

Electronic Supplementary Information

A single-site hydroxyapatite-bound zinc catalyst for highly efficient chemical fixation of carbon dioxide with epoxides

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General: $^1\text{H-NMR}$ spectra were obtained on JNM-AL400 spectrometers at 400 MHz in CDCl_3 with TMS as an internal standard. Analytical GLC was performed by Shimadzu GC-8A PF with flame ionization detector equipped with Silicon UC W-98, KOCL 3000T, Silicon SE-30, and OV-17 columns. XPS were recorded on Shimadzu ESCA-KM using $\text{MgK}\alpha$ radiation. $(\text{NH}_4)_2\text{HPO}_4$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were purchased from Wako Pure Chemical Ind., Ltd and used without further purification. Solvents and all commercially available chemicals were purified by standard procedures used before. *Trans*-1-deuterio-1,2-hexene oxide was synthesized according to the literature procedures (see: Ref. 3c).

Synthesis of hydroxyapatite-bound Zn complex (ZnHAP): $(\text{NH}_4)_2\text{HPO}_4$ (40.0 mmol) was dissolved in deionized water (150 mL) and pH was adjusted to 11 with an aqueous NH_3 solution. To a solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (66.7 mmol) in deionized water (120 mL) adjusted to pH 11 with an aqueous NH_3 solution was added drop-wise over 30 min into the above solution with vigorous stirring at room temperature, and then the obtained milky solution was heated at 90°C for 10 min. The precipitate was filtered, washed with deionized water, and dried at 110°C , giving stoichiometric hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HAP). 2.0 g of the HAP was stirred at room temperature for 24 h in a 100 mL of aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0×10^{-2} M). The obtained slurry was filtered, washed with deionized water and dried at 110°C overnight, yielded the ZnHAP (Zn content: $0.3 \text{ mmol}\cdot\text{g}^{-1}$) as a white powder.

A typical example for the coupling of epoxide and CO₂: Into a 150 ml of stainless autoclave were successively placed the ZnHAP (0.01 g, Zn²⁺: 0.003 mmol), DMAP (0.02 mmol), and epichlorohydrin (100 mmol), and then charged with CO₂ (10 atm). The reaction mixture was stirred at 100°C for 24 h. The reactor was cooled to room temperature and the reaction mixture was subjected to GC analysis after removal of catalyst to give 4-(chloromethyl)-1,3-dioxolan-2-one in 90 % yield.

A typical example for the coupling of epoxide and CO₂ under atmospheric pressure conditions: Into a reaction vessel equipped with a reflux condenser were successively placed the ZnHAP (0.01 g, Zn²⁺: 0.003 mmol), DMAP (0.02 mmol), and epichlorohydrin (100 mmol). The reaction mixture was stirred at 100°C for 24 h under 1 atm of CO₂ balloon conditions. The reactor was cooled to room temperature and the reaction mixture was subjected to GC analysis after removal of catalyst 4-(chloromethyl)-1,3-dioxolan-2-one in 86 % yield.

An example for the coupling of enantiomerically pure benzyl glycidyl ethers with CO₂: Into a 100 ml of stainless autoclave were successively placed the ZnHAP (0.1 g, Zn²⁺: 0.03 mmol), DMAP (0.2 mmol), and (*R*)- or (*S*)-benzyl glycidyl ethers (15 mmol), and then charged with CO₂ (5 atm). The reaction mixture was stirred at 100°C for 24 h. The reactor was cooled to room temperature and the reaction mixture was subjected to HPLC analysis after removal of catalyst. The enantiomeric excess of (*R*)- and (*S*)-4-(benzyloxymethyl)-1,3-dioxolan-2-one were determined by chiral HPLC (Daisel Chiracel OF, eluent: *n*-hexane/ethanol (8:2 v/v), flow rate: 1.0 mL/min, 254 nm, t_R of (*R*) = 20.9 min, t_R of (*S*) = 18.6 min).

The coupling reaction of *trans*-1-deuterio-1,2-hexene oxide with CO₂: Into a 15 ml of stainless autoclave were successively placed the ZnHAP (0.005 g, Zn²⁺: 0.0015 mmol), DMAP (0.01 mmol), and *trans*-1-deuterio-1,2-hexene oxide (5 mmol), and then charged with CO₂ (10 atm). The reaction mixture was stirred at 130°C for 24 h. The reactor was cooled to room temperature and the reaction mixture was subjected to ¹H NMR analysis after removal of catalyst. The total yield of the corresponding 1,2-hexene carbonate was 90 % and the *trans/cis* ratio was 9:2. ¹H NMR (400 MHz, TMS, CDCl₃), *trans*-1-deuterio-1,2-hexene carbonate; δ 0.93 (3H, t, *J*=7.2 Hz, CH₃), 1.34-1.46 (4H, m, -CH₂CH₂-), 1.68-1.82 (2H, m, CH₂), 4.06 (1H, d, *J*=6.9 Hz, CDH), 4.72 (1H, m, CH), *cis*-1-deuterio-1,2-hexene carbonate; δ 0.93 (3H, t, *J*=7.2 Hz, CH₃), 1.34-1.46 (4H, m, -CH₂CH₂-), 1.68-1.82 (2H, m, CH₂), 4.67 (1H, dt, *J*=7.8, 1.2 Hz, CDH), 4.72 (1H, m, CH).

