^3/g]	V_{meso} [cm^3/g]
LPCA-ZSM-5	447	0.37	0.11	0.26
PCA-silicalite-1	422	0.23	0.12	0.11
PCA-ZSM-5(seeds)	413	0.36	0.11	0.25

[a] S_{BET} is calculated from Brunauer–Emmett–Teller method; V_{total} is evaluated at P/P_0=0.99; V_{micro} is calculated from *t*-plot method; V_{meso}= V_{total}-V_{micro};

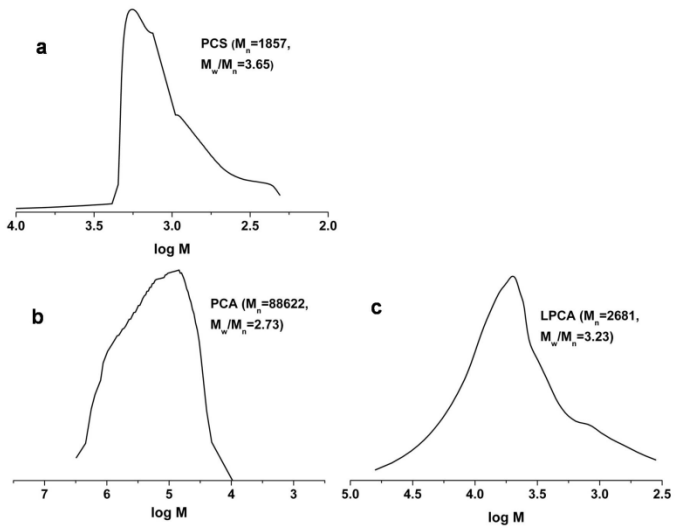

Fig. S1 GPC profiles (water, Polyethylene Oxide standard) of (a) PCS, (b) PCA and (c) LPCA.

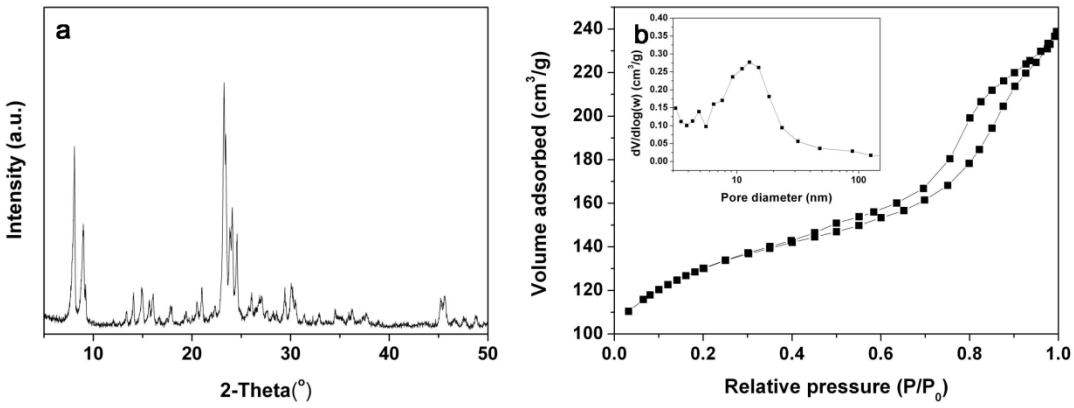

Fig. S2 (a) XRD pattern and (b) N_2 adsorption-desorption isotherms and the corresponding pore size distribution (inset) of LPCA-ZSM-5.

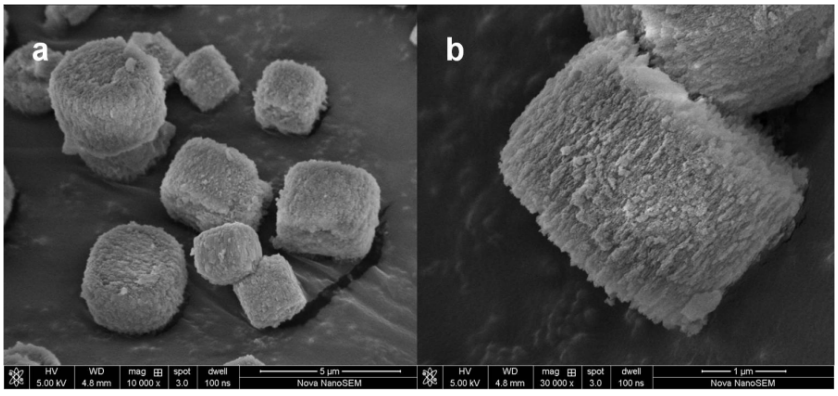

Fig. S3 SEM images of (a and b) LPCA-ZSM-5.

