

## Supplementary Information

# Fabrication of ZIF-on-Lamella-Zeolite Architecture as a Highly Efficient Catalyst for Aldol Condensation

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## Experimental

### Chemicals

All the chemicals and reagents were of analytical grade, obtained from commercial sources, and used as received unless otherwise stated. Methanol, NH<sub>4</sub>F (>96 wt%), cobalt nitrate, zinc nitrate and ethanol were purchased from Damao chemical reagent factory. 2-methylimidazole (Hmim), furfural (99 wt%), benzaldehyde (98 wt%), cinnamaldehyde (99 wt%), amylcinnamaldehyde (99 wt%), veratraldehyde (99 wt%), 4-methoxybenzaldehyde (97 wt%), 3,4,5-trimethoxybenzaldehyde (99 wt%), 4-

chlorobenzaldehyde (98 wt%), 4-(Trifluoromethyl)benzaldehyde (97 wt%) and hydrofluoric acid (HF, 40% aq) were supplied from Aladdin Industrial Corporation. N,N,N-trimethyl-1-adamantammonium hydroxide (TMA<sub>3</sub>AdOH, 25 wt%) and hexamethylenimine (HMI, 98 wt%) were purchased from Energy chemical. N-dodecane was obtained from Tianjin Kermel chemical reagent Co., Ltd. Tetraethyl orthosilicate (TEOS, 98 wt%), tetrabutylammonium hydroxide (TBAOH, 40 wt%), tetrapropylammonium hydroxide (TPAOH, 25 wt%), tetraethylammonium hydroxide (TEAOH, 25 wt%) and 5-hydroxymethylfurfural (5-HMF, 99 wt%) were purchased from Shanghai Titan scientific Co., Ltd. Acetone was obtained from Beijing chemical works. Deionized water was prepared in the laboratory.

### **Synthesis of ZIF-67/MWW(1/2), ZIF-67/MWW(1/4) and ZIF-67/MWW(1/8) Composites.**

The centrifugation product (0.106 g) of ZIF-67/MWW(U) was dispersed in a solution containing 0.5 g of 2-methylimidazole in 10 mL of ethanol. The resulting mixture, marked as Suspension A, was sonicated at room temperature for 10 min. Solution B was prepared by dissolving 0.175 g of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in 20 mL of ethanol. Suspension A and Solution B were then mixed and vigorously stirred for 120 min. Afterward, the mixture was centrifuged at 6000 rpm for 5 min to separate the solid product. Finally, the product was washed with ethanol three times and dried at 80 °C for 12 h. The obtained product was denoted as ZIF-67/MWW(1/2). ZIF-67/MWW(1/4) and ZIF-67/MWW(1/8) were prepared similarly to ZIF-67/MWW(1/2), but the precursor concentration was reduced to 1/4 and 1/8 of the initial concentration, respectively.

### **Synthesis of ZIF-8.**

To prepare Solution A, 1.6 g of 2-methylimidazole was dissolved in 10 mL of methanol and stirred for 10 min. For Solution B, 0.48 g of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in 5 mL of deionized water and 10 mL of methanol and stirred for 10 min. Both solutions were mixed together and stirred at room temperature for 2 h. The

mixture was then centrifuged at 8500 rpm for 20 min. The solid product was washed with ethanol three times and dried at 80 °C for 12 h.

#### **Synthesis of ZIF-8/MWW(U) Composite.**

To prepare Suspension A, 0.1 g of Si-MWW was dispersed in 10 mL of ethanol and stirred under ultrasonication at room temperature for 20 min. Solution B was prepared by dissolving 0.35 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 10 mL of ethanol. Suspension A and Solution B were mixed and subjected to ultrasonication for 60 min, followed by centrifugation at 6000 rpm for 5 min to separate the solid product. Then, a solution of 2-methylimidazole (1 g in 40 mL of ethanol) was added to the above solid product. The mixture was treated by ultrasonication at room temperature for 60 min. Finally, the solid product was collected by centrifugation, washed with ethanol three times, and dried at 80 °C for 12 h. The obtained sample was denoted as ZIF-8/MWW(U), where U represents the ultrasonication process.

