Supporting Information

The Role of MnO_x Doped in CeO_2 for Catalytic Synthesis of Aliphatic Carbamate from CO_2

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Table S1. Relative molar sensitivity of all the products toward toluene (internal standard)

Reactants or products	Relative molar sensitivity
n-butylamine (BA)	1.68
Dibutylurea (DBU)	2.51
dimethyl carbonate (DMC)	3.33
N-butylcarbamate (NBCB)	2.05

Table S2 The catalytic performance with the different ratios of BA to catalyst over $MnO_x(0.03)$-CeO_2 catalyst[a]

Entry	Sub./Cat. (molar ratio)	Conv. (%)	$Sel._{NBCB}$(%)	$Sel._{DBU}$(%)
1	3	81.8	68.1	31.9
2	4	79.1	67.3	32.7
3	9	61.8	60.7	39.3

[a]Reaction condition: BA: CH_3OH = 5 mmol : 200 mmol, t = 16 h, T = 170 ^oC, P = 5.0 MPa

Table S3 The catalytic performance with the different ratios of BA to CH_3OH over $MnO_x(0.03)$-CeO_2 catalyst[a]

Entry	BA/CH_3OH (molar ratio)	Conv. (%)	Sel.$_{NBCB}$(%)	Sel.$_{DBU}$(%)
1	5:100	80.6	53.7	46.3
2	5:200	86.5	74.5	25.5
3	5:400	88.4	87.4	12.6
4	5:500	91.1	89.3	10.7
5	5:600	91.3	92.7	7.3

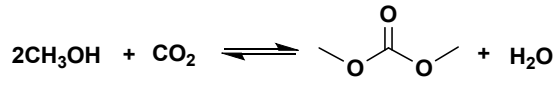
[a]Reaction condition: BA: 5 mmol, t = 8 h, T = 170 ^oC, P = 5.0 MPa, 0.3 g catalyst.

Table S4 BET surface area of CeO_2-based catalysts

Entry	Catalyst	BET surface /$m^2 \cdot g^{-1}$
1	Lab-com	8.0
2	Lab-CeO_2	31.7
3[a]	The spent Lab-CeO_2	24.1
4	MnO_x (0.03)-CeO_2	68.2
5[a]	The spent MnO_x (0.03)-CeO_2	52.9
6	MnO_x	14.9

[a]The BET surface area was measured after four catalytic recycles.

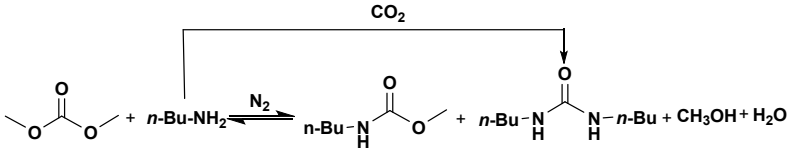
Table S5 The reaction of methanol with CO_2 over CeO_2-based catalysts[a]



Entry	Catalyst	Reactants /mmol		n_{DMC} /mmol
		CH_3OH	CO_2	
1	Lab-CeO_2	500	5 MPa	0.21
2	MnO_x(0.03)-CeO_2	500	5 MPa	0.28

[a]Reaction condition: T = 170 °C, P = 5.0 MPa, t = 8 h, catalyst 0.3 g. [b]DMC was detected as a sole product.

Table S6 The carbonylation of BA with DMC under the pressure of N_2 or CO_2[a].



Entry	Catalyst	Atmosphere	Reactants /mmol		Products /mmol	
			n_{BA}	n_{DMC}	n_{DBU}	n_{NBCB}
1	$MnO_x(0.03)$-CeO_2	N_2	5	2.5	0.058	0.65
[b]2	$MnO_x(0.03)$-CeO_2	CO_2	5	5	1.95	0.84

[a]Reaction condition: CH_3OH = 500 mmol, T = 170 °C, P = 5.0 MPa, t = 8 h, catalyst 0.3 g. [b]no solvent.

Table S7 Summary of the results of XPS analysis

Entry	Catalyst	u'''/ total area	[a]Mn/ Mn+Ce	Mn (%)	Ce (%)	O (%)	O distribution		
							O_L	O_s	O_a
1	Lab-CeO_2	0.126	-	0	29.1	70.9	61.5	6.9	2.5
2	the spent Lab-CeO_2	0.133	-	0	27.6	72.4	61.4	9.3	1.7
3	MnO_x (0.03)-CeO_2	0.125	0.03	1.0	32.0	67.0	60.1	5.6	1.3
4	the spent MnO_x (0.03)-CeO_2	0.126	0.037	1.2	29.8	69.0	57.6	8.8	2.6

