

## Electronic Supplementary Information (ESI)

# Mesoporous Zirconium Phosphonates as Efficient Catalysts for Chemical CO<sub>2</sub> Fixation

Xiu-Zhen Lin <sup>a</sup>, Zhen-Zhen Yang <sup>b</sup>, Liang-Nian He <sup>b</sup>, Zhong-Yong Yuan<sup>\*a,c</sup>

<sup>a</sup> Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), College of Chemistry, Nankai University, Tianjin 300071, China. E-mail address: zyyuan@nankai.edu.cn

<sup>b</sup> State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

<sup>c</sup> Material and Process Synthesis, College of Science, Engineering and Technology, University of South Africa, Johannesburg, South Africa

## Experimental.

**Materials.** Aziridines were synthesized according to the published procedure [*Tetrahedron* 2009, **65**, 6204-6210; *J. Org. Chem.* 2008, **73**, 4709-4712]. Carbon dioxide with a purity of 99.99% was commercially available. 1-Hydroxy ethylidene-1,1'-diphosphonic acid (HEDP, 60 wt%), amino tri(methylene phosphonic acid) (ATMP, 50 wt%) and sodium salt of ethylene diamine tetra(methylene phosphonic acid) (EDTMPS, 30 wt%) were received from Henan Qingyuan Chemical Co. Scheme S1 lists the structures of these three organophosphonic acids. Zirconium oxychloride (ZrOCl<sub>2</sub>·8H<sub>2</sub>O) and cetyltrimethyl ammonium bromide (CTAB) were obtained from Tianjin Guangfu Fine Chemical Institute and Tianjin Fine Chemical Co., Ltd., respectively. All chemicals were used as received without further purification except for the solvents, which were distilled by the known method prior to use.

**Synthesis of mesoporous zirconium phosphonates.** In the synthesis of mesoporous zirconium phosphonates, 1.82 g of CTAB was solved in 20 ml of deionized water, followed by addition of 1.72 g of HEDP or 3.0 g of ATMP or 4.5 g of EDTMPS under stirring at 45 °C. Because EDTMPS was in sodium salt instead of acid form, extra HCl (2 mol/L) was added to adjust the pH value of above mixture to 2. After 2 h of stirring, the mixed solution of 0.3–0.8 g of zirconium oxychloride and 5 ml of deionized water was added dropwise into the above solution and continued to stir overnight. The final molar ratio of HEDP : ZrOCl<sub>2</sub> : CTAB was 5.4 : 1 : 5.4 (P/Zr = 10.8), ATMP : ZrOCl<sub>2</sub> : CTAB was 2 : 1 : 2 (P/Zr = 6), and EDTMPS : ZrOCl<sub>2</sub> : CTAB was 0.89 : 1 : 2 (P/Zr = 3.5). The resulting gel containing HEDP was transferred into a Teflon-lined autoclave and heated at 110 °C for 24 h, while the gel with ATMP or EDTMPS was stirred for another 36 h at 75 °C. The white solid products were filtered, washed with water and dried under vacuum at 80 °C for 6 h, and denoted as ZrHEDP, ZrATMP and ZrEDTMPS for the samples synthesized with HEDP, ATMP and EDTMPS, respectively. The surfactant embedded in the product was removed by extraction with HCl/ethanol solution, namely, 1 g of sample in 150 ml of ethanol with 3.6 ml of con. HCl under 60 °C stirred for 8 h. The textural property of the synthesized zirconium phosphonates are listed in Table S1.

**Characterization.** X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Focus diffractometer with Cu K<sub>α</sub> radiation, operated at 40 kV and 40 mA. N<sub>2</sub> adsorption-desorption isotherms were recorded on a Quantachrome NOVA 2000e sorption analyzer at liquid nitrogen temperature (77 K). The samples were degassed at 120 °C for at least 6 h prior to the measurement. The surface areas were calculated by multi-point Brunauer-Emmett-Teller (BET) method, and the pore size distributions were calculated from the adsorption branch of the isotherms by Barret-Joyner-Halenda (BJH) method and the non-local density functional theory (NLDFT). The CO<sub>2</sub> adsorption isotherms of the samples were measured on a Quantachrome AUTOSORB-1MP analyzer at 0 °C and 25 °C. Each sample was outgassed at 120 °C overnight to remove the guest molecules from the pores before starting the adsorption measurements and then cooled down to room temperature, followed by the introduction of CO<sub>2</sub> into the system. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos Axis Ultra DLD (delay-line detector) spectrometer equipped with a

