Fabrication of MOF-based composite for synergistic catalysis

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Supplementary material

General information

Chemical reagents and solvents were purchased from commercial sources and used as received unless otherwise noted. X-ray diffraction (XRD) patterns were recorded with a MiniFlex300/600 (Rigaku) using Cu Kα radiation (λ = 1.5406 Å) over the range of 5°–50°. Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-7600 operated at an accelerating voltage of 5.0 kV. Transmission electron microscopy (TEM) images were obtained by a JEOL JEM-1400 operated at 100 kV. Nitrogen adsorption–desorption isotherms were measured with a Quantachrome ASIQM0V002-5 system at 77 K. The analyses of the substrates and products were performed with a GC (Shimazu, 2010) equipped with a chromatographic column HP-5.

UiO-66

5 mL N,N-dimethylformamide (DMF) solution of $ZrCl_4$ (20 mmol·L^{-1}) and 5 mL DMF solution of 1,4-benzenedicarboxylate (BDC, 20 mmol·L^{-1}) were mixed in the glass vial. Then 1.374 mL acetic acid was subsequently added. After that, the mixture was reacted at 120 °C for 24 h without stirring. Then, the products were collected by centrifugation and then washed with DMF and methanol, separately. Finally, the UiO-66 was dried in a vacuum oven at 120 °C for later use.

Pd/UiO-66

10 μmol $Pd(acac)_2$ (0.1 mol·L^{-1}) was added to the as-synthesized UiO-66 (20 mg). The solvent of obtained material was slowly evaporated at room temperature for 48 h. The Pd^{2+}/UiO-66 was then heated under vacuum at 150 °C for 4 h to produce Pd/UiO-66.

Pd/66/SA-$CaCl_2$

Sodium alginate (150 mg) was dissolved in the 5 mL DI water under high-frequency sonication. Then, the as-synthesized Pd/UiO-66 (75 mg) was dispersed in the above solution. The mixture was noted as Pd/66-SA. Then the Pd/66-SA (1 mL) was treated with liquid nitrogen and freeze-drying to obtain the further composite (Pd/66/SA). To improve the reusability of materials in catalytic reactions, the freeze-dried Pd/66/SA was added into the $CaCl_2$ solution to obtain the Pd/66/SA-$CaCl_2$ composite for further use.

Catalytic hydrogenation of olefin

Hydrogenation of olefins (styrene, cyclohexene, 1-hexene, and cyclooctene) was carried out in the ethanol solution in a static hydrogen atmosphere (1 atm) at 30 °C for 30 min. In a typical experiment,

the catalyst (solid Pd/66/SA-$CaCl_2$) was loaded in a reactor. Subsequently, an ethanol solution (10 mL) containing olefins (0.5 mmol) was added into the reactor and the mixture was sonicated for 10 min. The residual air in the reactor was expelled by flushing hydrogen for several times. After the catalytic reaction, the products were analyzed by using gas chromatograph. The used catalysts could be easily recovered by tweezer, followed by thoroughly washing with ethanol, and then reusing under the same experimental conditions to estimate its reusability.

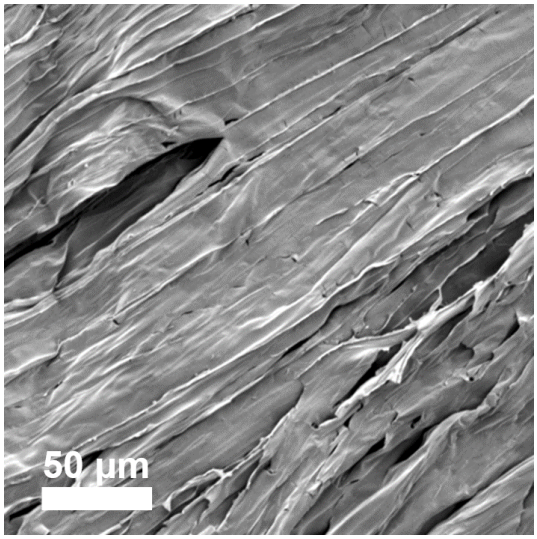

Fig. S1 SEM image of the as-prepared pure SA.

