Electronic Supplementary Information

Mechanistic insights into CeO_2-catalyzed direct synthesis of diethyl carbonate from CO_2 and ethanol assisted by zeolite and 2,2-deoxypropane

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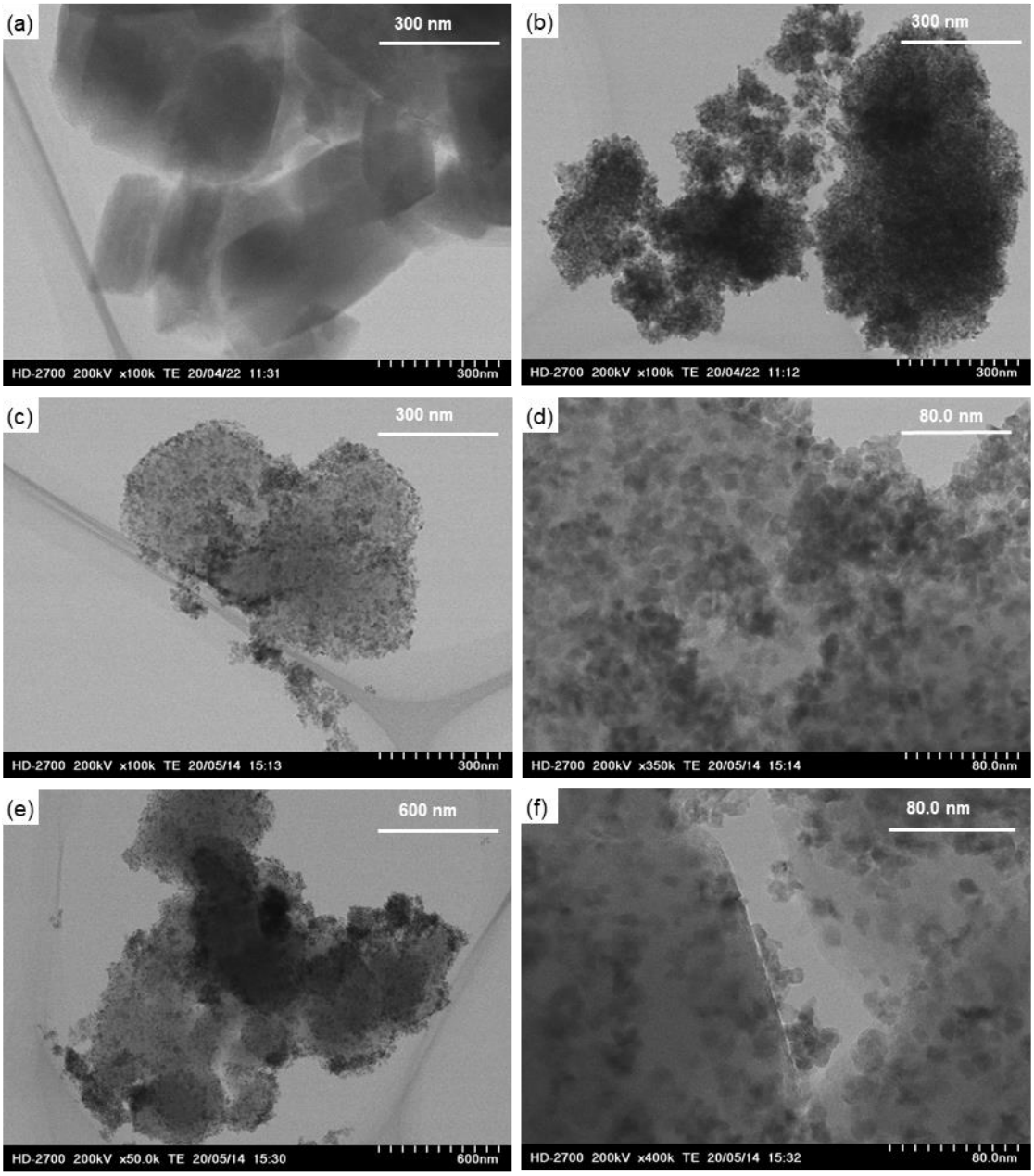

Fig. S1. TEM images of (a) H-FAU, (b) CeO_2, (c) mixture of CeO_2 and H-FAU after the reaction, (d) expanded image of the figure (c), (e) mixture of CeO_2 and H-FAU after reaction (another view), and (f) expanded image of the figure (e).

Reaction conditions: CeO_2 0.5 g; H-FAU 0.01 g; EtOH 140 mmol; DEP 21 mmol; CO_2 6.5 MPa (at 393 K); 393 K; 1 h.

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Table S1. Estimation of apparent activation energy for the DEC synthesis over CeO_2 in the presence of DEP and H-FAU (detailed data for Table 1 and Fig. S2).[a]

Entry	Temp. /K	Time /min	Reactant used /mmol		Product /mmol		DEP conv. /%	Balance /%		r_{DEC}[c] /mmol h^{-1}	$\ln(r_{DEC}$ /mmol $h^{-1})$
			DEP	EtOH	DEC	Acetone		Ethoxy moiety[b]	DEP		
1	363	3	21	140	0.015	0.58	4.7	93	96	0.19	–1.7
2	363	10	21	139	0.045	0.64	4.7	95	97		
3	363	20	21	139	0.070	0.63	5.1	97	99		
4	373	3	21	140	0.033	0.46	5.0	104	105	0.55	–0.59
5	373	10	21	139	0.10	0.54	4.8	106	107		
6	373	20	21	139	0.19	0.82	6.5	106	108		
7	383	3	21	140	0.049	0.51	6.8	104	103	0.72	–0.33
8	383	10	21	140	0.11	0.58	6.1	101	101		
9	383	20	21	140	0.25	0.79	7.0	103	103		
10	393	3	21	140	0.096	0.84	8.7	98	97	1.3	0.27
11	393	10	21	140	0.28	1.1	9.7	102	101		
12	393	20	21	140	0.47	1.3	10	100	100		