#### **Synthesis of ZIF-8/MWW(R) Composite.**

The above centrifugation product (0.105 g) of ZIF-8/MWW(U) was dispersed in a solution containing 1 g of 2-methylimidazole in 10 mL of ethanol, and the resulting mixture was sonicated at room temperature for 10 min, marked as Suspension A. Solution B was prepared by dissolving 1.2 mmol of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 20 mL of ethanol. Suspension A and Solution B were mixed and vigorously stirred for 120 min, followed by centrifugation at 6000 rpm for 5 min to separate the solid product. Finally, the product was washed with ethanol three times and dried at 80 °C for 12 h. The obtained product was denoted as ZIF-8/MWW(R), where R represents the regrowth process.

#### **Synthesis of Si-Beta.**

The Si-Beta zeolite was synthesized by modifying the route described by Tolborg et al.<sup>1</sup> 10.288 g of tetraethyl orthosilicate (TEOS) was added to 11 g of tetraethylammonium hydroxide (TEAOH, 25 wt%) under stirring. The solution was

stirred until a viscous gel formed. Then 1.03 g hydrofluoric acid (HF) diluted in 0.53 g of deionized water was added to the viscous gel, resulting in a solid gel with the molar composition:  $1.0\text{SiO}_2$ :  $0.55\text{TEAOH}$ :  $0.55\text{HF}$ :  $7.5\text{H}_2\text{O}$ . The solid gel was transferred to a Teflon lined stainless steel autoclave and heated at 150 °C for 10 d. The product was washed with deionized water until the pH was less than 8 and dried at 80 °C for 12 h. The dried sample was calcined at 600 °C for 10 h in a muffle furnace to remove the organic template. The resulting product was recorded as Si-Beta.

### **Caution!**

For synthesis of Si-Beta, HF is involved. HF is an extremely corrosive acid! When using HF acid, full safety protective gear must be worn, including a laboratory coat, rubber boots, an acid apron, goggles, a face shield, gloves, and long rubber gloves.

### **Synthesis of Silicalite-1.**

The sheet-like Silicalite-1 was prepared using the synthesis gel with composition of  $1\text{ SiO}_2$ :  $0.14\text{ TPAOH}$ :  $0.8\text{ NH}_4\text{F}$ :  $80\text{ H}_2\text{O}$ :  $x\text{ wt\% Silicalite-1 seed suspension}$ . 12 g of deionized water, 4.37 g of TPAOH, 8 g of TEOS, and 2.46 g of Silicalite-1 seed suspension (20 wt%, respect to the silica in TEOS) were mixed and stirred at 35 °C to hydrolyze TEOS. Then, 1.14 g of  $\text{NH}_4\text{F}$  was dissolved in deionized water (20 g), respectively, and added into the hydrolyzing mixture to obtain a synthesis gel. The gel was transferred into a 100 ml stainless-steel autoclave and heated at 170 °C for 24 h. The solid products were repeatedly filtered and washed with deionized water, then dried at 80 °C overnight and calcined at 540 °C for 6 h.

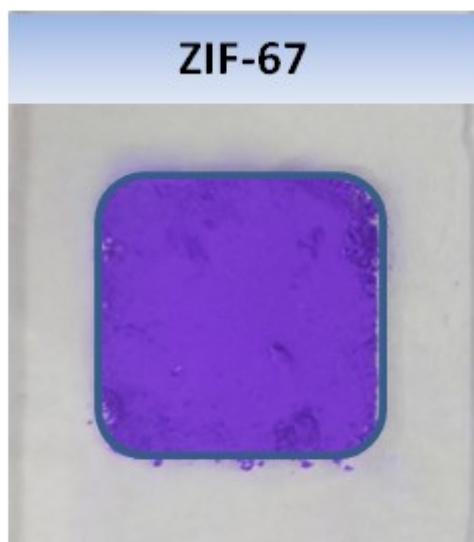
### **Synthesis of Si-SPP.**

The synthesis of Si-SPP, the self-pillared pentasil zeolite, was conducted as follows: 11.025 g of tetrabutylammonium hydroxide (TBAOH, 40 wt%) was added to 4.845 g of deionized water under stirring to form a clear solution. Subsequently, 11.250 g of tetraethyl orthosilicate (TEOS, 98 wt%) was added dropwise into the above mixture

