Supporting Information

Support Effect of Metal–Organic Frameworks on Ethanol Production through Acetic Acid Hydrogenation

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Preparation of MOF supports

Synthesis of UiO-66-NH₂ ({Zr₆O₄(OH)₄(bdc-NH₂)₆}∞)†

ZrCl₄ (11.52 g, 49.43 mmol) was dissolved in 2880 ml DMF by sonication for 15 minute. 2-aminoterephthalic acid (8.928 g, 49.29 mmol) was added into the solution. After sonication for 15 minute, the mixture was heated at 120 °C for 24 h. The yellow precipitate was collected by centrifugation. It was washed with DMF and MeOH, and dried under vacuum at 160 °C for a night.

Synthesis of HKUST-1 ({Cu₃(btc)₂}∞ (H₃btc = trimesic acid))†

Cu(NO₃)₂·3H₂O (20.8 g, 86.0 mmol) was dissolved in a mixed solvent (500 ml, DMF : EtOH : distilled water = 1 : 1 : 1). Trimesic acid (10.0 g, 47.6 mmol) was also dissolved in the mixture and sonicated for 15 minute. The solution was heated at 85 °C for 20 h. The precipitate was separated through decantation. After washing with DMF, the blue precipitate was immersed in chloroform for four days. This operation was repeated three times. The precipitate was separated by filtration and washed with MeOH and distilled water. To dry the powder, it was heated at 160 °C in vacuo. To remove unreacted chemicals and solvent,
reflux using MeOH was conducted for a day. After that, the sample was moved into DMF. The mixture was kept at 70 °C for 26 h. After separation by centrifugation, the resultant was washed with MeOH and head at 160 °C under vacuum until dryness.

**Synthesis of Zn-MOF-74 (\{Zn_2(dobdc)\}_x (H_4dobdc = 2,5-dihydroxyterephthalic acid))**

Zn(NO_3)_2·6H_2O (22.6 g, 76.0 mmol) was dissolved in 1000 ml DMF. 2,5-dihydroxyterephthalic acid (5.00 g, 26.0 mmol) was also dissolved in the mixture and sonicated 10 minute. 50 ml of distilled water was added to this solution and heated at 100 °C for 20 h. The precipitate was separated by decantation and washed with DMF. It was immersed in MeOH for five days. This operation was repeated two times. The precipitate was separated by filtration. After washing with MeOH and distilled water, it was refluxed in MeOH for 30 hours. The sample was dried in air after separation by centrifugation.

**Synthesis of Mg-MOF-74 (COP-27-Mg) (\{Mg_2(dobdc)\}_x)**

Mg(NO_3)_2·6H_2O (31.4 g, 122 mmol) was dissolved in a mixed solvent (198 ml of distilled water, 198 ml of EtOH and 2970 ml of DMF). 2,5-dihydroxyterephthalic acid (7.39 g, 37.3 mmol) was dissolved in the mixture and sonicated for 15 min. The solution was heated at 125 °C for 21 h. The precipitate was separated by decantation and immersed in MeOH for two days. This operation was repeated five times. The sample was separated by filtration and dried at 250 °C for 6 h under vacuum.

**Synthesis of DUT-5 (\{Al(OH)(bpydc)\}_x (H_2bypdc = 2,2’-bipyridyl-5,5’-dicarboxylic acid))**

Al(NO_3)_3·9H_2O (1.88 g, 5.0 mmol) and H_2bpydc (0.8 g, 3.3 mmol) were dissolved in 120 ml of DMF. After sonication, the solution was placed in Teflon-lined autoclaves and heated at 180 °C for 24 h. The precipitate was collected and washed with MeOH. The white powder was dried at 120 °C under vacuum for a night.

