Electronic Supplementary Information

Harnessing nanoscale spatial effect in inner-modified zeolitic imidazolate framework-8 for enhanced Knoevenagel condensation reaction

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Materials and Methods

Figures S1–S6

Table S1

Movies S1–S3

Materials and Methods

Section 1. Chemicals

Zinc nitrate hexahydrate (98%, $Zn(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich), 2-methylimidazole (99%, $C_4H_6N_2$, Sigma-Aldrich), hexadecyltrimethylammonium bromide (99%, $C_{19}H_{42}BrN$, Sigma-Aldrich), gold(III) chloride trihydrate (99.9%, $HAuCl_4 \cdot 3H_2O$, Sigma-Aldrich), silver nitrate (99%, $AgNO_3$, Sigma-Aldrich), sodium borohydride (99%, $NaBH_4$, Sigma-Aldrich), ascorbic acid (BioXtra, 99%, $C_6H_8O_6$, Sigma-Aldrich), methyl alcohol (99.5%, CH_3OH, Daejung), toluene (99.7%, C_7H_8, Daejung), malononitrile (99%, $CH_2(CN)_2$, Sigma-Aldrich), benzaldehyde (99.5%, C_7H_6O, Sigma-Aldrich) and dodecane (99.5%, $C_{12}H_{26}$, TCI) were purchased and used without further purification. Deionized water (18.2 MΩ·cm at 25°C) purified by a Merck Millipore Direct Q3 UV Water Purification System was used for all washing and solution preparation. All glassware were treated with aqua regia (a mixture of HCl and HNO_3 with a volume ratio of 3:1), repeatedly washed with deionized water and dried immediately before use.

Section 2. Synthesis of ZIF-8 nanocrystals

2.1. Gold nanorod

Gold nanorods were prepared via literature methods.[1,2] An aqueous solution of 10 mM $HAuCl_4$ (10 mL), 10 mM $AgNO_3$ (1.8 mL), 100 mM ascorbic acid (1.4 mL) and seed solution (240 μL) were added in sequence into 100 mM CTAB solution (200 mL) and mixed well. The solution was left undisturbed at 30 °C for 2 h. After centrifugation at 8000 rpm for 15 min twice, dark brownish gold nanorod solution was collected and stored in 50 mM CTAB (5 mL).

2.2. Pristine ZIF-8 nanocube (C-ZIF)

ZIF-8 nanocubes were synthesized according to a literature method with modifications.[3] an aqueous solution of 24 mM $Zn(NO_3)_2$ (4.5 mL) was injected to a mixture of aqueous solutions of 1.32 M 2-methylimidazole (4.5 mL) and 50 mM CTAB (90.9 μL) in a 20 mL scintillation vial while stirred at 500 rpm. The solution was stirred for 5 min and left undisturbed at room temperature for 3 h. The clear solution turned translucent during the initial 5-min agitation, which later became cloudy over 3 h. The cloudy solution was centrifuged at 8000 rpm for 15 min, and supernatant was discarded as much as possible. The remaining product was redispersed with methyl alcohol (10 mL). After centrifugation at 8000 rpm for 15 min, the product was collected and stored in methyl alcohol (15 mL). The absorbance of C-ZIF was ~1.0 at 400 nm after 4-fold dilution. For further characterizations (XRD, IR and XPS) and catalytic reaction, C-ZIF was dried under dynamic vacuum at room temperature overnight (product mass: ~5 mg).

2.3. Etching of ZIF-8 nanocube (E-ZIF)

The as-synthesized solution of C-ZIF was centrifuged at 8000 rpm for 15 min, and supernatant was discarded as much as possible. C-ZIF was redispersed with 50 mM CTAB in methyl alcohol (~15 mL) in a 50 mL Erlenmeyer flask, whose absorbance was adjusted to 2 at 400 nm. A methanolic solution of 10 mM $HAuCl_4$ (120 μL per 1.5 mL of 50 mM CTAB) was injected into the C-ZIF solution while stirred at 300 rpm under 40 °C, and it was stirred for 30 min. After centrifugation at 9000 rpm for 10 min twice, E-ZIF was collected and dispersed in methyl alcohol (3–5 mL). The absorbance of E-ZIF was ~1.0 at 400 nm after 4-fold dilution. For further characterizations (XRD, IR and XPS) and catalytic reaction, E-ZIF was dried under dynamic vacuum at room temperature overnight (product mass: ~2 mg). The above synthesis was conducted repeatedly to obtain a large amount of dry powder (> 5 mg) for the Knoevenagel condensation reaction.