monochromatic Al-K $\alpha$  X-ray source (1468.6 eV).  $^1\text{H}$  NMR spectra were recorded on a Bruker 300 or 400 spectrometer in  $\text{CDCl}_3$  and  $\text{CDCl}_3$  (7.26 ppm) was used as internal reference,  $^{13}\text{C}$  NMR was recorded at 75 or 100.6 MHz in  $\text{CDCl}_3$  and  $\text{CDCl}_3$  (77.0 ppm) was used as internal reference. GC analyses were performed on a Shimadzu GC-2014 chromatograph equipped with a capillary column (RTX-5, 30 m  $\times$  0.25  $\mu\text{m}$ ) using a flame ionization detector. ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage 4.8 KV.

### **Spectral characteristics for various oxazolidinones:**

#### **3-Ethyl-5-phenyloxazolidin-2-one (2a)**

Colorless liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.17 (t,  $^3J = 7.2$  Hz, 3H), 3.29–3.45 (m, 3H), 3.92 (t,  $^3J = 8.7$  Hz, 1H), 5.48 (t,  $^3J = 7.8$  Hz, 1H), 7.34–7.42 (m, 5H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  12.4, 38.8, 51.5, 74.2, 125.4, 128.6, 128.8, 138.8, 157.5; ESI-MS calcd for  $\text{C}_{11}\text{H}_{13}\text{NO}_2$  191.09, found 192.29 (M + H) $^+$ , 214.38 (M + Na) $^+$ , 405.01 (2M + Na) $^+$ .

#### **3-Ethyl-4-phenyloxazolidine (3a)**

Colorless liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.05 (t,  $^3J = 7.2$  Hz, 3H), 2.79–2.88 (m, 1H), 3.48–3.57 (m, 1H), 4.10 (t,  $^3J = 8.0$  Hz, 1H), 4.62 (t,  $^3J = 8.8$  Hz, 1H), 4.81 (t,  $^3J = 7.2$  Hz, 1H), 7.30–7.44 (m, 5H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  12.1, 36.8, 59.3, 69.7, 126.9, 129.0, 129.2, 137.8, 158.1; ESI-MS calcd for  $\text{C}_{11}\text{H}_{13}\text{NO}_2$  191.09, found 192.29 (M + H) $^+$ , 214.38 (M + Na) $^+$ , 405.01 (2M + Na) $^+$ .

#### **3-Propyl-5-phenyloxazolidin-2-one**

Colorless liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.91 (t,  $^3J = 7.2$  Hz, 3H), 1.52–1.61 (m, 2H), 3.18–3.31 (m, 2H) 3.40 (t,  $^3J = 8.0$  Hz, 1H), 3.90 (t,  $^3J = 8.8$  Hz, 1H), 5.46 (t,  $^3J = 8.0$  Hz, 1H), 7.31–7.37 (m, 5H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  10.7, 20.3, 45.5, 51.8, 74.0, 125.2, 128.4, 128.5, 138.7, 157.6; ESI-MS calcd for  $\text{C}_{12}\text{H}_{15}\text{NO}_2$  205.11, found 206.30 (M + H) $^+$ , 228.30 (M + Na) $^+$ , 433.04 (2M + Na) $^+$ .

### 3-Butyl-5-phenyloxazolidine-2-one

Colorless liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.94 (t,  $^3J = 7.2$  Hz, 3H), 1.31-1.40 (m, 2H), 1.51-1.58 (m, 2H), 3.23-3.38 (m, 2H) 3.43 (t,  $^3J = 8.0$  Hz, 1H), 3.92 (t,  $^3J = 8.8$  Hz, 1H), 5.49 (t,  $^3J = 8.0$  Hz, 1H), 7.28-7.42 (m, 5H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  13.4, 19.5, 29.1, 43.6, 51.8, 74.1, 125.2, 128.4, 128.5, 138.7, 157.7; ESI-MS calcd for  $\text{C}_{13}\text{H}_{17}\text{NO}_2$  219.13, found 220.34 (M + H) $^+$ , 259.48 (M + K) $^+$ , 461.05 (2M + Na) $^+$ .

