Supporting Information

Transesterification of dimethyl carbonate with ethanol to form ethyl methyl carbonate and diethyl carbonate: a comprehensive study on chemical equilibrium and reaction kinetics

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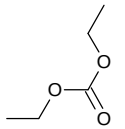
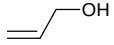
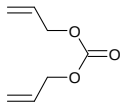
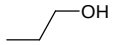
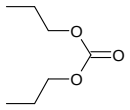
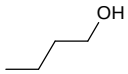
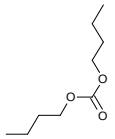
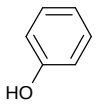
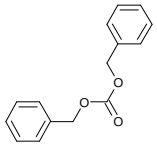
Transesterification of DMC with different alcohols

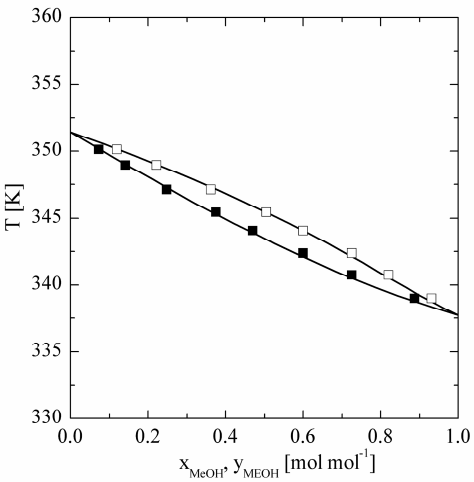
Table S-1: Transesterification of dimethyl carbonate with different alcohols reported in the literature (modified and expanded from Shaikh et al.[1]).

Hydroxy component (CAS number)		Catalyst (CAS number)	Reaction conditions (T, P)	Desired product (CAS number)		Yield	Ref.
	Ethanol (64-17-5)	Dipotassium carbonate (584-08-7) and phase transferring agent	303–373 K, 101.3 kPa		Diethyl carbonate (105-58-8)	45 %	(2)
		Dipotassium carbonate (584-08-7) coated on polyethylene glycol	348 K, 101.3 kPa			26 %	(3, 4)
		Potassium fluoride (nda*) supported on alumina	353 K, 101.3 kPa			59 %	(5)
		Samarium(III) trioxide (12060-58-1)	373 K, nda*			3 %	(6)
		Lanthanum nitrate hexahydrate (10277-43-7)	353 K, 101.3 kPa			61 %	(7)
		Lewatit K1221	348 K, 101.3 kPa			12 %	(3)
		Nafion SAC-13	348 K, 101.3 kPa			10 %	(3)
	2-Propen-1-ol (107-18-6)	Sodium (7440-23-5) and 15-Crown-5 (33100-27-5)	nda*		Diallyl carbonate (15022-08-9)	95 %	(8)
		Bis(butyl)tin oxide (818-08-6)	373–453 K, 101.3 kPa			50 %	(1)
		Sodium methoxide (124-41-4)	403 K, 20.27–101.3 kPa			99 %	(9)
	1-Propanol (71-23-8)	Dipotassium carbonate (584-08-7) coated on Hβ molecular sieves	363 K, 101.3 kPa		Dipropyl carbonate (623-96-1)	56 %	(10)
		Dipotassium carbonate (584-08-7) coated on NaY molecular sieves	359 K, 101.3 kPa			36 %	(11)
	1-Butanol (71-36-3)	Bis(butyl)tin oxide (818-08-6)	373–453 K, 101.3 kPa		Di-n-butyl carbonate (542-52-9)	48 %	(1)
	Phenol (108-95-2)	Vanadium(V) oxide (1314-62-1)	423–453 K, 101.3 kPa		Diphenyl carbonate (102-09-0)	40 %	(12)
		Tetrabutoxytitanium (5593-70-4)	433–475K, > 101.3 kPa			64 %	(13)
		Ammonium decamolybdate (nda)	473 K, 1000 kPa			nda*	(14)

