

Electronic Supplementary Information

(ESI)

Table S1 The SiO₂/Al₂O₃ and solid yields of ZM-X samples

| Samples | SiO ₂ /Al ₂ O ₃ | Solid yield (%) |
|---------|--|-----------------|
| ZM-1 | 30 | 92.32 |
| ZM-2 | 28 | 90.23 |
| ZM-3 | 26 | 86.56 |
| ZM-4 | 27 | 86.69 |
| ZM-5 | 25 | 83.69 |

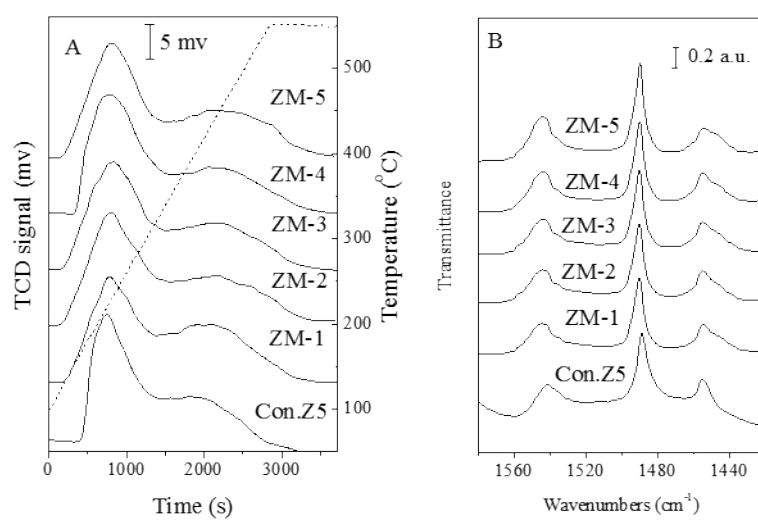


Figure S1 The NH_3 -TPD profiles (A) pyridine-FTIR spectra collected at 100 °C (B)

Table S2 The acidic properties data of NH₃-TPD and pyridine/collidine-FTIR

| Samples | NH ₃ -TPD | | pyridine-FTIR (100 °C) | | | collidine-FTIR (100 °C) | | | |
|---------|---|------------------|--|-------------------------------|------|---|---|--|--|
| | Concentration of acid sites | S/W ^a | Concentration of B acid sites ^b | Concentration of L acid sites | B/L | A ^c 1633 cm ⁻¹ [a.u.cm ⁻¹] | A 1639 & 1650 cm ⁻¹ [a.u.cm ⁻¹] | Concentration of B acid sites ^d | B _{coll} /B _{pyd} ^e |
| | [μmol NH ₃ g ⁻¹] | | [μmol pyd g ⁻¹] | [μmol pyd g ⁻¹] | | | | [μmol coll g ⁻¹] | [μmol coll/μmol pyd] |
| Con.Z5 | 758 | 1.35 | 291 | 140 | 2.09 | / | / | / | / |
| ZM-1 | 832 | 1.59 | 307 | 153 | 2.00 | 4.13 | 0.21 | 66 | 0.21 |
| ZM-2 | 812 | 1.56 | 318 | 166 | 1.92 | 7.00 | 0.32 | 102 | 0.32 |
| ZM-3 | 821 | 1.54 | 318 | 174 | 1.83 | 8.76 | 0.38 | 121 | 0.38 |
| ZM-4 | 866 | 1.66 | 343 | 172 | 1.99 | 3.5 | 0.15 | 50 | 0.15 |
| ZM-5 | 875 | 1.73 | 380 | 169 | 2.25 | 3.16 | 0.12 | 45 | 0.12 |

^a the ratio of strong acid amount to weak acid amount

^b calculated with the the corresponding extinction coefficients (Brønsted: 1.67 cm/μmol; Lewis: 2.22 cm/μmol)

^c the area of the bands integration in collidine FTIR sprctra.

^e calculated with the the corresponding extinction coefficients (Brønsted: 8.1 cm/μmol)

^d the proportion of external Brønsted acid sites concentration detected by collidine absorption in bulky Brønsted acid sites concentration detected by pyridine absorption.

Table S3 The conversion of IPB over the Con Z5 and hierarchical zeolite microspheres

| Samples | Conversion (%) ^a |
|---------|-----------------------------|
| Con.Z5 | 92.6 |
| ZM-1 | 95.3 |
| ZM-2 | 97.6 |
| ZM-3 | 96.9 |
| ZM-4 | 96.1 |
| ZM-5 | 95.3 |

^a Conversion(Conv.) = 100% – area percent of reactant and its isomers calculated by normalization method.

The cracking reaction of isopropylbenzene (IPB, 97%, Aldrich) was evaluated in a micro-reactor with a quartz-tube of 6 mm inner diameter. 50 mg of 20–60 mesh zeolite ZSM-5 pellets without a binder was pretreated at 510 °C for 60 min in a stream of N₂ before reaction. Maintaining the catalyst at the scheduled temperature, 0.5 μL substrate was injected into the catalyst bed with N₂ from the top of the reactor. The flow of the carrier gas is 80 mL min⁻¹. The IPB cracking products were analyzed by an on-line gas chromatograph of GC-9800A (Shanghai Kechuang, FFAP capillary column, 30 m × 0.25 mm × 0.25 μm) equipped with a flame ionization detector.