2.4. Gold nanorod encapsulated with ZIF-8 (Rod@ZIF)

Aqueous solutions of 1.32 M 2-methylimidazole (3 mL), 24 mM $Zn(NO_3)_2$ (3 mL) and the gold nanorod solution (3 mL, extinction = 25 at 720–780 nm) were injected sequentially in a 20 mL scintillation vial while stirred at 500 rpm. The solution was stirred for 5 min and left undisturbed at room temperature for 3 h. The brownish cloudy solution was centrifuged at 6000 rpm for 15 min, and supernatant was discarded as much as possible. The remaining product was redispersed with methyl alcohol (10 mL) upon ultrasonication. After centrifugation at 5000 rpm for 15 min, the product was collected and stored in methyl alcohol (15 mL). Rod@ZIF showed an extinction around 780–830 nm with ~1.0 in intensity after 5-fold dilution. For further characterizations (XRD, IR and XPS) and catalytic reaction, Rod@ZIF was dried under dynamic vacuum at room temperature overnight (product mass: ~2 mg). The above synthesis was conducted repeatedly to obtain a large amount of dry powder (> 5 mg) for the Knoevenagel condensation reaction.

2.5. Etching of Rod@ZIF (E-Rod@ZIF)

The as-synthesized solution of Rod@ZIF was centrifuged at 8000 rpm for 15 min, and supernatant was discarded as much as possible. Rod@ZIF was redispersed with 50 mM CTAB in methyl alcohol (25–30 mL) in a 50 mL Erlenmeyer flask, whose absorbance was adjusted to 2 at 780–830 nm. A methanolic solution of 10 mM $HAuCl_4$ (120 µL per 1.5 mL of 50 mM

CTAB) was injected into the Rod@ZIF solution while stirred at 300 rpm under 40 °C, and it was stirred for 30 min. After centrifugation at 9000 rpm for 10 min twice, E-Rod@ZIF was collected and dispersed in methyl alcohol (3–5 mL). The absorbance of E-Rod@ZIF was ~1.0 at 400 nm. For further characterizations (XRD, IR and XPS) and catalytic reaction, E-Rod@ZIF was dried under dynamic vacuum at room temperature overnight (product mass: ~1.5 mg). The above synthesis was conducted repeatedly to obtain a large amount of dry powder (> 5 mg) for the Knoevenagel condensation reaction.

Section 3. Materials characterization

A Talos L120C Transmission Electron Microscope at 120 kV (Thermo Fisher Scientific) was used for morphology analysis. A UV-visible absorption measurement was conducted using a Genesis 150 UV-visible spectrophotometer with a quartz cuvette (path length = 1 cm). Powder X-ray diffraction was measured using a D8 Advanced A25 diffractometer (BRUKER). Infrared spectra were obtained using a Nicolet iS5 FTIR spectrometer (Thermo Fisher Scientific) with iD7 ATR Accessory. X-ray photoelectron spectroscopy spectra were measured using a NEXSA G2 X-ray photoelectron spectrometer (Thermo Fisher Scientific). Elemental analysis for gold and zinc was conducted using an OPTIMA 8300DV inductively coupled plasma (ICP–OES) spectrometer (PerkinElmer).

Section 4. Knoevenagel condensation reaction

Dry ZIF-8 nanocrystals (5 mg) were mixed with benzaldehyde (200 μL), dodecane (200 μL) and toluene (4 mL), followed by ultrasonication for 2 min. The mixture was transferred into 1 mL of toluene with malononitrile (0.25 g) and stirred at 200 rpm. An aliquot (200 μL) was collected at 30 min, 1 h, 2 h, 4 h and 6 h and centrifuged to remove ZIF-8 crystals (10000 rpm, 1 min). The supernatant was measured using an Agilent 7890A gas chromatography (Agilent Technologies). Dodecane was used as an internal standard.

Figures S1−S6

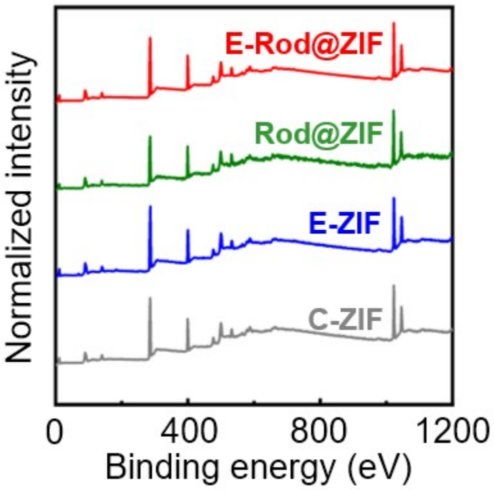

Figure S1. Full-range XPS spectra of C-ZIF (gray line), E-ZIF (blue line), Rod@ZIF (green line) and E-Rod@ZIF (red line).