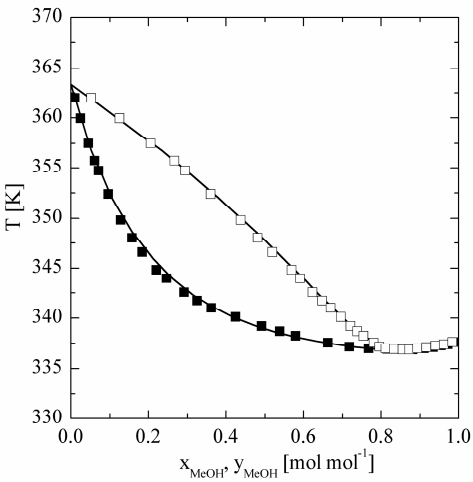
*nda: no data available

Binary vapour-liquid equilibria

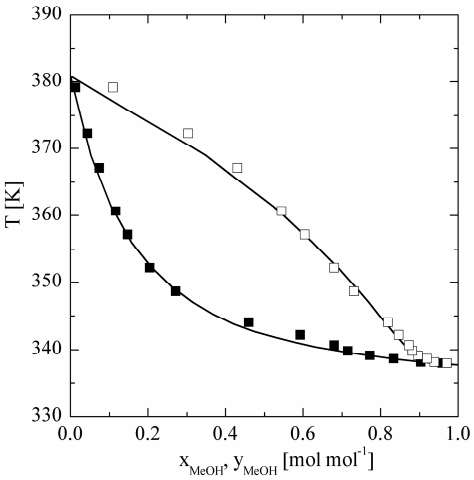
Figure S-1displays the vapour-liquid equilibria of all binary systems. Compared are the experimental values with the simulated values obtained from the UNIQUAC model.