[a] The values estimated by XPS analysis; The ICP value of Mn/Mn+Ce was 0.03

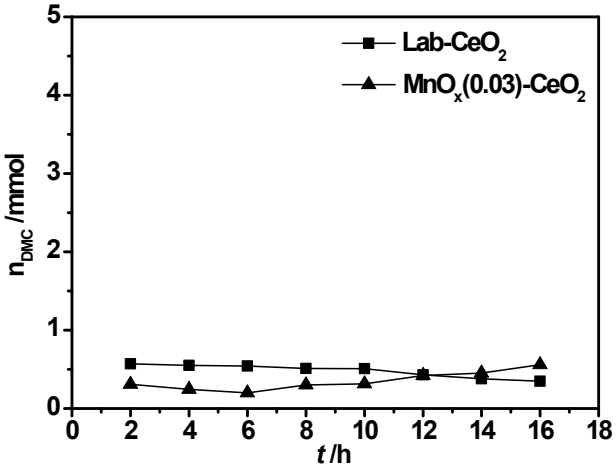


Figure S1 The n_{DMC} versus time profile over Lab-CeO_2 (A) and MnO_x (0.03)-CeO_2 (B) catalysts. Reaction condition: BA: CH_3OH = 5 mmol : 200 mmol, T = 170 ^oC, P = 5.0 MPa, catalyst 0.3 g.

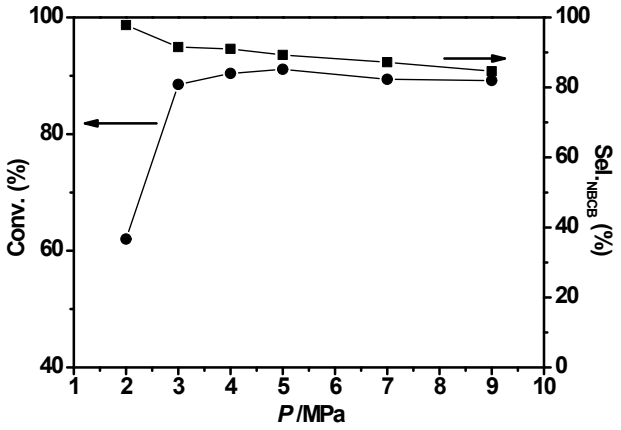


Figure S2 The effect of pressure on the reaction of BA+CO_2+CH_3OH over the MnO_x (0.03)-CeO_2 catalyst. Reaction condition: BA: CH_3OH = 5 mmol : 500 mmol, T = 170 ^oC, t = 8 h, catalyst 0.3 g.

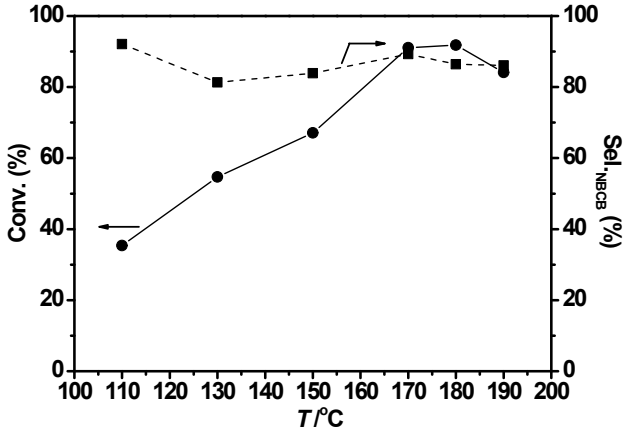


Figure S3 The effect of temperature in the reaction of BA+CO_2+CH_3OH over the MnO_x (0.03)-CeO_2 catalyst. Reaction condition: BA: CH_3OH = 5 mmol : 500 mmol, P = 5 MPa, t = 8 h, catalyst 0.3 g.

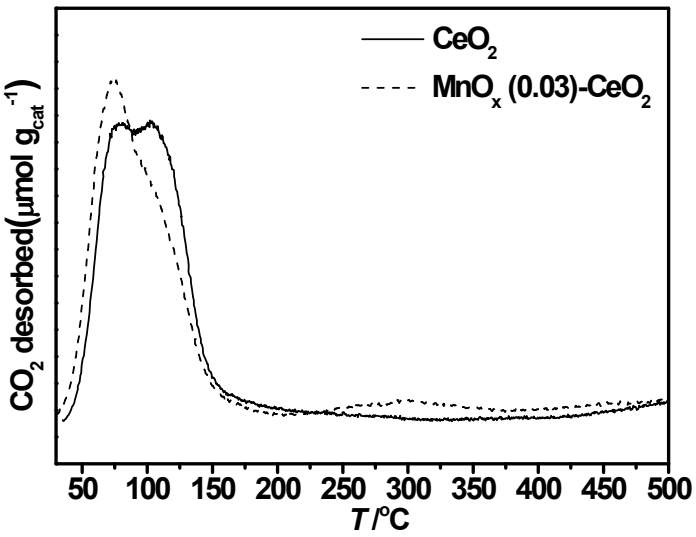


Figure S4 CO_2-TPD profiles of Lab-CeO_2 (solid line) and MnO_x(0.03)-CeO_2 (dashed line). Conditions: He 50 ml·min^{-1}; CO_2 adsorbed at 25 ^{o}C for 30 min.