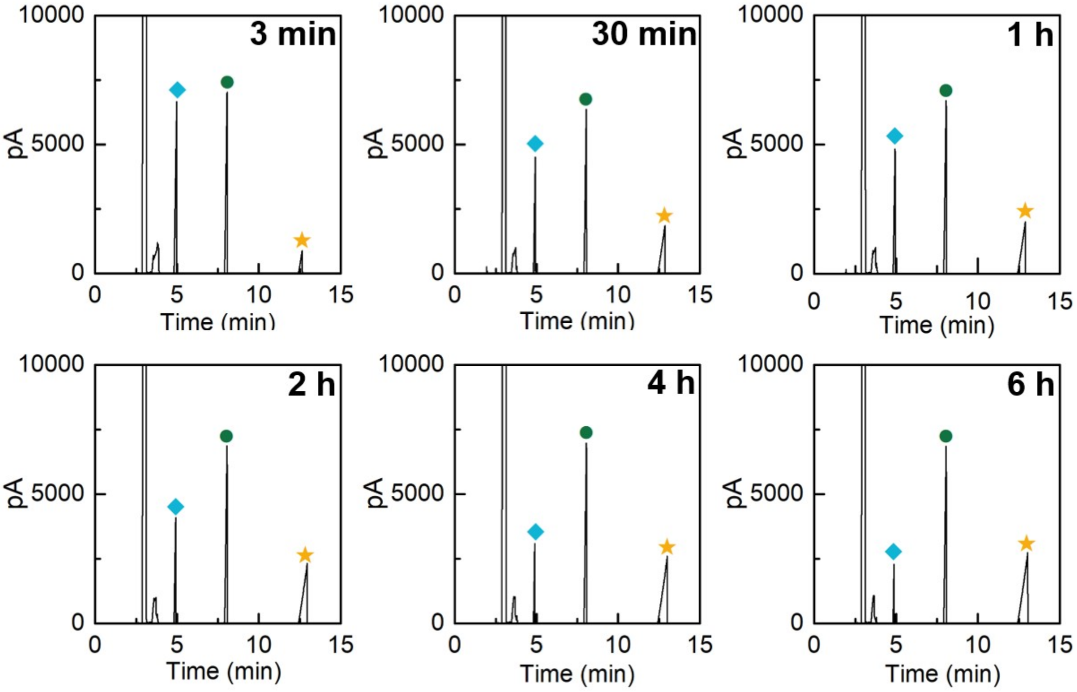

Figure S2. GC spectra of product species collected at different reaction times for the Knoevenagel condensation between malononitrile and benzaldehyde using C-ZIF, where peaks were assigned as sky-blue rhombus for benzaldehyde, green circle for dodecane and orange star for benzalmalononitrile.