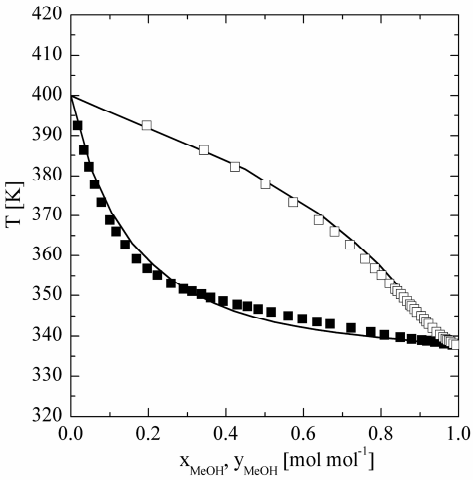
(a) Methanol/Ethanol



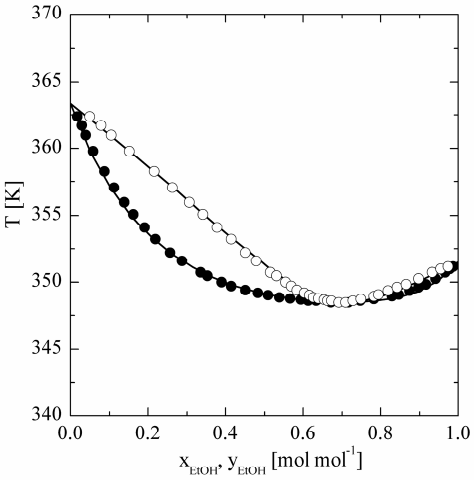
(b) Methanol/Dimethyl carbonate



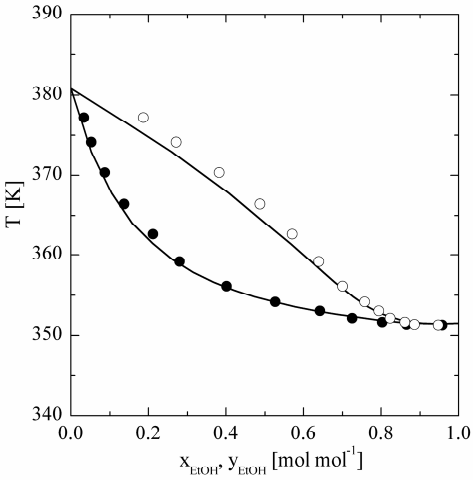
(c) Methanol/Ethyl methyl carbonate



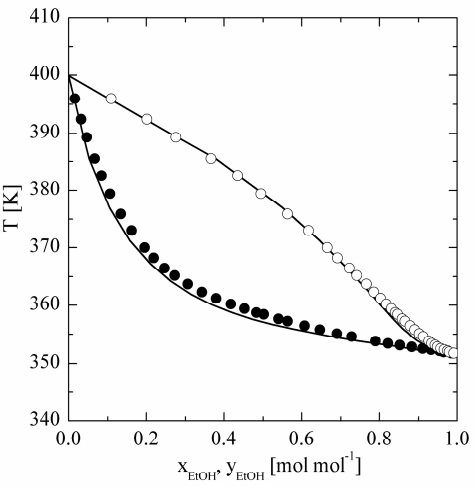
(d) Methanol/Diethyl carbonate



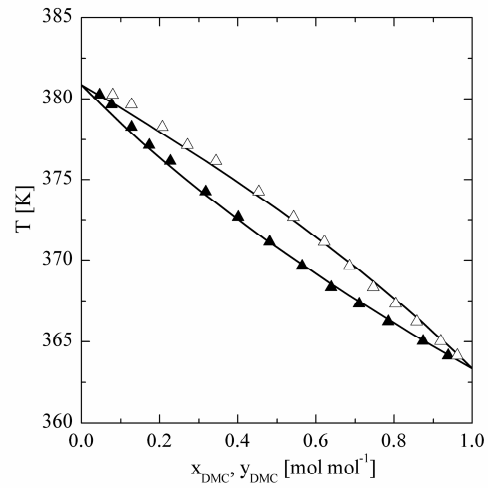
(e) Ethanol/Dimethyl carbonate



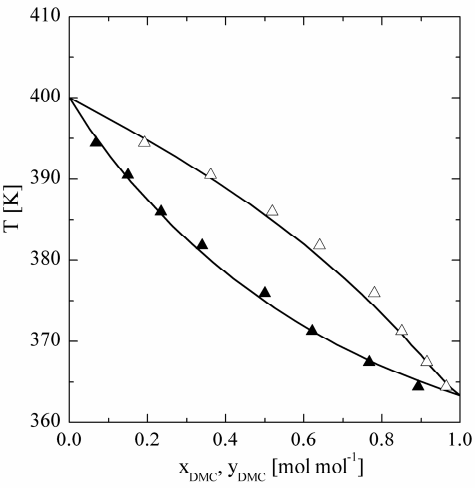
(f) Ethanol/Ethyl methyl carbonate



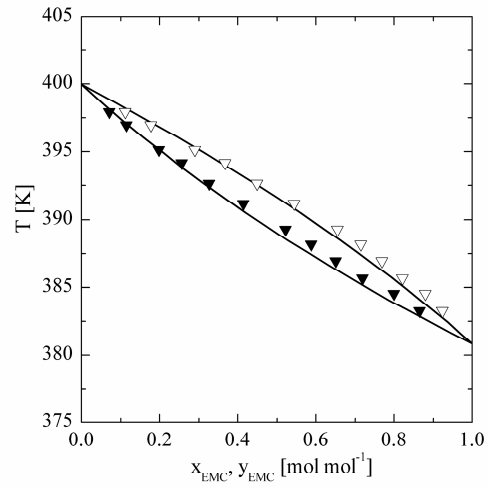
(g) Ethanol/Diethyl carbonate



(h) Dimethyl carbonate/Ethyl methyl carbonate



(i) Dimethyl carbonate/Diethyl carbonate



(j) Ethyl methyl carbonate/Diethyl carbonate

Figure S-1: Binary vapour-liquid equilibria at P = 101.3 kPa. The symbols represent the experimental data, the lines represent the calculated data obtained from the UNIQUAC model.

