Surface reaction kinetics of the methanol synthesis and the water-gas shift reaction on $Cu/ZnO/Al_2O_3$

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Supplementary Material

1. Thermodynamic Consistency – Solving the minimization problem

The constrained minimization problem of the thermodynamic consistency can be solved with the method of the Lagrangean multipliers. The Lagrangean function is:

$$L\left(E^{+,TC}_{A,k},E^{-,TC}_{A,k},\Delta S^{\neq,+,TC}_{k},\Delta S^{\neq,-,TC}_{k},\beta^{+,TC}_{k},\beta^{-,TC}_{k},\lambda_{1-3m}\right) = \int_{T_1}^{T_2}\left\{\sum_{k=1}^{Nr} w_k \cdot \left\{\left[E_{A,f} - T\cdot\left(\Delta S^{\neq,+,TC}_{k} + \ln(T)\cdot\beta^{+,TC}_{k}\right) - \left(E^{+,Orig.}_{A,k} - T\cdot\Delta S^{\neq,+,Orig.}_{k}\right)\right]^2 + \left[E_{A,rk}{}^{TC} - T\cdot\left(\Delta S^{\neq,-,TC}_{k} + \ln(T)\cdot\beta^{-,TC}_{k}\right) - \left(E^{-,Orig.}_{A,k} - T\cdot\Delta S^{\neq,-,Orig.}_{k}\right)\right]^2\right\} dT\right\} + \sum_{m=1}^{Nm}\left(\lambda_{1m}\cdot q_{1m} + \lambda_{2m}\cdot q_{2m} + \lambda_{3m}\cdot q_{3m}\right) \quad \text{(S1)}$$

Where $\lambda_{1\text{-}3,m}$ are the Lagrangean multipliers. The solution of this problem (minimum) lies when all partial derivatives of the Lagrangean function are zero.

$$\frac{\partial L}{\partial E^{+,TC}_{A,k}} = \frac{\partial L}{\partial E^{-,TC}_{A,k}} = \frac{\partial L}{\partial \Delta S^{\neq,+,TC}_{k}} = \frac{\partial L}{\partial \Delta S^{\neq,-,TC}_{k}} = \frac{\partial L}{\partial \beta^{+,TC}_{k}} = \frac{\partial L}{\partial \beta^{-,TC}_{k}} = \frac{\partial L}{\partial \lambda_{1-3m}} : \quad \text{(S2)}$$

The calculation of the partial derivatives leads to a linear system, whose solution gives the corrected values of E_A, $\Delta S^{\neq}$, and β.

2. Reactor simulation – Solving the differential equations of the Plug Flow Reactor (PFR)

The steady-state solution of the surface intermediate coverages (Eq. (45) in the article) can be found either by integrating the equations in time or by setting all time derivatives to zero and solving the non-linear algebraic system. The latter has a much lower computational time, but it requires a significantly close initial guess to converge to the correct answer.

Therefore, in this work, a database of initial guesses was built for different temperatures, pressures and gas phase concentrations, both by integrating the equations in time, and by solving the non-linear algebraic system of equations with initial guesses chosen by trial and error. With this database, an initial guess method was created (Fig. S3), which gives sufficiently good initial guesses for the studied region of operating conditions. This algebraic system has to be solved for each axial position in the reactor, as the coverage of the species vary along the reactor length. A scheme of the procedure used to solve the PFR model is described in Fig. S4. The numerical simulations were performed using the commercial software Matlab 2018. By informing the analytical Jacobian matrix of the algebraic system (Eq. (45) in the article) to the mathematical solver, the computational time dropped significantly.

3. Reactor simulation – Solving the differential equations of the Continuous Stirred Tank Reactor (CSTR)

The ordinary set of differential equations of the CSTR requires a certain strategy to be solved. On one hand, the steady-state achievement by integrating the gas phase equations in time (Eq. (48) in the article) usually requires an integration period around 1 to 10^3 s (depending on the GHSV), while the steady-state achievement by integrating the surface coverages equations (Eq. (49) in the article) usually requires an integration period around 10^{-5} to 10^{-3} s. This large difference between integration periods creates numerical instability if attempting to integrate all equations together, unless a tiny time step is used, e.g. 10^{-7} s, which would require a longish computational time.

On the other hand, setting all the time derivatives to zero (steady-state definition) and solving the non-linear system of equations is also challenging, as it would only converge to the correct answer if a sufficiently good initial guess for all y_j and θ_i is given. The strategy chosen was somewhat similar to the approach of the PFR: the gas phase equations (Eq. (48) in the article) were integrated in time until steady-state was achieved. For each time step, the time derivatives of the surface species equations (Eq. (49) in the article) were set to zero and the non-linear algebraic system was solved. A schematic description of the procedure used to solve the CSTR model is described in Fig. S5.

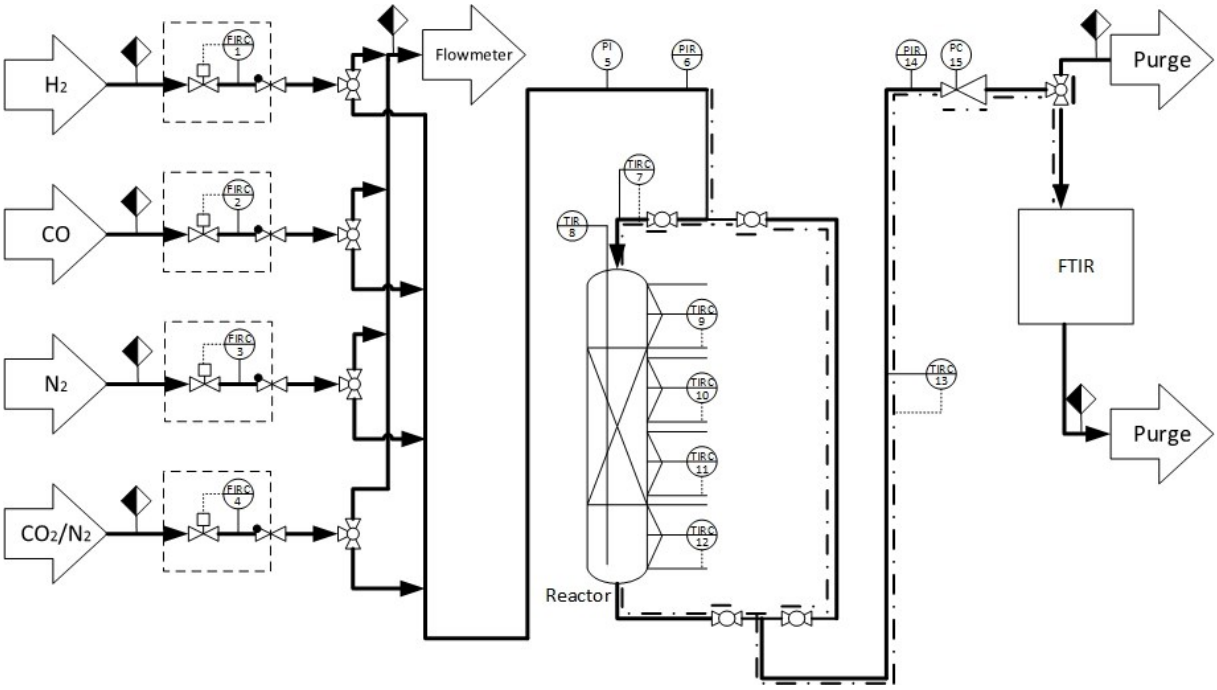

Fig. S1. Flow diagram of the experimental setup of the fixed-bed plug flow reactor.

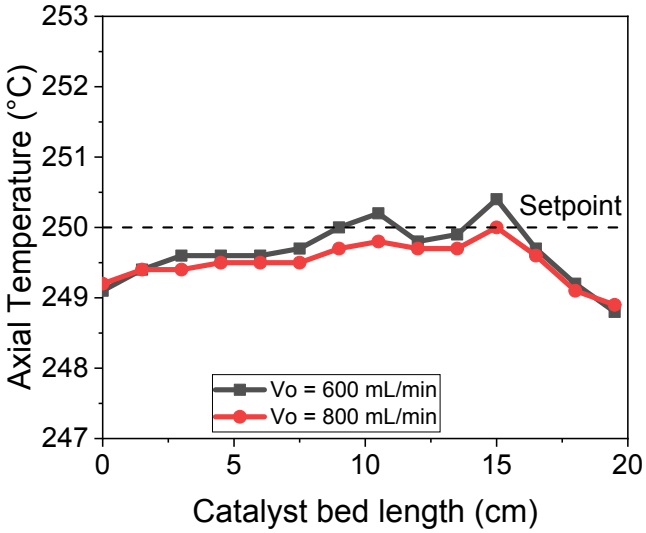

Fig. S2. Temperature axial profile of the reactor at 61 bar (abs.), 250 °C, $H_2/CO/CO_2/N_2$ = 55/12/3/30% v/v.

