Supporting Information

Functionalized dicyandiamide-formaldehyde polymers as efficient heterogeneous catalysts for conversion of CO_2 into organic carbonates

Xiang-Lei Meng,[a,b] Yi Nie,*[a,b] Jian Sun,[b] Wei-Guo Cheng,[b] Jin-Quan Wang,[b] Hong-Yan He[b] and Suo-Jiang Zhang*[b]

[a]*College of Chemistry and Chemical Engineering, Qufu Normal University, Shandong, 273165, China, E-mail: ynie@home.ipe.ac.cn*

[b]*Beijing Key Laboratory of Ionic Liquids Clean Process, Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China. Fax: (+86) 10 8262 7080; E-mail: sjzhang@home.ipe.ac.cn*

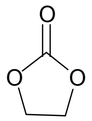
Supporting information

5. *1. General information*

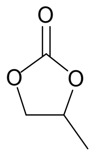
Carbon dioxide was supplied by Beijing Analytical Instrument Factory with a purity of 99.95%. Ammonium iodide, 1,2-Epoxyoctane and cyclohexene oxide were purchased from Alfa Aesar-A Johnson Matthey Company, Other reagents and chemicals (analytic grade) were bought from Sinopharm Chemical Reagent Co. , Ltd, and were used without further purification. GC-MS were measured on a Finnigan HP G1800 A. GC analyses were performed on a Agilent GC-6890 equipped with a capillary column (DB-624, 30 m×0.32 μm) using a flame ionization detector. NMR spectra were recorded on a Bruker 300 or Varian 400 spectrometer in $CDCl_3$. ^1H and ^{13}C NMR chemical shifts (δ) were given in ppm relative to TMS. ^1H and ^{13}C positive chemical shifts (δ) in ppm were downfield from tetramethylsilane ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm). Glass Transition was measured by DSC (DSC1, Mettler-Toledo Corp.). Samples (about 4~8 mg) were placed in aluminium pans with pierced lids at a heating rate of 10 °C/min in N_2 atmosphere.

2. Supporting NMR data

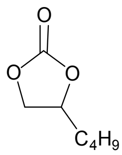
Spectra of product ^{1}H NMR and ^{13}C NMR of Products



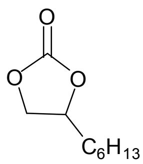
^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 4.2 (t, J = 10 Hz, 4H); ^{13}C NMR ($CDCl_3$, TMS, 100.4 MHz): 63.3, 155 (C=O).



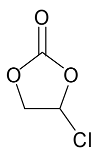
^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 1.49 (d, J = 6.0 Hz, 3H); 4.05 (t, J = 8.8 Hz, 1H); 4.60 (t, J = 8.0 Hz, 1H); 4.86 - 4.94 (m, 1H); ^{13}C NMR ($CDCl_3$, TMS, 100.4 MHz): 18.95, 70.46, 73.51, 154.95 (C=O)



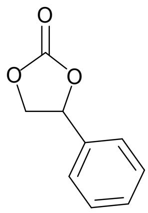
^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 0.96 (t, J = 7.2 Hz, 3H); 1.33 - 1.38 (m, 2H); 1.29 - 1.31 (m, 2H); 1.53 (m, 2H); 4.16 (d, J = 8.0 Hz, 2H); 4.19 (t, J = 6.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS, 100.4 MHz): 14.00, 23.12, 26.19, 36.23, 68.04, 75.61, 155.07 (C=O).



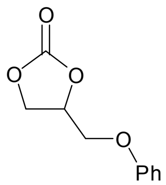
^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 0.84 (t, J = 13.1 Hz, 3H); 1.24 - 1.28 (m, 7H); 1.34 (t, J = 9.6 Hz, 1H); 1.65 (t, J = 11.7 Hz, 2H); 4.08 (t, J = 15.8 Hz, 1H); 4.53 (t, J = 15.8 Hz, 1H); 4.74 (t, J = 6.9 Hz, 1H); ^{13}CNMR ($CDCl_3$, TMS, 100 MHz): 14.29, 22.52, 24.45, 28.87, 31.63, 33.44, 69.69, 77.49, 155.35 (C=O).



^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 1.490 (d, 2H, J = 6.0 Hz); 4.05 (t, 1H, J = 8.4 Hz); 4.60 (t, 1H, J = 8.0 Hz); 4.86 – 4.94 (m, 1H); ^{13}C NMR ($CDCl_3$, TMS, 100.4 MHz): 18.95, 70.46, 73.51, 154.95 (C=O).



^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 4.34 (t, 1H, J = 8.4 Hz); 4.80 (t, 1H, J = 8.4 Hz); 5.68 (t, 1H, J = 8.0 Hz); 7.35 – 7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, TMS, 100.4 MHz): 71.10, 77.92, 125.81, 129.12, 129.63, 135.70, 154.81 (C=O).