Experimental data of chemical equilibrium measurements

Table S-2 provides the experimentally determined chemical equilibrium molar fractions, x_i^{eq}, of each component and the molar-based chemical equilibrium constants, $K_{x,Ri}$, for the experiments E1–E21. Further, the corresponding activity coefficients, γ_i^{eq}, and activity-based chemical equilibrium constants, $K_{a,Ri}$, are given.

Table S-2: Experimental results of chemical equilibrium measurements. Note that the molar fractions were calculated from reconciled mass fractions.

		Molar-based							Activity-based						
	T	x_{MeOH}^{eq}	x_{EtOH}^{eq}	x_{DMC}^{eq}	x_{EMC}^{eq}	x_{DEC}^{eq}	$K_{x,R1}$	$K_{x,R2}$	γ_{MeOH}^{eq}	γ_{EtOH}^{eq}	γ_{DMC}^{eq}	γ_{EMC}^{eq}	γ_{DEC}^{eq}	$K_{a,R1}$	$K_{a,R1}$
	[K]	[mol·mol^{-1}]	[mol·mol^{-1}]	[mol·mol^{-1}]	[mol·mol^{-1}]	[mol·mol^{-1}]	[-]	[-]	[-]	[-]	[-]	[-]	[-]	[-]	[-]
E1	323	0.2875	0.4608	0.0454	0.1238	0.0825	1.70	0.42	1.1251	1.0915	1.5521	1.8386	1.7963	2.08	0.42
E2	323	0.2869	0.4610	0.0458	0.1243	0.0821	1.69	0.41	1.1254	1.0918	1.5520	1.8372	1.7935	2.06	0.41
E3	323	0.3119	0.3763	0.0775	0.1568	0.0776	1.68	0.41	1.1834	1.1400	1.4141	1.6520	1.5333	2.04	0.40
E4	323	0.2905	0.4553	0.0465	0.1241	0.0835	1.70	0.43	1.1275	1.0933	1.5433	1.8295	1.7853	2.09	0.42
E5	323	0.2876	0.4608	0.0448	0.1236	0.0833	1.72	0.42	1.1250	1.0914	1.5503	1.8386	1.7984	2.10	0.42
E6	333	0.2881	0.4599	0.0450	0.1241	0.0829	1.73	0.42	1.1207	1.0895	1.5441	1.7976	1.7803	2.07	0.43
E7	333	0.2885	0.4615	0.0447	0.1227	0.0826	1.72	0.42	1.1192	1.0881	1.5505	1.8039	1.7879	2.05	0.43
E8	333	0.3177	0.3472	0.0915	0.1681	0.0755	1.68	0.41	1.2007	1.1566	1.3703	1.5632	1.4448	1.99	0.39
E9	343	0.2873	0.4653	0.0431	0.1212	0.0832	1.74	0.42	1.1125	1.0842	1.5505	1.7747	1.7839	2.04	0.44
E10	343	0.2884	0.4658	0.0433	0.1200	0.0825	1.72	0.43	1.1113	1.0831	1.5569	1.7800	1.7893	2.01	0.44
E11	343	0.3183	0.3519	0.0887	0.1643	0.0768	1.68	0.42	1.1878	1.1474	1.3787	1.5506	1.4592	1.95	0.41
E12	353	0.2845	0.4680	0.0436	0.1223	0.0815	1.71	0.41	1.1081	1.0824	1.5474	1.7397	1.7636	1.96	0.42
E13	353	0.2858	0.4666	0.0426	0.1212	0.0838	1.74	0.42	1.1083	1.0825	1.5426	1.7384	1.7657	2.01	0.44
E14	353	0.3170	0.3517	0.0889	0.1666	0.0759	1.69	0.41	1.1819	1.1445	1.3759	1.5238	1.4491	1.93	0.40
E15	363	0.2849	0.4729	0.0422	0.1195	0.0805	1.71	0.41	1.1002	1.0770	1.5572	1.7221	1.7654	1.93	0.43
E16	363	0.2850	0.4661	0.0453	0.1217	0.0818	1.64	0.41	1.1051	1.0815	1.5384	1.7022	1.7378	1.86	0.43
E17	363	0.3231	0.3550	0.0872	0.1613	0.0735	1.68	0.42	1.1669	1.1324	1.3967	1.5219	1.4654	1.89	0.41
E18	373	0.2863	0.4662	0.0439	0.1210	0.0826	1.69	0.42	1.1002	1.0787	1.5345	1.6749	1.7259	1.89	0.44
E19	383	0.2851	0.4668	0.0450	0.1212	0.0819	1.65	0.41	1.0968	1.0773	1.5290	1.6444	1.7033	1.80	0.44
E20	393	0.2853	0.4689	0.0431	0.1199	0.0827	1.69	0.42	1.0916	1.0742	1.5276	1.6226	1.6939	1.83	0.45
E21	403	0.2832	0.4720	0.0432	0.1200	0.0816	1.67	0.41	1.0872	1.0720	1.5263	1.5996	1.6777	1.77	0.43

