Fabricationof2DMetal–OrganicFrameworkNanosheetswithTailorableThicknessUsingBio-basedSurfactantandApplicationinCatalysis

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Experimental Section

Materials: 1, 4-benzenedicarboxylic acid (BDC), 2, 5-dihydroxyterephthalic acid (BDC- $(OH)_2$), 2-aminoterephthalic acid (BDC- NH_2), 2-bromoterephthalic acid (BDC-Br), nitroterephthalic acid (BDC- NO_2) and 1,2,4-benzene tricarboxylic acid (BDC-COOH), levulinic acid (LA) were purchased from Alfa Aesar. $ZrCl_4$ and γ -valerolactone (GVL) was purchased from Beijing Innochem Technology. Co., Ltd. Acetic acid and N,N-Dimethyl formamide (DMF) were obtained from Beijing Chemical Industry. Co., Ltd. H₂ (> 99.99%) was supplied by Beijing Analytical Instrument Company. The commercial Ru/C catalyst (5 wt% Ru) was purchased from Baoji Ruike Corporation, China. The surfactant sorbitol-alkylamine (SAAS- C_m , m = 6, 8, 10, 12, 14, 16) was synthesized in our group, and the structure is shown in Scheme S1.¹



m = 6, 8, 10, 12, 14, 16

Scheme S1. The structure of bio-based surfactant sorbitol-alkylamine SAAS-C_m.

Characterizations: Powder XRD analysis of the samples was performed on the X-ray diffractometer (Model D/MAX2500, Rigaka) with Cu-K α radiation, and the scan speed was 5°/min. The morphologies were characterized by transmission electron microscope (TEM) (JEOL-1011, JEOL-2100F) and scanning electron microscope (SEM) (TECNAI 20PHILIPS electron microscope). The N₂ adsorption-desorption isotherms were determined using a Micromeritics ASAP 2020M system. X-ray photoelectron spectroscopy (XPS) analysis was performed on the Thermo Scientific ESCALab 250Xi using a 200 W monochromated Al Ka radiation. Inductively coupled plasma-mass spectroscopy (ICP-AES) was used to determine the exact compositions of the catalysts. The XAFS experiment was carried out at Beamline 1W2B at Beijing Synchrotron Radiation Facility (BSRF). All spectra were collected in fluorescence mode. The raw data were energy-calibrated, background corrected, and normalized using Ifeffit software. For the Zr K-edge measurements, Zr foil was used as reference. The AFM images were obtained on a Dimension Fast Scan (Bruker) using Scan Asyst mode under ambient conditions. Standard silicon AFM probes (FASTSCAN-B) with cantilever spring constants of 4 N/m and resonance frequencies around 400 kHz were used for the scan. The AFM samples were prepared by dropping suspensions onto a mica sheet.

Preparation of UiO-66: The method was similar to that reported previously.² In the

experiment, ZrCl₄ (116 mg, 0.5 mmol) and 1, 4-benzenedicarboxylic acid (BDC) (83 mg, 0.5 mmol) were added into a 12.5 mL of DMF solution, followed by adding 1.5 mL of acetic acid. Then the mixture was heated in oil bath at 120 °C for 48 h. After reaction, the mixture was cooled down to room temperature. The bulk Zr-MOF (UiO-66) was obtained by centrifugation and washed with DMF for three times and ethanol for another five times. Then the white solids were suspended in ethanol overnight. Finally, the obtained UiO-66 was dried at 60 °C for 24 h under vacuum.

Synthesis of Zr-BDC MOF nanosheets using bio-based surfactant SAAS-C₁₂. The procedures were similar to that described above, and the main difference was that a bio-based surfactant was used. In a typical experiment, $ZrCl_4$ (116 mg, 0.5 mmol), BDC (83 mg, 0.5 mmol) and SAAS-C₁₂ (51.6 mg, 0.1 mmol) were added to 12.5 mL DMF, then 1.5 mL of acetic acid was added dropwise. The mixture was refluxed in oil bath at 120 °C for 24 h. After reaction, the mixture was cooled down to room temperature. Zr-MOF was obtained by centrifugation and washed with DMF for three times and ethanol for another five times. Then the white solids were suspended in ethanol overnight. Finally, nanosheets were dried at 60 °C for 24 h under vacuum.

The influence of chain length of SAAS- C_m on the thickness of nanosheets was studied by using different surfactants SAAS- C_m with alkyl chain length varying from 6 to 16. The procedures to prepare Zr-BDC MOFs using surfactants SAAS- C_m (m = 6, 8, 10, 14, 16) with other alkyl chain lengths were similar, and the corresponding amounts of surfactants were 0.1 mmol.