[a]Reaction conditions: CeO_2 0.030 g; H-FAU 0.010 g; EtOH 140 mmol; DEP 21 mmol; CO_2 5 MPa (at each reaction temperature); 3–20 min. [b]Balance of ethoxy moiety involved in DEC, DEP, and EtOH. [c]Formation rate of DEC, estimated from each slope in Fig. S2.

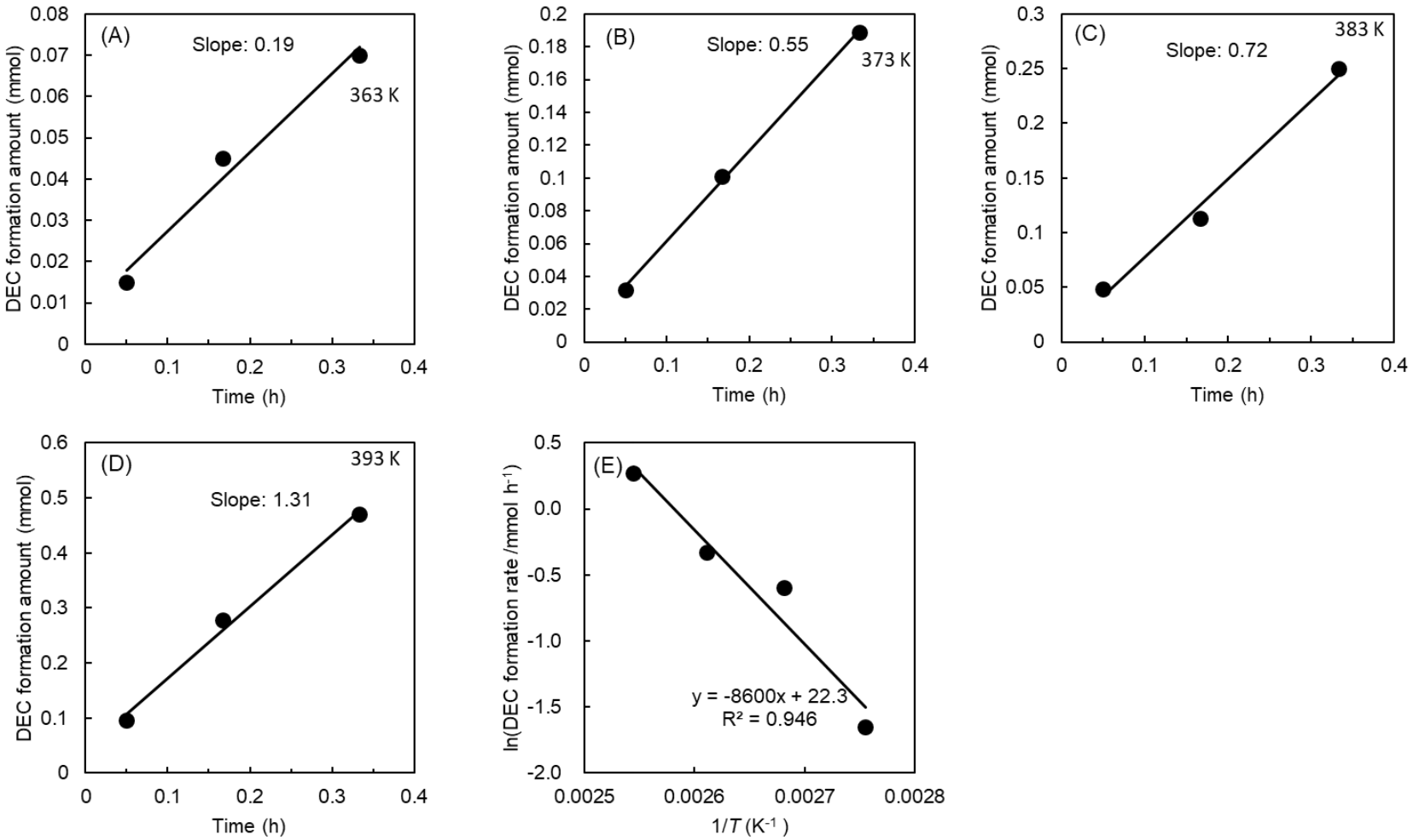

Fig. S2. Time courses for the DEC formation over CeO_2 in the presence of DEP and H-FAU at (A) 363 K, (B) 373 K, (C) 383 K, and (D) 393 K. (E) Arrhenius plot based on the initial reaction rates at the different temperatures determined from the figures A–D. The detailed data are summarized in Table S1. Reaction conditions: CeO_2 0.03 g; H-FAU 0.01 g; EtOH 140 mmol; DEP 21 mmol; CO_2 5 MPa (at each reaction temperature); 3–20 min.