Experimental data of kinetics experiments

Table S-3 and Table S- 4 provide the experimentally determined molar fractions of each component for the example of the kinetic experiments E10 and E13, respectively.

Table S-3: Experimental results of the kinetic experiment E10. The molar fractions were calculated from reconciled mass fractions.

Time [min]	x_{MeOH} [mol·mol^{-1}]	x_{EtOH} [mol·mol^{-1}]	x_{DMC} [mol·mol^{-1}]	x_{EMC} [mol·mol^{-1}]	x_{DEC} [mol·mol^{-1}]
0	0	0.7499	0.2501	0	0
1	0.1644	0.5866	0.1027	0.1215	0.0248
2	0.2292	0.5233	0.0629	0.1396	0.0450
3	0.2568	0.4976	0.0506	0.1357	0.0593
4	0.2680	0.4855	0.0474	0.1325	0.0666
5	0.2717	0.4810	0.0456	0.1297	0.0720
6	0.2782	0.4748	0.0444	0.1272	0.0754
7	0.2841	0.4710	0.0445	0.1249	0.0754
10	0.2860	0.4674	0.0437	0.1228	0.0801
20	0.2889	0.4644	0.0433	0.1210	0.0826
115	0.2888	0.4650	0.0432	0.1202	0.0828
125	0.2884	0.4658	0.0433	0.1200	0.0825

Table S- 4: Experimental results of the kinetic experiment E13. The molar fractions were calculated from reconciled mass fractions.

Time [min]	x_{MeOH} [mol·mol^{-1}]	x_{EtOH} [mol·mol^{-1}]	x_{DMC} [mol·mol^{-1}]	x_{EMC} [mol·mol^{-1}]	x_{DEC} [mol·mol^{-1}]
0	0	0.7536	0.2464	0	0
1	0.2042	0.5482	0.0817	0.1248	0.0412
2	0.2538	0.4986	0.0541	0.1303	0.0632
3	0.2747	0.4778	0.0449	0.1278	0.0749
4	0.2803	0.4721	0.0435	0.1249	0.0792
5	0.2831	0.4692	0.0430	0.1232	0.0815
6	0.2755	0.4770	0.0474	0.1219	0.0782
7	0.2824	0.4700	0.0433	0.1232	0.0811
10	0.2853	0.4672	0.0426	0.1217	0.0832
20	0.2863	0.4661	0.0424	0.1211	0.0841
110	0.2862	0.4662	0.0423	0.1215	0.0838
125	0.2858	0.4666	0.0426	0.1212	0.0838