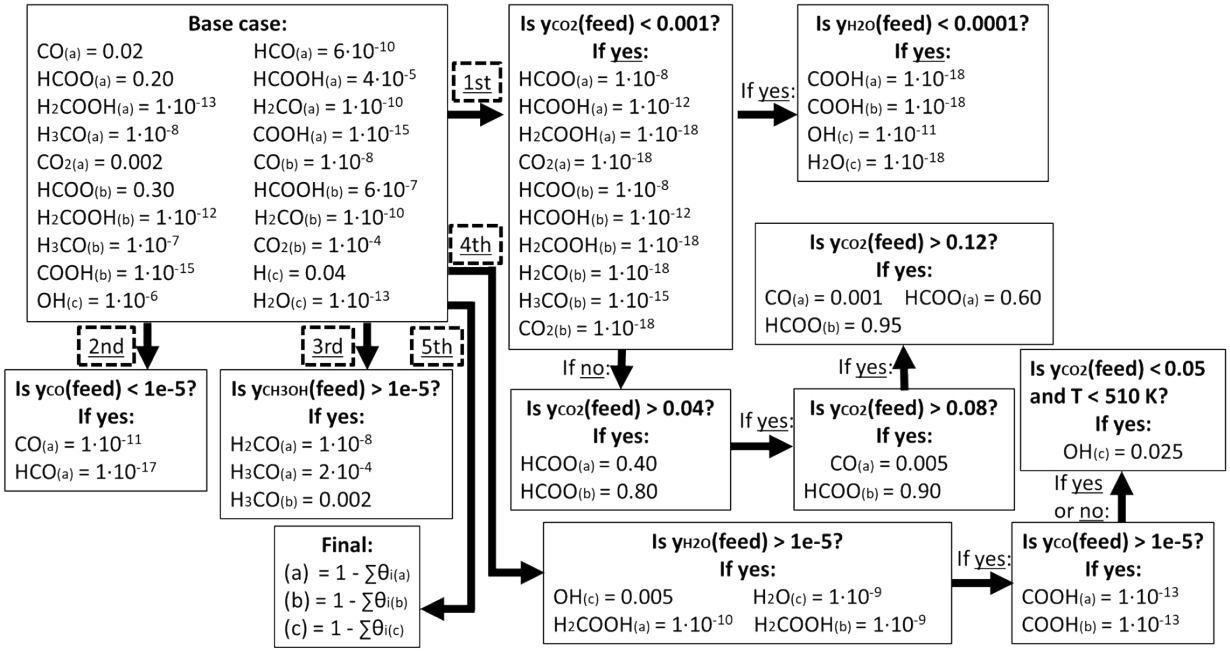

Fig. S3. Initial guess method: finding a proper initial guess to calculate the coverages with the Newton-Raphson method instead of integrating the differential equations in time.

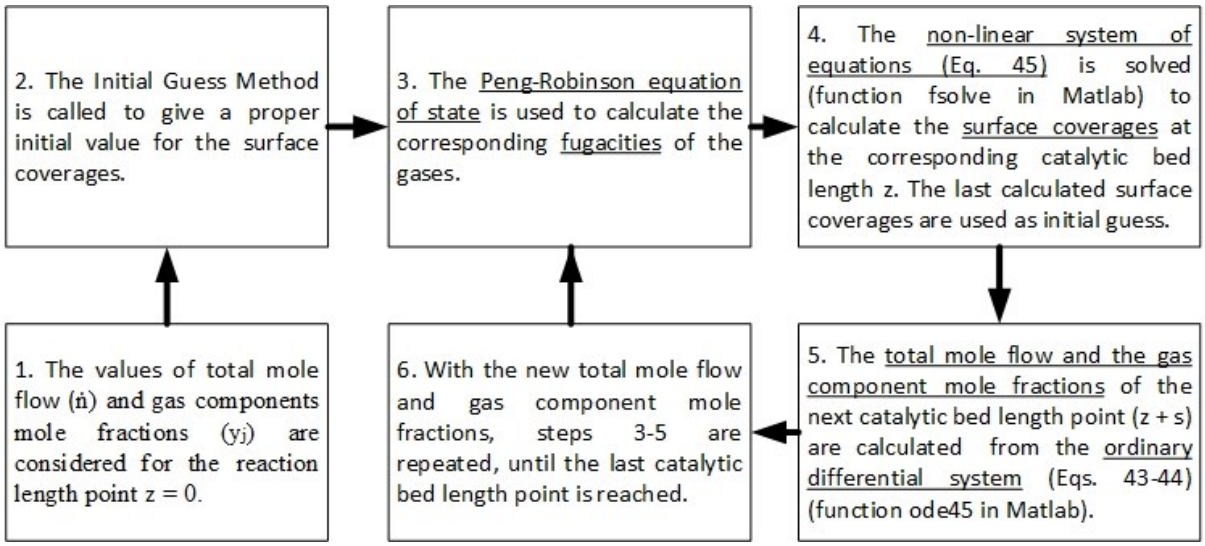

Fig. S4. Step-by-step method to solve the kinetic model of the PFR.

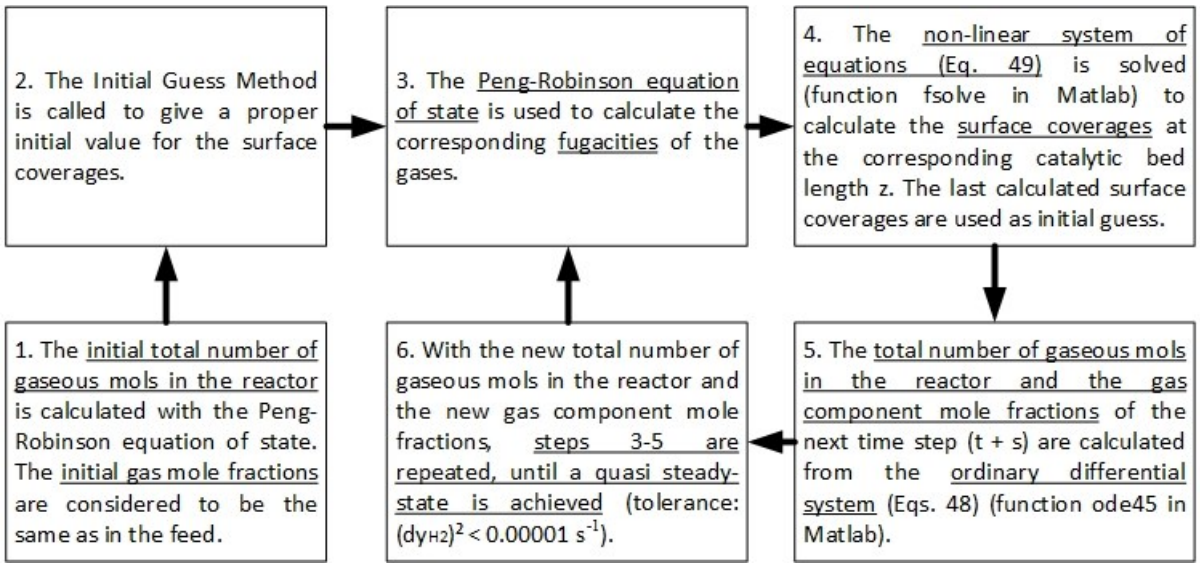

Fig. S5. Step-by-step method to solve the kinetic model of the CSTR.

