Supporting Information

Unseeded organotemplate-free hydrothermal synthesis of heteroatomic MFI zeolite poly-nanocrystallites

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1 Syntheses of control samples

1.1 Synthesis of Fe-Silicalite-1(100)

Synthesis of Fe-Silicalite-1 was attempted by the “acidic cohydrolysis route” in the absence of seed, organic template and Al source. Ferric nitrate (0.18 g) was added into the solution of TEOS (10.0 g) and deionized water (32.5 g), pH of which was adjusted to 1.0 by drop-wise adding sulfuric acid. Then, the mixture was stirred at 20 °C for 20 h to get a complete cohydrolysis and condensation of TEOS with ferric salt. Afterwards, the aqueous NaOH solution (12.5 mol/L) was added drop-wise to get a synthesis gel with pH of 9.8, followed with the aging at room temperature for 12 h. The final gel composition was SiO_2:0.01Fe:40H_2O. Finally, the slurry was transferred to a Teflon-lined stainless steel autoclave and left to crystallize statically at 180 °C for 5 days. Because the above template-free synthesis of Fe-Silicalite-1 was not effective, the following TPABr-aided synthesis of Fe-Silicalite-1 was carried out. After the cohydrolysis/condensation of TEOS with ferric salt, TPABr (1.2 g) was added into the mixture followed with the dripping of NaOH solution to get a basic gel (pH=9.8). The final gel composition was SiO_2:0.01Fe:40H_2O:0.1TPABr. The other procedures followed the above template-free synthesis.

1.2 Synthesis of Silicalite-1

Synthesis of Silicalite-1 zeolite was also attempted by the “acidic cohydrolysis route” in the absence of seed, organic template, Al and Fe sources. Under vigorous stirring, sulfuric acid was dripped into the solution of TEOS (10.0 g) and deionized water (32.5 g). After solution was stirred at 20 °C for 20 h, the aqueous NaOH solution (12.5 mol/L) was added drop-wise to get a synthesis gel with pH of 9.8. Then, the obtained synthesis gel was aged at room temperature for 12 h. The gel composition was SiO_2:40H_2O. Finally, the synthesis gel was transferred to a Teflon-lined stainless steel autoclave and hydrothermally crystallized at 180 °C for 5 days. Since the above synthesis was not successful, Silicalite-1 was prepared with the aid of the organic template TPABr with otherwise the similar conditions. After the acidic hydrolysis/condensation of TEOS, TPABr (1.2 g) was added into the mixture followed with the dropping of NaOH solution to gel pH of 9.8. The final gel composition was SiO_2:40H_2O:0.1TPABr.

1.3 Synthesis of Me-ZSM-5(100) (Me: Mo, Ti, Co, Cr)

Other than Fe-ZSM-5, the MFI-structured metalloaluminosilicate zeolites, Mo(Ti, Co, or Cr)-ZSM-5, were synthesized following the same procedures as the “acidic cohydrolysis route” for Fe-ZSM-5(100). The corresponding aqueous solutions of sodium molybdate, titanium sulfate, cobaltum nitrate, or chromium nitrate were used as the transition metal sources in stead of ferric nitrate. The molar ratios of Si to Me in the synthesis gels are 100:1.

1.4 Preparations of Fe^{3+}-ion-exchanged and Fe_2O_3-impregnated ZSM-5

The Fe^{3+}-ion-exchanged ZSM-5 sample (Fe(Ex)-ZSM-5) was prepared from the ion-exchange of the pure ZSM-5 (*i.e.*, the Fe-ZSM-5(∞) sample obtained by the present “acidic cohydrolysis route” in the absence of Fe source) with the aqueous solution of ferric nitrate twice. Pure ZSM-5 (10.0 g) was ion-exchanged with aqueous solution of $Fe(NO_3)_3$ (0.1 mol/L, 100 mL) at 70 °C for 1 h under vigorous stirring. The obtained solid was recovered by centrifugation, washing with deionized water, and air-drying at 120 °C for 12 h.

The Fe_2O_3-impregnated ZSM-5 sample (Fe(Im)-ZSM-5) was prepared by the impregnation of the pure ZSM-5 in an aqueous solution of ferric nitrate with stirring at room temperature for 10 h. The ratio of pure ZSM-5 to the aqueous solution was 1 g to 10 mL. Afterwards, the mixture was evaporated at 100 °C to get the dryness of the sample. Finally, the solid was calcined at 550 °C for 5 h to give the final impregnated product.