Table S2. Estimation of apparent activation energy for the DEC synthesis over CeO_2 (detailed data for Table 1 and Fig. S3).[a]

Entry	Temp. /K	Time /min	Reactant used /mmol	Product /mmol	Balance /%	r_{DEC}[c] /mmol h^{-1}	$\ln(r_{DEC}$ /mmol $h^{-1})$
			EtOH	DEC	Ethoxy moiety[b]		
1	373	3	140	0.0010	94	0.012	–4.4
2	373	10	139	0.0018	91		
3	373	21	139	0.0042	93		
4	383	3	140	0.0044	100	0.024	–3.7
5	383	10	140	0.0080	100		
6	383	20	140	0.011	98		
7	393	3	140	0.0057	94	0.075	–2.6
8	393	13	140	0.018	94		
9	393	23	140	0.031	94		
10	403	0	140	0.017	94	0.16	–1.8
11	403	10	140	0.039	95		
12	403	20	140	0.062	95		

[a]Reaction conditions: CeO_2 0.03 g; EtOH 140 mmol; CO_2 5 MPa (at each reaction temperature); 3–23 min. [b]Balance of ethoxy moiety involved in DEC and EtOH. [c]Formation rate of DEC, estimated from each slope in Fig. S3.

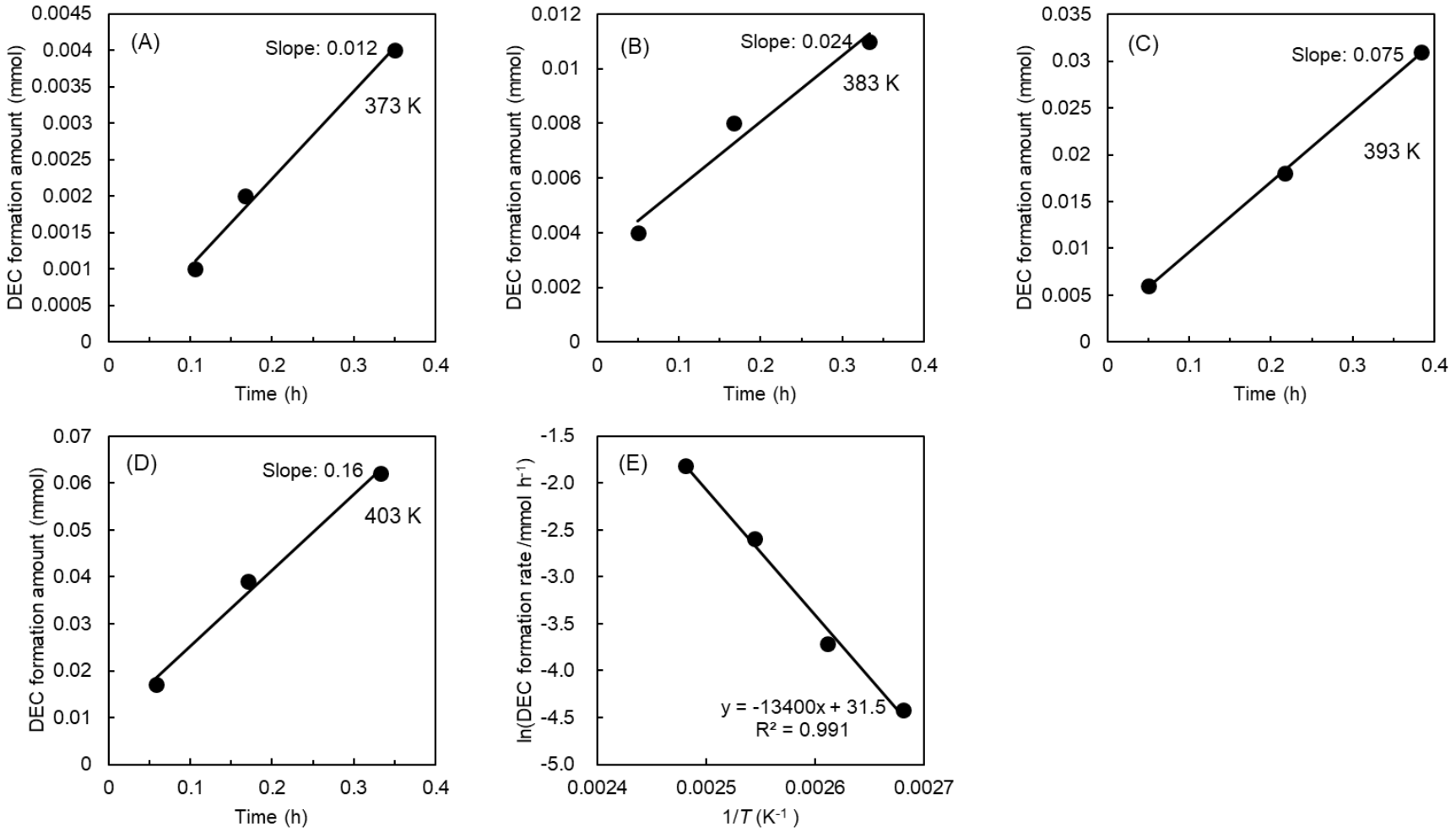

Fig. S3. Time courses for the DEC formation over CeO_2 at (A) 363 K, (B) 373 K, (C) 383 K, and (D) 393 K. (E) Arrhenius plot based on the initial reaction rates at the different temperatures determined from the figures A–D. The detailed data are summarized in Table S2.
Reaction conditions: CeO_2 0.03 g; EtOH 140 mmol; CO_2 5 MPa (at each reaction temperature); 3–23 min.