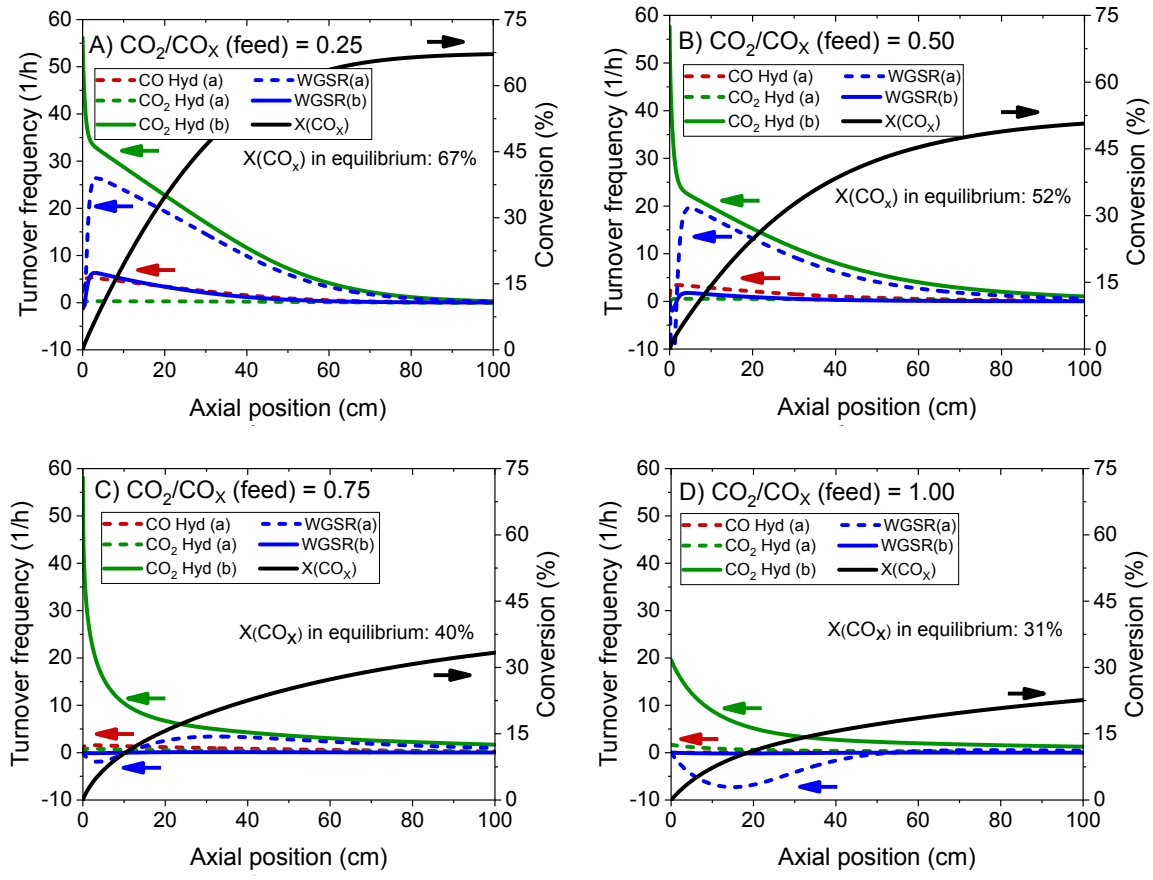

Fig. S6. Turnover frequency and conversion along a methanol synthesis reactor with a length of 100 cm. Operating conditions: 250 °C, 60 bar, GHSV = 4.8 $L_S \cdot h^{-1} \cdot (g_{cat})^{-1}$, feed concentration: H_2/CO_x = 80/20% v/v. A) CO_2/CO_x = 0.25. B) CO_2/CO_x = 0.50. C) CO_2/CO_x = 0.75. D) CO_2/CO_x = 1.00.

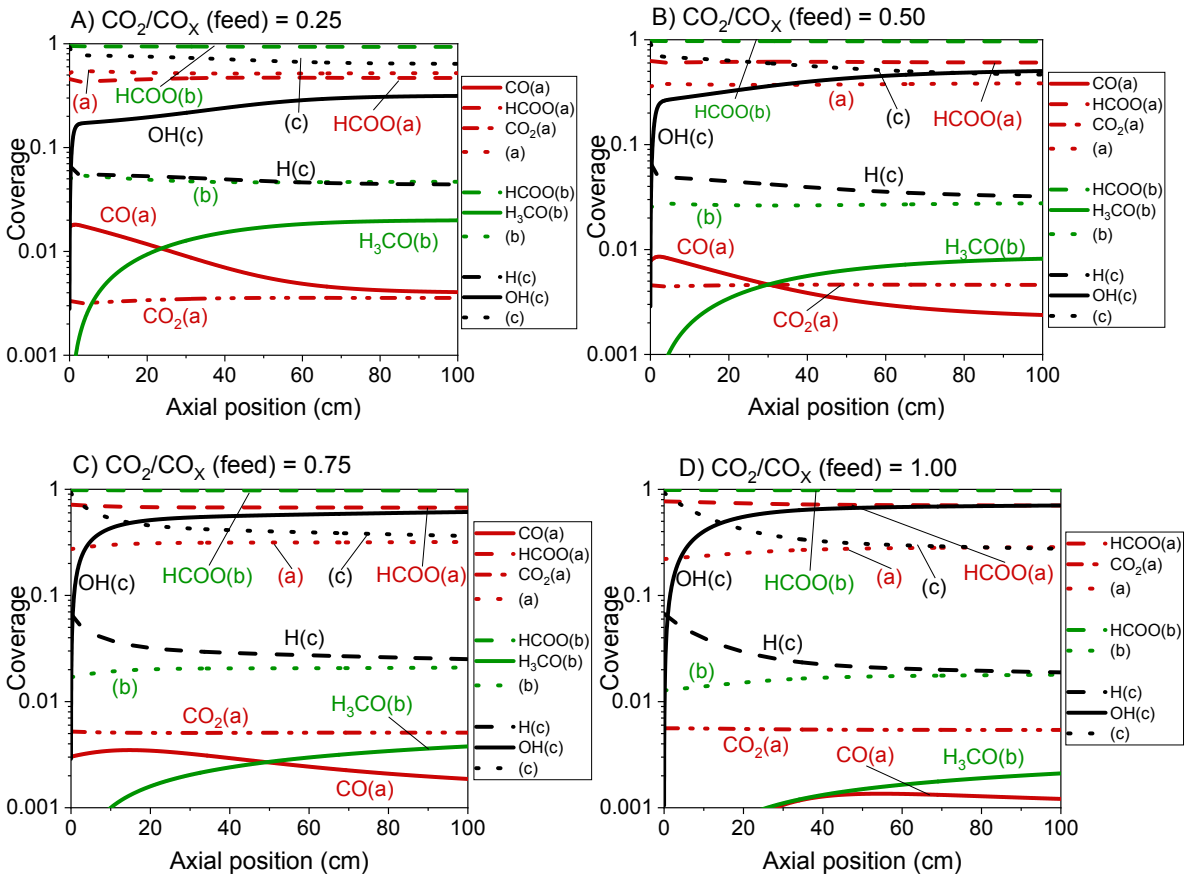

Fig. S7. Coverage of the surface species along the methanol synthesis reactor with a length of 100 cm. Operating conditions: 250 °C, 60 bar, GHSV = 4.8 $L_S \cdot h^{-1} \cdot (g_{cat})^{-1}$, feed concentration: H_2/CO_x = 80/20% v/v. A) CO_2/CO_x = 0.25. B) CO_2/CO_x = 0.50. C) CO_2/CO_x = 0.75. D) CO_2/CO_x = 1.00.

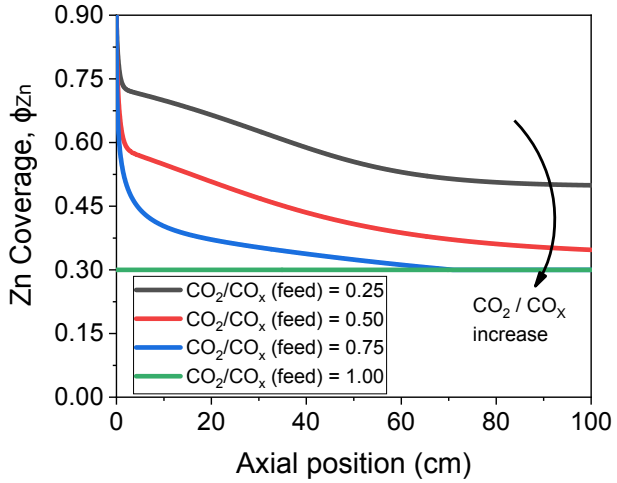

Fig. S8. Zinc coverage along the methanol synthesis reactor with a length of 100 cm. Operating conditions: 250 °C, 60 bar, GHSV = 4.8 $L_S \cdot h^{-1} \cdot (g_{cat})^{-1}$, feed concentration: H_2/CO_x = 80/20% v/v. A) CO_2/CO_x = 0.25. B) CO_2/CO_x = 0.50. C) CO_2/CO_x = 0.75. D) CO_2/CO_x = 1.00.