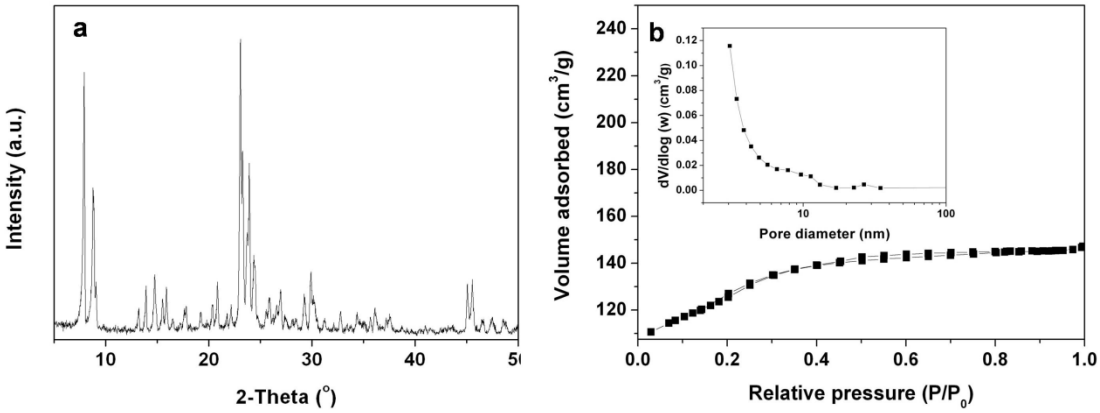

Fig. S4 (a) XRD pattern and (b) N_2 adsorption-desorption isotherms and the corresponding pore size distribution (inset) of PCA-silicalite-1.

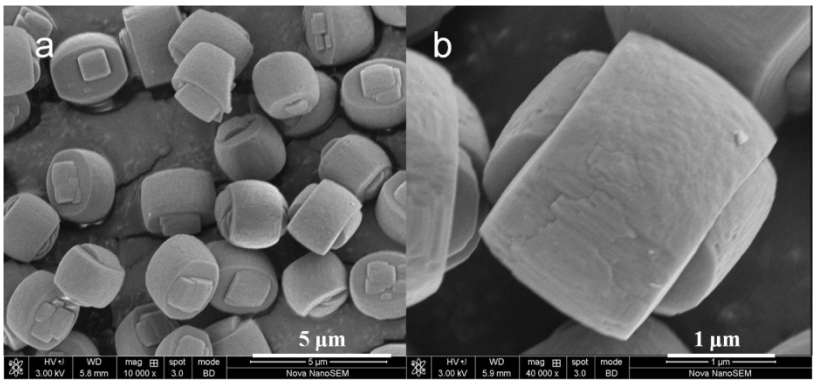

Fig. S5 SEM images of PCA-silicalite-1.

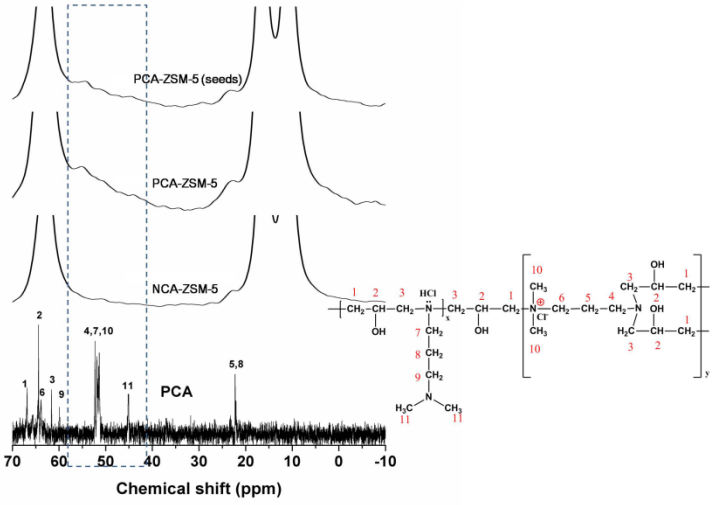

Fig. S6 ^{13}C NMR spectrum of PCA and ^{13}C MAS NMR spectra of as-synthesized NCA-ZSM-5, PCA-ZSM-5 and PCA-ZSM-5(seeds).