Calculation of standard enthalpy and Gibbs energy of reaction

In addition to the evaluation of experimental data, the standard enthalpies and the standard Gibbs energies of reaction can be obtained by calculating them from tabulated, component-specific standard enthalpies of formation $\Delta H_{f,i}^{0}$ and Gibbs energies of formation $\Delta G_{f,i}^{0}$:

$$\Delta H_r^0 = \sum_{i=1}^{n_C} \nu_i \cdot \Delta H_{f,i}^0 \qquad \text{(A-1)}$$

$$\Delta G_r^0 = \sum_{i=1}^{n_C} \nu_i \cdot \Delta G_{f,i}^0 \qquad \text{(A-2)}$$

Because the transesterification of DMC with ethanol investigated in this study occurs in the liquid phase, the corresponding standard thermodynamic data must refer to the liquid phase. Liquid-phase standard enthalpies of formation were found in the literature for all of the components except for EMC. A QSPR model (QSPR: quantitative structure-property relationship) published by Vatani et al.[15] was used to calculate the missing EMC value. In contrast, liquid-phase standard Gibbs energies of formation were only reported for methanol and ethanol. Because gas-phase standard Gibbs energies of formation were found for DMC and DEC, we followed an approach proposed by Jensen et al.[16] to determine the corresponding values for the liquid-phase standard state. For EMC, the averaged values from the DMC and DEC data were used. According to Jensen et al., the liquid-phase standard Gibbs energy of formation can be related to the gas-phase value by the following equation:

$$\frac{\Delta G_{f,i}^{0,l}}{\Re \cdot T} = \frac{\Delta G_{f,i}^{0,g}}{\Re \cdot T} + \frac{1}{\Re} \cdot \int_{T_{b,i}}^{T} \frac{\Delta H_{v,i}}{T^2} dT \qquad \text{(A-3)}$$

The temperature dependence of the enthalpy of vaporisation $\Delta H_{v,i}$ was considered using Kirchhoff's equation, where $\Delta H_{v,i}^{0}$ is the standard enthalpy of vaporisation of component *i*:[17]

$$\Delta H_{v,i}(T) = \Delta H_{v,i}^0 + \int_{T^0}^{T} \left(c_{P,i}^g - c_{P,i}^l \right) dT \qquad \text{(A-4)}$$

For a better overview, the standard thermodynamic data of the components involved in the transesterification of DMC with ethanol are listed in Table S-5. Furthermore, the required polynomial constants are given in Table S-6, and these values are needed to calculate the temperature dependence of the molar heat capacities $c_{P,i}$.

Table S-5: Standard thermodynamic data for the components involved in the transesterification of DMC with ethanol for the liquid-phase standard state.

	MeOH[18]	EtOH[18]	DMC[19,20]	EMC	DEC[19,21]
Standard enthalpy of formation, $\Delta H_{f,i}^{0,l}$ [kJ·mol^{-1}]	-239.20	-277.60	-605.27	-645.80[a]	-682.65
Standard Gibbs energy of formation, $\Delta G_{f,i}^{0,l}$ [kJ·mol^{-1}]	-166.60	-174.80	-459.46[c]	-468.86[c]	-475.62[c]
Standard enthalpy of vaporisation, $\Delta H_{v,i}^{0}$ [kJ·mol^{-1}]	37.43	42.32	37.70	41.025[b]	44.35

[a] calculated with the QSPR model published by Vatani et al.[15].

[b] averaged value from the DMC and DEC data.

[c] calculated with Equation A-3 using the following gas-phase standard Gibbs energies of formation: $\Delta G_{f,DMC}^{0,g}$ = -452.40 kJ·mol^{-1} (Ref. 22), $\Delta G_{f,EMC}^{0,g}$ = -458.53 kJ·mol^{-1} (averaged value from the DMC and DEC data), $\Delta G_{f,DEC}^{0,g}$ = -464.65 kJ·mol^{-1} (Ref. 22).