^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 4.15 [dd, 3J = 4.4 Hz, 2J = 10.8 Hz, 1H, OCH_2], 4.24 [dd, 3J = 3.6 Hz, 2J = 10.8 Hz, 1H, OCH_2], 4.55 [dd, 3J = 8.4 Hz, 2J = 6 Hz, 1H, $PhOCH_2$], 4.62 [t, 3J = 8.4 Hz, 1H, $PhOCH_2$], 5.03 [m, 1H, OCH], 6.91 [d, 3J = 8.0 Hz, 2H, C_6H_5], 7.02 [t, 3J = 7.4 Hz, 2H, C_6H_5], 7.31 [t, 3J = 8.0 Hz, 2H, C_6H_5]. ^{13}C NMR ($CDCl_3$, TMS, 100.4 MHz): 66.17, 68.84, 74.11, 114.57, 121.92, 129.62, 154.65(C=O), 157.71.

3. The cartesian coordinates

N	0.84412000	-1.02966700	2.06290200
H	1.58673100	-0.43614000	2.41699300
C	1.22280600	-2.45247800	1.98560900
H	1.21105900	-2.87645200	2.99268300
H	0.46840700	-2.94975000	1.36792700
O	2.52502400	-2.59408700	1.50393200
H	2.53979100	-2.28348700	0.56460200
C	-0.06651000	-0.43866200	1.25785700
C	-0.81367700	1.80147000	0.36552800
H	-0.63248200	1.85821000	-0.71586600
H	-1.83071900	1.45247100	0.54510800
N	0.13125600	0.85598700	0.96093700
H	1.08755500	1.21048900	0.99344700
O	-0.68947900	3.06321100	0.97058100
H	0.18999900	3.42059100	0.74760900
C	-1.72009500	-1.16049700	-0.26701100
N	-1.17592700	-1.13121700	0.93488400
N	-1.10106600	-0.84415800	-1.41782200
H	-0.05955500	-0.86279500	-1.46045200
H	-1.57556700	-1.00772700	-2.29694500
N	-3.04345000	-1.53549100	-0.33139800
H	-3.40085800	-1.91755800	0.53634900
H	-3.35772300	-2.03076400	-1.15742300
Br	2.14239700	-1.12783000	-1.42285600
C	2.86421900	2.50938800	-0.93607100
H	2.86984900	1.45357400	-1.20471400
H	2.62922000	3.21878800	-1.72790400
C	3.60336600	2.97957100	0.24116700
H	3.91737300	4.01976100	0.30680700
H	4.18418500	2.26978600	0.82720400
O	2.17298200	2.78741800	0.31781100
C	-5.31433800	0.69021900	-0.30039100
O	-6.06088300	-0.20869400	-0.36409400
O	-4.57893300	1.59625300	-0.23849500

4. Supporting Figure

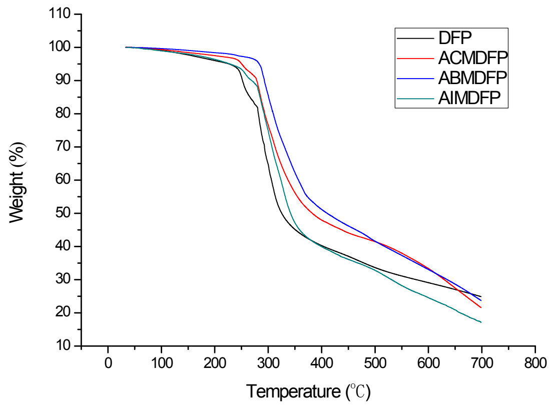


Fig. S1 The thermo-gravimetric analysis of DFP, ACMDFP, ABMDFP and AIMDFP.

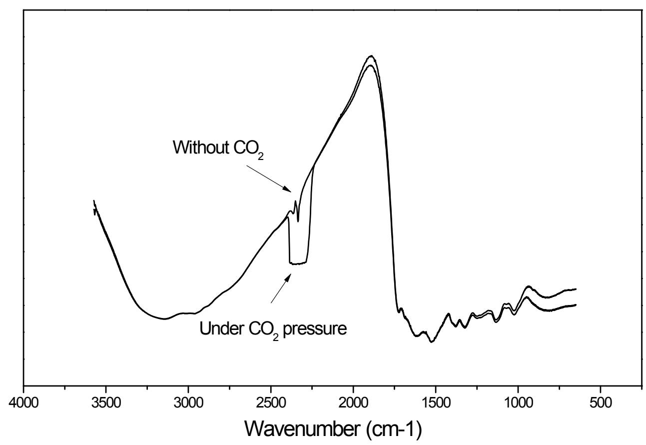


Fig. S2 *In situ* FTIR of ABMDFP under CO_2 pressure and without CO_2. Conditions: T (130°C), P (0.2 MPa).

Table S1 DSC of the DFP, ACMDFP, ABMDFP and AIMDFP.

Entry	Catalyst	Glass Transition (°C)	
		Onset	Midpoint
1	DFP	112.77	120.72
2	ACMDFP	96.94	115.92
3	ABMDFP	98.12	116.73
4	AIMDFP	83.62	113.27