Table S3. Estimation of apparent activation energy for the DEC synthesis over CeO_2 in the presence of DEP (detailed data for Table 1 and Fig. S4).[a]

Entry	Temp. /K	Time /min	Reactant used /mmol		Product /mmol		DEP conv. /%	Balance /%		r_{DEC}[c] /mmol h^{-1}	$\ln(r_{DEC}$ /mmol $h^{-1})$
			DEP	EtOH	DEC	Acetone		Ethoxy moiety[b]	DEP		
1	373	3	21	140	0.0020	0.056	1.9	93	96	0.025	–3.7
2	373	10	21	139	0.0047	0.11	2.4	93	96		
3	373	20	21	139	0.0095	0.16	3.0	97	100		
4	383	3	21	140	0.0035	0.071	2.2	94	96	0.064	–2.8
5	383	10	21	140	0.0087	0.13	3.0	95	98		
6	383	20	21	140	0.021	0.20	3.9	95	97		
7	393	3	21	140	0.0066	0.084	2.5	93	94	0.13	–2.0
8	393	10	21	140	0.021	0.16	3.9	95	96		
9	393	20	21	140	0.044	0.23	5.1	94	96		
10	403	3	21	140	0.016	0.094	3.0	92	95	0.25	–1.4
11	403	10	21	139	0.049	0.18	4.9	94	95		
12	403	20	21	139	0.086	0.26	6.3	94	95		

[a]Reaction conditions: CeO_2 0.03 g; EtOH 140 mmol; DEP 21 mmol; CO_2 5 MPa (at each reaction temperature); 3–20 min. [b]Balance of ethoxy moiety involved in DEC, DEP, and EtOH. [c]Formation rate of DEC, estimated from each slope in Fig. S4.

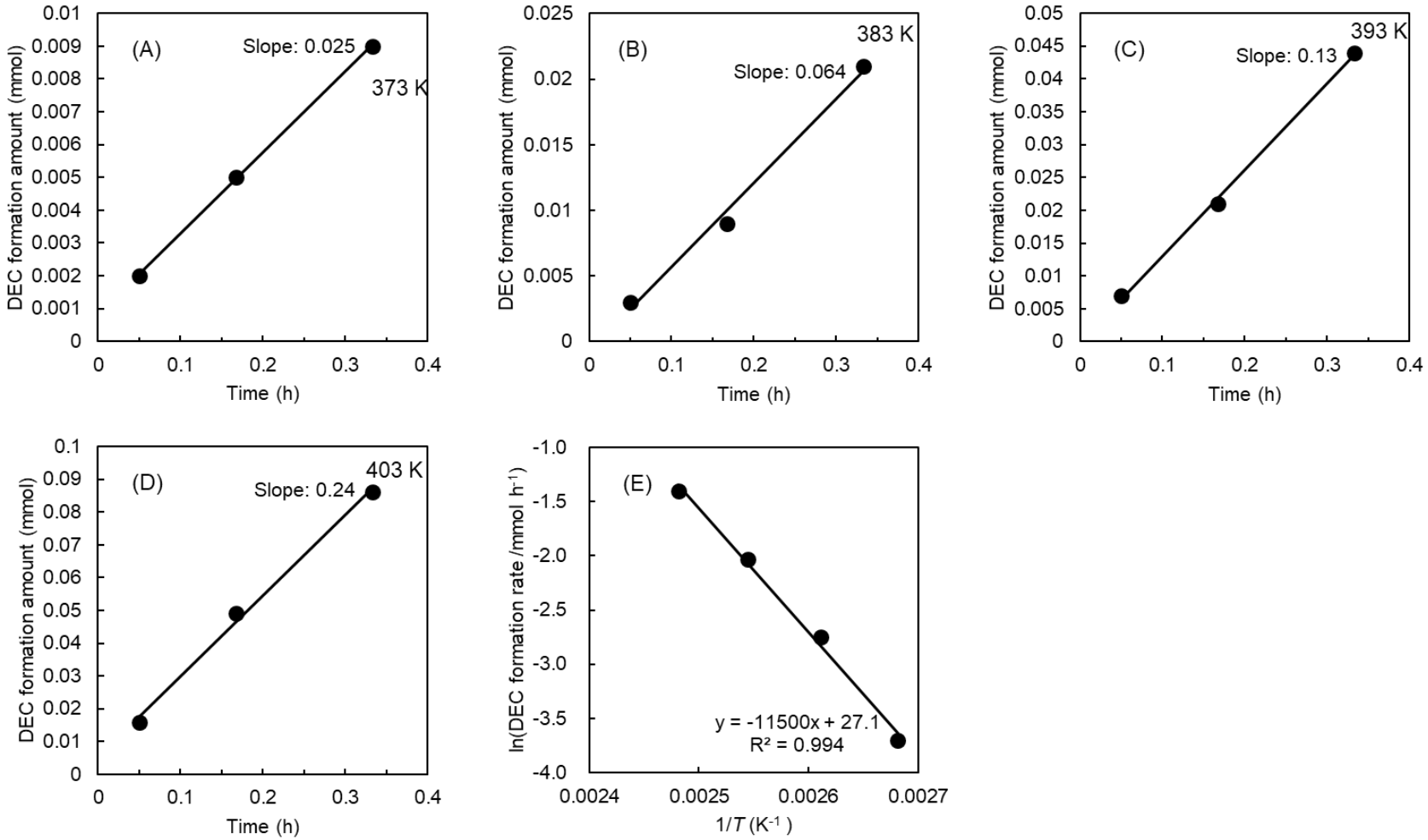

Fig. S4. Time courses for the DEC formation over CeO_2 in the presence of DEP at (A) 373 K, (B) 383 K, (C) 393 K, and (D) 403 K. (E) Arrhenius plot based on the initial reaction rates at the different temperatures determined from the figures A–D. The detailed data are summarized in Table S3.
Reaction conditions: CeO_2 0.03 g; EtOH 140 mmol; DEP 21 mmol; CO_2 5 MPa (at each reaction temperature); 3–20 min.