### 3-Ethyl-5-(4-chlorophenyl)oxazolidin-2-one

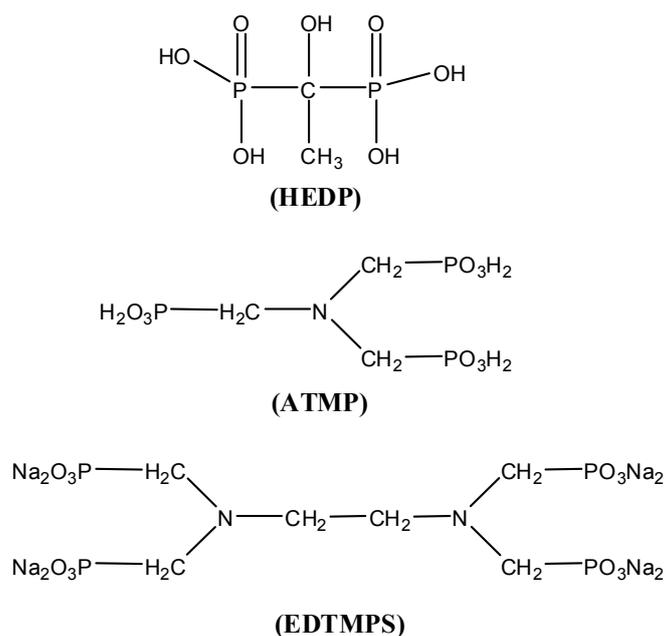
White solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.17 (t,  $^3J = 7.3$  Hz, 3H), 3.30-3.43 (m, 2H), 3.69-3.76 (m, 1H), 3.92 (t,  $^3J = 8.7$  Hz, 1H), 5.44 (t,  $^3J = 8.0$  Hz, 1H), 7.27-7.38 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.6, 38.9, 51.5, 73.6, 126.9, 129.1, 134.7, 137.4, 157.4; ESI-MS calcd for  $\text{C}_{11}\text{H}_{12}\text{ClNO}_2$  225.67, found 451.64 (2M + H) $^+$ .

### 3-Ethyl-5-p-tolyloxazolidin-2-one

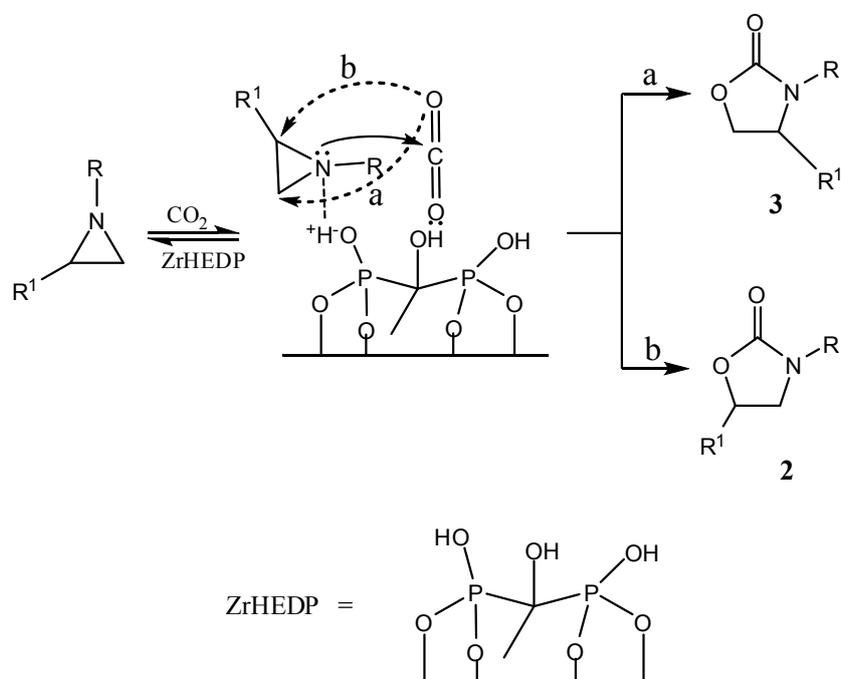
White solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.18 (t,  $^3J = 7.3$  Hz, 3H), 1.62 (d,  $^3J = 6.4$  Hz, 1H), 1.87 (d,  $^3J = 3.2$  Hz, 1H), 2.27 (dd,  $^3J = 6.6$  Hz,  $^2J = 3.2$  Hz, 1H), 2.31 (s, 3H), 2.36-2.48 (m, 2H), 7.09- 7.15 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.6, 21.2, 38.9, 51.6, 74.3, 125.6, 129.5, 135.8, 138.7, 157.7; ESI-MS calcd for  $\text{C}_{12}\text{H}_{15}\text{NO}_2$  205.25, found 206.45 (M + H) $^+$ , 411.15 (2M + H) $^+$ .