**Synthesis of UiO-66 (\{Zr_6O_4(OH)_4(bdc)_6\}_x)**

ZrCl_4 (1.66 g, 7.1 mmol) and terephthalic acid (1.16 g, 7.0 mmol) were dissolved in 30 ml of DMF and 0.8 ml of 35% HCl. The mixture was heated and stirred at 60 °C for complete dissolution. After that, it was put in Teflon-lined autoclaves and heated at 220 °C for 17h. Resulting white precipitate was separated by filtration and washed with DMF and MeOH. The white powder was dried at 180 °C under vacuum over a night.
**Synthesis of UiO-67** \(\{\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_6\}_{\infty}\) (H<sub>2</sub>bpdc = 4,4'-biphenyldicarboxylic acid))

ZrCl<sub>4</sub> (2.3 g, 9.7 mmol) was mixed into 300 ml of DMF and stirred until completely dissolved. 4,4'-biphenyldicarboxylic acid (2.4 g, 10.0 mmol) was added into the mixture and stirred for 20 min. Then, 0.25 ml of H<sub>2</sub>O and 50 ml of DMF were also added into the mixture. The mixture was heated at 95 °C for 99 h without stirring. After cooling to room temperature, the precipitate was filtrated and washed with ethanol. The resulting powder was dried at 90 °C under vacuum for 3h.

**Synthesis of MIL-125** \(\{\text{Ti}_8\text{O}_8(\text{OH})_4(\text{bdc})_6\}_{\infty}\)

Titanium (IV) isopropoxide (0.78 ml, 2.6 mmol), terephthalic acid (1.50 g, 9.0 mmol) were added in mixture of 22.5 ml of DMF and 3.0 ml of ethanol. The mixture was stirred until dissolved. Then, it was heated at 130 °C for 15 h in Teflon-lined autoclaves. The precipitate was separated by filtration and washed with MeOH and acetone. At last, the resulting white powder was heated at 70 °C under vacuum.

**Synthesis of ZIF-8** \(\{\text{Zn(mIm)}_2\}_{\infty}\) (HmIm = 2-methylimidazole)

Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (9.70 g, 33.3 mmol) and 2-methylimidazole (22.00 g, 266.6 mmol) were dissolved in 1000 ml of MeOH. The mixture was stayed for 24 h without stirring. The precipitate was separated and washed by centrifugation. The sample was dried under vacuum at room temperature.

**Synthesis of ZIF-67** \(\{\text{Co(mIm)}_2\}_{\infty}\)

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (9.70 g, 33.3 mmol) and 2-methylimidazole (22.00 g, 266.6 mmol) were dissolved in 1000 ml of MeOH. The mixture was stayed for 24 h without stirring. The precipitate was separated and washed by centrifugation. The sample was dried under vacuum at room temperature.

**Figure S1.** Schematic illustration of the tolerance test for MOFs against AcOH.
Table S1. List of the tolerances of MOFs against AcOH.

| MOF          | Tolerance |
|--------------|-----------|
| MIL-125      | ×         |
| MIL-125-NH₂  | ⃝        |
| UiO-66       | ×         |
| UiO-66-NH₂   | ⃝        |
| UiO-67       | ×         |
| HKUST-1      | ⃝        |
| MIL-101      | ⃝        |
| Zn-MOF-74    | ⃝        |
| Mg-MOF-74    | ⃝        |
| MIL-121      | ⃝        |
| DUT-5        | ×         |
| ZIF-8        | ×         |
| ZIF-67       | ×         |

Figure S2. Home-made fixed-bed flow reactor for online gas analysis of the AH reaction.
Figure S3. N₂ adsorption isotherms of (a) MIL-125-NH₂, (b) UiO-66-NH₂, (c) HKUST-1, (d) MIL-101, (e) Zn-MOF-74, (f) Mg-MOF-74, and (g) Pt/MIL-121 at 77 K.
Figure S4. Charts of the TPD-MS (at mass number = 60) of Zn-MOF-74, Mg-MOF-74, and MIL-121.

