Supporting Information

Acid-Base Bifunctional Periodic Mesoporous Metal Phosphonates for Synergistically and Heterogeneously Catalyzing CO_2 Conversion

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1. Supplementary tables

Table S1. Summary of physicochemical properties of the synthesized titanium phosphonates.

Sample	S_{BET} ($m^2\ g^{-1}$)	$D_{BJH\text{-}ads}$ (nm)	V_{pore} ($cm^3\ g^{-1}$)	Mesophase	P/Ti molar ratio*	Phosphonic acid used
Ti-AST	540	2.4	0.43	hexagonal	5/3	AST
Ti-AST’	531	2.4	0.42	hexagonal	1/1	AST
Ti-MDA	627	2.5	0.50	hexagonal	5/3	MDA
Bulk-Ti-AST	35	–	0.03	–	5/3	AST

* Molar ratios used in the feeding materials during catalyst preparation.

Table S2. Recyclability of Ti-AST.

Run*	Conversion (%)	Yield (%)	Regioselectivity
1	>99	98	98:2
2	>99	98	98:2
3	>99	98	98:2
4	>99	97	98:2
5	99	97	98:2
6	99	98	97:3
7	99	97	98:2
8	98	97	98:2
9	99	97	98:2
10	97	96	97:3

* Reaction conditions: 30 min, 3.0 MPa, 80 ^{o}C, R, R’ = Et, Ph.

2. Supplementary figures

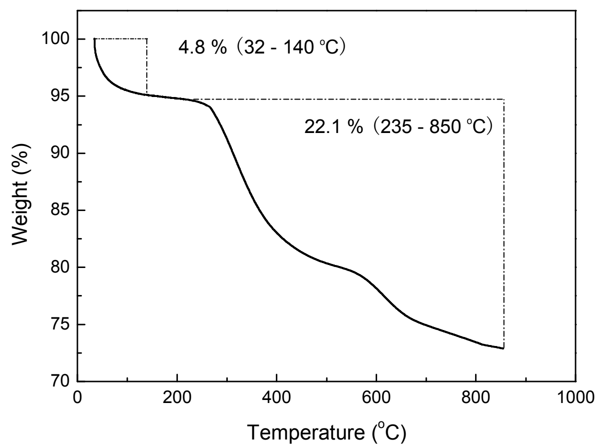

Figure S1. TG curve of Ti-AST.

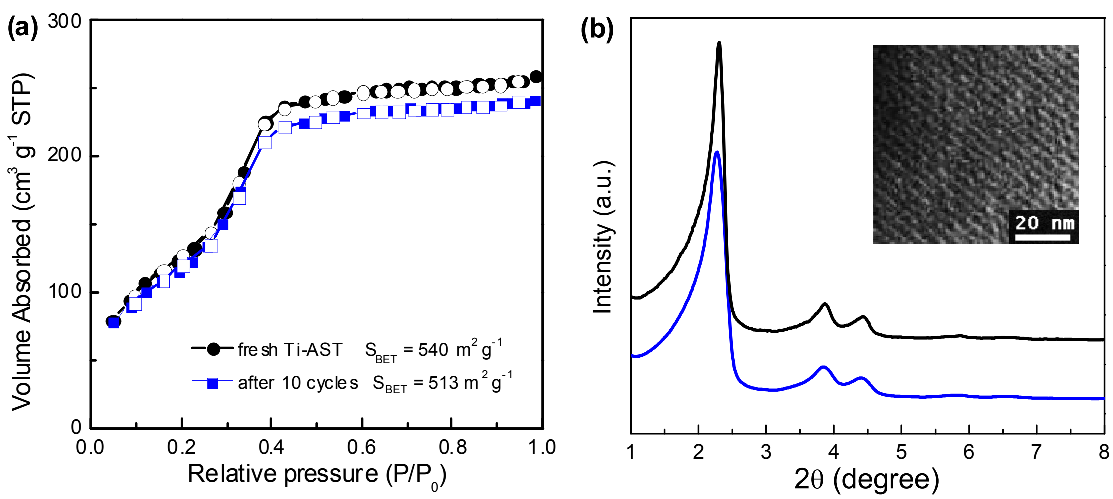

Figure S2. (a) N_2 adsorption isotherm, (b) XRD pattern, and (inset of b) TEM image of Ti-AST after used for 10 cycles in comparison to those of the fresh Ti-AST.

3. Spectroscopic data of oxazolidinones

3-cyclohexyl-5-phenyloxazolidin-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.0–1.9 (m, 10H), 3.39 (t, ^{3}J=8.0 Hz, 1H), 3.71–3.78 (m, 1H), 3.88 (t, ^{3}J=8.6 Hz, 1H), 5.46 (t, ^{3}J=8.0 Hz, 1H), 7.33–7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ25.1, 29.9, 30.4, 48.2, 52.4, 74.4, 125.3, 128.6, 128.7, 138.9, 157.1; MS (EI) *m/z*: 246.30 $(M + H)^+$, 757.75 $(3M + Na)^+$.

