Supporting information

Seed-induced and additive-free synthesis of oriented nanorodassembled meso/macroporous zeolites: toward efficient and costeffective catalysts for the MTA reaction

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Figure S1. SEM images of (a, c) C-ZSM-5 and (b, d) C-ZSM-11 under different magnification. For comparisons, conventional ZSM-5 and ZSM-11 (denoted as C-ZSM-5 and C-ZSM-11, respectively) were also synthesized by using TPABr or TBABr as the templates under seed-free crystallization conditions. The molar composition of the synthesis mixture for C-ZSM-5 and C-ZSM-11 were 3.5 NaOH : $60 \text{ SiO}_2 : 4 \text{ NaAlO}_2 : 2500 \text{ H}_2\text{O} : 8 \text{ TPABr}$ and 3.5 NaOH : $60 \text{ SiO}_2 : 4 \text{ NaAlO}_2 : 2500 \text{ H}_2\text{O} : 8 \text{ TBABr}$, respectively.



Figure S2. SEM images of silicalite-1 (a) and silicalite-2 seeds (b). It was obvious that the as-prepared silicalite-1 and silicalite-2 seeds had similar particle size of about 150 nm but with slightly different crystal morphologies of near-sphere shape and olive shape, respectively.



Figure S3. Low-resolution TEM images of (a) N-ZSM-5 and (b) N-ZSM-11, which showed the existence of zeolite nanorods that assembled into hedgehog-shaped submicron particles, in which substantial mesopores were formed due to the stacking of these nanorods, resulting in quite different structure properties from C-ZSM-5 and C-ZSM-11.



Figure S4. Nitrogen adsorption/desorption isotherms of Zn/N-ZSM-5 and Zn/N-ZSM-11.



Figure S5. TG curves of Zn/N-ZSM-5, Zn/N-ZSM-11, Zn/C-ZSM-5, and Zn/C-ZSM-11 after MTA reaction tested at 748 K ($W_{cat} = 0.7$ g; GHSV = 0.75 h⁻¹). Clearly, both of Zn/N-ZSM-5 and Zn/N-ZSM-11 have much slower coke formation rate (about 4.41 mg g_{cat}^{-1} h⁻¹) than Zn/C-ZSM-5 and Zn/C-ZSM-11 (26.33 mg g_{cat}^{-1} h⁻¹).

Sample name	S_{BET} (m ² g ⁻¹)	$\frac{S_{Micro}^{a}}{(m^2 g^{-1})}$	S_{Meso} (m ² g ⁻¹)	V_{Micro}^{a} (cm ³ g ⁻¹)	$\frac{V_{Meso}^{b}}{(cm^3 g^{-1})}$
Zn/N-ZSM-5	415	371	44	0.15	0.23
Zn/N-ZSM-11	417	369	48	0.15	0.18

Table S1. Textural properties and compositions of various samples.

^{*a*} *t*-plot method.

 ${}^{b}V_{meso} = V_{tot} - V_{micro.}$