Supporting Information

Zeolitic Imidazole Framework-67 as an Efficient Heterogeneous Catalyst in the Conversion of CO_2 to Cyclic Carbonate

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sample	BET (m^2/g)	Langmuir (m^2/g)	Pore volume (cm^3/g) HK	Pore size (Å)HK
ZIF-8	1753	1792	0.7092	12.86
ZIF-67	1514	1721	0.5588	12.54

Table S1. The surface area of ZIF-67 evaluated from BET and Langmuir theoretical calculations.

Samples	Acidic sites mmol/g, NH_3-TPD	Basic sites μmol/g, CO_2-TPD
(Zn)ZIF-8	(0.13775*0.294)/0.1=**0.405**	(0.00852*0.0176)/0.03 =**4.99**
(Co)ZIF-67	(0.10721*0.294)/0.1=**0.315**	(0.00898* 0.0176)/0.03=**5.26**

Table S2. NH_3-TPD and CO_2-TPD profiles of ZIF-67 and ZIF-8.

CALCULATION OF ACIDITY

Calculation of total acidity.

Total acidity is calculated from the NH_3-TPD profiles:

The NH_3-TPD profiles:

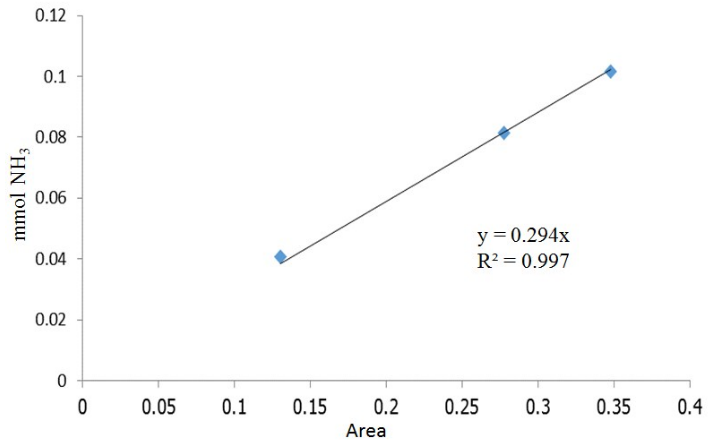
- area of the NH_3-TPD profiles of the sample = A
- The mole of NH_3 was calculated from the calibration curve of NH_3 as formula:

The mole of NH_3 of the sample = 0.294×A mmole.

- Amount of sample = B g.

$$\text{The total acidity of sample} = \frac{\text{mmole of } NH_3 \text{ of the sample}}{\text{Amount of dry catalyst}}$$

$$= \frac{0.294 \times A}{B} \quad \text{mmol } NH_3/\text{g catalyst}$$



The calibration curve of ammonia from Micromeritics Chemisorp 2750

CALCULATION OF BASICITY

Calculation of total basicity.

Total basicity is calculated from the CO_2-TPD profiles:

The CO_2-TPD profiles:

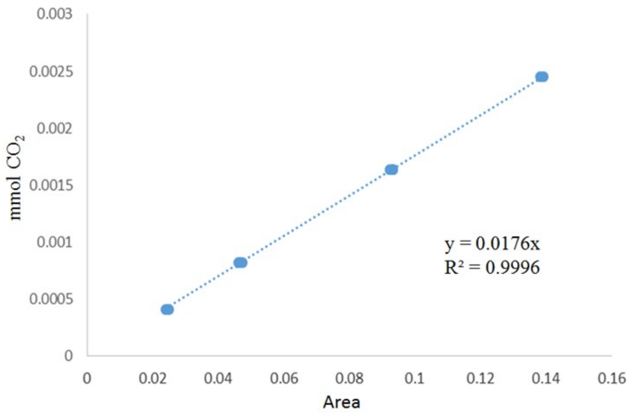
- area of the CO_2-TPD profiles of the sample = A
- The mole of CO_2 was calculated from the calibration curve of CO_2 as formula:

The mole of CO_2 of the sample = 0.0176×A mmole.