Table S4. Estimation of apparent activation energy for the DEC synthesis over CeO_2 in the presence of H-FAU (detailed data for Table 1 and Fig. S5).[a]

Entry	Temp. /K	Time /min	Reactant used /mmol	Product /mmol	Balance /%	r_{DEC}[c] /mmol h^{-1}	$\ln(r_{DEC}$ /mmol $h^{-1})$
			EtOH	DEC	Ethoxy moiety[b]		
1	373	3	140	0.0016	91	0.012	–4.4
2	373	13	140	0.0036	92		
3	373	23	140	0.0056	91		
4	383	3	140	0.0034	91	0.030	–3.5
5	383	10	139	0.0076	92		
6	383	23	139	0.013	92		
7	393	3	140	0.0042	92	0.078	–2.6
8	393	13	140	0.017	93		
9	393	23	140	0.030	94		

[a]Reaction conditions: CeO_2 0.03 g; H-FAU 0.01 g; EtOH 140 mmol; CO_2 5 MPa (at each reaction temperature); 3–23 min.
[b]Balance of ethoxy moiety involved in DEC and EtOH. [c]Formation rate of DEC, estimated from each slope in Fig. S5.

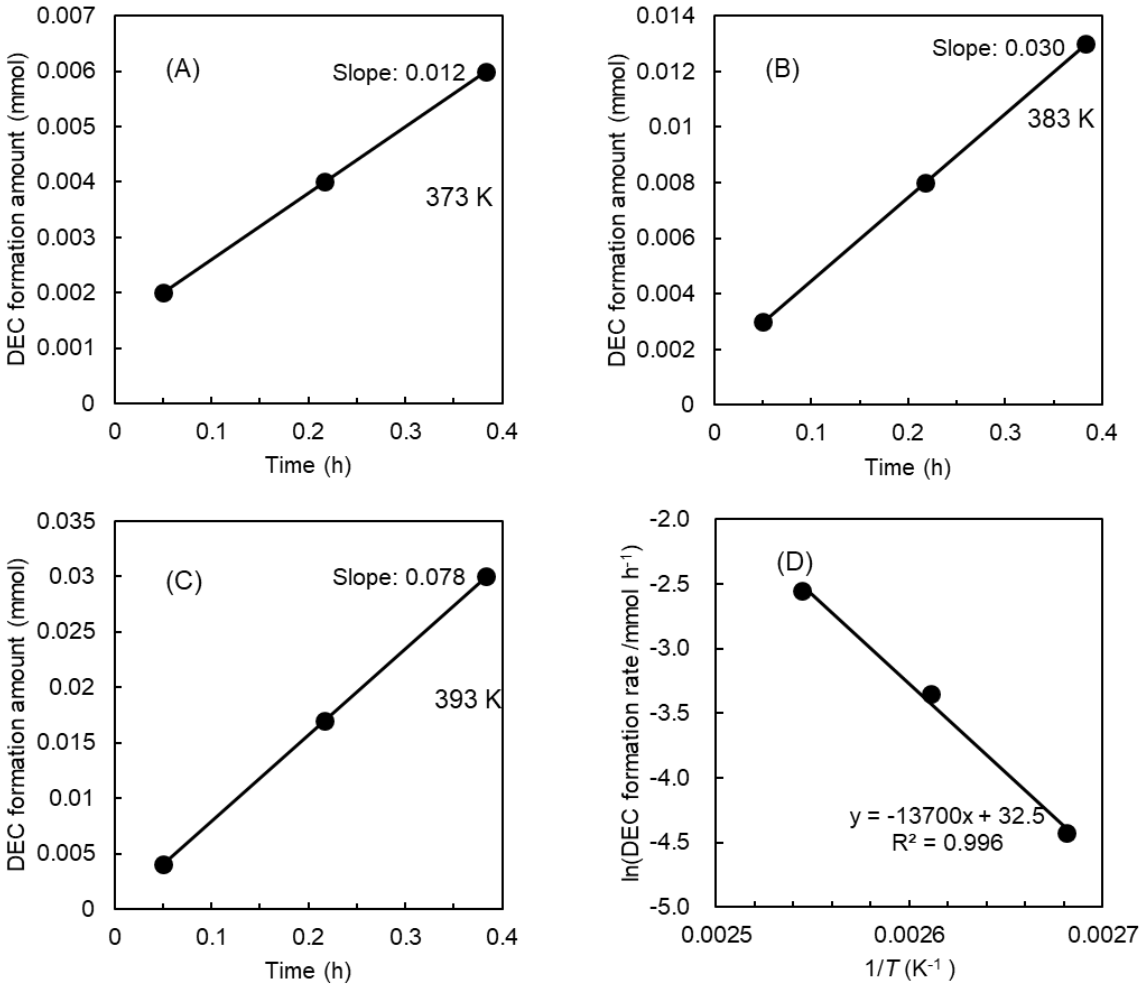

Fig. S5. Time courses for the DEC formation over CeO_2 in the presence of H-FAU at (A) 373 K, (B) 383 K, and (C) 393 K. (D) Arrhenius plot based on the initial reaction rates at the different temperatures determined from the figures A–C. The detailed data are summarized in Table S4.
Reaction conditions: CeO_2 0.03 g; H-FAU 0.01 g; EtOH 140 mmol; CO_2 5 MPa (at each reaction temperature); 3–23 min.