Table S1 Unit cell volumes for the as-synthesized Me-ZSM-5(100) (Me = Mo, Ti, Co, Cr) obtained by the unseeded organotemplate-free acidic cohydrolysis route.

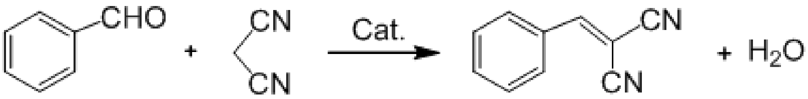
Sample	V_{cell} [a] (nm^3)
Mo-ZSM-5(100)	5.300
Ti-ZSM-5(100)	5.362
Co-ZSM-5(100)	5.274
Cr-ZSM-5(100)	5.348

[a] Unit cell volumes determined by MDI Jade software (Jade 7 XRD pattern Processing Software) [Hedin, N.; DeMartin, G. J.; Roth, W. J.; Strohmaier, K. G.; Reyes, S. C. *Microporous Mesoporous Mater*. **2008**, *109*, 327-334].

Table S2. The ferric content of ion-exchanged (Fe(Ex)-ZSM-5) and ferric oxide impregnated (Fe(Im)-ZSM-5) analogues.

Catalyst	n_{Si}/n_{Fe} [a] (mol/mol)
Fe(Ex)-ZSM-5	73
Fe(Im)-ZSM-5	65

[a] The molar ratio of Si to Fe; the data in parentheses are the Si/Fe molar ratios measured after the samples were treated by aqueous nitric acid.



Scheme S1 Knoevenagel condensation of benzaldehyde with malononitile catalyzed by Fe-ZSM-5(n), Fe(Ex)-ZSM-5 and Fe(Im)-ZSM-5.

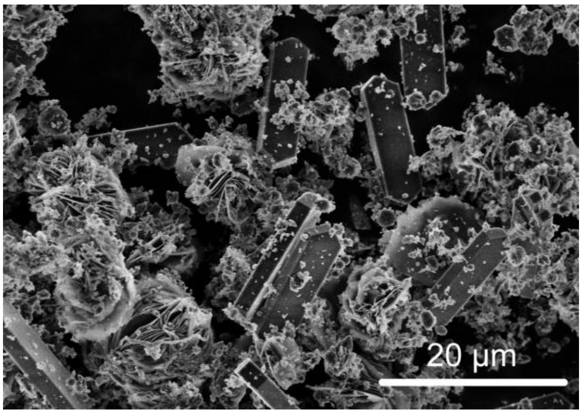


Figure S1. The SEM image for Fe-Silicalite-1(100) obtained by the unseeded organotemplate-free acidic cohydrolysis route.

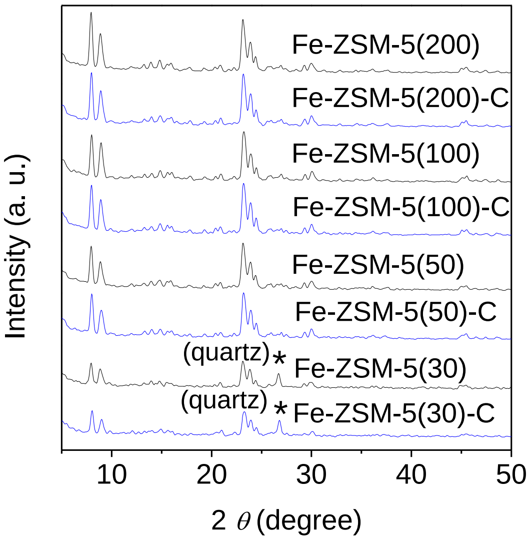


Figure S2. XRD patterns for as-synthesized and as-calcined Fe-ZSM-5(*n*) series.