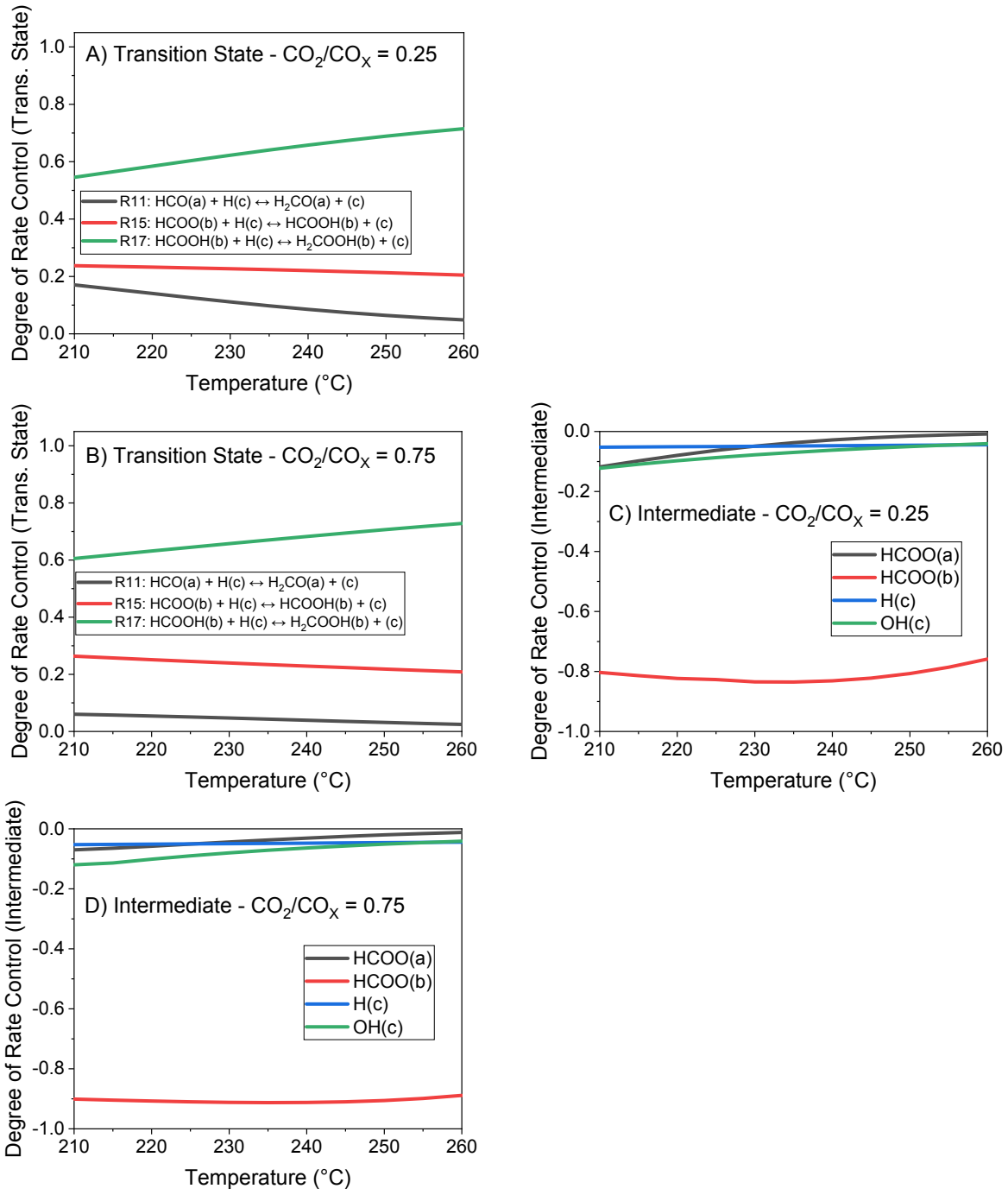

Fig. S9. Degree of Rate Control (DRC) analysis of the methanol production at 30 bar and 210-260 °C. Gas concentration: $H_2/CO_x/CH_3OH/H_2O$ = 79.8/19.8/0.2/0.2% v/v. A) Trans. State - CO_2/CO_x = 0.25. B) Trans. State - CO_2/CO_x = 0.75. C) Intermediate - CO_2/CO_x = 0.25. D) Intermediate - CO_2/CO_x = 0.75.

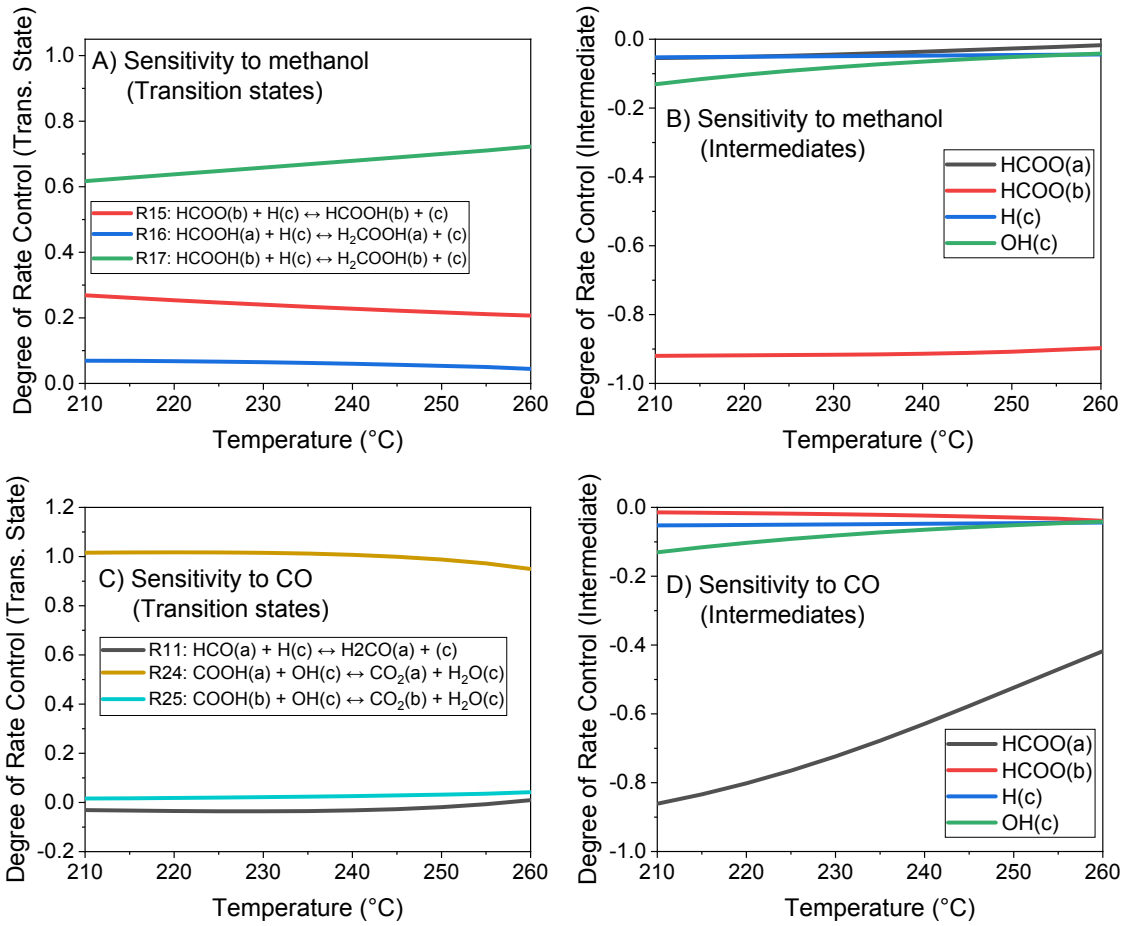

Fig. S10 Degree of Rate Control (DRC) analysis at 210-260 °C, 30 bar, and a gas concentration of $H_2/CO/CO_2/CH_3OH/H_2O$ = 79.8/0.2/19.6/0.2/0.2% v/v. A) Sensitivity to methanol, transition states. B) Sensitivity to methanol, intermediates. C) Sensitivity to CO, transition states. D) Sensitivity to CO, intermediates.