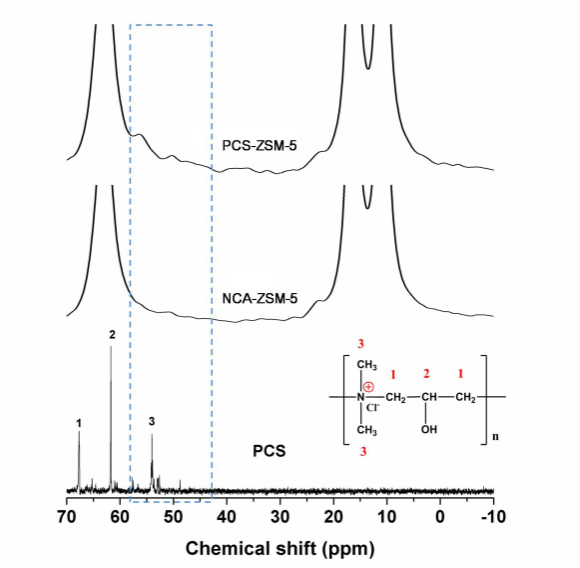

Fig. S7 ^{13}C NMR spectrum of PCS and ^{13}C MAS NMR spectra of as-synthesized NCA-ZSM-5 and PCS-ZSM-5.

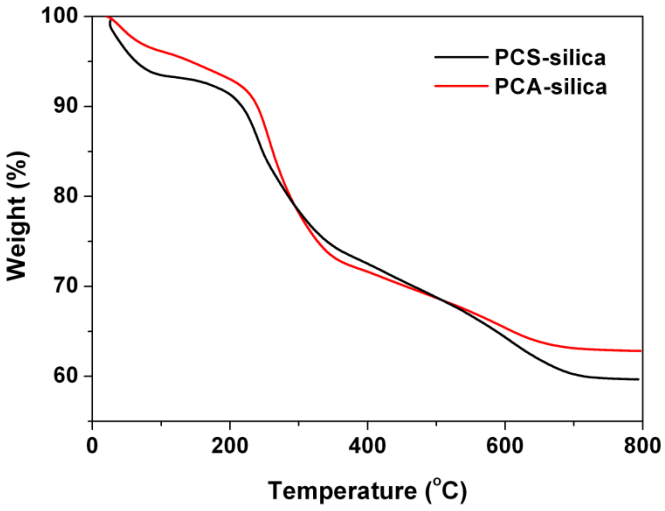

Fig. S8 Thermogravimetric analysis (TG) curves of PCS-silica and PCA-silica composites.

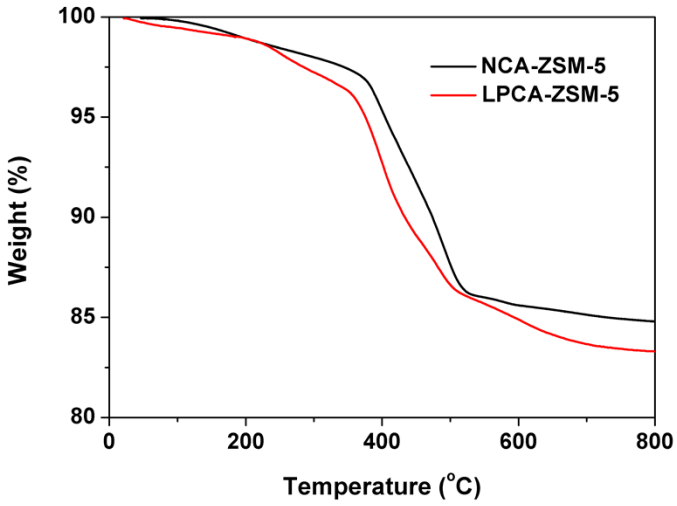

Fig. S9 Thermogravimetric analysis (TG) curves of as-synthesized NCA-ZSM-5 (extracted from Fig. 4) and LPCA-ZSM-5.