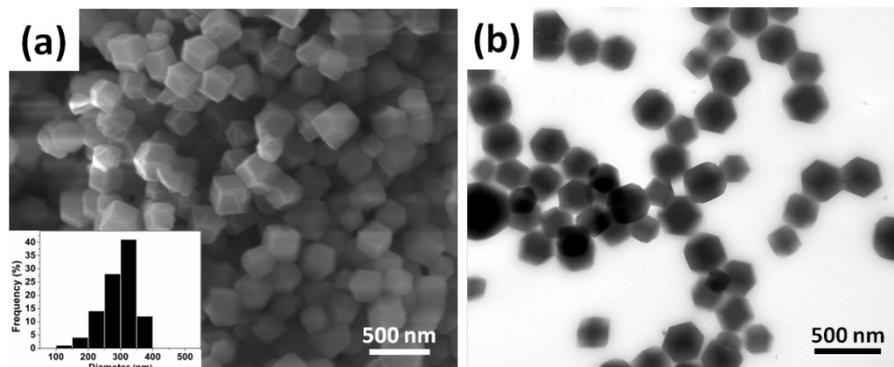
with vigorous stirring until a clear sol was formed. The composition of the final silicate sol was 1.0SiO<sub>2</sub>: 0.32TBAOH: 8H<sub>2</sub>O: 4ethanol. After overnight stirring, the final mixture was sealed in a stainless steel autoclave with a Teflon liner, and the crystallization was conducted at 120 °C for 3 d. The product was centrifuged, washed with deionized water, and dried at 80 °C for 12 h. The dry powder was then calcined in air at 550 °C for 10 h to remove the organic structure directing agent.

**Synthesis of ZIF-67/Beta, ZIF-67/Silicalite-1 and ZIF-67/SPP Composites.**

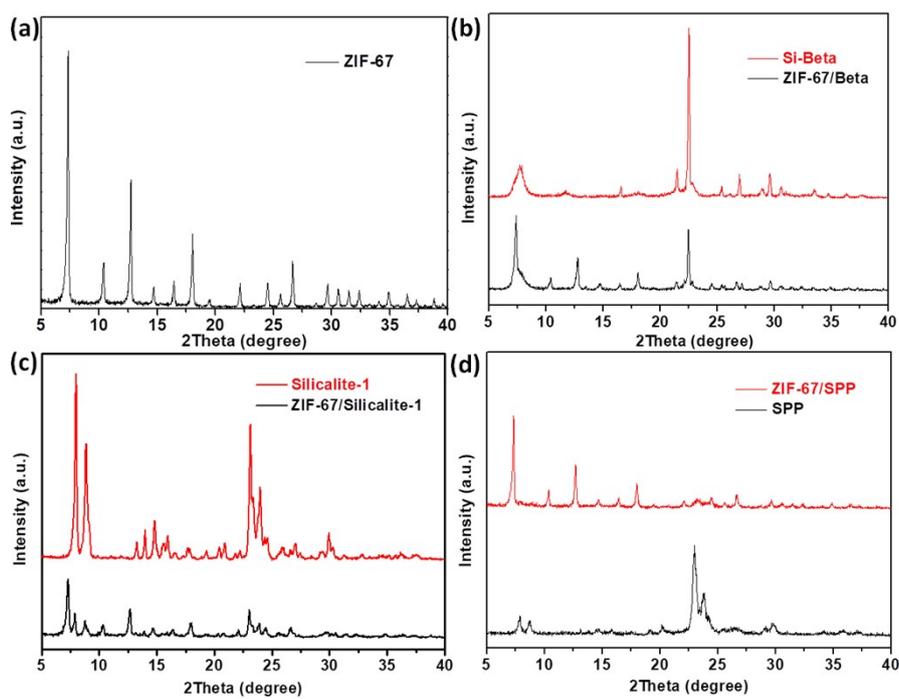
ZIF-67/Beta, ZIF-67/Silicalite-1, and ZIF-67/SPP were prepared using similar procedures to that of ZIF-67/MWW(R), with the only difference being that the Si-MWW support was replaced by Si-SPP, Silicalite-1, or Si-Beta.