Table S1. Experimental data performed in the PFR. *The volume flow description considers the standard temperature of 298.15 K and the pressure of 1 bar.

N°	Abs. Pres. (bar)	Vol. Flow* $\left(\frac{Ls}{min}\right)$	Temp. (°C)	Inlet Flow (% v/v)				Outlet Flow (% v/v)		
				H_2	CO	CO_2	N_2	CO	CO_2	CH_3OH
1	41	600	220	35.33	11.51	2.68	0.00	10.9	2.58	0.77
2	41	600	235	35.33	11.51	2.68	0.00	10.82	2.61	1.13
3	41	600	250	35.33	11.51	2.68	0.00	10.47	2.66	1.65
4	41	800	220	35.32	11.55	2.68	0.00	11.11	2.58	0.58
5	41	800	235	35.32	11.55	2.68	0.00	11.02	2.60	0.87
6	41	800	250	35.32	11.55	2.68	0.00	10.69	2.64	1.34
7	41	600	220	35.37	8.61	5.50	0.00	8.23	5.28	0.80
8	41	600	235	35.37	8.61	5.50	0.00	8.11	5.32	1.11
9	41	600	250	35.37	8.61	5.50	0.00	7.83	5.41	1.52
10	41	800	220	35.36	8.63	5.50	0.00	8.43	5.26	0.62
11	41	800	235	35.36	8.63	5.50	0.00	8.31	5.29	0.86
12	41	800	250	35.36	8.63	5.50	0.00	8.12	5.37	1.24
13	41	600	220	35.34	5.80	8.37	0.00	5.55	7.98	0.78
14	41	600	235	35.34	5.80	8.37	0.00	5.49	7.98	1.02
15	41	600	250	35.34	5.80	8.37	0.00	5.34	7.99	1.23
16	41	800	220	35.36	5.75	8.37	0.00	5.65	7.97	0.63
17	41	800	235	35.36	5.75	8.37	0.00	5.68	7.94	0.83
18	41	800	250	35.36	5.75	8.37	0.00	5.55	7.98	1.03
19	41	600	210	45.38	12.94	1.34	0.00	12.71	1.25	0.54
20	41	600	220	45.38	12.94	1.34	0.00	12.65	1.28	0.74
21	41	600	230	45.38	12.94	1.34	0.00	12.45	1.30	1.12
22	41	600	240	45.38	12.94	1.34	0.00	12.13	1.32	1.59
23	41	600	250	45.38	12.94	1.34	0.00	11.78	1.34	2.02
24	41	600	260	45.38	12.94	1.34	0.00	11.59	1.36	2.27
25	41	800	210	45.34	13.01	1.35	0.00	12.83	1.26	0.39
26	41	800	220	45.34	13.01	1.35	0.00	12.73	1.28	0.54
27	41	800	230	45.34	13.01	1.35	0.00	12.64	1.29	0.83
28	41	800	240	45.34	13.01	1.35	0.00	12.36	1.31	1.19
29	41	800	250	45.34	13.01	1.35	0.00	12.09	1.33	1.61
30	41	800	260	45.34	13.01	1.35	0.00	11.87	1.35	1.89
31	41	600	210	45.32	11.71	2.69	0.00	11.48	2.59	0.51
32	41	600	220	45.32	11.71	2.69	0.00	11.35	2.56	0.79
33	41	600	230	45.32	11.71	2.69	0.00	11.03	2.59	1.16
34	41	600	240	45.32	11.71	2.69	0.00	10.68	2.62	1.70
35	41	600	250	45.32	11.71	2.69	0.00	10.26	2.65	2.21
36	41	600	260	45.32	11.71	2.69	0.00	10.05	2.68	2.51
37	41	800	210	45.29	11.76	2.70	0.00	11.62	2.56	0.39
38	41	800	220	45.29	11.76	2.70	0.00	11.49	2.55	0.59
39	41	800	230	45.29	11.76	2.70	0.00	11.32	2.57	0.88
40	41	800	240	45.29	11.76	2.70	0.00	11	2.60	1.27
41	41	800	250	45.29	11.76	2.70	0.00	10.63	2.62	1.74
42	41	800	260	45.29	11.76	2.70	0.00	10.34	2.65	2.09
43	41	1000	210	45.26	11.79	2.71	0.00	11.72	2.56	0.32
44	41	1000	220	45.26	11.79	2.71	0.00	11.56	2.55	0.47
45	41	1000	230	45.26	11.79	2.71	0.00	11.43	2.56	0.70
46	41	1000	240	45.26	11.79	2.71	0.00	11.18	2.58	1.02
47	41	1000	250	45.26	11.79	2.71	0.00	10.9	2.62	1.43
48	41	1000	260	45.26	11.79	2.71	0.00	10.61	2.64	1.79
49	41	600	210	45.33	11.72	5.68	0.00	11.65	5.44	0.64
50	41	600	220	45.33	11.72	5.68	0.00	11.55	5.51	0.86

51	41	600	230	45.33	11.72	5.68	0.00	11.23	5.57	1.22
52	41	600	240	45.33	11.72	5.68	0.00	10.88	5.64	1.73
53	41	600	250	45.33	11.72	5.68	0.00	10.49	5.73	2.23
54	41	600	260	45.33	11.72	5.68	0.00	10.33	5.79	2.48
55	41	800	210	45.34	11.72	5.66	0.00	11.74	5.45	0.50
56	41	800	220	45.34	11.72	5.66	0.00	11.69	5.48	0.66
57	41	800	230	45.34	11.72	5.66	0.00	11.53	5.53	0.92
58	41	800	240	45.34	11.72	5.66	0.00	11.21	5.56	1.30
59	41	800	250	45.34	11.72	5.66	0.00	10.87	5.64	1.75
60	41	800	260	45.34	11.72	5.66	0.00	10.68	5.72	2.06
61	41	600	210	45.37	10.10	4.20	0.00	9.93	3.99	0.61
62	41	600	220	45.37	10.10	4.20	0.00	9.93	4.06	0.82
63	41	600	230	45.37	10.10	4.20	0.00	9.63	4.09	1.18
64	41	600	240	45.37	10.10	4.20	0.00	9.22	4.14	1.66
65	41	600	250	45.37	10.10	4.20	0.00	8.90	4.20	2.09
66	41	600	260	45.37	10.10	4.20	0.00	8.74	4.23	2.25
67	41	800	210	45.36	10.12	4.20	0.00	10.09	4.00	0.48
68	41	800	220	45.36	10.12	4.20	0.00	10.08	4.03	0.63
69	41	800	230	45.36	10.12	4.20	0.00	9.87	4.05	0.89
70	41	800	240	45.36	10.12	4.20	0.00	9.62	4.11	1.26
71	41	800	250	45.36	10.12	4.20	0.00	9.24	4.14	1.66
72	41	800	260	45.36	10.12	4.20	0.00	9.06	4.18	1.90
73	41	600	210	45.36	8.54	2.76	0.00	8.41	2.55	0.59
74	41	600	220	45.36	8.54	2.76	0.00	8.38	2.59	0.78
75	41	600	230	45.36	8.54	2.76	0.00	8.09	2.62	1.13
76	41	600	240	45.36	8.54	2.76	0.00	7.75	2.66	1.56
77	41	600	250	45.36	8.54	2.76	0.00	7.42	2.69	1.89
78	41	600	260	45.36	8.54	2.76	0.00	7.31	2.70	1.98
79	41	800	210	45.33	8.63	2.73	0.00	8.52	2.55	0.45
80	41	800	220	45.33	8.63	2.73	0.00	8.46	2.59	0.59
81	41	800	230	45.33	8.63	2.73	0.00	8.37	2.60	0.86
82	41	800	240	45.33	8.63	2.73	0.00	8.05	2.63	1.19
83	41	800	250	45.33	8.63	2.73	0.00	7.79	2.66	1.53
84	41	800	260	45.33	8.63	2.73	0.00	7.60	2.68	1.71
85	41	600	210	45.35	8.76	5.58	0.00	8.63	5.28	0.60
86	41	600	220	45.35	8.76	5.58	0.00	8.53	5.28	0.86
87	41	600	230	45.35	8.76	5.58	0.00	8.36	5.31	1.19
88	41	600	240	45.35	8.76	5.58	0.00	7.98	5.35	1.63
89	41	600	250	45.35	8.76	5.58	0.00	7.61	5.39	2.05
90	41	600	260	45.35	8.76	5.58	0.00	7.50	5.40	2.20
91	41	800	210	45.30	8.84	5.59	0.00	8.72	5.29	0.47
92	41	800	220	45.30	8.84	5.59	0.00	8.69	5.29	0.66
93	41	800	230	45.30	8.84	5.59	0.00	8.54	5.27	0.91
94	41	800	240	45.30	8.84	5.59	0.00	8.37	5.31	1.25
95	41	800	250	45.30	8.84	5.59	0.00	8.08	5.31	1.61
96	41	800	260	45.30	8.84	5.59	0.00	7.82	5.35	1.87
97	41	1000	210	45.27	8.88	5.61	0.00	8.81	5.33	0.39
98	41	1000	220	45.27	8.88	5.61	0.00	8.72	5.28	0.54
99	41	1000	230	45.27	8.88	5.61	0.00	8.70	5.28	0.75
100	41	1000	240	45.27	8.88	5.61	0.00	8.50	5.30	1.03
101	41	1000	250	45.27	8.88	5.61	0.00	8.33	5.30	1.34
102	41	1000	260	45.27	8.88	5.61	0.00	8.04	5.33	1.62
103	41	600	210	45.19	8.82	8.84	0.00	8.84	8.37	0.67
104	41	600	220	45.19	8.82	8.84	0.00	8.72	8.38	0.87
105	41	600	230	45.19	8.82	8.84	0.00	8.52	8.41	1.16
106	41	600	240	45.19	8.82	8.84	0.00	8.26	8.47	1.51
107	41	600	250	45.19	8.82	8.84	0.00	8.06	8.54	1.83
108	41	600	260	45.19	8.82	8.84	0.00	8.00	8.59	2.01