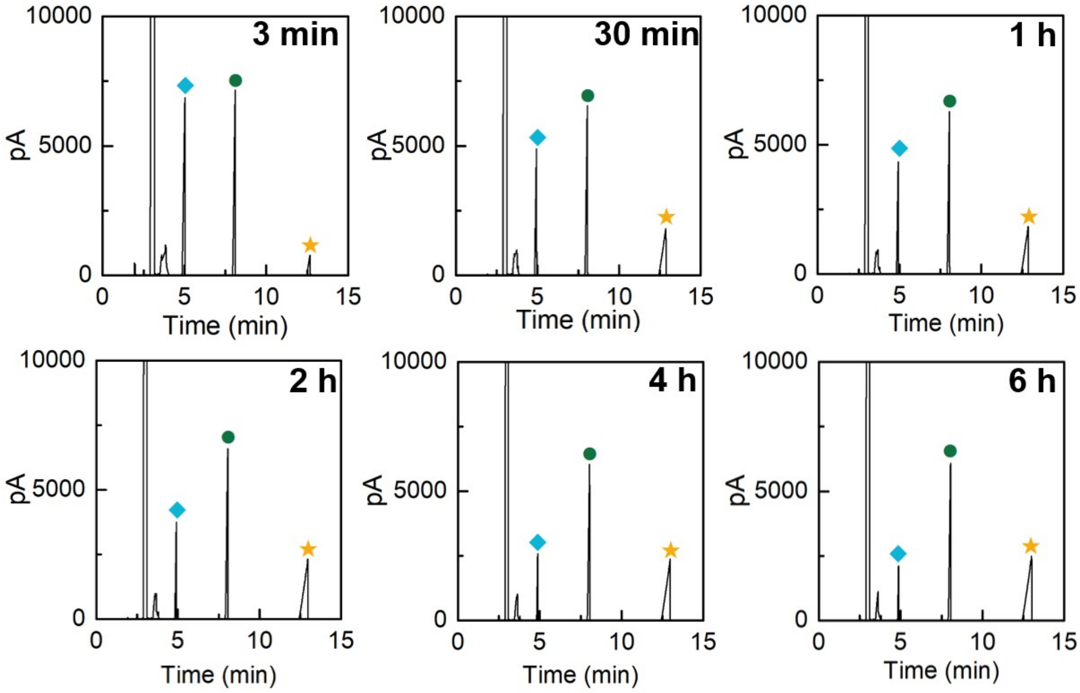

Figure S3. GC spectra of product species collected at different reaction times for the Knoevenagel condensation between malononitrile and benzaldehyde using E-ZIF, where peaks were assigned as sky-blue rhombus for benzaldehyde, green circle for dodecane and orange star for benzalmalononitrile.

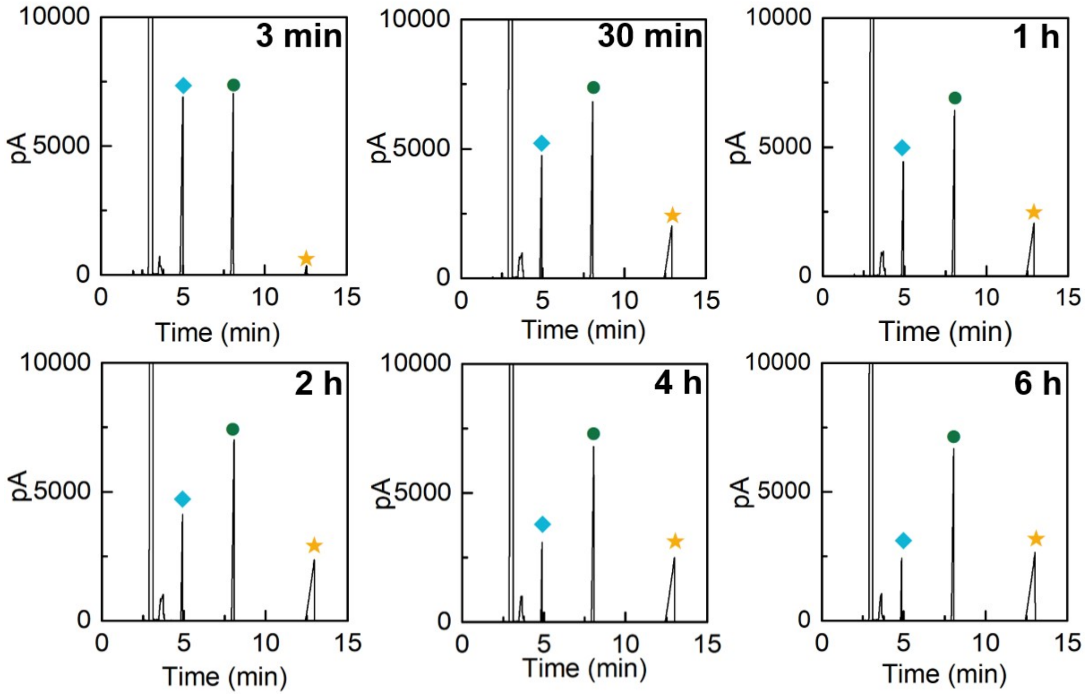

Figure S4. GC spectra of product species collected at different reaction times for the Knoevenagel condensation between malononitrile and benzaldehyde using Rod@ZIF, where peaks were assigned as sky-blue rhombus for benzaldehyde, green circle for dodecane and orange star for benzalmalononitrile.