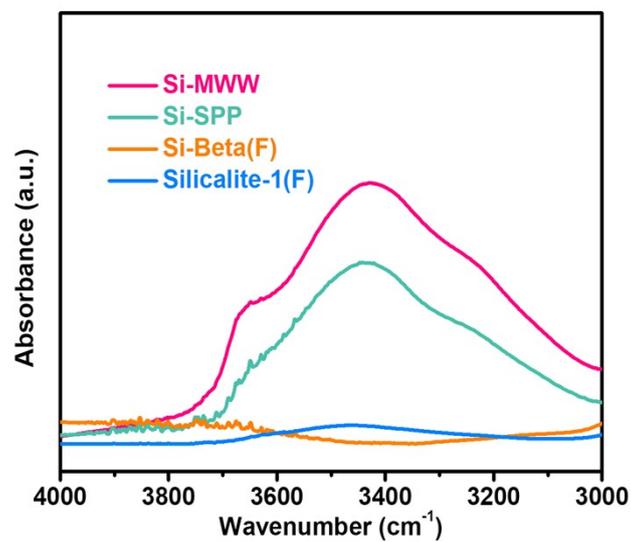
**Fig. S1** Photograph of the ZIF-67 powder.



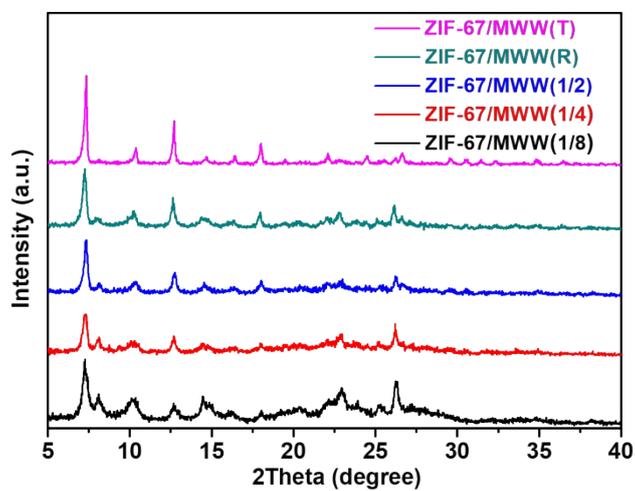
**Fig. S2** (a) SEM and (b) TEM images of ZIF-67.



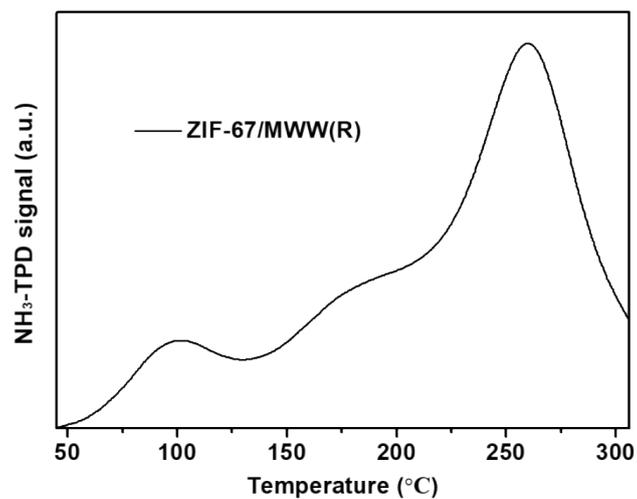
**Fig. S3** XRD patterns of (a) ZIF-67, (b) Si-Beta and ZIF-67/Beta, (c) Silicalite-1 and ZIF-67/Silicalite-1 and (d) Si-SPP and ZIF-67/SPP.