**Table S1.** The textural property of the mesoporous zirconium phosphonate catalysts.

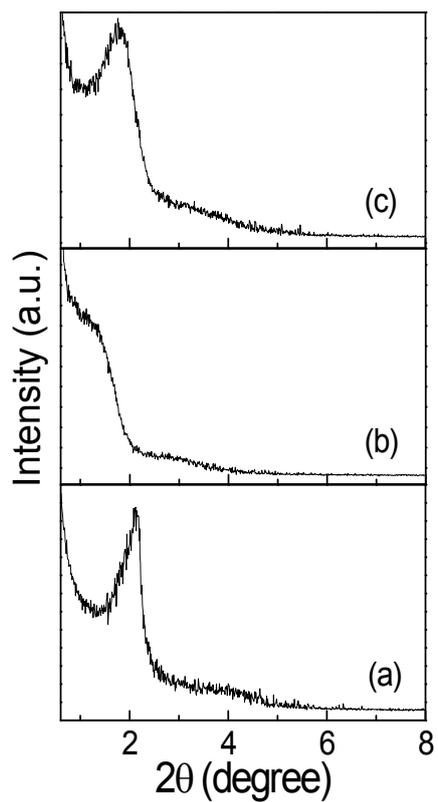
Samples	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{pore}}$ ( $\text{cm}^3/\text{g}$ )	$D_{\text{DFT}}$ (nm)	$D_{\text{BJH}}$ (nm)	Acid content (mmol $\text{H}^+/\text{g}$ )
ZrHEDP	749	0.74	3.4	2.3	1.92
ZrHEDP used	569	0.68	3.8	2.5	-
ZrATMP	310	0.42	4.2	3.3	1.25
ZrEDTMPS	670	0.67	3.6	2.6	1.42



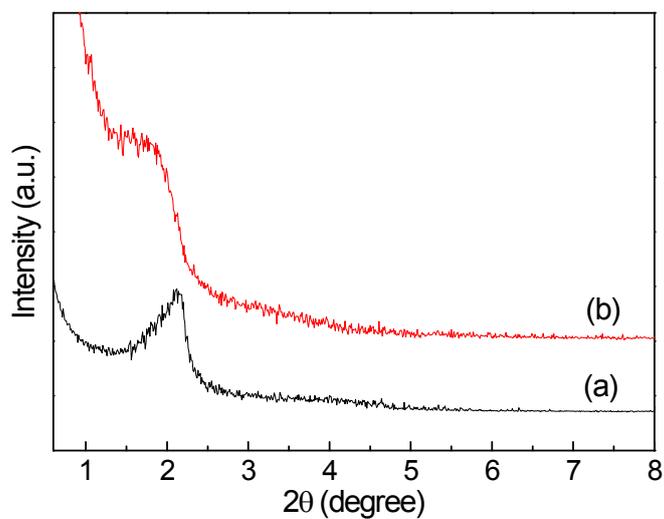
**Scheme S1.** The organophosphonic acids used for synthesis of zirconium phosphonates.



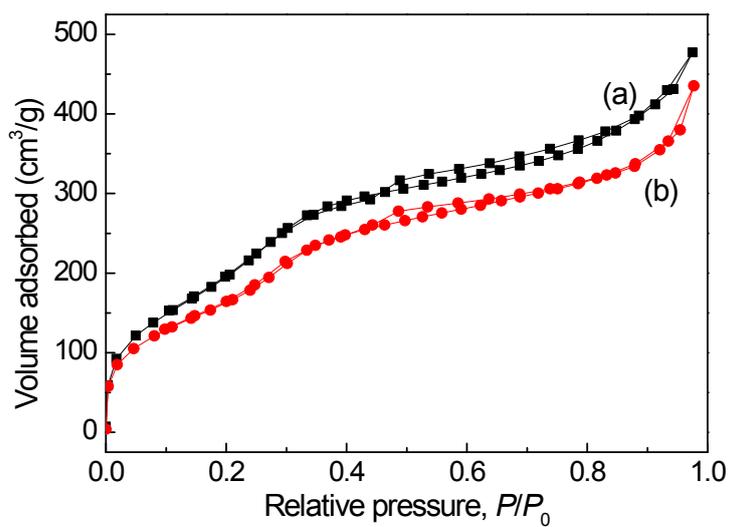
**Scheme S2.** A plausible reaction mechanism for the cyclization of aziridine with  $\text{CO}_2$  catalyzed by mesoporous ZrHEDP.