Characterization by Zn K-edge X-ray absorption fine structure (XAFS): X-ray absorption spectra were recorded using at the beam line 7C station with attached Si (111) monochromator at PF, KEK, Tsukuba, Japan (Proposal number : 2002G102). Details of data analysis are referred to the reported procedure (See: Tanaka, T.; Yamashita, H.; Tsuchitani, R.; Funabiki, T.; Yoshida, S. *J. Chem. Soc., Faraday Trans.* 1988, **84**, 2987). The Zn K-edge XANES and the inverse Fourier-transforms of EXAFS experimental data are shown in Figure 1S. The results of curve-fitting analysis for the ZnHAP are summarized in Table 1S.

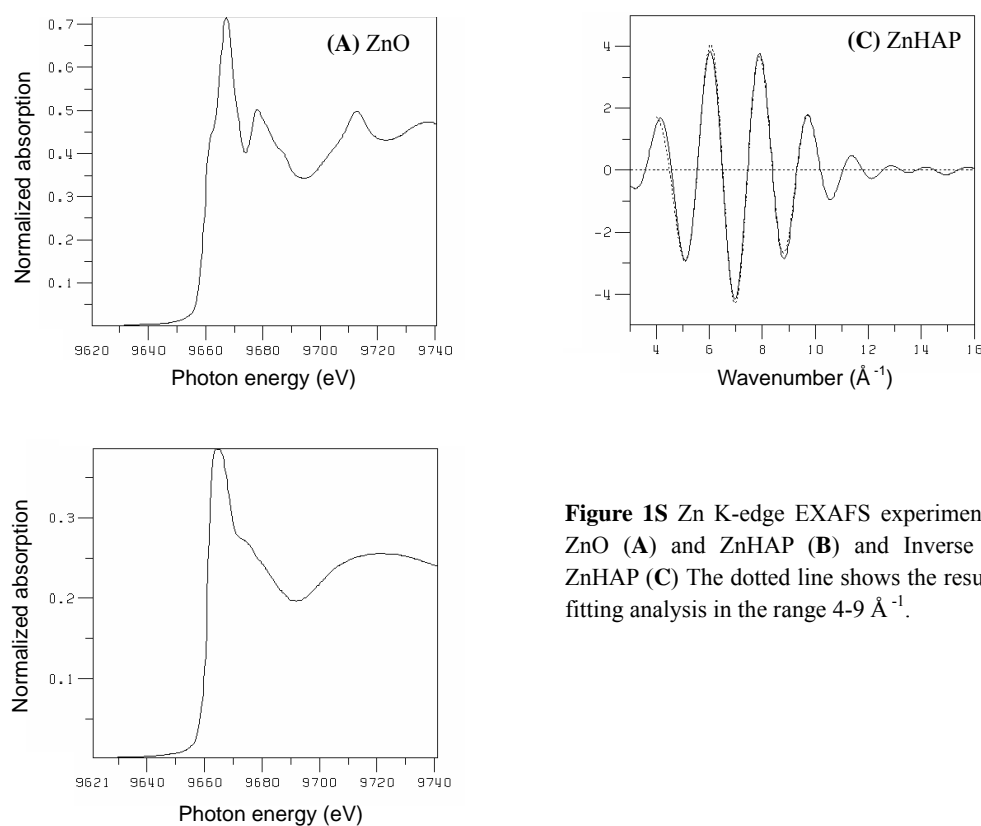


Figure 1S Zn K-edge EXAFS experimental data for ZnO (A) and ZnHAP (B) and Inverse FT of the ZnHAP (C) The dotted line shows the results of curve fitting analysis in the range 4-9 Å⁻¹.

Table 1S Results of Curve-fitting Analysis for ZnHAP^a

shell	C.N. ^b	R ^c / Å	σ ^d / Å ²
Zn-O(1)	4.0	1.88	0.0019
Zn-O(2)	3.0	2.28	0.0025

^a The region of 1.1-2.2 Å was inversely Fourier transformed.

^b Coordination number. ^c Interatomic distance. ^d Difference between Debye-Waller factor of ZnHAP and that of the reference sample.