Table S2. Preparation details of all the catalysts used for AH reaction. Support amount used for the arc plasma deposition, number of shots of the arc plasma gun, loading amount of Pt, and diameter of the loaded Pt NPs are listed. **Pt/UIO-66-NH$_2$, Pt/HKUST-1, Pt/Zn-MOF-74, and Pt/Mg-MOF-74** were already reported in our previous literature.$^1$

|                  | Pt/UIO-66-NH$_2$ | Pt/UIO-66-NH$_2$ | Pt/HKUST-1 | Pt/MIL-101 | Pt/Zn-MOF-74 |
|------------------|------------------|------------------|------------|------------|--------------|
| **Support (g)**  | 1.83             | 6.05             | 4.45       | 2.78       | 7.32         |
| **Shot**         | 2600             | 8600             | 5200       | 2800       | 6600         |
| **Pt (wt%)**     | 0.56             | 0.44             | 0.47       | 0.58       | 0.48         |
| **Diameter (nm)**| 2.0 ± 0.2        | 1.9 ± 0.2        | 2.0 ± 0.2  | 1.9 ± 0.3  | 2.0 ± 0.3    |

|                  | Pt/MIL-121 | Pt/MIL-121 | Pt/TiO$_2$ | Pt/Al$_2$O$_3$ |
|------------------|------------|------------|------------|----------------|
| **Support (g)**  | 7.28       | 3.46       | 2.05       | 2.15           |
| **Shot**         | 8200       | 6500       | 7500       | 8000           |
| **Pt (wt%)**     | 0.41       | 0.41       | 0.50       | 0.52           |
| **Diameter (nm)**| 1.8 ± 0.3  | 2.0 ± 0.2  | 1.9 ± 0.3  | 1.3 ± 0.3      |
Figure S5. Temperature dependence of XRPD patterns of (a) MIL-125-NH$_2$, (b) UiO-66-NH$_2$, (c) HKUST-1, (d) MIL-101, (e) Zn-MOF-74, (f) Mg-MOF-74, and (g) MIL-121 under AcOH vapor ($\lambda = 1.080$ Å).
Figure S6. XRPD patterns of (a) Pt/MIL-125-NH$_2$, (b) Pt/MIL-101, (c) Pt/MIL-121, (d) Pt/TiO$_2$, and (e) Pt/Al$_2$O$_3$ before and after the APD experiments.
Figure S7. XRPD patterns before (blue) and after (red) AcOH introduction into (a) Pt/MIL-125-NH$_2$, (b) Pt/UiO-66-NH$_2$, (c) Pt/HKUST-1, (d) Pt/MIL-101, (e) Pt/Zn-MOF-74, (f) Pt/Mg-MOF-74, and (g) Pt/MIL-121.
Figure S8. Comparison of XPS spectra of (a) Pt/MIL-125-NH$_2$, (b) Pt/MIL-101, and (c) Pt/MIL-121.

Table S3. Comparison of binding energies of Pt$^0$ 4f$_{7/2}$ of Pt/MOFs determined from XPS measurements.

| Pt/MOF             | Binding energy (eV) |
|--------------------|---------------------|
| Pt/MIL-125-NH$_2$  | 71.03               |
| Pt/UiO-66-NH$_2$   | 71.72               |
| Pt/HKUST-1         | 71.21               |
| Pt/MIL-101         | 71.35               |
| Pt/Zn-MOF-74       | 70.83               |
| Pt/Mg-MOF-74       | 71.07               |
| Pt/MIL-121         | 70.74               |
Figure S9. Comparison of AcOH conversions on Pt/MIL-125-NH₂, MIL-125-NH₂ (only support), and Pt/Al₂O₃ (Pt NPs on an inactive support). Note that the MIL-125-NH₂ support did not produce any EtOH but produced ethyl acetate and acetaldehyde.
Figure S10. Product selectivity on (a) Pt/HKUST-1, (b) Pt/MIL-101, (c) Pt/Zn-MOF-74, (d) Pt/Mg-MOF-74, (e) Pt/MIL-121, and (f) Pt/TiO$_2$. 
Table S4. Reaction steps for AH.²

(a) Hydrogen dissociation on Pt

\[ \text{H}_2(\text{g}) + 2^* \rightleftharpoons 2\text{H}^* \quad (\text{*: active site on Pt}) \]

\[ \text{H}^* \rightleftharpoons \text{H}_{sp} \quad (\text{H}_{sp}: \text{spillover hydrogen}) \]

(b) Adsorption of AcOH on support

\[ \text{CH}_3\text{COOH}_{(g)} + \text{S} \rightleftharpoons \text{CH}_3\text{COOH}–\text{S} \quad (\text{S: support}) \]

