Supplementary information

Effect of pore sizes on catalytic activities of arenetricarbonyl metal complexes constructed within Zr-based MOFs

Masakazu Saito,[a] Takashi Toyao,[a] Kozo Ueda,[a] Takashi Kamegawa,[b]
Yu Horiuchi[*,a] and Masaya Matsuoka*[*,a]*

[a]*Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University 1-1, Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan.*

[b]*Division of Materials and Manufacturing Science, Graduate School of Engineering Osaka University, 2-1, Yamada-oka, Suita, Osaka 565-0871, Japan.*

E-mail: horiuchi@chem.osakafu-u.ac.jp; matsumac@chem.osakafu-u.ac.jp
Tel: +72-254-9288; Fax: +72-254-9910

Experimental procedures

Synthesis of UiO-66 and UiO-67. Zr-based MOFs named UiO-66 and UiO-67 was prepared by a conventional solvothermal method using 1,4-benzenedicarboxylic acid (BDC) and 4,4'-biphenyldicarboxylic acid (BPDC) as organic linkers, respectively. The typical synthesis procedure for UiO-66 was as follows. BDC (1.64 mmol) and zirconium tetrachloride ($ZrCl_4$, 1.80 mmol) were dissolved in N,N-dimethylformamide (DMF, 211 mL) and stirred for few minutes at room temperature. The mixture was then placed in a Teflon-lined stainless-steel autoclave and heated in oven at 393 K for 24 h. After cooling to room temperature, the precipitate was filtered, washed repeatedly with DMF and dried at room temperature for 24 h. The obtained white powder sample was then dried under vacuum at 473 K for 2 h to remove residual DMF, yielding UiO-66. UiO-67 was prepared by a similar procedure using BPDC as an organic linker. The precursor solution prepared by mixing BPDC (1.36 mmol), $ZrCl_4$ (1.36 mmol) and DMF (158 mL) was stirred for 30 min at room temperature, placed in a Teflon-lined stainless-steel autoclave and heated in oven at 393 K for 48 h. After cooling to room temperature, the precipitate was filtered, washed repeatedly with DMF and dried at room temperature for 24 h. The obtained white powder sample was then dried under vacuum at 473 K for 2 h to remove residual DMF.

General methods. XRD (X-ray diffraction) data were recorded on a Shimadzu XRD-6100 using Cu Kα radiation (λ = 1.5406 Å). FT-IR (Fourier-transform infrared spectroscopy) data were recorded with a Jasco FT/IR-660 plus.

Selective oxidation reaction. The epoxidation of cyclooctene was carried out in a closed glass reaction vessel (20 mL) at 328 K under N_2 atmosphere. The reaction vessel was loaded with 30 mg of catalyst, 1.7 mmol of cyclooctene and 2.7 mmol of tert-butyl hydroperoxide (TBHP, 5.5 M in decane). In order to avoid the photodissociation of the carbonyl ligands caused by interaction with reagents or solvent, the catalytic tests were carried out in the dark. After the reaction (15 min or 3 h), the reaction mixture was cooled down to 298 K and then filtered to remove the catalyst. Analysis of the products was performed on a gas chromatograph (Shimadzu GC-14B with a flame ionization detector) equipped with an InertCap®1 capillary column.

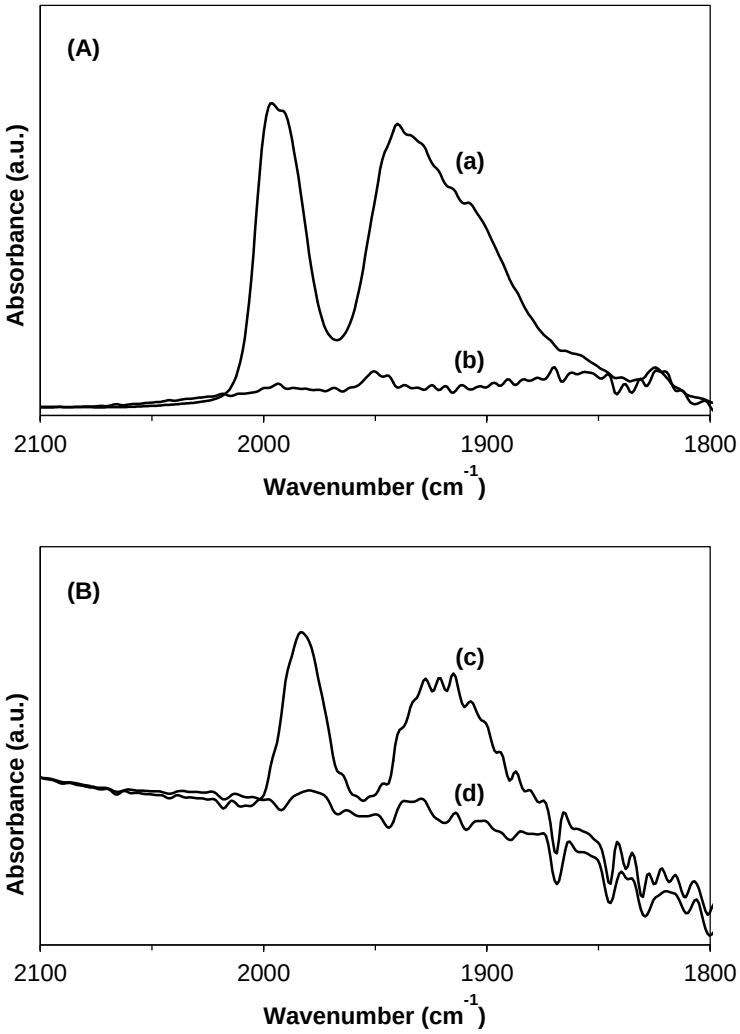

Figure S1 FT-IR spectra of (A) UiO-66-Cr$(CO)_3$ and (B) UiO-67-Cr$(CO)_3$ recorded after evacuation at (a,c) 473 K and (b,d) 523 K for 1 h.