Table S4 The performance of LDPE cracking

| Samples | Reaction temperature /°C | Conversion /% | Selectivity /% | | | | | | | |
|---------------------|--------------------------|---------------|----------------|----------------|----------------|----------------|----------------|---------------------------------|----------------------------------|------------------------------|
| | | | C ₁ | C ₂ | C ₃ | C ₄ | C ₅ | C ₆ -C ₁₂ | C ₁₃ -C ₁₆ | C ₁₆ ⁺ |
| LDPE-T ₁ | 340 | 5.11 | / | / | / | / | / | / | / | / |
| LDPE-T ₂ | 400 | 19.23 | 0.36 | 1.78 | 4.65 | 4.85 | 6.23 | 40.04 | 22.69 | 19.40 |
| Con.Z5 | 340 | 37.85 | 0.02 | 0.26 | 9.53 | 19.09 | 28.51 | 34.13 | 5.86 | 2.60 |
| ZM-1 | 340 | 75.32 | 0.04 | 0.77 | 8.77 | 14.06 | 9.06 | 47.72 | 11.82 | 7.75 |
| ZM-2 | 340 | 79.32 | 0.02 | 0.36 | 7.90 | 13.14 | 7.37 | 53.07 | 12.89 | 5.26 |
| ZM-3 | 340 | 82.88 | 0.03 | 0.37 | 7.41 | 11.65 | 6.54 | 51.34 | 15.56 | 7.17 |
| ZM-4 | 340 | 73.25 | 0.03 | 0.47 | 9.52 | 14.96 | 8.41 | 46.69 | 11.46 | 5.91 |
| ZM-5 | 340 | 66.32 | 0.01 | 0.64 | 9.53 | 16.04 | 14.57 | 45.96 | 8.44 | 4.81 |

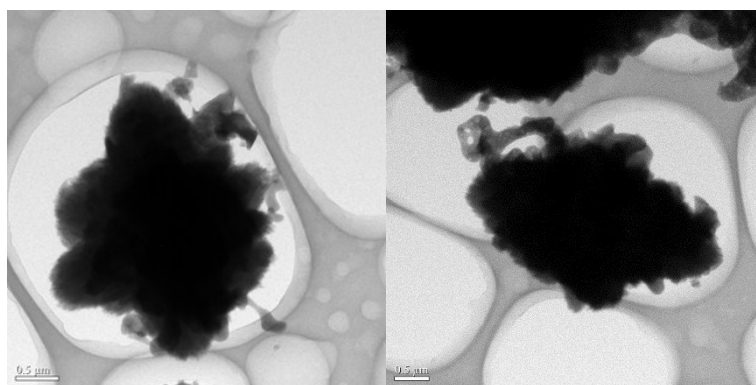


Figure S2 The TEM images of ZM-3 intermediate at crystallization of 28 h

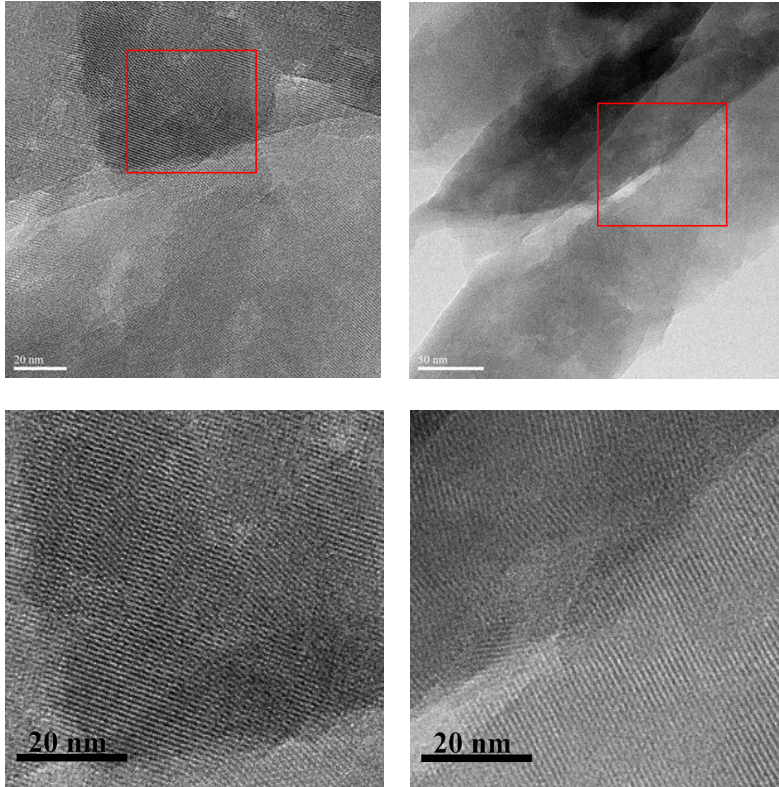


Figure S3 The TEM images of ZM-3 inner section