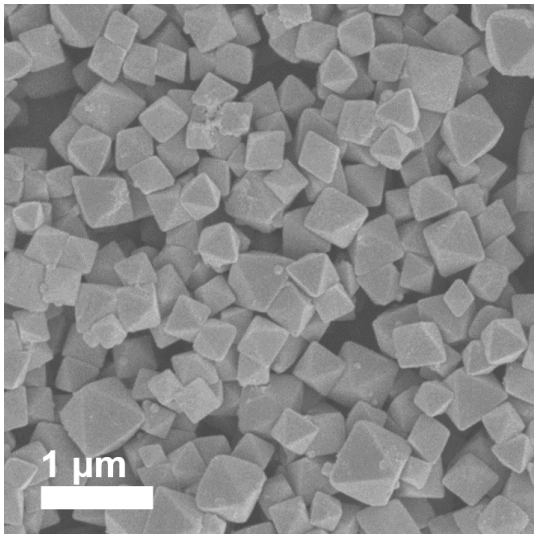

Fig. S2 SEM image of the as-prepared Pd/UiO-66.

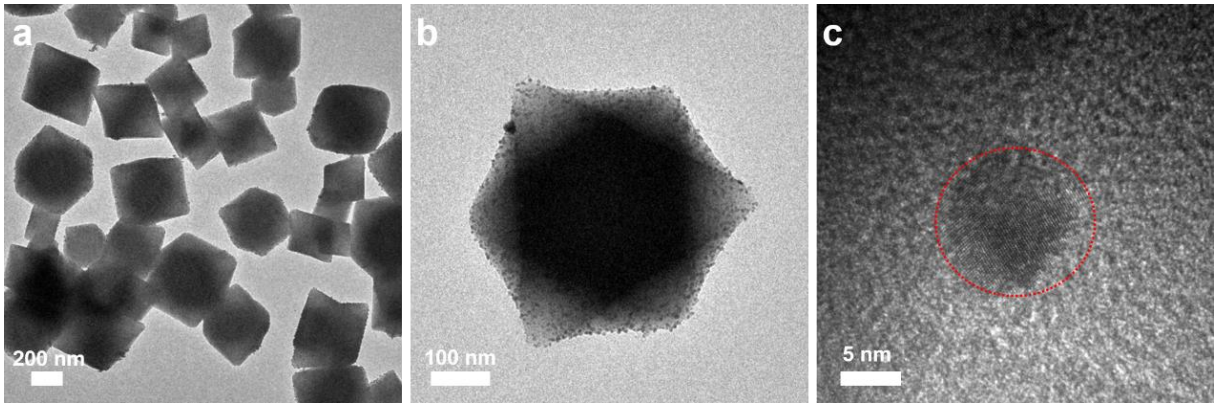

Fig. S3 (a) TEM and **(b)** magnified TEM images of Pd/UiO-66. **(c)** High-resolution TEM image of Pd nanoparticle.