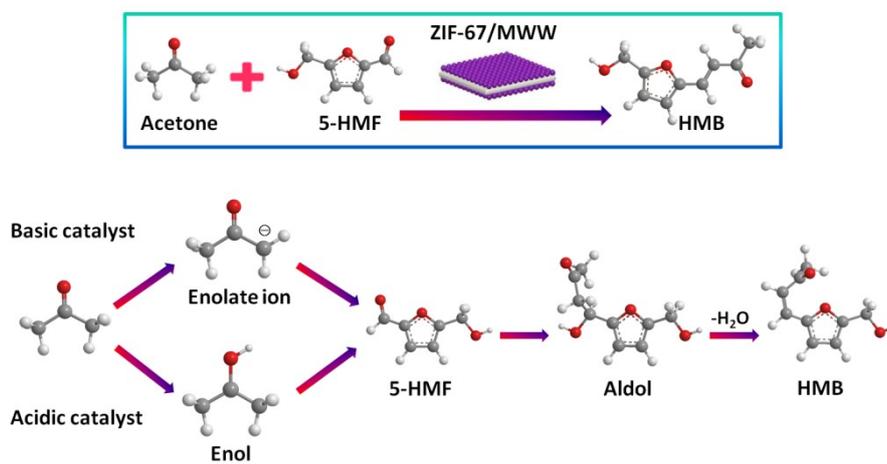
**Fig. S4** FTIR spectra in the hydroxyl stretching vibration region for the Si-MWW, Si-SPP, Si-Beta(F) and Silicalite-1(F) zeolites.



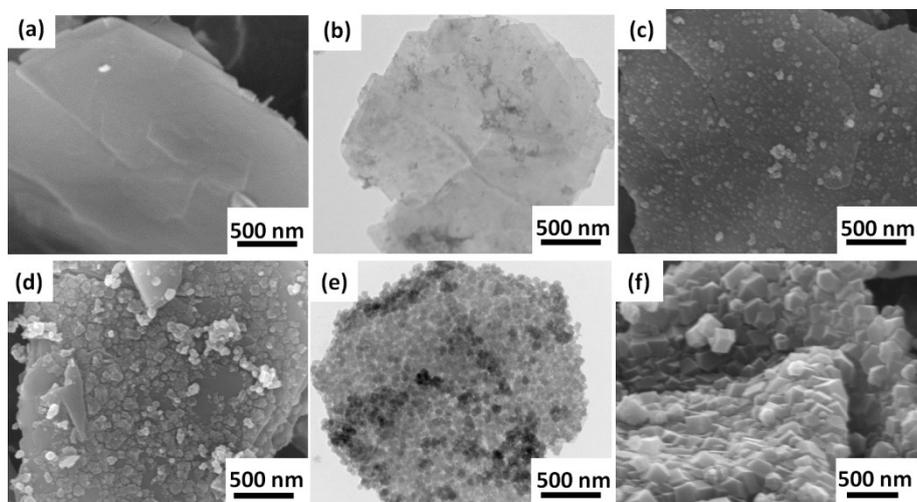
**Fig. S5** XRD patterns of ZIF-67/MWW(T), ZIF-67/MWW(R), ZIF-67/MWW(1/2), ZIF-67/MWW(1/4) and ZIF-67/MWW(1/8).



**Fig. S6**  $\text{NH}_3$ -TPD profile of ZIF-67/MWW(R).



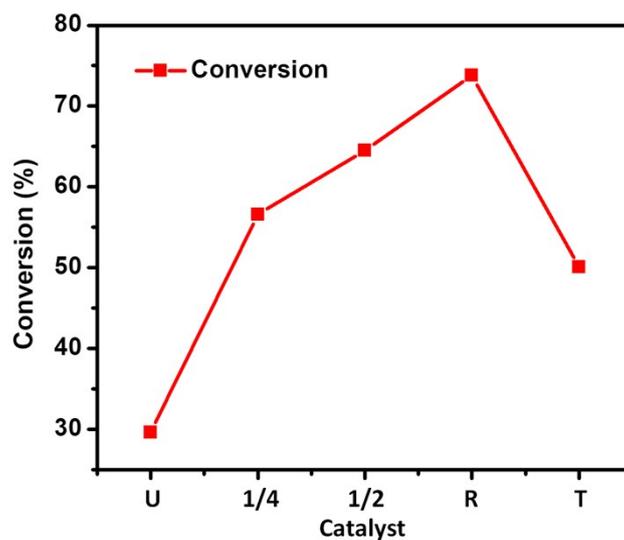
**Fig. S7** Reaction mechanisms of the aldol condensation of 5-HMF with acetone over the acid and base catalysts.<sup>3</sup>



**Fig. S8** SEM images of (a) Si-MWW, (c) ZIF-67/MWW(1/4), (d) ZIF-67/MWW(1/2) and (f) ZIF-67/MWW(T); TEM images of (b) ZIF-67/MWW(U) and (e) ZIF-67/MWW(R).