109	41	800	210	45.15	8.89	8.83	0.00	8.86	8.39	0.54
110	41	800	220	45.15	8.89	8.83	0.00	8.89	8.41	0.69
111	41	800	230	45.15	8.89	8.83	0.00	8.74	8.37	0.91
112	41	800	240	45.15	8.89	8.83	0.00	8.54	8.39	1.21
113	41	800	250	45.15	8.89	8.83	0.00	8.36	8.41	1.52
114	41	800	260	45.15	8.89	8.83	0.00	8.28	8.47	1.73
115	41	600	210	45.19	7.32	7.33	0.00	7.28	6.82	0.66
116	41	600	220	45.19	7.32	7.33	0.00	7.21	6.86	0.85
117	41	600	230	45.19	7.32	7.33	0.00	6.99	6.86	1.12
118	41	600	240	45.19	7.32	7.33	0.00	6.74	6.90	1.44
119	41	600	250	45.19	7.32	7.33	0.00	6.48	6.92	1.72
120	41	600	260	45.19	7.32	7.33	0.00	6.49	6.97	1.76
121	41	800	210	45.17	7.35	7.32	0.00	7.39	6.86	0.53
122	41	800	220	45.17	7.35	7.32	0.00	7.36	6.87	0.67
123	41	800	230	45.17	7.35	7.32	0.00	7.19	6.82	0.89
124	41	800	240	45.17	7.35	7.32	0.00	7.03	6.84	1.16
125	41	800	250	45.17	7.35	7.32	0.00	6.79	6.87	1.43
126	41	800	260	45.17	7.35	7.32	0.00	6.69	6.88	1.58
127	41	600	210	45.19	5.82	5.81	0.00	5.74	5.30	0.64
128	41	600	220	45.19	5.82	5.81	0.00	5.65	5.30	0.82
129	41	600	230	45.19	5.82	5.81	0.00	5.45	5.30	1.08
130	41	600	240	45.19	5.82	5.81	0.00	5.20	5.32	1.36
131	41	600	250	45.19	5.82	5.81	0.00	5.03	5.36	1.56
132	41	600	260	45.19	5.82	5.81	0.00	5.05	5.35	1.55
133	41	800	210	45.18	5.84	5.80	0.00	5.79	5.3	0.51
134	41	800	220	45.18	5.84	5.80	0.00	5.78	5.32	0.65
135	41	800	230	45.18	5.84	5.80	0.00	5.64	5.28	0.86
136	41	800	240	45.18	5.84	5.80	0.00	5.45	5.27	1.10
137	41	800	250	45.18	5.84	5.80	0.00	5.31	5.31	1.32
138	41	800	260	45.18	5.84	5.80	0.00	5.24	5.30	1.39
139	41	600	210	45.31	5.87	8.54	0.00	5.85	8.08	0.67
140	41	600	220	45.31	5.87	8.54	0.00	5.79	8.04	0.88
141	41	600	230	45.31	5.87	8.54	0.00	5.65	7.98	1.15
142	41	600	240	45.31	5.87	8.54	0.00	5.43	7.98	1.45
143	41	600	250	45.31	5.87	8.54	0.00	5.28	7.98	1.67
144	41	600	260	45.31	5.87	8.54	0.00	5.29	7.97	1.70
145	41	800	210	45.31	5.89	8.52	0.00	5.92	8.14	0.54
146	41	800	220	45.31	5.89	8.52	0.00	5.90	8.06	0.71
147	41	800	230	45.31	5.89	8.52	0.00	5.83	7.98	0.92
148	41	800	240	45.31	5.89	8.52	0.00	5.70	7.94	1.16
149	41	800	250	45.31	5.89	8.52	0.00	5.56	7.94	1.39
150	41	800	260	45.31	5.89	8.52	0.00	5.48	7.90	1.51
151	41	1000	210	45.29	5.92	8.53	0.00	5.91	8.17	0.46
152	41	1000	220	45.29	5.92	8.53	0.00	5.96	8.08	0.6
153	41	1000	230	45.29	5.92	8.53	0.00	5.94	8.01	0.79
154	41	1000	240	45.29	5.92	8.53	0.00	5.87	7.94	0.99
155	41	1000	250	45.29	5.92	8.53	0.00	5.75	7.90	1.19
156	41	1000	260	45.29	5.92	8.53	0.00	5.62	7.84	1.33
157	41	600	210	45.14	4.34	10.39	0.00	4.44	9.74	0.70
158	41	600	220	45.14	4.34	10.39	0.00	4.45	9.68	0.87
159	41	600	230	45.14	4.34	10.39	0.00	4.39	9.58	1.03
160	41	600	240	45.14	4.34	10.39	0.00	4.34	9.57	1.19
161	41	600	250	45.14	4.34	10.39	0.00	4.29	9.45	1.32
162	41	600	260	45.14	4.34	10.39	0.00	4.40	9.39	1.33
163	41	800	210	45.12	4.37	10.41	0.00	4.47	9.79	0.58
164	41	800	220	45.12	4.37	10.41	0.00	4.50	9.70	0.72
165	41	800	230	45.12	4.37	10.41	0.00	4.51	9.61	0.89
166	41	800	240	45.12	4.37	10.41	0.00	4.50	9.52	1.04