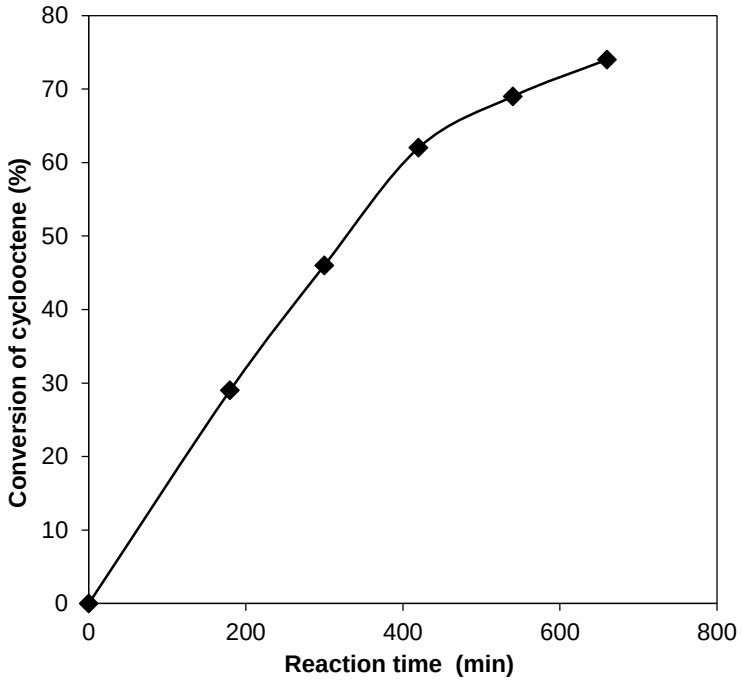

Figure S2 Time course of epoxidation of cyclooctene at 328 K over UiO-66-Cr(CO)$_3$.

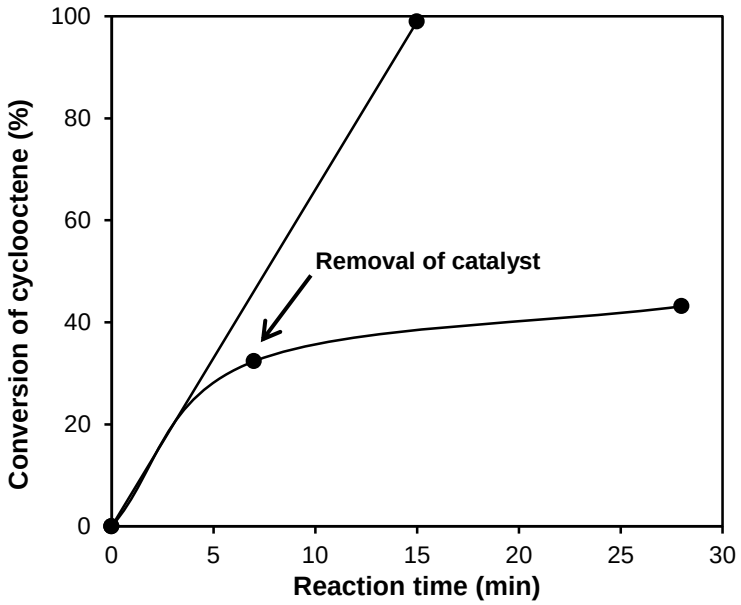

Figure S3 Verification of heterogeneous catalysis of epoxidation reaction of cyclooctene at 328 K over UiO-67-Mo$(CO)_3$. The arrow indicates the removal of UiO-67-Mo$(CO)_3$ catalyst by hot filtration at reaction temperature.

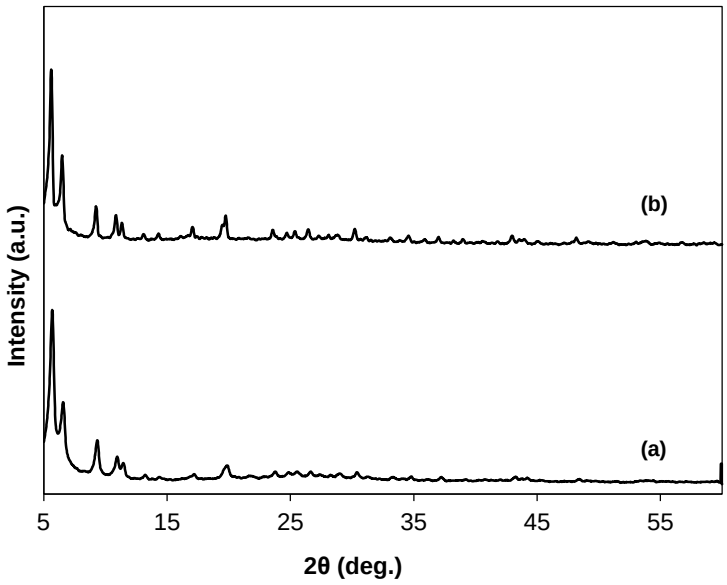

Figure S4 XRD patterns of UiO-67-$Mo(CO)_3$ (a) before and (b) after epoxidation reaction.