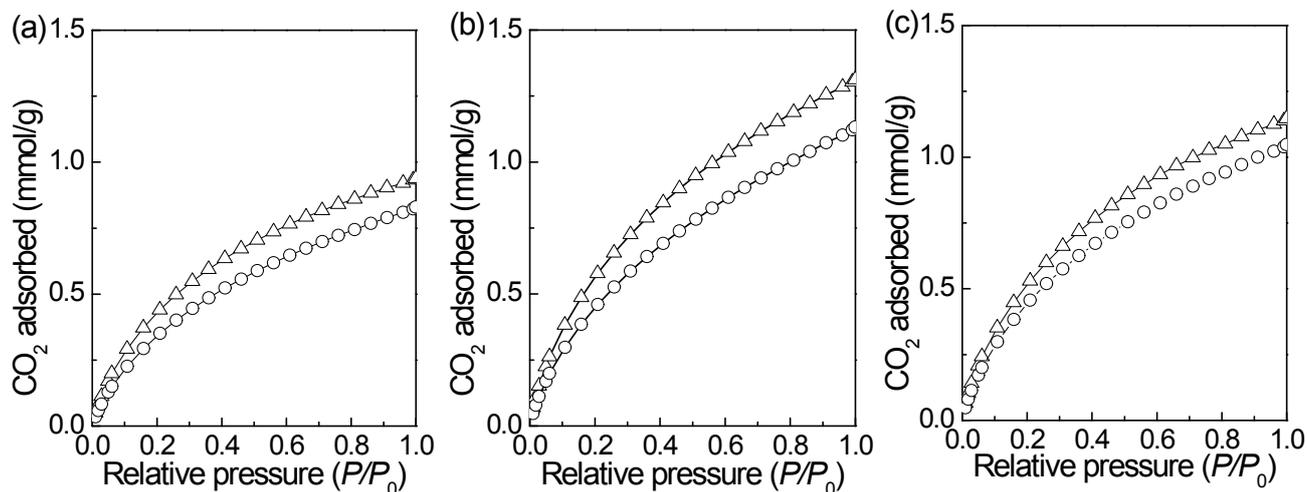
**Figure S1.** Low-angle XRD patterns of the mesoporous zirconium organophosphonates: (a) ZrHEDP, (b) ZrATMP and (c) ZrEDTMPS.



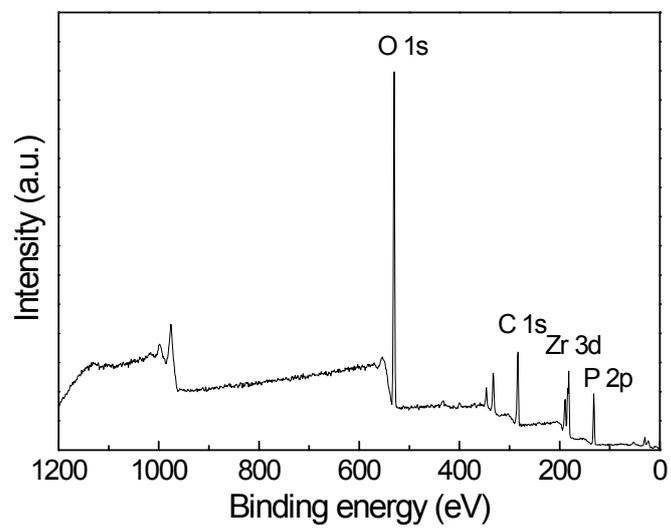
**Figure S2.** Low-angle XRD patterns of ZrHEDP before (a) and after (b) catalytic reaction.



**Figure S3.**  $N_2$  adsorption-desorption isotherms of ZrHEDP before (a) and after (b) catalytic reaction.



**Figure S4.**  $CO_2$  adsorption isotherms at 0 °C ( $\Delta$ ) and 25 °C (O) for the mesoporous zirconium organophosphonates: (a) ZrHEDP, (b) ZrATMP and (c) ZrEDTMPS.



**Figure S5.** XPS survey spectrum of mesoporous ZrHEDP.