3-cyclohexyl-5-p-tolyloxazolidin-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02–1.82 (m, 10 H), 2.36 (s, 3 H), 3.38 (t, ^{3}J = 8.0 Hz, 1 H), 3.71–3.75 (m, 1 H), 3.85 (t, ^{3}J = 8.7 Hz, 1 H), 5.43 (t, ^{3}J = 8.0 Hz, 1 H), 7.17–7.26 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 25.2, 25.3, 25.4, 30.1, 30.5, 48.3, 52.5, 74.5, 125.5, 129.5, 136.0, 138.6, 157.3; MS (EI) *m/z*: 260.02 $(M + H)^+$, 799.55 $(3M + Na)^+$.

5-(4-chlorophenyl)-3-cyclohexyloxazolidin-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05–1.83 (m, 10 H), 3.34 (t, ^{3}J = 8.0 Hz, 1 H), 3.69–3.76 (m, 1 H), 3.89 (t, ^{3}J = 8.7 Hz, 1 H), 5.44 (t, ^{3}J = 8.0 Hz, 1 H), 7.27–7.38 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 25.3, 30.0, 30.4, 48.2, 52.6, 73.8, 126.8, 129.0, 134.5, 137.6, 156.8; MS (EI) *m/z*: 280.10 $(M + H)^+$.

3-propyl-5-phenyloxazolidin-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, ^{3}J = 7.2 Hz, 3H), 1.54–1.63 (m, 2H), 3.21–3.33 (m, 2H) 3.43 (t, ^{3}J = 8.0 Hz, 1H), 3.93 (t, ^{3}J = 8.8 Hz, 1H), 5.48 (t, ^{3}J = 8.0 Hz, 1H), 7.32–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.9, 20.4, 45.6, 52.0, 74.1, 125.3, 128.6, 128.7, 138.9, 157.8; MS (EI) *m/z*: 206.31 $(M + H)^+$, 228.32 $(M + Na)^+$.

3-butyl-5-phenyloxazoidine-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, ^{3}J = 7.2 Hz, 3H), 1.29–1.38 (m, 2H), 1.48–1.56 (m, 2H), 3.21–3.35 (m, 2H) 3.40 (t, ^{3}J = 8.0 Hz, 1H), 3.89 (t, ^{3}J = 8.8 Hz, 1H), 5.45 (t, ^{3}J = 8.0 Hz, 1H), 7.32–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ13.6, 19.7, 29.2, 43.7, 52.0, 74.2, 125.4, 128.6, 128.7, 138.8, 157.8; MS (EI) *m/z*: 220.30 $(M + H)^+$, 461.07 $(2M + Na)^+$.

3-ethyl-5-(4-chlorophenyl)oxazolidin-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (t, ^{3}J = 7.3 Hz, ^{3}H), 3.29–3.41 (m, 2H), 3.67–3.75 (m, 1H), 3.90 (t, ^{3}J = 8.7 Hz, 1H), 5.41 (t, ^{3}J = 8.0 Hz, 1H), 7.24–7.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 39.1, 51.6, 73.8, 127.1, 129.3, 134.9, 137.5, 157.6; MS (EI) *m/z*: 451.66 $(2M + H)^+$.

3-ethyl-5-p-tolyloxazolidin-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, ^{3}J = 7.3 Hz, 3H), 1.62 (d, ^{3}J = 6.4 Hz, 1H), 1.88 (d, ^{3}J = 3.2 Hz, 1H), 2.30 (dd, ^{3}J = 6.6 Hz, ^{2}J = 3.2 Hz, 1H), 2.32 (s, 3H), 2.36–2.49 (m, 2H), 7.10–7.15 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 21.3, 38.9, 51.7, 74.3, 125.8, 129.7, 135.9, 138.7, 157.9; MS (EI) *m/z*: 206.40 $(M + H)^+$, 411.12 $(2M + H)^+$.

3-ethyl-5-phenyloxazolidin-2-one: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, ^{3}J = 7.2 Hz, 3H), 1.29–1.38 (m, 2H), 1.48–1.56 (m, 2H), 3.21–3.35 (m, 2H), 3.40 (t, ^{3}J = 8.0 Hz, 1H), 3.89 (t, ^{3}J = 8.8 Hz, 1H), 5.45 (t, ^{3}J = 8.0 Hz, 1H), 7.32–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ13.6, 19.7, 29.2, 43.7, 52.0, 74.2, 125.4, 128.6, 128.7, 138.8, 157.8; MS (EI) *m/z*: 192.25 $(M + H)^+$, 214.33 $(M + Na)^+$.