- Amount of sample = B g.

$$\text{The total basicity of sample} = \frac{\text{The mmole of } CO_2 \text{ of the sample}}{\text{Amount of dry catalyst}}$$

$$= \frac{0.0176 \times A}{B} \quad \text{mmol } CO_2\text{/g catalyst}$$



The calibration curve of carbon dioxide from Micromeritics Chemisorp 2750

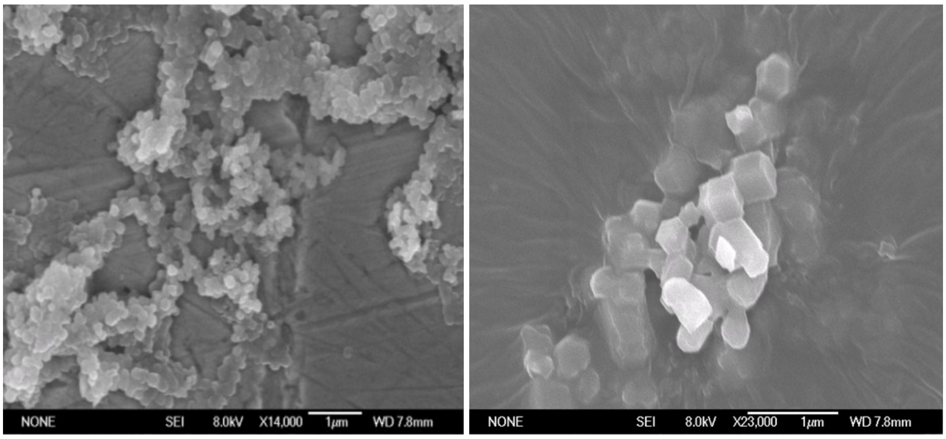


Figure S1. (left) Scanning electron microscope image (SEM) of ZIF-67 before reaction, (right) Scanning electron microscope image (SEM) of ZIF-67 after reaction (scale bar: 1.0 μm).

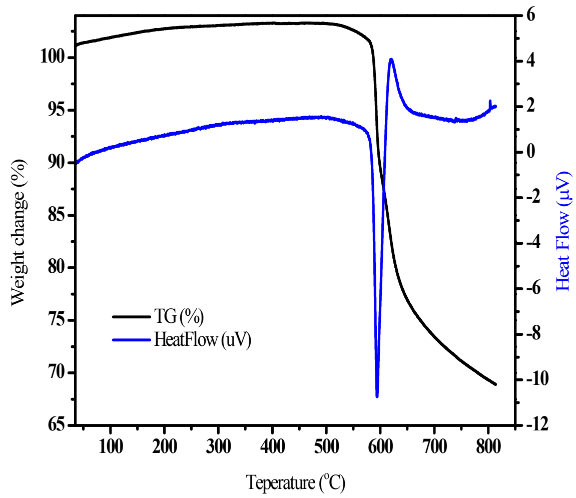


Figure S2. Thermal gravimetric analysis (TGA) curve of ZIF-67.

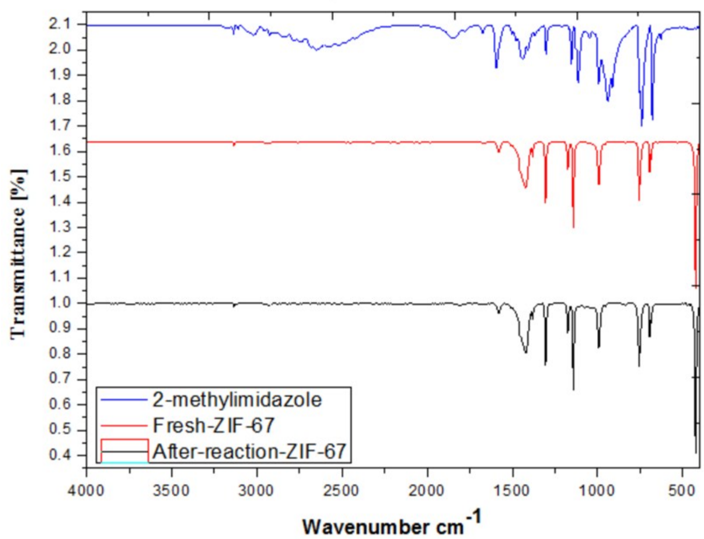


Figure S3. FT-IR spectra of 2-methylimidazole (blue), fresh ZIF-67 and reused ZIF-67.