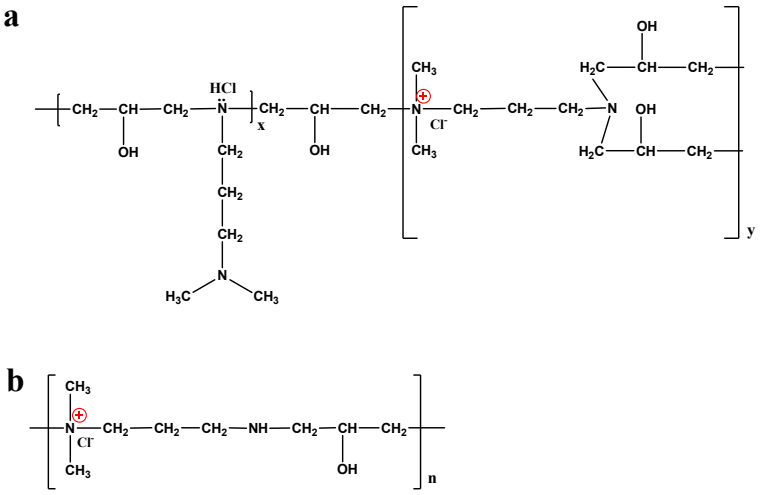

Fig. S10 Proposed PCA structures formed by (a) di-N-alkylation and (b) mono-N-alkylation of primary amine group on DMDAP by ECH.

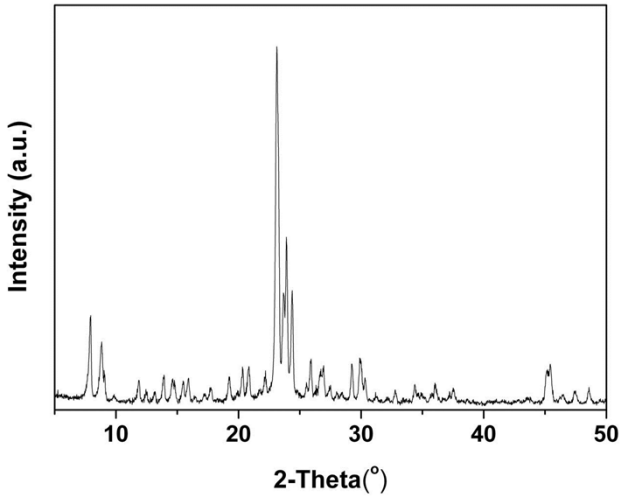

Fig. S11 XRD pattern of PCA-ZSM-5 (seeds).

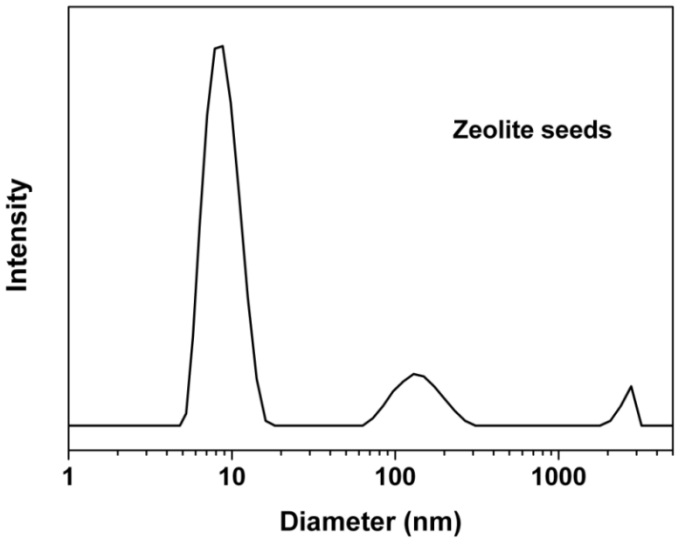

Fig. S12 Particle size distributions of zeolite seeds measured using dynamic light scattering (DLS) after pre-crystallization at 90 °C for 20 hours (The average size of zeolite seeds is around 10 nm, and the size peaks at about 150 and 2500 nm are attributed to the aggregation of zeolite seeds).