Other Zr-MOF nanosheets using 2-Bromoterephthalic acid, 2-aminoterephthalic acid, and 2, 5-dihydroxyterephthalicacid as ligands were also obtained in the presence of SAAS-C₁₂. The procedures to prepare other 2D Zr-MOFs are discussed taking 2D Zr-MOF-Br as the example. $ZrCl_4$ (116 mg, 0.5 mmol), 2-Bromoterephthalic acid (121.5 mg, 0.5 mmol) and SAAS-C₁₂ (51.6 mg, 0.1 mmol) were added into 12.5 mL DMF solution, followed by adding 1.5 mL of acetic acid. Then the mixture was refluxed in oil bath at 120 °C for 24 h. After being cooled down to room temperature, Zr-MOF was obtained by washing with DMF for three times and ethanol for five times. Then the white solids were suspended in ethanol overnight. Finally, Zr-MOF nanosheets were dried at 60 °C for 24 h under vacuum.

Synthesis of Ru/Zr-MOFs hybrid nanomaterials (Ru/Zr-BDC nanosheets, Ru/UiO-66).

The as-prepared 2D Zr-BDC nanosheets or Bulk Zr-MOFs (0.1 g) was dispersed in 30 mL water. Subsequently, 2.0 mL of 5 mg/mL RuCl₃ solution was added and stirred evenly for 30 min, and then freshly prepared NaBH₄ (20 mmol) solution was added slowly. The mixture was stirred at room temperature for 2 h. Then 2D nanosheets or Bulk Zr-MOFs loading with Ru nanoparticles were obtained after washing with water and ethanol for five times. The Ru loading of Ru/nanosheets and Ru/Bulk Zr-MOFs

determined by ICP-AES were 1.66 wt% and 1.72 wt%, respectively.

Catalyst Testing.

LA hydrogenation. Hydrogenation of LA to GVL was carried out in a 20 mL stainless steel batch reactor. In the experiment, desired amount of LA with solvent and certain amount of catalyst were added into the reactor. H₂ was introduced into the system to 3 MPa, and pressure was maintained during the reaction. The reactor was placed in air bath of desired temperature and the stirrer was started. After reaction, the reactor was cooled in ice-water and H₂ was released. The reaction mixture was analyzed using a gas chromatograph (GC, HP 4890) equipped with a flame ionization detector (FID), and toluene was used as the internal standard. In the reuse experiments, the catalyst was washed with ethanol and centrifuged, used for the next run after drying at 60 °C under vacuum. The structural stability of the 2D Zr-BDC MOF was also confirmed by TEM and XRD.

Results and discussion



Fig. S1. Representative TEM and SEM images of 2D Zr-BDC MOF nanosheets synthesized with

 $SAAS-C_{12}$.



Fig. S2. (A) Representative SEM image of UiO-66 (Zr); (B-E) SEM images of Zr-BDC MOF synthesized with SAAS- C_{12} at different time; (F) the enlarged image of 2D Zr-BDC MOF synthesized at 16 h.



Fig. S3. SEM images of Zr-BDC MOF synthesized with variable molar ratios of SAAS- C_{12} to BDC: (A) 0.01 g, 0.02N BDC; (B) 0.03 g, 0.1 N BDC; (C) 0.05 g, 0.2 N BDC; (D) XRD patterns of Zr-BDC MOF synthesized with variable molar ratios of SAAS- C_{12} .



Fig. S4. (A-D) TEM images of 2D Zr-BDC MOF synthesized using surfactants SAAS-C₆, SAAS-C₁₀, SAAS-C₁₄, SAAS-C₁₆, respectively; (E) AFM image of 2D Zr-BDC MOF synthesized using SAAS-C₁₆ and the corresponding height profiles of 2D nanosheets; (F) The correlation of thickness with hydrophobic chain length of surfactant.



Fig. S5. Characterizations of Zr-MOFs synthesized with BDC derivatives as ligands in the presence of SAAS-C₁₂: (A) BDC-OH₂; (B) BDC-Br; (C) BDC-NH₂; (D) XRD patterns of 2D Zr-MOF synthesized with BDC derivatives; (E) BDC-NO₂; (F) BDC-COOH.



Fig. S6. Characterizations of Ru/2D Zr-BDC nanosheets: (A) TEM image; (B) XPS spectra of Ru 3p;

(C) STEM-EDX elemental mapping of Ru/2D Zr-BDC nanosheets.



Fig. S7. Characterizations of Ru/3D Zr-BDC: (A) TEM image; (B) the enlarged TEM image; (C) XRD pattern of Ru/3D Zr-BDC.



Fig. S8. N₂ adsorption/desorption isotherms and the mesopore size distribution (inset) of 2D Zr-BDC nanosheets and 3D Zr-BDC MOF.



Fig. S9. A) Reusability of Ru/2D Zr-BDC nanosheets catalyst at the condition of entry 2 of Table 1; XRD pattern (B) and TEM image (C) of the catalyst after used for six times.

References

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