Table S-6: Standard molar heat capacities in the gas ($c_{P,i}^{g}$) and liquid phase ($c_{P,i}^{l}$) needed in Equation A-4. These values represent the polynomial constants needed to calculate the temperature dependence: $c_{P,i} = a + b \cdot T + c \cdot T^2 + d \cdot T^3$.[17]

	$c_{P,i}^{g}$	[J·mol^{-1}·K^{-1}]	MeOH[23]	EtOH[23]	DMC[24]	EMC[a]	DEC[24]
Gas phase	*a*	[J·mol^{-1}·K^{-1}]	57.01	63.56	67.59	50.15	85.67
	b	[J·mol^{-1}·K^{-2}]	-0.21	-0.27	-0.16	0.27	-0.22
	c	[J·mol^{-1}·K^{-3}]	7.00E-04	1.30E-03	1.30E-03	1.00E-05	2.00E-03
	d	[J·mol^{-1}·K^{-4}]	-6.00E-07	-1.00E-06	-2.04E-06	2.34E-06	-4.08E-06
	$c_{P,i}^{l}$	[J·mol^{-1}·K^{-1}]	MeOH[23]	EtOH[23]	DMC[25]	EMC[b]	DEC[26]
Liquid phase	*a*	[J·mol^{-1}·K^{-1}]	20.64	22.38	63.68	43.73	100.05
	b	[J·mol^{-1}·K^{-2}]	0.59	0.59	0.24	0.64	0.08
	c	[J·mol^{-1}·K^{-3}]	-2.00E-03	-1.70E-03	-2.00E-05	-1.20E-03	1.10E-03
	d	[J·mol^{-1}·K^{-4}]	2.74E-06	2.96E-06	2.43E-07	1.87E-06	-6.06E-07

[a] Estimated with the group-contribution model of Joback et al.[27]

[b] Estimated with the group-contribution model of Zábranský et al.[28]

Effect of the initial molar reactant ratio

A kinetic model of a reaction, in this work for the homogeneously catalysed transesterification reaction of DMC with EtOH, must be able to describe the reaction kinetics at different temperatures, catalyst molar fractions and also at different compositions of the liquid phase. The latter is especially important for reactive distillation processes because the reaction often takes place over a large area of the composition space. Consequently, several experiments with two different initial reactant ratios between EtOH and DMC were performed to study the influence of the initial composition on the conversion of EtOH and DMC. Figure S-2 compares the experimentally determined temporal course of reactant conversions for E10 and E11. Both experiments were carried out at the same temperature (343 K) and with the same molar fraction of catalyst ($4 \cdot 10^{-4}$ mol·mol^{-1}) but with different initial reactant ratios: $\chi_{EtOH/DMC}$ = 2.0 for E11 and $\chi_{EtOH/DMC}$ = 3.0 for E10. The symbols represent the experimentally determined values, and the lines represent the predicted results of the kinetic model using the individually fitted forward reaction rate constants.