167	41	800	250	45.12	4.37	10.41	0.00	4.45	9.40	1.16
168	41	800	260	45.12	4.37	10.41	0.00	4.54	9.34	1.20
169	41	600	210	45.34	2.86	11.49	0.00	3.04	11.18	0.66
170	41	600	220	45.34	2.86	11.49	0.00	3.13	11.24	0.82
171	41	600	230	45.34	2.86	11.49	0.00	3.22	11.09	0.96
172	41	600	240	45.34	2.86	11.49	0.00	3.16	10.94	1.07
173	41	600	250	45.34	2.86	11.49	0.00	3.38	10.86	1.17
174	41	600	260	45.34	2.86	11.49	0.00	3.52	10.74	1.13
175	41	800	210	45.35	2.87	11.46	0.00	3.05	11.30	0.55
176	41	800	220	45.35	2.87	11.46	0.00	3.13	11.31	0.68
177	41	800	230	45.35	2.87	11.46	0.00	3.24	11.16	0.84
178	41	800	240	45.35	2.87	11.46	0.00	3.25	10.94	0.95
179	41	800	250	45.35	2.87	11.46	0.00	3.47	10.84	1.07
180	41	800	260	45.35	2.87	11.46	0.00	3.60	10.70	1.06
181	41	1000	210	45.33	2.89	11.48	0.00	3.05	11.35	0.47
182	41	1000	220	45.33	2.89	11.48	0.00	3.13	11.42	0.59
183	41	1000	230	45.33	2.89	11.48	0.00	3.22	11.19	0.74
184	41	1000	240	45.33	2.89	11.48	0.00	3.32	11.01	0.87
185	41	1000	250	45.33	2.89	11.48	0.00	3.50	10.81	0.98
186	41	1000	260	45.33	2.89	11.48	0.00	3.64	10.67	1.00
187	41	600	220	55.22	11.94	2.72	0.00	11.62	2.53	0.88
188	41	600	235	55.22	11.94	2.72	0.00	11.00	2.59	1.73
189	41	600	250	55.22	11.94	2.72	0.00	10.18	2.66	2.89
190	41	800	220	55.15	12.03	2.74	0.00	11.72	2.53	0.66
191	41	800	235	55.15	12.03	2.74	0.00	11.34	2.56	1.28
192	41	800	250	55.15	12.03	2.74	0.00	10.59	2.62	2.22
193	41	600	220	55.23	8.99	5.66	0.00	8.74	5.26	0.96
194	41	600	235	55.23	8.99	5.66	0.00	8.25	5.29	1.73
195	41	600	250	55.23	8.99	5.66	0.00	7.56	5.41	2.62
196	41	800	220	55.20	9.02	5.67	0.00	8.91	5.27	0.76
197	41	800	235	55.20	9.02	5.67	0.00	8.54	5.25	1.31
198	41	800	250	55.20	9.02	5.67	0.00	8.06	5.33	2.04
199	41	600	220	55.17	6.01	8.72	0.00	5.98	8.06	1.04
200	41	600	235	55.17	6.01	8.72	0.00	5.68	8.00	1.60
201	41	600	250	55.17	6.01	8.72	0.00	5.31	8.01	2.15
202	41	800	220	55.16	6.03	8.72	0.00	6.08	8.09	0.85
203	41	800	235	55.16	6.03	8.72	0.00	5.93	7.95	1.29
204	41	800	250	55.16	6.03	8.72	0.00	5.65	7.93	1.75
205	41	600	220	60.31	15.84	3.75	0.00	15.68	3.79	0.96
206	41	600	250	60.31	15.84	3.75	0.00	14.44	4.02	3.18
207	41	800	220	60.19	16.01	3.74	0.00	15.85	3.76	0.74
208	41	800	250	60.19	16.01	3.74	0.00	14.93	3.91	2.37
209	41	600	220	60.10	12.12	7.75	0.00	11.84	7.85	1.07
210	41	600	250	60.10	12.12	7.75	0.00	10.61	8.05	2.80
211	41	800	220	60.07	12.16	7.75	0.00	11.98	7.88	0.83
212	41	800	250	60.07	12.16	7.75	0.00	11.25	7.90	2.17
213	41	600	220	60.27	8.01	11.63	0.00	8.07	11.95	1.13
214	41	600	250	60.27	8.01	11.63	0.00	7.45	11.94	2.33
215	41	800	220	60.31	8.00	11.59	0.00	8.23	11.98	0.92
216	41	800	250	60.31	8.00	11.59	0.00	7.91	11.82	1.92
217	61	600	220	35.37	11.47	2.64	0.00	11.02	2.56	0.96
218	61	800	220	35.33	11.52	2.67	0.00	11.25	2.57	0.72
219	61	600	220	45.38	11.66	2.63	0.00	11.01	2.52	1.07
220	61	800	220	45.31	11.75	2.67	0.00	11.30	2.51	0.81
221	61	1000	220	45.31	11.73	2.69	0.00	11.49	2.51	0.64
222	61	600	220	55.28	11.84	2.72	0.00	11.27	2.50	1.39
223	61	800	220	55.21	11.94	2.74	0.00	11.57	2.48	1.02
224	61	600	235	45.38	11.66	2.63	0.00	10.41	2.59	2.07

225	61	800	235	45.31	11.75	2.67	0.00	10.85	2.56	1.51
226	61	1000	235	45.31	11.73	2.69	0.00	11.17	2.55	1.18
227	61	600	250	45.38	11.66	2.63	0.00	9.33	2.69	3.64
228	61	800	250	45.31	11.75	2.67	0.00	9.93	2.64	2.81
229	61	1000	250	45.31	11.73	2.69	0.00	10.36	2.61	2.26
230	61	600	250	55.28	11.84	2.72	0.00	8.35	2.78	5.33
231	61	800	250	55.21	11.94	2.74	0.00	9.20	2.71	4.57
232	61	600	220	45.37	8.75	5.56	0.00	8.35	5.20	1.12
233	61	800	220	45.35	8.78	5.56	0.00	8.56	5.20	0.87
234	61	1000	220	45.36	8.77	5.55	0.00	8.70	5.22	0.72
235	61	600	235	45.37	8.75	5.56	0.00	7.73	5.29	1.91
236	61	800	235	45.35	8.78	5.56	0.00	8.18	5.23	1.47
237	61	1000	235	45.36	8.77	5.55	0.00	8.39	5.22	1.18
238	61	600	250	45.37	8.75	5.56	0.00	6.76	5.42	3.21
239	61	800	250	45.35	8.78	5.56	0.00	7.41	5.34	2.51
240	61	1000	250	45.36	8.77	5.55	0.00	7.82	5.29	2.03
241	61	600	220	35.37	5.75	8.36	0.00	5.54	7.94	0.99
242	61	800	220	35.36	5.75	8.37	0.00	5.72	7.95	0.79
243	61	600	220	45.33	5.86	8.52	0.00	5.68	7.94	1.10
244	61	800	220	45.35	5.85	8.48	0.00	5.84	7.94	0.93
245	61	1000	220	45.33	5.89	8.49	0.00	5.91	7.97	0.78
246	61	600	220	55.19	5.97	8.74	0.00	5.80	7.94	1.41
247	61	800	220	55.17	6.01	8.73	0.00	5.99	7.95	1.17
248	61	600	235	45.33	5.86	8.52	0.00	5.30	7.96	1.72
249	61	800	235	45.35	5.85	8.48	0.00	5.59	7.89	1.38
250	61	1000	235	45.33	5.89	8.49	0.00	5.75	7.84	1.17
251	61	600	250	35.37	5.75	8.36	0.00	4.62	8.08	2.17
252	61	800	250	35.36	5.75	8.37	0.00	5.04	8.00	1.78
253	61	600	250	45.33	5.86	8.52	0.00	4.67	7.97	2.60
254	61	800	250	45.35	5.85	8.48	0.00	5.14	7.90	2.05
255	61	1000	250	45.33	5.89	8.49	0.00	5.41	7.84	1.73
256	61	600	250	55.19	5.97	8.74	0.00	4.41	8.02	3.44
257	61	800	250	55.17	6.01	8.73	0.00	5.04	7.94	2.69
258	61	600	220	45.32	2.90	11.49	0.00	3.08	10.66	1.06
259	61	800	220	45.33	2.91	11.46	0.00	3.13	10.74	0.94
260	61	1000	220	45.31	2.94	11.48	0.00	3.13	10.78	0.83
261	61	600	235	45.32	2.90	11.49	0.00	3.07	10.40	1.42
262	61	800	235	45.33	2.91	11.46	0.00	3.18	10.42	1.24
263	61	1000	235	45.31	2.94	11.48	0.00	3.23	10.48	1.14
264	61	600	250	45.32	2.90	11.49	0.00	2.97	10.26	1.82
265	61	800	250	45.33	2.91	11.46	0.00	3.18	10.23	1.52
266	61	1000	250	45.31	2.94	11.48	0.00	3.31	10.23	1.41
267	41	600	220	20.67	28.30	4.53	0.00	28.00	4.53	0.53
268	41	600	230	20.67	28.30	4.53	0.00	27.92	4.54	0.82
269	41	600	240	20.67	28.30	4.53	0.00	27.95	4.59	1.16
270	41	600	250	20.67	28.30	4.53	0.00	27.88	4.64	1.40
271	41	600	260	20.67	28.30	4.53	0.00	27.77	4.66	1.42
272	41	800	220	20.62	28.51	4.49	0.00	28.10	4.52	0.39
273	41	800	230	20.62	28.51	4.49	0.00	28.21	4.53	0.61
274	41	800	240	20.62	28.51	4.49	0.00	28.03	4.55	0.89
275	41	800	250	20.62	28.51	4.49	0.00	28.11	4.62	1.15
276	41	800	260	20.62	28.51	4.49	0.00	27.88	4.63	1.23
277	41	600	220	30.78	28.56	2.70	0.00	28.40	2.68	0.71
278	41	600	230	30.78	28.56	2.70	0.00	28.38	2.70	1.12
279	41	600	240	30.78	28.56	2.70	0.00	28.21	2.74	1.67
280	41	600	250	30.78	28.56	2.70	0.00	27.98	2.79	2.16
281	41	600	260	30.78	28.56	2.70	0.00	27.83	2.84	2.39
282	41	800	220	30.74	28.64	2.71	0.00	28.39	2.67	0.52