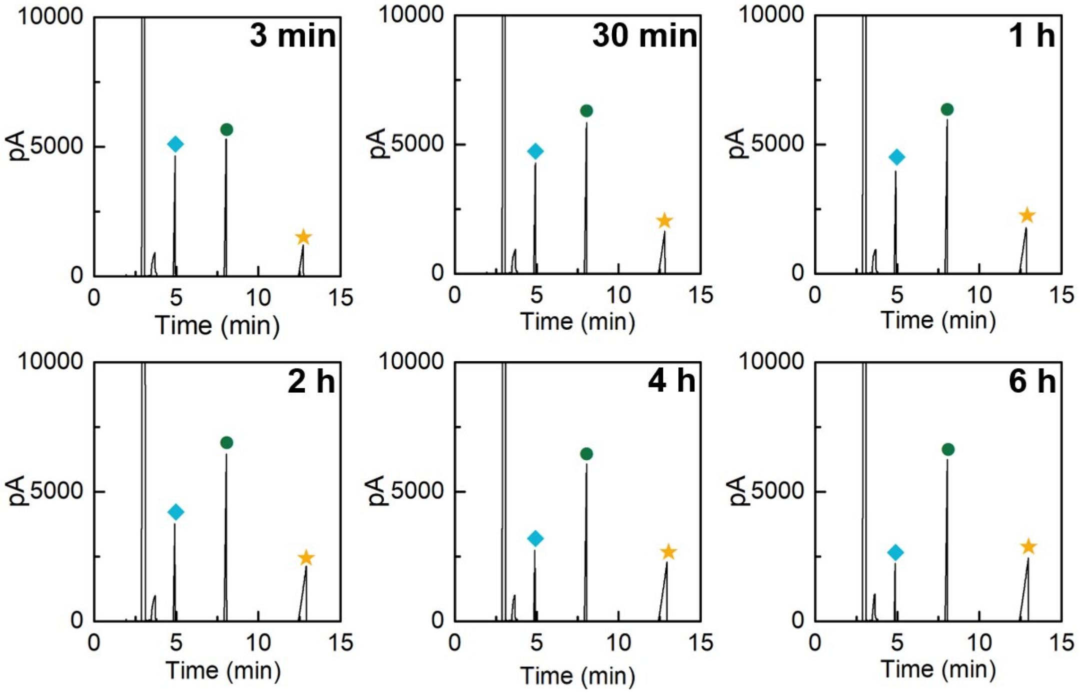

Figure S5. GC spectra of product species collected at different reaction times for the Knoevenagel condensation between malononitrile and benzaldehyde using E-Rod@ZIF, where peaks were assigned as sky-blue rhombus for benzaldehyde, green circle for dodecane and orange star for benzalmalononitrile.

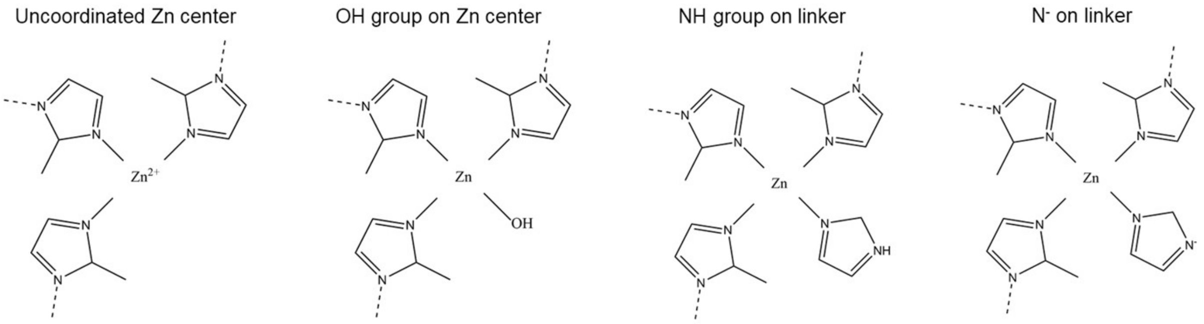

Figure S6. Potential catalytic sites in the framework for ZIF-8 nanocrystals after etching (E-Rod@ZIF and E-ZIF).

Table S1

Table S1. Elemental analysis (Zn and Au) of C-ZIF, E-ZIF and E-Rod@ZIF from ICP-OES. The detected amount of Au (< 1 ppm) in each sample can be considered non-existent.

Element	C-ZIF	E-ZIF	E-Rod@ZIF
Zn (ppm)	407.809	441.875	447.662
Au (ppm)	0.139	0.348	0.718

Movies S1−S3

Movie S1. A series of tilt TEM images of the E-Rod@ZIF particle shown in Figure 3.

Movie S2. A series of *xy*-slice images of the E-Rod@ZIF particle shown in Figure 3.

Movie S3. 3D reconstruction of the E-Rod@ZIF particle and its cross-sectional view shown in Figure 3.

<u>**References**</u>

1. M. N. O'Brien, M. R. Jones, K. A. Brown and C. A. Mirkin, Universal noble metal nanoparticle seeds realized through iterative reductive growth and oxidative dissolution reactions, *J. Am. Chem. Soc.*, 2014, **136**, 7603-7606.
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3. Y. Pan, D. Heryadi, F. Zhou, L. Zhao, G. Lestari, H. Su and Z. Lai, Tuning the crystal morphology and size of zeolitic imidazolate framework-8 in aqueous solution by surfactants, *CrystEngComm*, 2011, **13**, 6937-6940.