**Table S1** Co content of the ZIF-67/MWW samples determined by ICP analysis

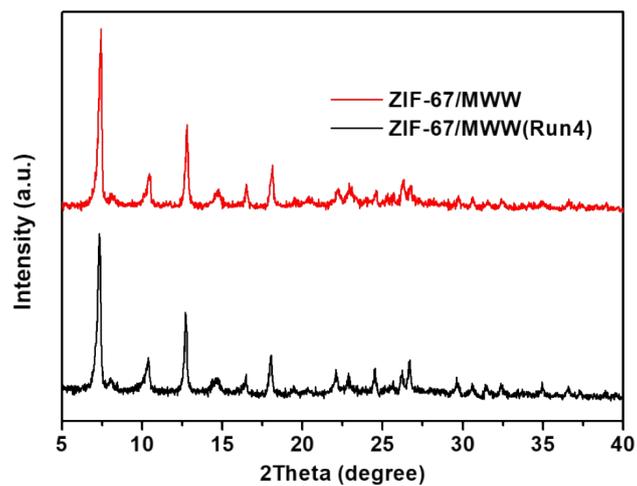
| Sample          | Co content (wt%) |
|-----------------|------------------|
| ZIF-67/MWW(U)   | 1.8              |
| ZIF-67/MWW(1/4) | 4.1              |
| ZIF-67/MWW(1/2) | 8.7              |
| ZIF-67/MWW(R)   | 13.4             |
| ZIF-67/MWW(T)   | 28.0             |



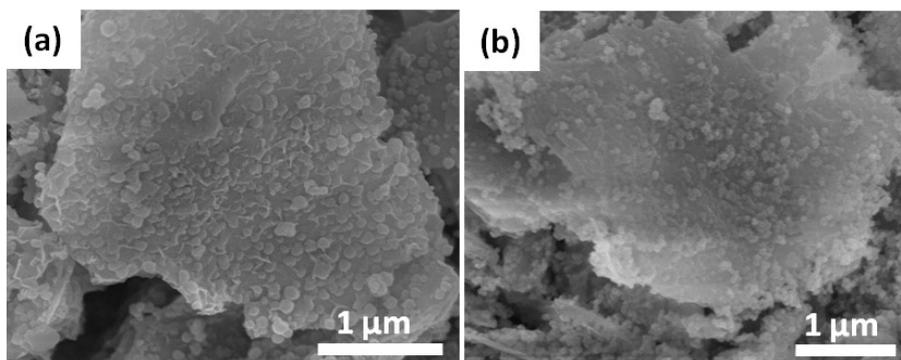
**Fig. S9** A comparison of different ZIF-67/MWW(X) catalysts for the aldol reaction of acetone and 5-hydroxymethylfurfural. (X were defined as U, 1/4, 1/2, R and T)

**Table S2** Comparison of catalytic activities of various catalysts for the aldol reaction of acetone and 5-hydroxymethylfurfural