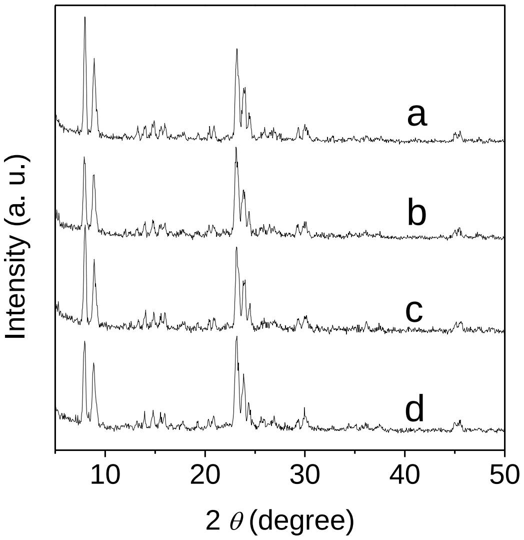


Figure S3. XRD patters for the as-synthesized Me-ZSM-5(100) (Me = Mo, Ti, Co, Cr) obtained by the unseeded organotemplate-free acidic cohydrolysis route. (a) Mo-ZSM-5(100), (b) Ti-ZSM-5(100), (c) Co-ZSM-5(100), (d) Cr-ZSM-5(100).

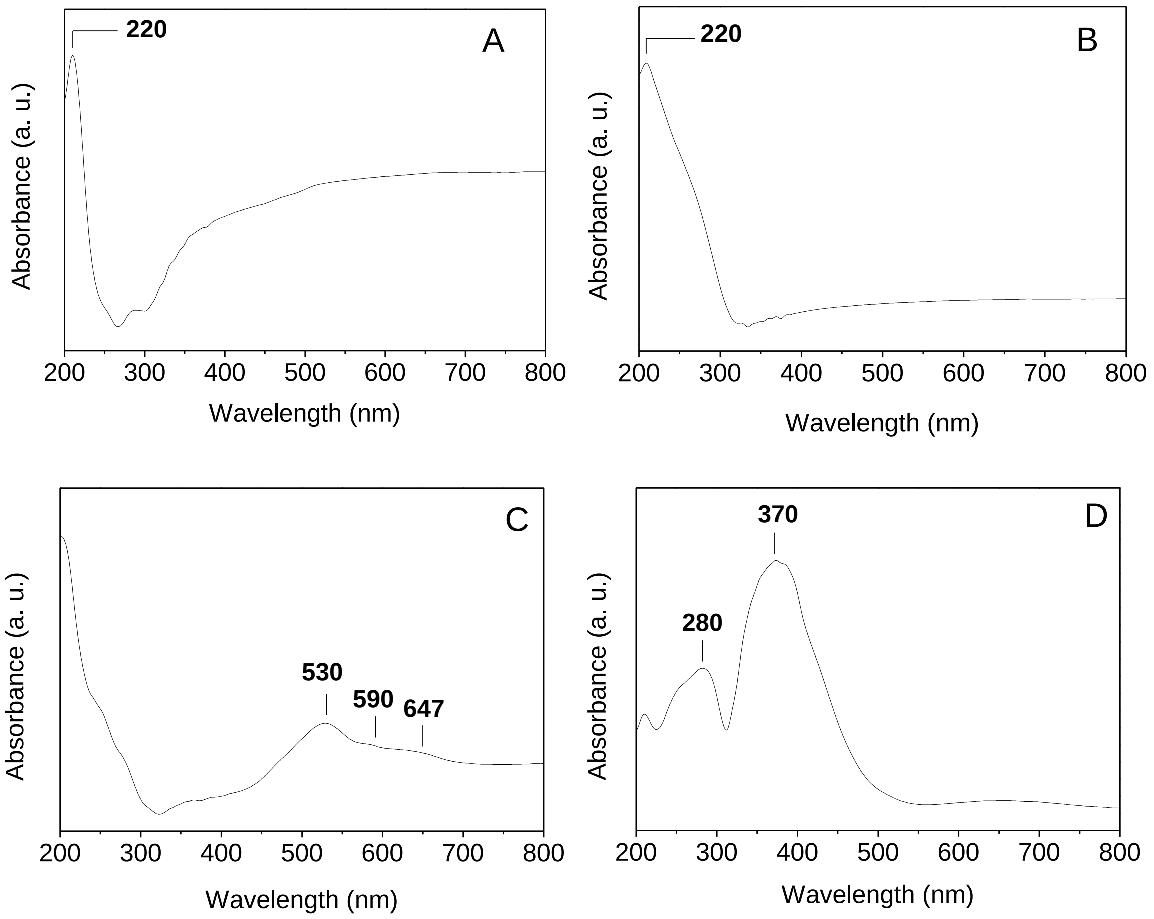


Figure S4. UV-Vis spectra for Me-ZSM-5(100) (Me = Mo, Ti, Co, Cr) obtained by the unseeded organotemplate-free acidic cohydrolysis route. (A) Mo-ZSM-5(100), (B) Ti-ZSM-5(100), (C) Co-ZSM-5(100), (D) Cr-ZSM-5(100).