(c) Acetaldehyde production by hydrogenation of AcOH

\[ \text{CH}_3\text{COOH}–\text{S} + \text{H}_{sp} \rightarrow \text{CH}_3\text{COOH}_2–\text{S} \]

\[ \text{CH}_3\text{COOH}_2–\text{S} + \text{H}_{sp} \rightarrow \text{CH}_3\text{CHO}–\text{S} + \text{H}_2\text{O}_{(g)} \]

\[ \text{CH}_3\text{CHO}–\text{S} \rightleftharpoons \text{CH}_3\text{CHO}_{(g)} + \text{S} \]

(d) EtOH production by hydrogenation of acetaldehyde

\[ \text{CH}_3\text{CHO}–\text{S} + \text{H}_{sp} \rightarrow \text{CH}_3\text{CHOH}–\text{S} \]

\[ \text{CH}_3\text{CHOH}–\text{S} + \text{H}_{sp} \rightarrow \text{CH}_3\text{CH}_2\text{OH}–\text{S} \]

\[ \text{CH}_3\text{CH}_2\text{OH}–\text{S} \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH}_{(g)} + \text{S} \]

(e) Ethane production by hydrogenation of EtOH

\[ \text{CH}_3\text{CH}_2\text{OH}–\text{S} + \text{H}_{sp} \rightarrow \text{CH}_3\text{CH}_2\text{OH}_2–\text{S} \]

\[ \text{CH}_3\text{CH}_2\text{OH}_2–\text{S} + \text{H}_{sp} \rightarrow \text{CH}_3\text{CH}_3–\text{S} + \text{H}_2\text{O}_{(g)} \]

\[ \text{CH}_3\text{CH}_3–\text{S} \rightleftharpoons \text{CH}_3\text{CH}_3_{(g)} + \text{S} \]

(f) Possible side reactions

\[ \text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O} \quad (\text{esterification}) \]

\[ 2\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad (\text{ketonisation}) \]

\[ \text{CH}_3\text{COOH} + \text{H}_2 \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2\text{O} \quad (\text{decarbonylation}) \]

\[ \text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2 \quad (\text{decarbonylation}) \]

Table S5. Adsorbed H₂ on Pt/MOFs and Pt/TiO₂ determined using H₂-pulse chemisorption after the pretreatment with H₂ at 200 °C.

| Pt/MOF            | Adsorbed H₂ (μmol g⁻¹) |
|-------------------|------------------------|
| Pt/MIL-125-NH₂    | 1.89                   |
| Pt/UiO-66-NH₂     | 1.46                   |
| Pt/HKUST-1        | 1.58                   |
| Pt/MIL-101        | 4.65                   |
| Pt/Zn-MOF-74      | 0.98                   |
| Pt/Mg-MOF-74      | 1.02                   |
| Pt/MIL-121        | 1.73                   |
| Pt/TiO₂           | 1.20                   |
| Pt/Al₂O₃          | 2.70                   |
Figure S11. TOF for EtOH production on Pt/MOFs and Pt/TiO$_2$.

Figure S12. Modulation of IR spectra in Pt/MIL-125-NH$_2$, Pt/UiO-66-NH$_2$, Pt/TiO$_2$, and Pt/Al$_2$O$_3$, observed at $t = 99$ s.
Figure S13. Optimized structures of (a) MIL-125-NH$_2$ with AcOH, (b) MIL-125-NH$_2$ with EtOH, (c) UiO-66-NH$_2$ with AcOH, and (d) UiO-66-NH$_2$ with EtOH. Magnified views around the adsorbed guest molecules are shown in right. Gray, red, blue, green, cyan, white colors indicate C, O, N, Zr, Ti, and H atoms, respectively.

(Reference)
(1) Yoshimaru, S.; Sadakiyo, M.; Staykov, A.; Kato, K.; Yamauchi, M. Chem. Commun. 2017, 53, 6720–6723.
(2) Rachmady, W.; Vannice, M. A. J. Catal. 2000, 192, 322–334.