Table S5. Effect of CeO_2 amount on the DEC synthesis over CeO_2 in the presence of DEP and H-FAU (detailed data for Figs. 2A and S6).[a]

Entry	CeO_2 /g	Time /min	Product /mmol		DEC yield /%	Balance /%		r_{DEC}[c] /mmol h^{-1}	$\log_{10}(r_{DEC}$ /mmol $h^{-1})$
			DEC	Acetone		Ethoxy moiety[b] (in DEP + EtOH)	DEP		
1	0.03	3	0.13	0.68	0.60	101	106	1.1	0.058
2	0.03	10	0.23	0.88	1.1	101	105		
3	0.03	20	0.45	1.2	2.2	97	101		
4	0.06	3	0.20	0.82	0.95	99	105	2.4	0.38
5	0.06	7	0.32	1.0	1.5	99	103		
6	0.06	15	0.67	1.5	3.2	98	102		
7	0.09	3	0.24	1.0	1.2	96	105	3.2	0.51
8	0.09	7	0.45	1.3	2.1	101	106		
9	0.09	15	0.88	1.9	4.2	101	103		
10	0.15	3	0.35	1.2	1.7	100	106	4.2	0.62
11	0.15	7	0.56	1.5	2.7	98	103		
12	0.15	15	1.2	2.1	5.6	93	100		
13	0.20	3	0.40	1.4	1.9	101	108	5.1	0.70
14	0.20	7	0.74	1.8	3.6	101	106		
15	0.20	15	1.4	2.6	6.7	100	103		
16	0.25	3	0.33	1.4	1.6	98	104	6.4	0.81
17	0.25	7	0.82	2.0	3.9	101	106		
18	0.25	15	1.6	2.9	7.8	101	105		
19	0.35	3	0.54	1.8	2.6	102	109	7.0	0.85
20	0.35	7	0.96	2.2	4.6	99	103		
21	0.35	15	1.9	3.3	9.1	100	103		
22	0.70	3	0.71	2.8	3.4	99	108	8.7	0.94
23	0.70	7	1.2	3.4	5.9	100	106		
24	0.70	15	2.4	4.6	12	99	103		
25	1.5	3	0.62	4.5	2.9	100	109	7.0	0.84
26	1.5	7	1.1	5.2	5.3	100	107		
27	1.5	15	2.0	6.1	9.6	96	102		

[a]Reaction conditions: CeO_2 0.03–1.5 g; H-FAU 0.01 g; EtOH 6.5 g; DEP 2.8 g; toluene 20 g; CO_2 5 MPa (at 393 K); 393 K; 3–20 min. [b]Balance of ethoxy moiety involved in DEC, DEP, and EtOH. [c]Formation rate of DEC, estimated from each slope in Fig. S6.