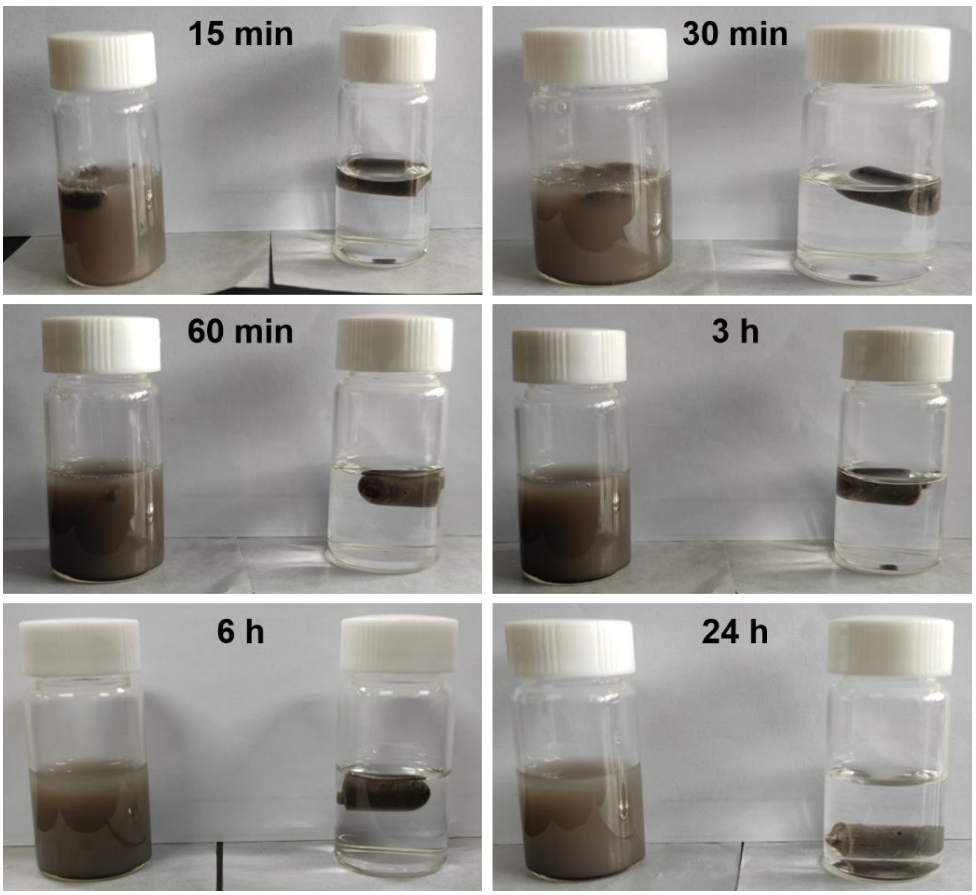

Fig. S4 Pd/66/SA composite in the aqueous solution (left) and the ethanol solution (right) with different hours.

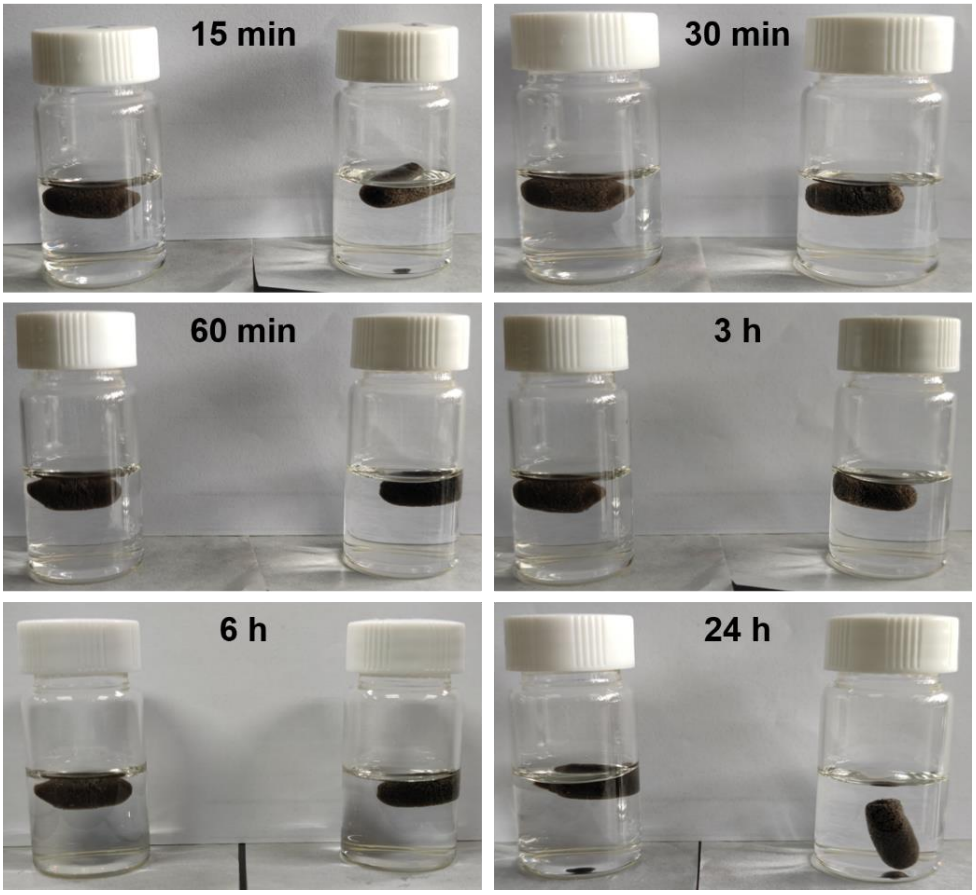

Fig. S5 Pd/66/SA-$CaCl_2$ composite in the aqueous solution (left) and the ethanol solution (right) with different hours.