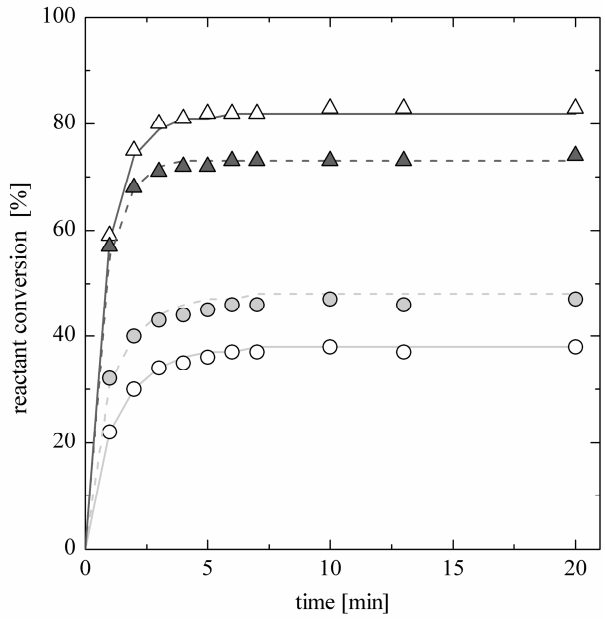


Figure S-2: Effect of the initial molar ratio between ethanol and dimethyl carbonate on the temporal course of reactant conversions. Closed symbols represent experiment E10 ($\chi_{EtOH/DMC}$ =3.0) and open symbols represent experiment E11 ($\chi_{EtOH/DMC}$ =2.0). The symbols are experimental values, and the lines are the values predicted with the kinetic model: -●- ethanol, -▲- dimethyl carbonate.

Chemical equilibrium is achieved in both experiments after nearly the same time, which supports the fact that the reaction rate constants are not affected by the initial reactant composition. In contrast, Grob et al.[29]investigated the homogeneously catalysed esterification reaction of 1-Butanol with acetic acid and observed a strong influence of the initial molar ratio on the reaction rate constants. They found that the mixture composition has an influence on the activity of the catalyst sulphuric acid and thus on the reaction kinetics. We did not make a similar observation

during our experimental study of the transesterification reaction of dimethyl carbonate with ethanol. However, we only investigated two different initial molar ratios between EtOH and DMC. Nevertheless, Figure S-2 shows that the experimental reactant conversions are well in line with the predicted values, even at a different liquid mixture composition. Thus, our proposed kinetic model of the homogeneously catalysed transesterification reaction of dimethyl carbonate with ethanol seems to be suitable to reproduce the experimental results.

Linear relationship between reaction rate and catalyst molar fraction

The kinetic model assumes a linear relationship between the reaction rate and the molar fraction of catalyst. To verify this assumption, Figure S-3 shows the time required to reach 98 % of the chemical equilibrium as a function of the reciprocal molar fraction of catalyst. At the highest catalyst molar fraction ($2 \cdot 10^{-3}$ mol·mol^{-1}, E5), 98 % of the chemical equilibrium was achieved after just 2 minutes. This time increased to about 30 minutes for the lowest catalyst molar fraction ($4 \cdot 10^{-4}$ mol·mol^{-1}, E1). Overall, the linear dependence of the reaction rate on the catalyst molar fraction assumed in the kinetic model is verified.

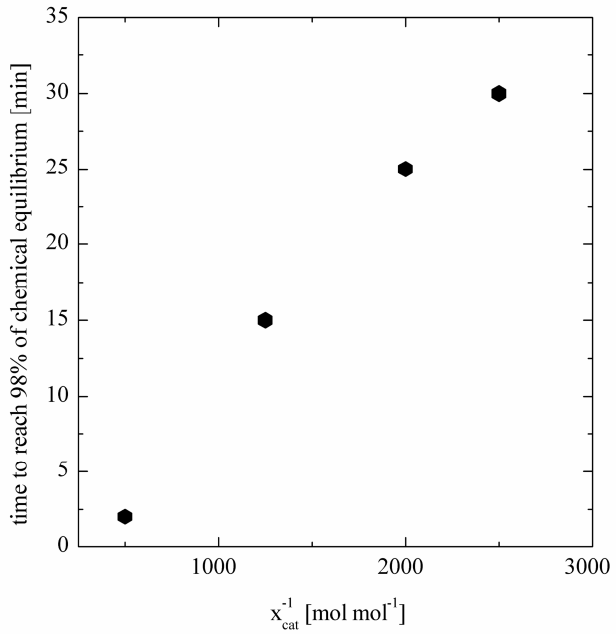


Figure S-3: Effect of the applied catalyst molar fraction on the time to reach 98 % of the chemical equilibrium conversion. The reciprocal catalyst molar fraction x_{cat}^{-1} is plotted here. The experiments were performed with the same initial molar ratio between ethanol and dimethyl carbonate ($\chi_{EtOH/DMC}$ = 3.0) and at the same temperature of 323 K, but with varying catalyst molar fractions.

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