Supporting On-Line Information

Formation of glycerol carbonate from glycerol and urea catalysed by metal monoglycerolates

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Table S1: Effect of catalyst loading on glycerol + urea conversion and yield of glycerol carbonate

Catalyst (%)	Conversion (%)	Selectivity (%)				Yield (%)
		Glyc. carb.	SP1	SP3	SP4	
0	26	82	16	0	0	22
0.1	53	63	37	0	0	34
0.5	61	76	24	0	0	46
1.0	79	87	5	2	6	69
5.0	58	90	4	1	2	52

Reaction conditions: a 1:1 molar ratio of glycerol to urea with various loadings of ZMG (% wt ZMG w.r.t glycerol) at 140˚C/40 mbar over 6 h, monitored and quantified by gas chromatography.

Table S2: ZnO as a catalyst for the formation glycerol carbonate

Time (h)	Conversion (%)	% Selectivity					Yield* (%)
		Glyc. Carb.	SP1	SP2	SP3	SP4	
0.5	17	62	38	0	0	0	10
1.5	35	77	23	0	0	0	27
2	45	79	21	0	0	0	36
3	69	86	10	0	2	2	59
4	66	89	7	0	2	2	59
5	72	93	4	0	1	2	67
6	75	91	2	2	1	4	68
7	76	94	1	2	1	2	71

Reaction conditions: catalyst (ZnO) amount 5% wt with respect to glycerol, time 7h, molar ratio of glycerol:urea = 1:1, pressure 40 mbar, T = 140^0C. * Yields determined by gas chromatography.

Table S3: Effectiveness of cobalt monoglycerolate as a catalyst in the formation of glycerol carbonate

Time (h)	Conversion (%)	Selectivity				
		Glyc. carb.	SP1	SP3	SP4	Yield Glycerol Carbonate (%)
2	56	69	27	4	0	39
3	53	71	22	4	3	38
4	58	72	19	4	6	41
5	66	75	14	5	6	50
6	63	82	11	3	4	52

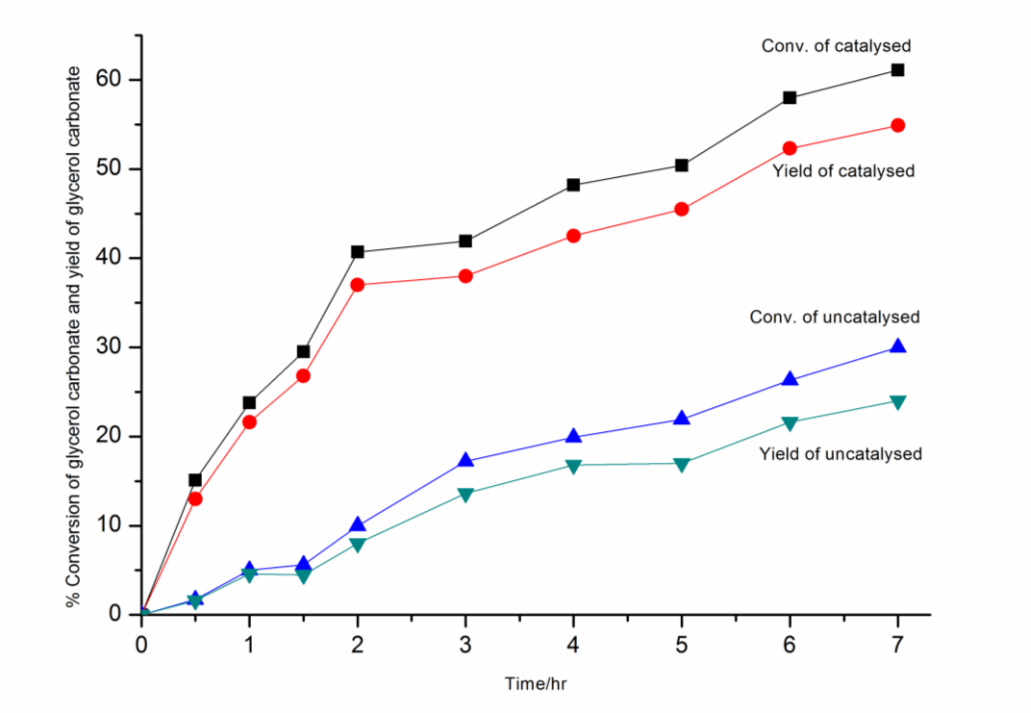
Reaction conditions: Molar ratio of glycerol : urea = 1:1 with 5% wt. CMG at 140˚C/40 mbar.