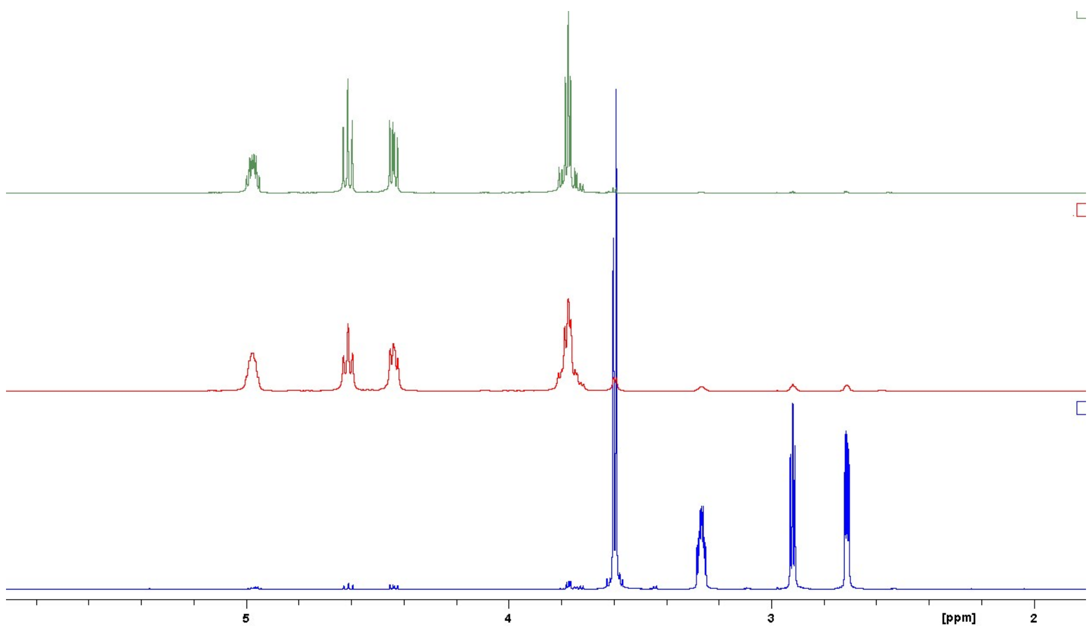


Figure S4. ^{1}H NMR in $CDCl_3$ (500 MHz) at different temperatures, Blue: 60 °C, Red 80 °C, Green 95 °C

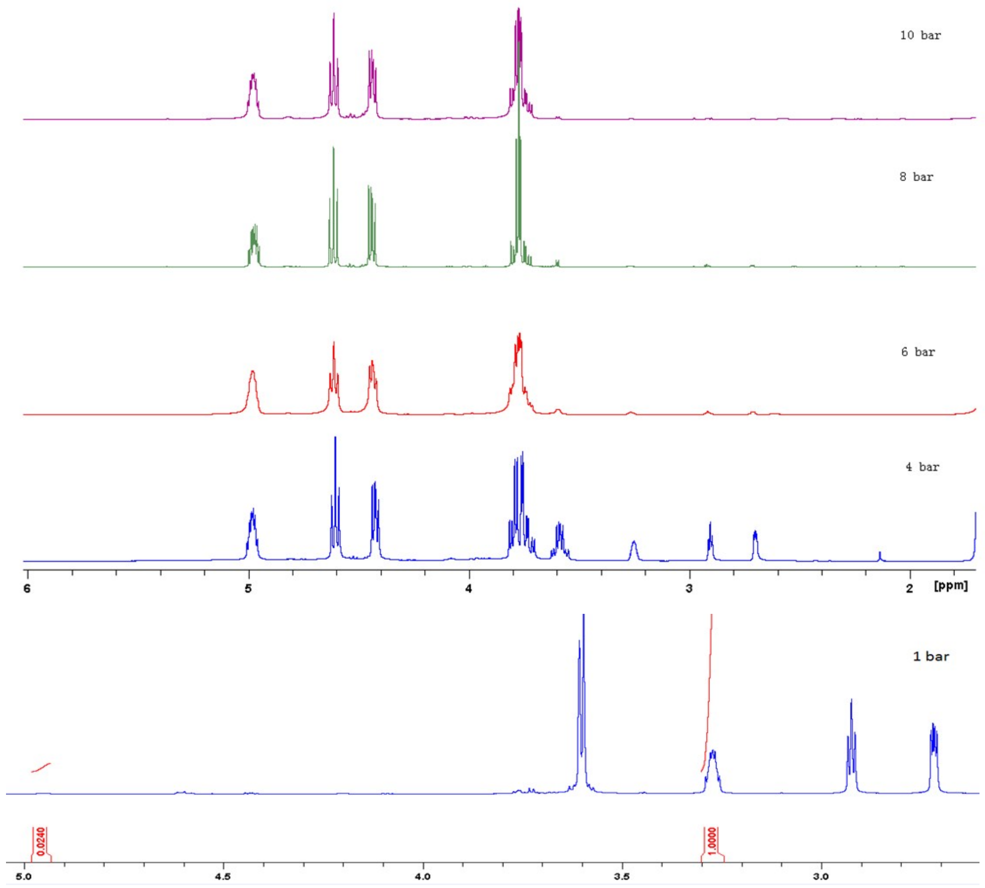


Figure S5. The effect of different CO_2 pressure ZIF-67. (^{1}H NMR in $CDCl_3$ (500 MHz)).