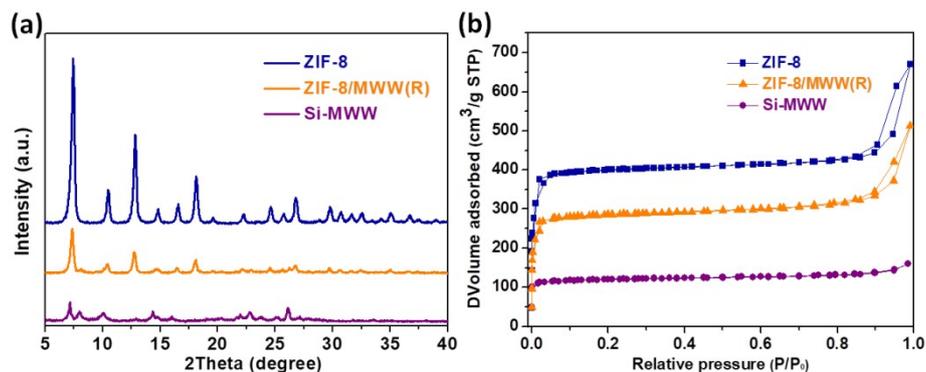
| Entry | Catalysts            | T(°C) | T(h) | Con. (%) | Sel. (%) | Ref.      |
|-------|----------------------|-------|------|----------|----------|-----------|
| 1     | MgZr                 | 50    | 24   | 68.0     | 20.7     | 4         |
| 2     | MgAl                 | 50    | 24   | 27.2     | 12.1     | 4         |
| 3     | Hie-FAUZIF-8         | 130   | 6    | 68.3     | 97.8     | 3         |
| 4     | Nit-NaY              | 120   | 24   | 51.4     | 63.6     | 5         |
| 5     | MgO-ZrO <sub>2</sub> | 120   | 24   | 68.5     | 48.6     | 5         |
| 6     | ZIF-67/MWW           | 150   | 4    | 73.8     | 70.8     | This work |



**Fig. S10** XRD patterns of fresh ZIF-67/MWW(R) catalyst and after repeated use for 4 times.



**Fig. S11** SEM images of ZIF-67/MWW(R) catalyst (a) fresh and (b) after repeated use for 4 times.



**Fig. S12** (a) PXRD patterns and (b) N<sub>2</sub> adsorption-desorption isotherms of the Si-MWW, ZIF-8/MWW(R) and ZIF-8.

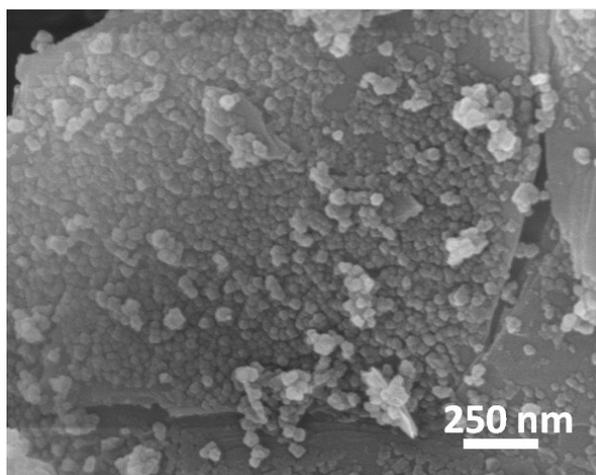
**Table S3** Structural properties of the Si-MWW zeolite, ZIF-8 and ZIF-8/MWW samples.

| Sample       | $S_{\text{BET}}$<br>( $\text{m}^2 \text{g}^{-1}$ ) | $S_{\text{ext}}^{\text{a}}$<br>( $\text{m}^2 \text{g}^{-1}$ ) | $V_{\text{micro}}^{\text{a}}$<br>( $\text{cm}^3 \text{g}^{-1}$ ) | $V_{\text{meso}}^{\text{b}}$<br>( $\text{cm}^3 \text{g}^{-1}$ ) | $V_{\text{total}}^{\text{c}}$<br>( $\text{cm}^3 \text{g}^{-1}$ ) |
|--------------|--|---|--|---|--|
| Si-MWW       | 460  | 57  | 0.16   | 0.09  | 0.25   |
| ZIF-8/MWW(R) | 1118   | 103   | 0.40   | 0.39  | 0.79   |
| ZIF-8        | 1553   | 114   | 0.57   | 0.47  | 1.04   |

<sup>a</sup> External surface areas ( $S_{\text{ext}}$ ) and micropore volumes ( $V_{\text{micro}}$ ) were determined using the  $t$ -plot analysis.

<sup>b</sup> Mesopore volumes ( $V_{\text{meso}}$ ) were calculated as  $V_{\text{total}} - V_{\text{micro}}$ .

<sup>c</sup> Total pore volumes were determined at  $P/P_0 = 0.99$ .



**Fig. S13** SEM image of ZIF-8/MWW(R).

## References

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