Table S4: Re-using ZMG over two reaction cycles in a glycerol/urea mixture[1]

Time	% Conv		Yield of GC		Yield of SP1	
h	1ST Cycle	2nd	1ST	2nd	1ST	2nd
3	42	40	39	37	3	4
4	48	45	43	39	2	2
5	51	49	46	45	2	1
6	59	55	55	53	5	4
ZMG Recovery[2]	90%	84%				

1. Reaction Conditions: glycerol : urea = 1 : 1 molar with 5% wt. ZMG at 6h/140^{o}C/ 40 mbar pressure. 2. Isolated product after MeOH wash of reaction mixture.

Figure S1: Effect of time on glycerol conversion and glycerol carbonate yields in the catalysed and uncatalysed reaction of glycerol with urea



Reaction conditions: 1:1 molar ratio of glycerol to urea with 5% wt. ZMG in the catalysed reaction, performed at 140^0C/40 mbar.

Figure S2. FTIR of reaction profile with ZnO

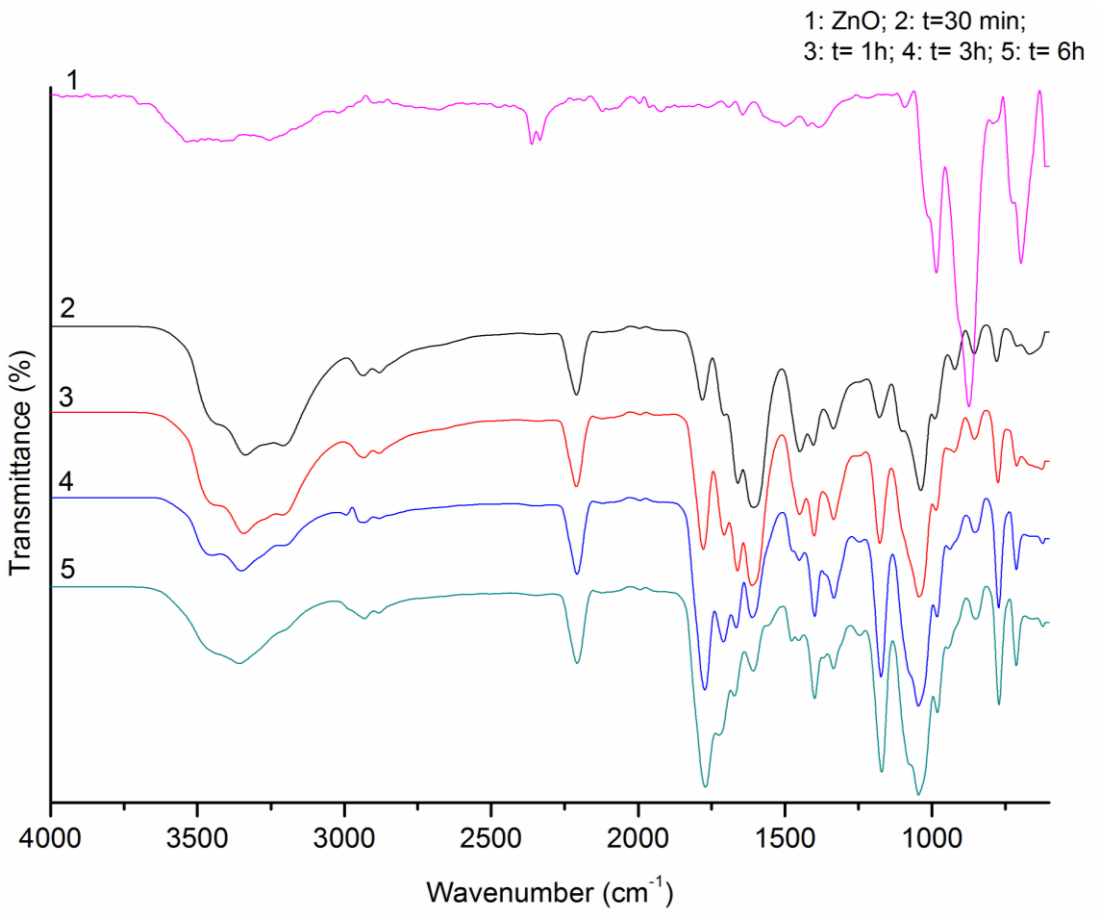
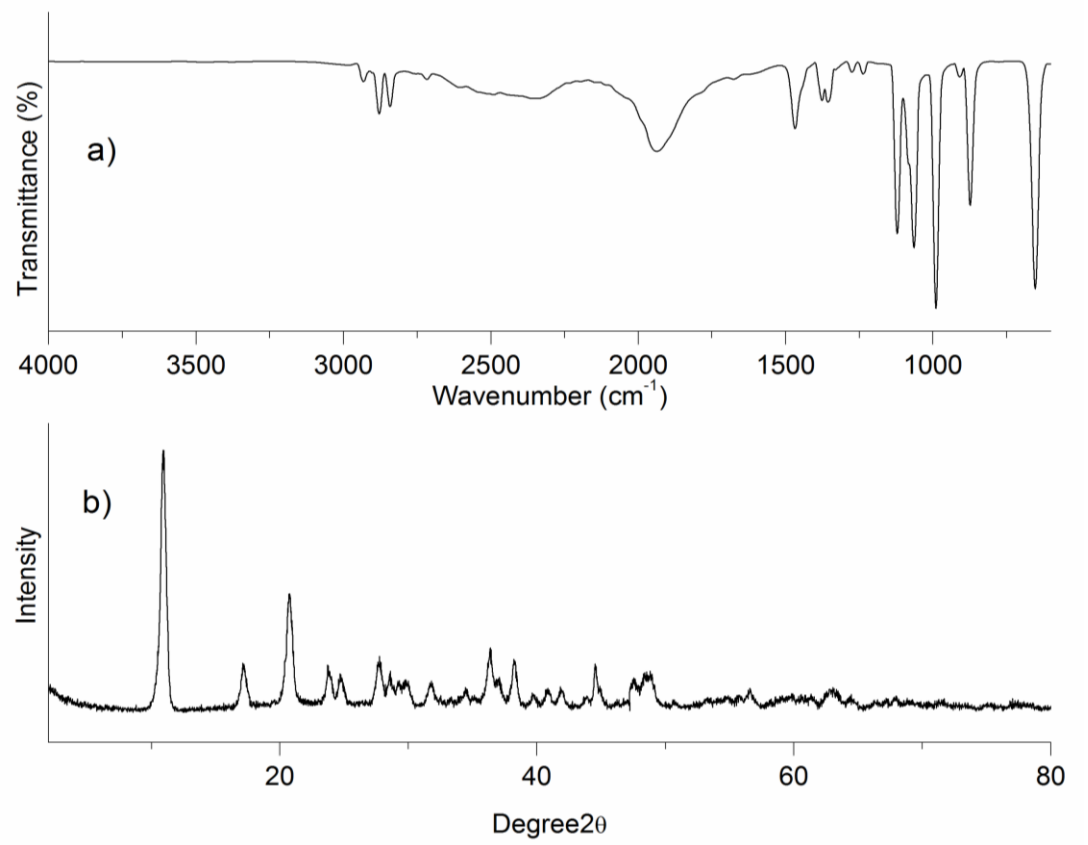


Figure S3. Recovered solid from ZnO reaction after MeOH work-up



a) FTIR spectrum of solid residue and b) powder XRD diffraction pattern of solid, showing the predominant crystalline phase to be ZMG.