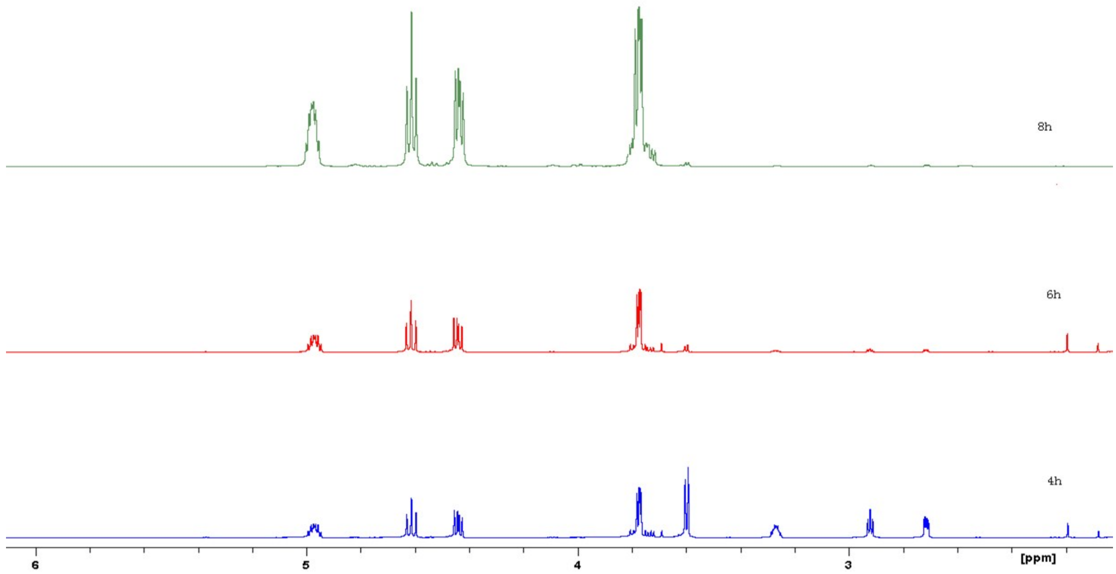


Figure S6. H^1 NMR in $CDCl_3$ (500 MHz) for different reaction times

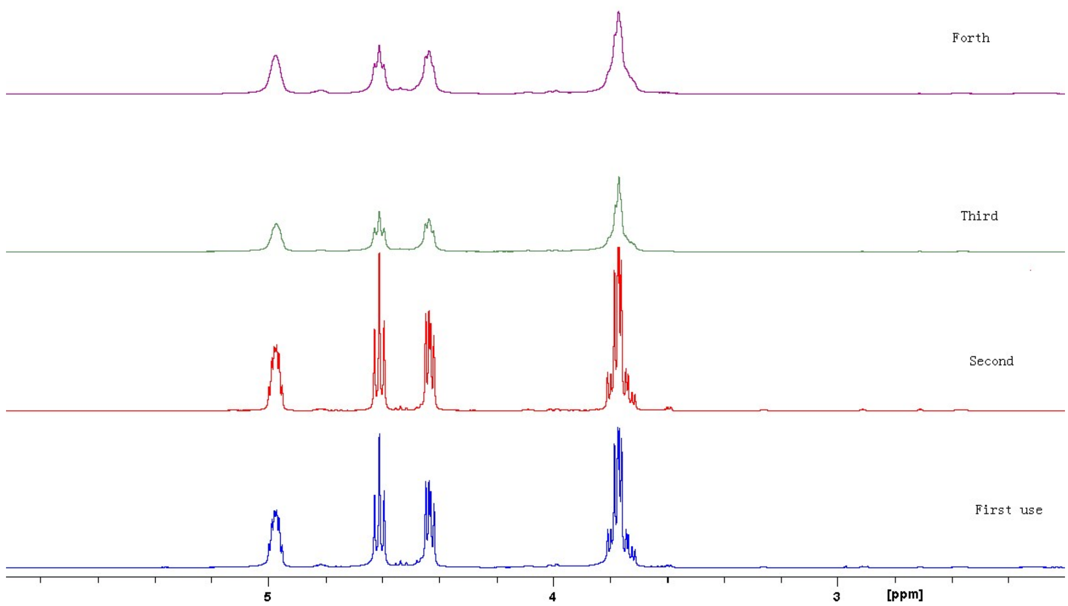


Figure S7. Reusability of ZIF-67 catalyst. (^1H NMR in $CDCl_3$, 500 MHz.)