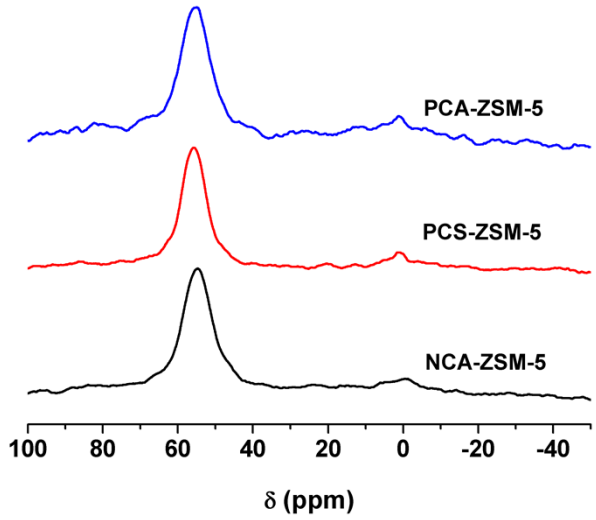

Fig. S13 ^{27}Al MAS NMR spectra of calcined NCA-ZSM-5, PCS-ZSM-5 and PCA-ZSM-5.

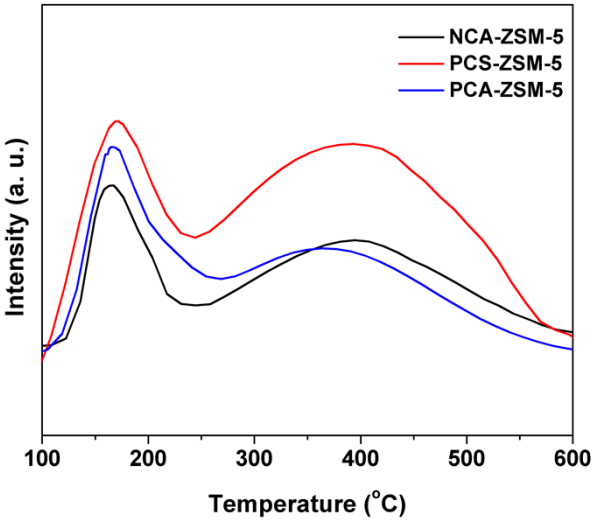

Fig. S14 NH_3-TPD profiles of NCA-ZSM-5, PCS-ZSM-5 and PCA-ZSM-5

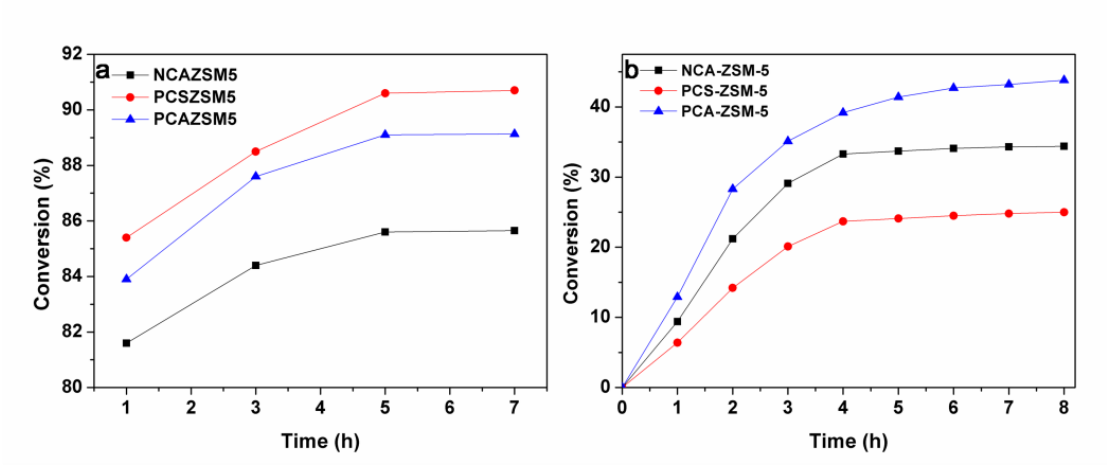

Fig. S15. The effect of reaction time on the conversion of (a) acetalization of cyclohexanone with methanol (ACM) and (b) aldol condensation of benzaldehyde with n-butyl alcohol (CBB) over various catalysts (The selectivities of the two reactions are close to 100%).