Figure S4. Powder XRD of synthesised $Zn(NCO)_2(NH_3)_2$

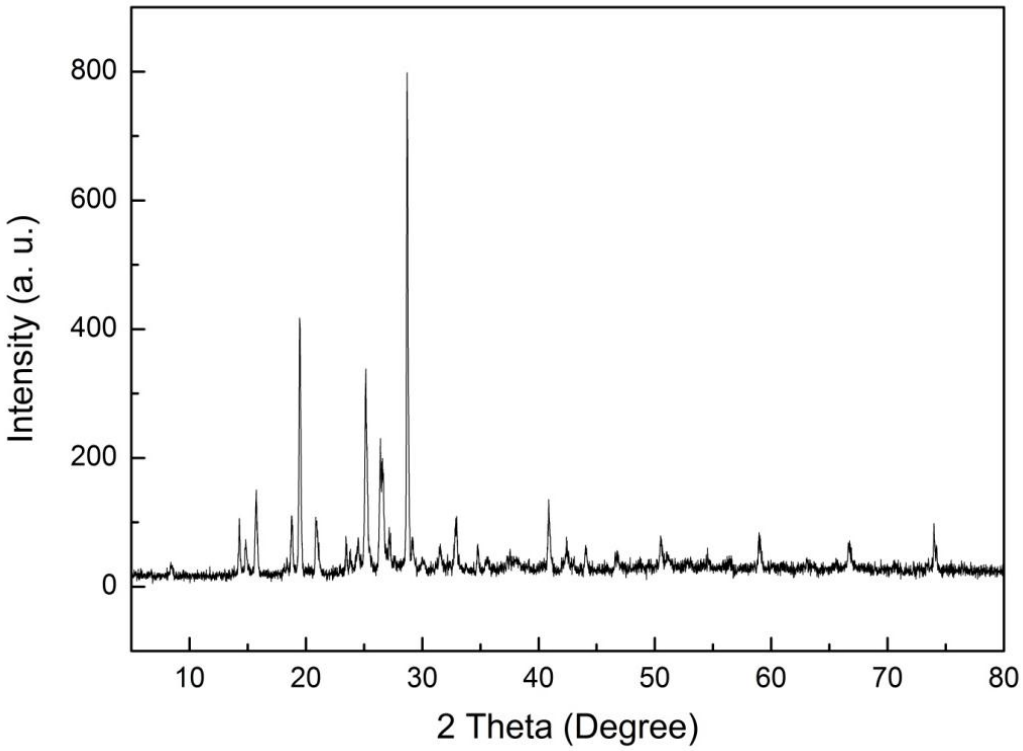


Figure S5. FTIR spectrum of synthesised $Zn(NCO)_2(NH_3)_2$

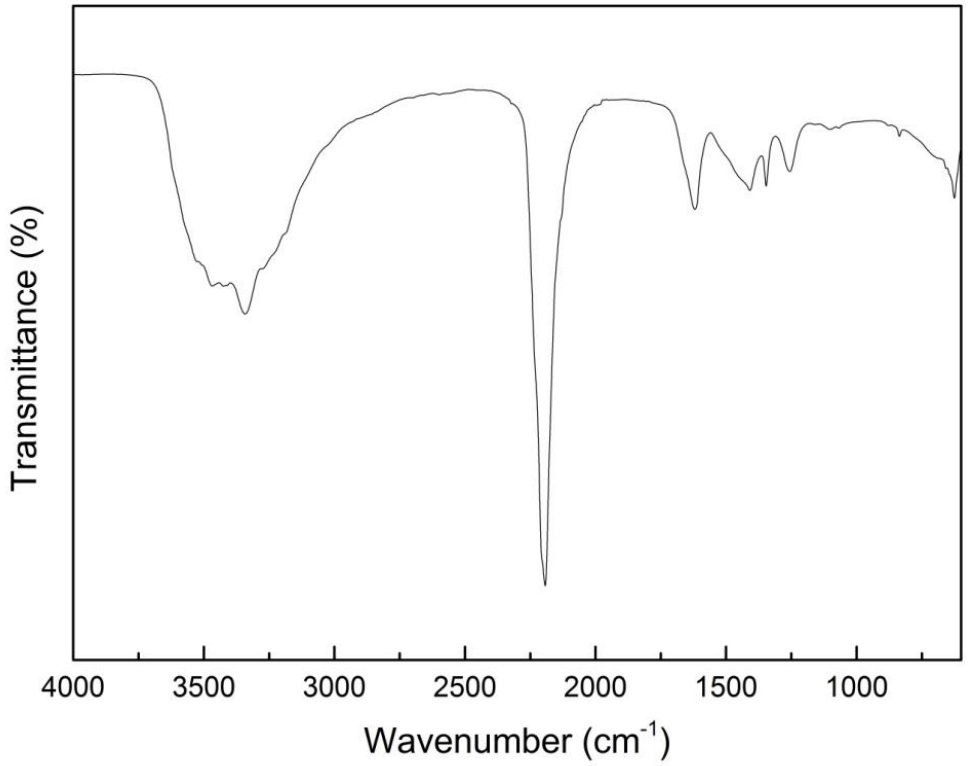
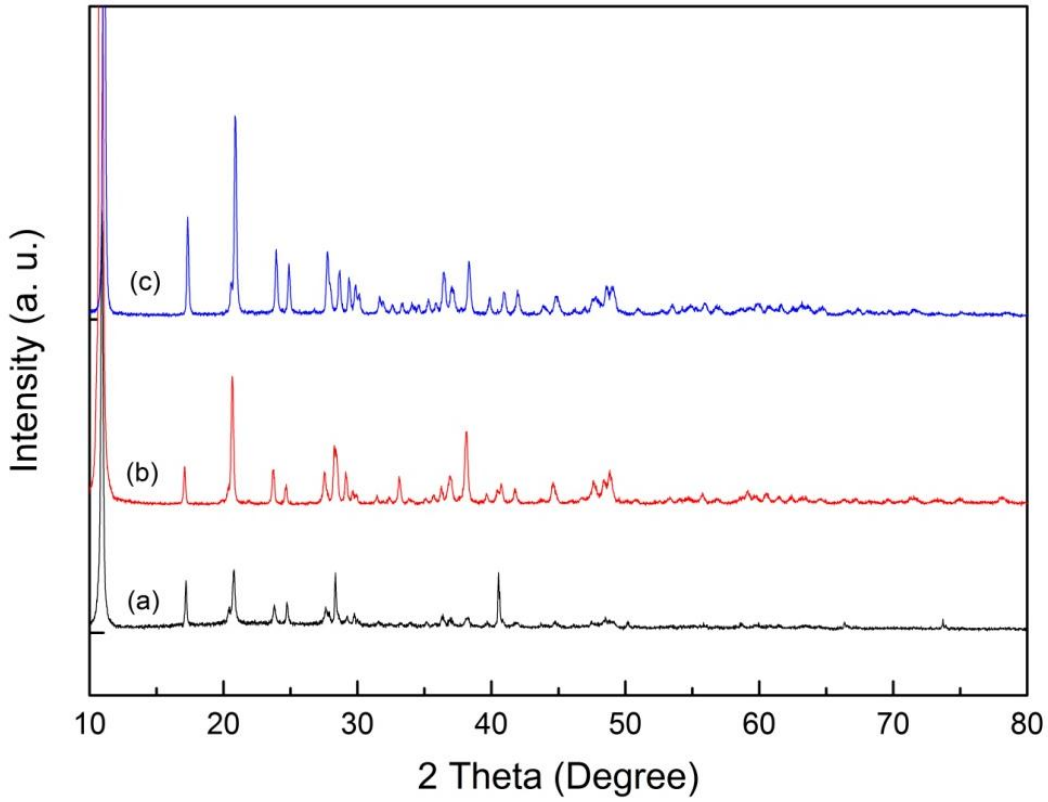


Figure S6. XRD of reaction mixture containing $Zn(NCO)_2(NH_3)_2$ and glycerol (1:1.5 molar eq.)



a) XRD of reaction suspension at 30 min., prior to MeOH work-up. b) XRD of solid at 6 h, after methanol work-up. c) XRD of commercial ZMG.

Figure S7. FTIR of reaction mixture of CMG + urea (1:2 molar ratio) after 1 h heating at 140^0C/40 mbar