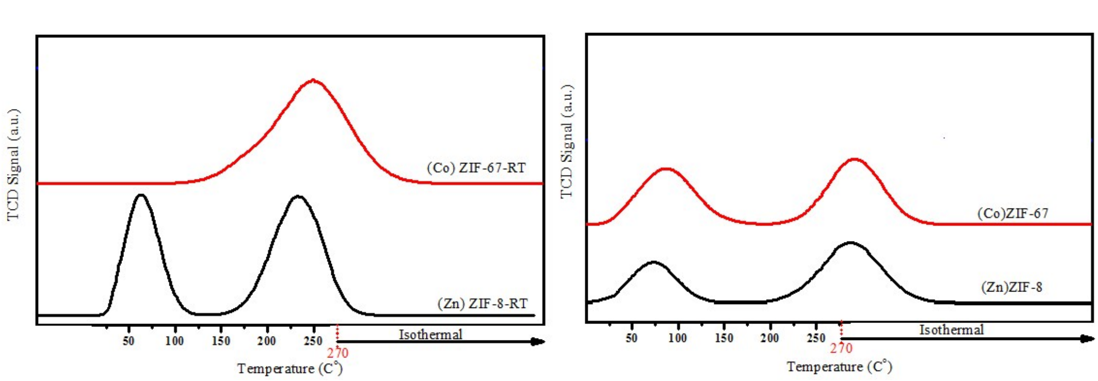
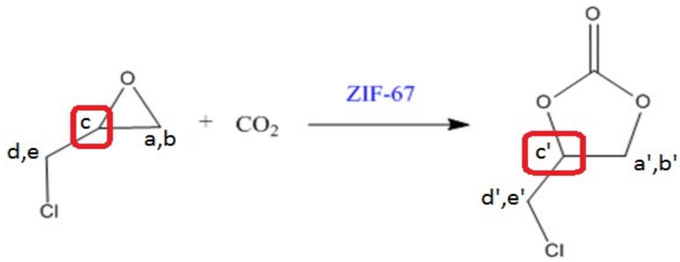


Figure S8. (left) NH_3-TPD and (right) CO_2-TPD profiles of ZIF-67 (red) and ZIF-8 (black).



^{1}H NMR in $CDCl_3$ 500 MHz

Epichlorohydrin: ^{1}H NMR (500 MHz, CDCl3): δ [d,e] 3.57-3.63 (m, 2H), [c] 3.23 (m, 1H), [a,b] 2.68 (m, 1H), 2.88 (m, 1H).

Chloropropene carbonate: ^{1}H NMR (500 MHz, CDCl3): δ [c']: 4.90-5.02 (m, 1H), [a',b']: 4.61 (t, J = 8.6 Hz, 1H), 4.45 (dd, J = 8.9, 5.7 Hz, 1H), [d']: 3.68-3.78 (m, 1H). ^{13}C NMR (100 MHz, CDCl3): δ 154.5, 74.5, 67.0, 44.1.

The conversion of the reaction was calculated by measuring the ratio of peak c integration to c'.

^{1}H and ^{13}C

4-phenyloxymethyl-1,3-dioxolan-2-one: ^{1}H NMR (500 MHz, $CDCl_3$); δ (ppm) 4.17 (dd, 1H), 4.24 (dd, 1H), 4.54 (dd, 1H), 4.61(t, 1H), 5.03 (m, 1H), 6.94 (m, 2H), 7.03 (t, 1H), 7.31(m, 2H)

4-phenyl-1,3-dioxolan-2-one: ^{1}H NMR (500 MHz, $CDCl_3$); 4.36 (t, 1H), 4.8 (t, 1H) 5.68 (t, 1H) 7.30-7.45(m, 5H)

Propylene carbonate: ^{1}H NMR (500 MHz, $CDCl_3$); 1.50 (t, 3H), 4.04(m, 1H), 4.55(m, 1H), 4.86(m, 1H)

Hexahydrobenzo[*d*][1,3]dioxol-2one: ^{1}H NMR (500 MHz, $CDCl_3$); 1.41-1.54 (m, 4H), 1.81 (m, 2H), 4.52 (m,2H). ^{13}C NMR (100 MHz, CDCl3): 20.1 , 27.8, 76.3, 156.1