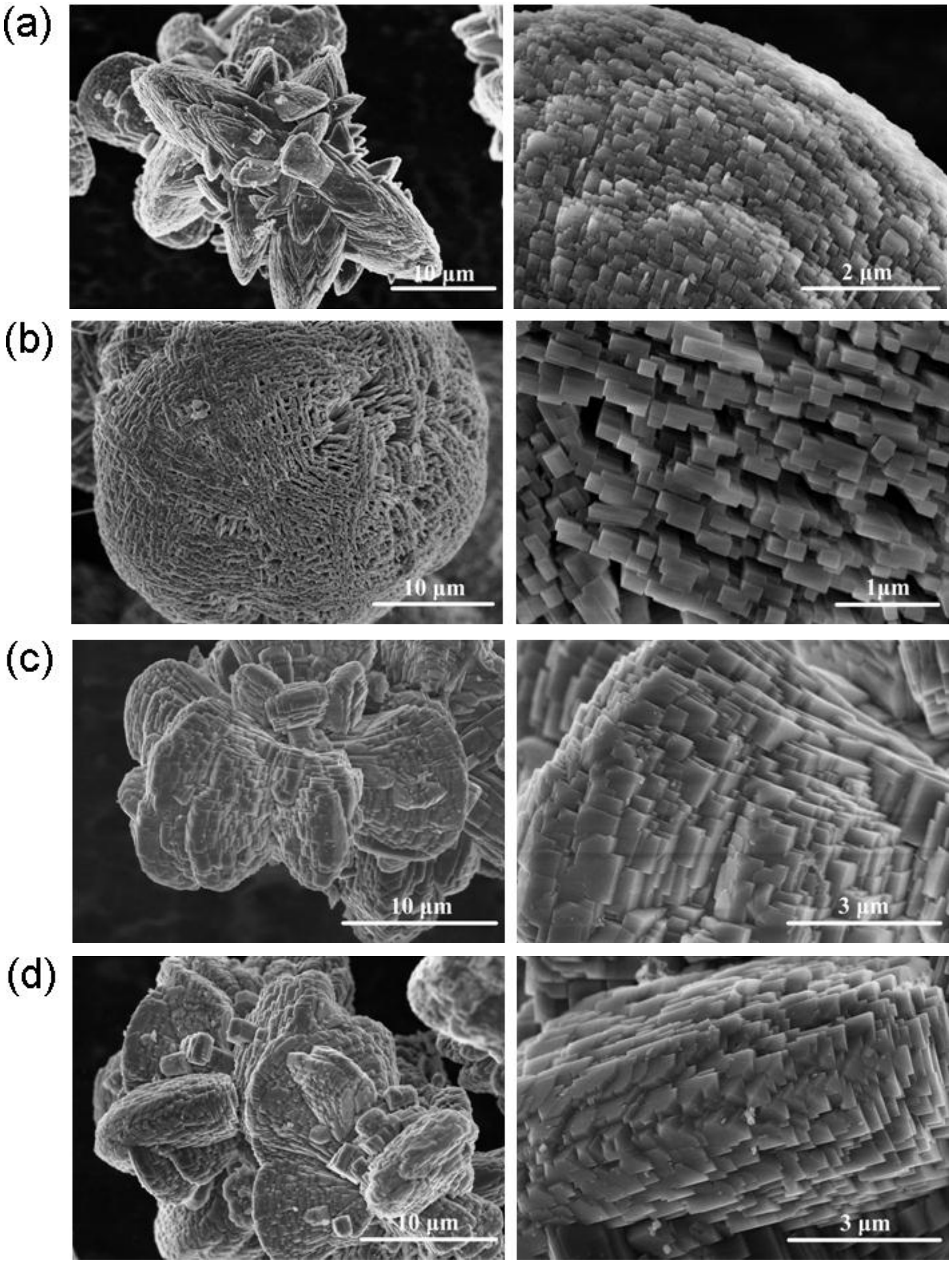


Figure S5. SEM images for the as-synthesized Me-ZSM-5(100) (Me = Mo, Ti, Co, Cr) obtained by the unseeded organotemplate-free acidic cohydrolysis route.(a) Mo-ZSM-5(100), (b) Ti-ZSM-5(100), (c) Co-ZSM-5(100), (d) Cr-ZSM-5(100).