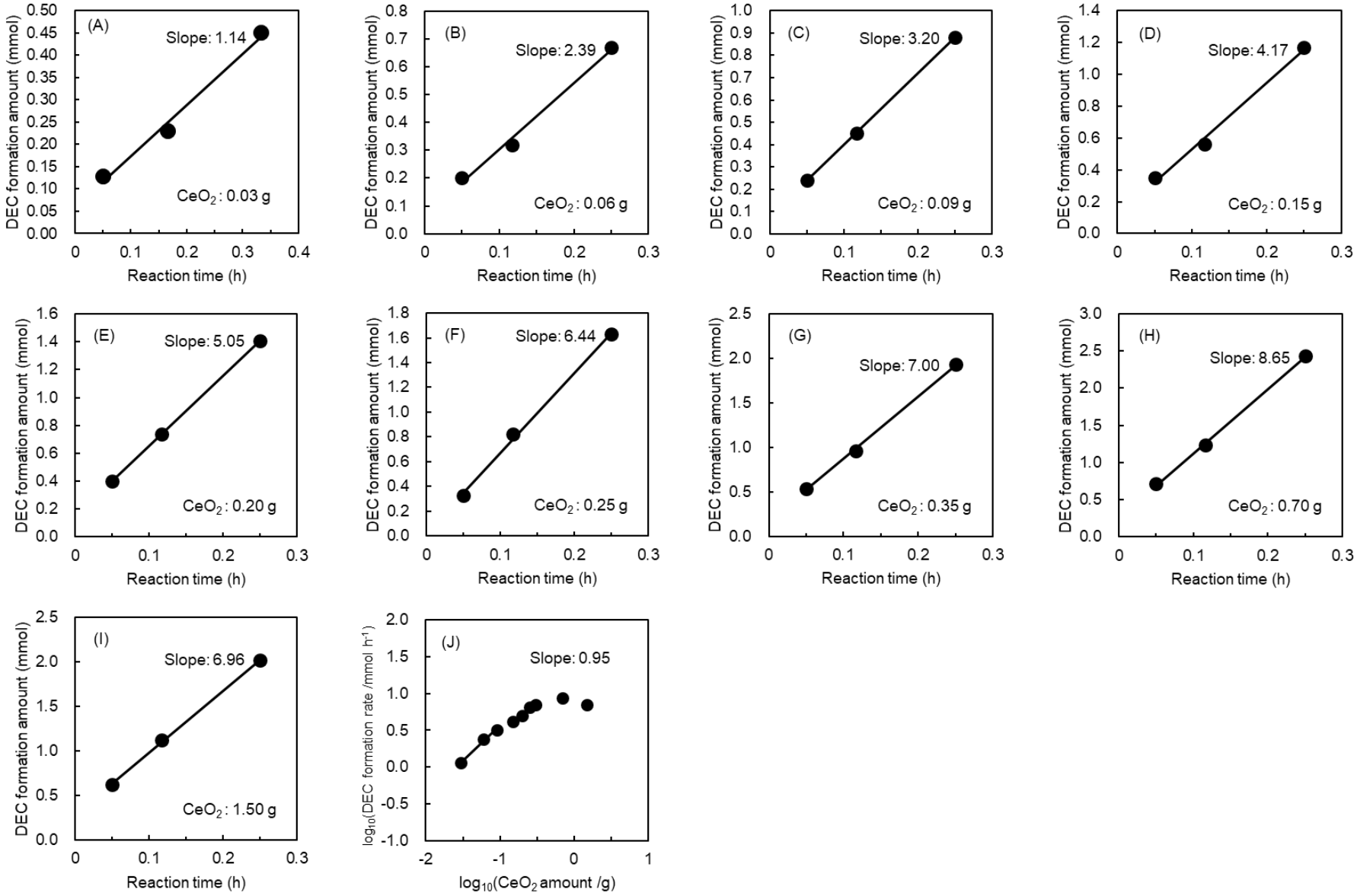

Fig. S6. Effect of CeO_2 amount on time courses for the DEC formation over CeO_2 in the presence of DEP and H-FAU. CeO_2 amount = (A) 0.03 g; (B) 0.06 g; (C) 0.09 g; (D) 0.15 g; (E) 0.20 g; (F) 0.25 g; (G) 0.35 g; (H) 0.70 g; (I) 1.5 g. (J) Double logarithmic plot of DEC formation rate as a function of CeO_2 amount at constant H-FAU loading (same figure as Fig. 2A). The detailed data are summarized in Table S5.
Reaction conditions: CeO_2 0.03–1.5 g; H-FAU 0.01 g; EtOH 6.5 g; DEP 2.8 g; toluene 20 g; CO_2 5 MPa (at 393 K); 393 K; 3–20 min.

Table S6. Effect of H-FAU amount on the DEC synthesis over CeO_2 in the presence of DEP and H-FAU (detailed data for Figs. 2B and S7).[a]

Entry	H-FAU /g	Time /min	Product /mmol		DEC yield /%	Balance /%		r_{DEC}[c] /mmol h^{-1}	$\log_{10}(r_{DEC}$ /mmol $h^{-1})$
			DEC	Acetone		Ethoxy moiety[b]	DEP		
1	0.00	3	0.020	0.12	>0.1	92	98	0.36	–0.44
2	0.00	10	0.068	0.30	0.32	96	97		
3	0.00	20	0.12	0.41	0.57	95	98		
4	0.01	3	0.24	1.0	1.2	96	105	3.2	0.51
5	0.01	7	0.45	1.3	2.1	101	106		
6	0.01	15	0.88	1.9	4.2	101	103		
7	0.02	3	0.35	1.2	1.7	96	103	5.1	0.71
8	0.02	7	0.66	1.6	3.2	100	103		
9	0.02	15	1.4	2.5	6.6	99	100		
10	0.03	3	0.43	1.6	2.0	100	103	6.5	0.81
11	0.03	7	0.75	1.9	3.6	96	99		
12	0.03	15	1.7	3.3	8.1	100	99		
13	0.04	3	0.50	1.6	2.4	96	98	7.3	0.86
14	0.04	7	0.83	1.9	4.0	94	97		
15	0.04	15	1.9	3.4	9.2	100	102		
16	0.07	3	1.1	2.1	5.0	104	103	7.6	0.88
17	0.07	7	1.6	2.3	7.5	101	100		
18	0.07	15	2.7	3.3	13	100	98		
19	0.09	3	1.0	2.4	4.8	102	97	7.8	0.89
20	0.09	7	1.5	2.6	7.1	104	102		
21	0.09	15	2.6	3.6	12	104	100		
22	0.12	3	0.96	2.5	4.6	101	98	7.3	0.86
23	0.12	7	1.5	3.1	7.2	103	97		
24	0.12	15	2.4	3.8	12	109	102		

[a]Reaction conditions: CeO_2 0.09 g; H-FAU 0.00–0.12 g; EtOH 6.5 g; DEP 2.8 g; toluene 20 g; CO_2 5 MPa (at 393 K); 393 K; 3–15 min. [b]Balance of ethoxy moiety involved in DEC, DEP, and EtOH. [c]Formation rate of DEC, estimated from each slope in Fig. S7.

