Supporting Information

Development of a novel one-pot reaction system utilizing a bifunctional Zr-based metal-organic framework

Takashi Toyao, Masakazu Saito, Yu Horiuchi* and Masaya Matsuoka*

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University
1-1, Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531 (Japan)

horiuchi@chem.osakafu-u.ac.jp and matsumac@chem.osakafu-u.ac.jp
Materials

ZrCl$_4$, 2-aminobenzene-1,4-dicarboxylic acid (H$_2$BDC-NH$_2$), 1,4-benzenedicarboxylic acid (H$_2$BDC), N’N-dimethylformamide (DMF) and 1,4-dioxane were purchased from Nacalai Tesque Inc. Malononitrile, benzyl alcohol, benzaldehyde and benzaldehyde dimethylacetal were purchased from Tokyo Chemical Industry Co., Ltd. p-Xylene was purchased from Kishida Chemicals Co., Ltd.

Synthesis

Zr-MOF-NH$_2$ was synthesized according to the literature.$^{1,2}$ The mixture of ZrCl$_4$ (0.42 g), H$_2$BDC-NH$_2$ (0.30 g) and ion-exchanged water (50 µl) were added in DMF (40 ml) and dispersed by ultrasound for 10 min. The mixture was subject to react under solvothermal conditions in a Teflon-lined stainless steel autoclave at 393 K for 24 h under autogenous pressure. The precipitate was filtrated, washed repeatedly with acetone and dried under vacuum at 473 K for 3 h. For comparison purposes, Zr-MOF was also prepared by using H$_2$BDC.

Characterization

Standard θ–2θ X-ray diffraction (XRD) data were recorded on a Shimadzu X-ray diffractmeter XRD-6100 using Cu Kα radiation (λ = 1.5406 Å). N$_2$ adsorption isotherms were collected by using a BEL-SORP mini (BEL Japan, Inc.) after degassing of samples under vacuum at 473 K for 2 h. Diffuse reflectance UV–vis spectra were obtained with a Shimadzu UV–vis recording spectrophotometer 2200A. FT-IR spectra were recorded in transmittance mode by a FT-IR spectrophotometer equipped with a DTGS detector (JASCO FT/IR 660Plus, resolution 4 cm$^{-1}$). Self-supporting pellets of the samples were loaded in a specially constructed IR cell, which was equipped with CaF$_2$ windows.
One-pot reaction

The catalyst (100 mg) and 4 ml of p-xylene containing benzyl alcohol (0.1 mmol) and malononitrile (3 mmol) or ethyl cyanoacetate were added to a quartz reaction vessel. Subsequently, the sample was irradiated with a high pressure Hg lamp (500 W; Ushio USH-500BY) with stirring at 363 K under air. The progression of the reaction was monitored by a GC (Shimadzu GC-14B with a flame ionization detector) equipped with an InertCap®1 capillary column.

Reusability of the catalyst was studied as follows. After the first run, the catalyst was washed three times with 1, 4-dioxane, dried at 313 K in air and reused for the next run.

Photocatalytic oxidation of benzyl alcohol

The catalyst (100 mg) and 4 ml of p-xylene containing benzyl alcohol (0.1 mmol) were added to a quartz reaction vessel. Subsequently, the sample was irradiated with the high pressure Hg lamp with stirring at 298 K under air. The progression of the reaction was monitored by the GC.

Knoevenagel condensation of benzaldehyde with malononitrile

The catalyst (100 mg) and 4 ml of p-xylene containing benzaldehyde (0.1 mmol) and malononitrile (3 mmol) were added to a quartz reaction vessel. Subsequently, the mixture was heated to 363 K with stirring under air. The progression of the reaction was monitored by the GC.
Figure S1. XRD patterns of Zr-MOF and Zr-MOF-NH$_2$. 
**Figure S2.** N$_2$ adsorption isotherms and pore size distribution curves (inset) of Zr-MOF and Zr-MOF-NH$_2$. 
Figure S3. Diffuse reflectance UV-Vis spectra of Zr-MOF and Zr-MOF-NH₂.
**Figure S4.** FT-IR spectra of Zr-MOF and Zr-MOF-NH$_2$. 
Figure S5. Time course of the photocatalytic oxidation of benzyl alcohol over Zr-MOF-NH$_2$ (●), Zr-MOF (◆) and Al-MOF-NH$_2$ (■) under UV-light irradiation at room temperature.
Figure S6. Time course of Knoevenagel condensation of benzaldehyde with malononitrile over Zr-MOF-NH$_2$ (●), Zr-MOF (◆) and Al-MOF-NH$_2$ (■) at 363 K.
Figure S7. Time course of Knoevenagel condensation of benzaldehyde with malononitrile over Zr-MOF-NH$_2$ under UV-light irradiation (◆) and without UV-light irradiation (●) at 363 K.
References