283	41	800	230	30.74	28.64	2.71	0.00	28.35	2.68	0.83
284	41	800	240	30.74	28.64	2.71	0.00	28.47	2.72	1.26
285	41	800	250	30.74	28.64	2.71	0.00	28.19	2.76	1.72
286	41	800	260	30.74	28.64	2.71	0.00	27.92	2.80	2.01
287	41	600	230	30.78	28.72	4.58	0.00	28.51	4.62	1.12
288	41	600	240	30.78	28.72	4.58	0.00	28.53	4.70	1.70
289	41	600	250	30.78	28.72	4.58	0.00	28.22	4.77	2.26
290	41	600	260	30.78	28.72	4.58	0.00	28.16	4.83	2.54
291	41	800	230	31.07	28.16	4.53	0.00	28.72	4.59	0.84
292	41	800	240	31.07	28.16	4.53	0.00	28.59	4.64	1.27
293	41	800	250	31.07	28.16	4.53	0.00	28.59	4.73	1.77
294	41	800	260	31.07	28.16	4.53	0.00	28.27	4.76	2.12
295	41	600	220	30.72	29.02	7.49	0.00	28.93	7.46	0.77
296	41	600	230	30.72	29.02	7.49	0.00	28.96	7.58	1.20
297	41	600	240	30.72	29.02	7.49	0.00	28.78	7.68	1.84
298	41	600	250	30.72	29.02	7.49	0.00	28.59	7.82	2.48
299	41	600	260	30.72	29.02	7.49	0.00	28.19	7.86	2.76
300	41	800	220	30.72	29.03	7.49	0.00	28.90	7.42	0.57
301	41	800	230	30.72	29.03	7.49	0.00	28.89	7.47	0.89
302	41	800	240	30.72	29.03	7.49	0.00	28.95	7.58	1.37
303	41	800	250	30.72	29.03	7.49	0.00	28.83	7.69	1.92
304	41	800	260	30.72	29.03	7.49	0.00	28.42	7.75	2.30
305	41	600	220	30.31	30.32	19.17	0.00	30.36	19.33	0.79
306	41	600	230	30.31	30.32	19.17	0.00	30.13	19.39	1.18
307	41	600	240	30.31	30.32	19.17	0.00	29.95	19.61	1.74
308	41	600	250	30.31	30.32	19.17	0.00	29.89	19.97	2.37
309	41	600	260	30.31	30.32	19.17	0.00	29.57	20.11	2.75
310	41	800	220	30.17	30.42	19.29	0.00	30.37	19.15	0.61
311	41	800	230	30.17	30.42	19.29	0.00	30.32	19.26	0.89
312	41	800	240	30.17	30.42	19.29	0.00	30.34	19.46	1.30
313	41	800	250	30.17	30.42	19.29	0.00	30.18	19.72	1.81
314	41	800	260	30.17	30.42	19.29	0.00	29.78	19.86	2.22
315	41	600	220	40.66	29.25	4.68	0.00	28.96	4.62	0.91
316	41	600	230	40.66	29.25	4.68	0.00	29.09	4.69	1.47
317	41	600	240	40.66	29.25	4.68	0.00	28.85	4.78	2.31
318	41	600	250	40.66	29.25	4.68	0.00	28.71	4.92	3.27
319	41	600	260	40.66	29.25	4.68	0.00	28.46	5.01	3.91
320	41	800	220	40.65	29.27	4.68	0.00	29.16	4.60	0.68
321	41	800	230	40.65	29.27	4.68	0.00	28.89	4.61	1.06
322	41	800	240	40.65	29.27	4.68	0.00	29.06	4.71	1.69
323	41	800	250	40.65	29.27	4.68	0.00	28.90	4.81	2.47
324	41	800	260	40.65	29.27	4.68	0.00	28.59	4.91	3.16
325	41	600	210	35.42	13.98	0.00	0.00	13.84	0.00	0.07
326	41	600	250	35.42	13.98	0.00	0.00	13.64	0.01	0.30
327	41	800	210	35.42	13.97	0.00	0.00	13.91	0.00	0.05
328	41	800	250	35.42	13.97	0.00	0.00	13.75	0.01	0.21
329	41	600	210	45.40	14.24	0.00	0.00	14.14	0.00	0.09
330	41	600	220	45.40	14.24	0.00	0.00	14.03	0.00	0.12
331	41	600	230	45.40	14.24	0.00	0.00	14.02	0.00	0.17
332	41	600	240	45.40	14.24	0.00	0.00	14.01	0.00	0.25
333	41	600	250	45.40	14.24	0.00	0.00	13.87	0.01	0.40
334	41	600	260	45.40	14.24	0.00	0.00	13.77	0.02	0.51
335	41	800	210	45.28	14.47	0.00	0.00	14.16	0.00	0.06
336	41	800	220	45.28	14.47	0.00	0.00	14.15	0.00	0.09
337	41	800	230	45.28	14.47	0.00	0.00	14.12	0.00	0.12
338	41	800	240	45.28	14.47	0.00	0.00	14.10	0.00	0.17
339	41	800	250	45.28	14.47	0.00	0.00	14.06	0.01	0.28
340	41	800	260	45.28	14.47	0.00	0.00	13.96	0.01	0.34

341	41	600	210	55.34	14.46	0.00	0.00	14.32	0.00	0.10
342	41	600	250	55.34	14.46	0.00	0.00	14.05	0.01	0.46
343	41	800	210	55.69	13.93	0.00	0.00	14.42	0.00	0.08
344	41	800	250	55.69	13.93	0.00	0.00	14.27	0.01	0.31
345	61	600	220	45.35	14.26	0.00	0.00	14.19	0.00	0.21
346	61	800	220	45.33	14.35	0.00	0.00	14.27	0.00	0.15
347	61	1000	220	45.29	14.44	0.00	0.00	14.39	0.00	0.12
348	61	600	220	55.19	14.69	0.00	0.00	14.52	0.00	0.32
349	61	800	220	55.16	14.76	0.00	0.00	14.58	0.00	0.21
350	61	600	235	45.35	14.26	0.00	0.00	14.01	0.00	0.37
351	61	800	235	45.33	14.35	0.00	0.00	14.16	0.00	0.25
352	61	1000	235	45.29	14.44	0.00	0.00	14.28	0.00	0.19
353	61	600	250	35.35	14.16	0.00	0.00	13.76	0.02	0.54
354	61	800	250	35.31	14.24	0.00	0.00	13.94	0.01	0.39
355	61	600	250	45.35	14.26	0.00	0.00	13.89	0.02	0.64
356	61	800	250	45.33	14.35	0.00	0.00	14.14	0.01	0.44
357	61	1000	250	45.29	14.44	0.00	0.00	14.19	0.00	0.33
358	61	600	250	55.19	14.69	0.00	0.00	14.13	0.01	0.75
359	61	800	250	55.16	14.76	0.00	0.00	14.35	0.01	0.54

Table S2. Estimated parameters of the free Gibbs energy change (Eq. 19 of the article) of the global reactions involved in the methanol synthesis.

	CO Hyd.	**CO_2 Hyd.**	**WGSR**
m	1 (site a)	2 (site a) - 3 (site b)	4 (site a) - 5 (site b)
A_1 [kJ·mol^{-1}]	- 83.913	- 39.541	- 44.378
$A_2 \cdot 10^3$ [kJ·mol^{-1}·K^{-1}]	34.924	- 69.587	104.505
$A_3 \cdot 10^3$ [kJ·mol^{-1}·K^{-1}]	28.138	37.259	- 9.118
ΔH_{Tr}^0 [kJ·mol^{-1}]	- 75.524	- 28.432	- 47.096
$\Delta S_{Tr}^0 \cdot 10^3$ [kJ·mol^{-1}·K^{-1}]	- 223.384	- 179.957	- 43.438
$\Delta c_p \cdot 10^3$ [kJ·mol^{-1}·K^{-1}]	- 28.138	- 37.259	9.118