Supporting Information

Continuous CO₂ esterification to diethyl carbonate (DEC) at atmospheric pressure: Application of porous membranes for *in-situ* H₂O removal

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Figure SI1 The dependence of reaction time and catalyst weight on the formed DEC amount in the reaction of C₂H₅OH and CO₂ over Ce_{0.8}Zr_{0.2}O₂ in fixed bed reactor (FBR). Catalyst weight: 2.5 g (\Box), 2.0 g (\circ). Reaction condition: reaction temperature = 100 °C, n_{Ethanol}/n_{CO2}=3:1, $\dot{n}_{CO2,feed}$ = 62 mmol/h.

With a higher available catalyst surface steady state was reached faster, e.g. different amounts of $Ce_{0.8}Zr_{0.2}O_2$ were placed into the reactor and the production of DEC over time was recorded. When 2.5 g of catalyst were used, the amount of DEC formed increased with the reaction time faster than with only 2.0 g catalyst. In each of the two cases, a flattening in DEC productivity was detected after a certain time. DEC amount reached a value of about 0.039 mmol h⁻¹ over 2.5 and 0.030 mmol h⁻¹ over 2.0 g of catalyst in steady state.



Figure SI2 a) Effect of n_{EtOH}/n_{CO2} on the amount of DEC formed. Reaction condition: $\dot{n}_{CO2,feed} = 62 \text{ mmol/h}$, 100 °C. b) Effect of GHSV on the amount of DEC formed. Reaction condition: 100 °C, $n_{EtOH}/n_{CO2} = 3:1$. C) Effect of temperature on the amount of DEC formed. Reaction condition: $n_{EtOH}/n_{CO2} = 3:1$, GHSV = 3200 h⁻¹, $\dot{n}_{CO2,feed} = 62 \text{ mmol/h}$.

Under different conditions it also can be seen that the DEC amount increases in all cases with the reaction time and eventually reaches steady state after several hours.

n _{Ethanol} /n _{CO2} (mmol/mmol)	n _{CO2,feed} (mmol h ⁻¹)	Feed flux CO ₂ (mL/min)	Sweep flux CO ₂ (mL/min)	GHSV (h ⁻¹)	Temperature (°C)	Productivity (mmol L ⁻¹ h ⁻¹)	DEC amount (mmol)
2	62	25	25	3000	100	20	0.027 ±0.002
3	62	25	25	3900	100	27	0.037±0.001
4	62	25	25	4900	100	16	0.020±0.003
3	62	25	10	3000	100	19	0.024 ±0.004
3	62	25	50	3000	100	16	0.021 ±0.001
3	25	10	10	1600	100	9	0.010 ±0.003
3	124	50	50	7900	100	47	0.065 ±0.003
3	248	100	100	16800	100	47	0.066 ±0.001

Table SI1 The effect of reaction conditions on the formed DEC amount and productivity overMFI-57 CMR, 2.0 g $Ce_{0.8}Zr_{0.2}O_2$.



Figure SI3 The dependence of reaction time on the formed DEC amount from the reaction of C_2H_5OH and CO_2 over $Ce_{0.8}Zr_{0.2}O_2$ in the FBR and CMR. Catalyst weight: 2.0 g. Reaction condition: reaction temperature: 100 °C, $n_{Ethanol}/n_{CO2}$ =3:1, GHSV=980 h⁻¹, $\dot{n}_{CO2,feed}$ = 62 mmol/h.

Catalyst	Temperature (°C)	Pressure (bar)	Reaction time (h)	Catalyst weight (g)	Reaction mode	DEC Yield	Ref.
CeO ₂	140	80	2	1	Batch	0.176%	17
ZrO ₂ (with3 A molecular sieve)	150	70	2	ZrO ₂ :0.5g; 3A:1g	Batch	-	18
CeO ₂	180	90	25	1	Batch	-	19
CeO ₂ -ZrO ₂	110	60	2	1.4	Batch	0.200%	15
CeO ₂	130	50	2	0.1	Batch	0.205%	16
$Ce_{0.8}Zr_{0.2}O_{2}$	100	1	2	2	Continuous	0.056% ^{a)}	This work
Ce _{0.8} Zr _{0.2} O ₂ (with membrane)	100	1	2	2	Continuous	0.060% ^{a)}	This work

Table SI2 Comparative analysis of DEC yield on different catalysts and reaction modes used for the direct synthesis of DEC from CO_2 .

 $^{a)}$ Reaction condition: reaction temperature: 100 °C, $n_{Ethanol}/n_{CO2}$ =3:1, CO₂ feed flux: 25mL/min (in case of CMR, feed flux=sweep flux)