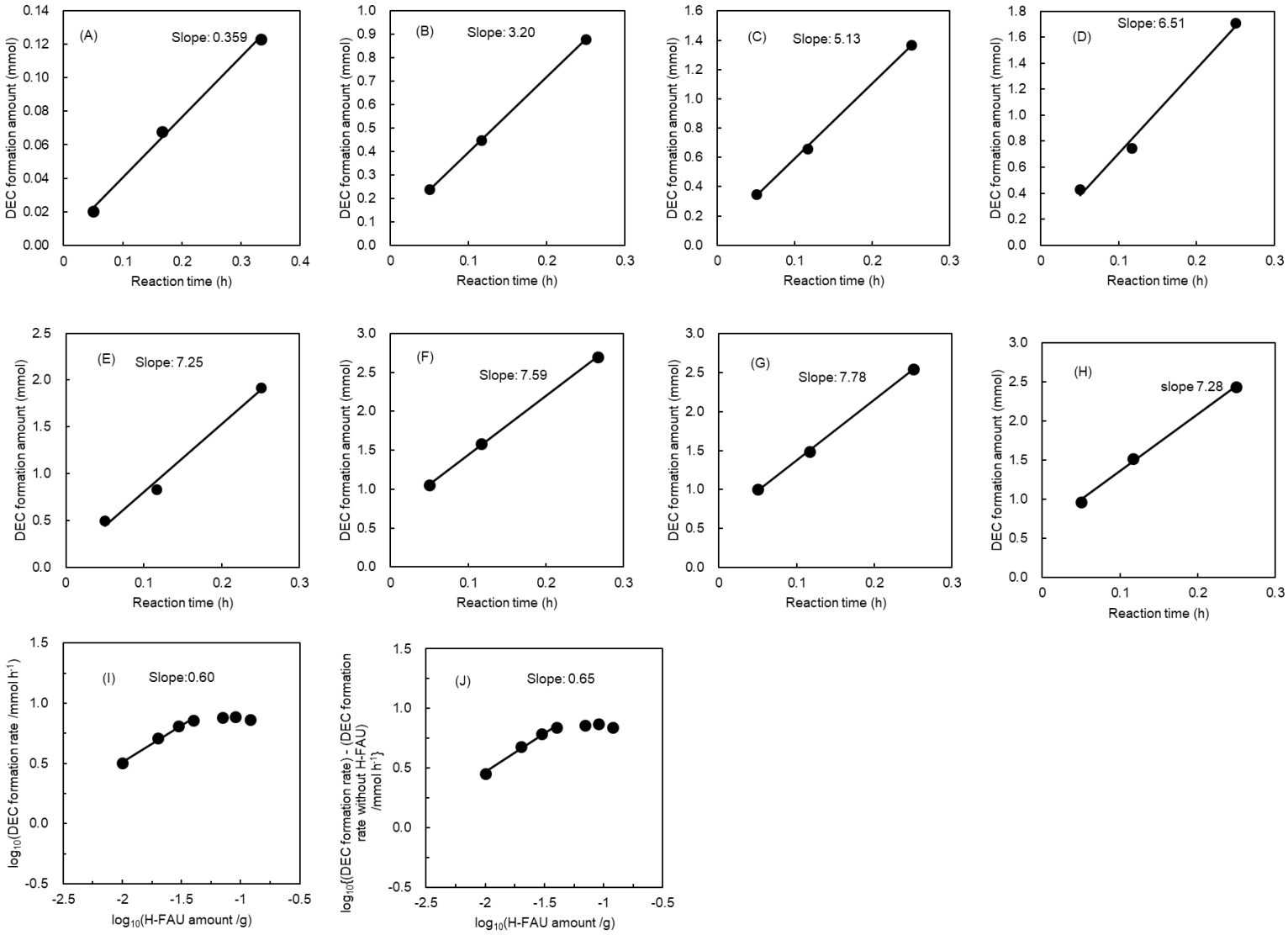

Figure S7. Effect of H-FAU amount on time courses for the DEC formation over CeO_2 in the presence of DEP and H-FAU. H-FAU amount =(A) 0 g; (B) 0.01 g; (C) 0.02 g; (D) 0.03 g; (E) 0.04 g; (F) 0.07 g; (G) 0.09 g; (H) 0.12 g. (I) Double logarithmic plot of DEC formation rate as a function of H-FAU amount at constant CeO_2 loading (same figure as Fig. 2B). (J) Double logarithmic plot of (DEC formation rate – DEC formation rate without H-FAU) as a function of H-FAU amount at constant CeO_2 loading. The detailed data are summarized in Table S6.
Reaction conditions: CeO_2 0.09 g; H-FAU 0.00–0.12 g; EtOH 6.5 g; DEP 2.8 g; toluene 20 g; CO_2 5 MPa (at 393 K); 393 K; 3–15 min.

Table S7. Effect of the amounts of CeO_2 and H-FAU at their constant weight ratio on the DEC synthesis over CeO_2 in the presence of DEP and H-FAU (detailed data for Figs. 2C and S8).[a]

Entry	CeO_2 /g	Time /min	Product /mmol		DEC yield /%	Balance /%		r_{DEC}[c] /mmol h^{-1}	$\log_{10}(r_{DEC}$ /mmol $h^{-1})$
			DEC	Acetone		Ethoxy moiety[b]	DEP		
1	0.03	3	0.13	0.68	0.60	101	106	1.1	0.058
2	0.03	10	0.23	0.88	1.1	101	105		
3	0.03	20	0.45	1.2	2.2	97	101		
4	0.06	3	0.28	1.2	1.3	101	105	3.3	0.52
5	0.06	7	0.42	1.4	2.0	101	103		
6	0.06	15	0.93	2.0	4.5	97	100		
7	0.09	3	0.43	1.6	2.0	100	103	6.5	0.81
8	0.09	7	0.75	1.9	3.6	96	99		
9	0.09	15	1.7	3.3	8.1	100	99		

[a]Reaction conditions: CeO_2 0.03–0.09 g; H-FAU 0.01–0.03 g (CeO_2/H-FAU weight ratio = 3); EtOH 6.5 g; DEP 2.8 g; toluene 20 g; CO_2 5 MPa (at 393 K); 393 K; 3–20 min. [b]Balance of ethoxy moiety involved in DEC, DEP, and EtOH. [c]Formation rate of DEC, estimated from each slope in Fig. S8.

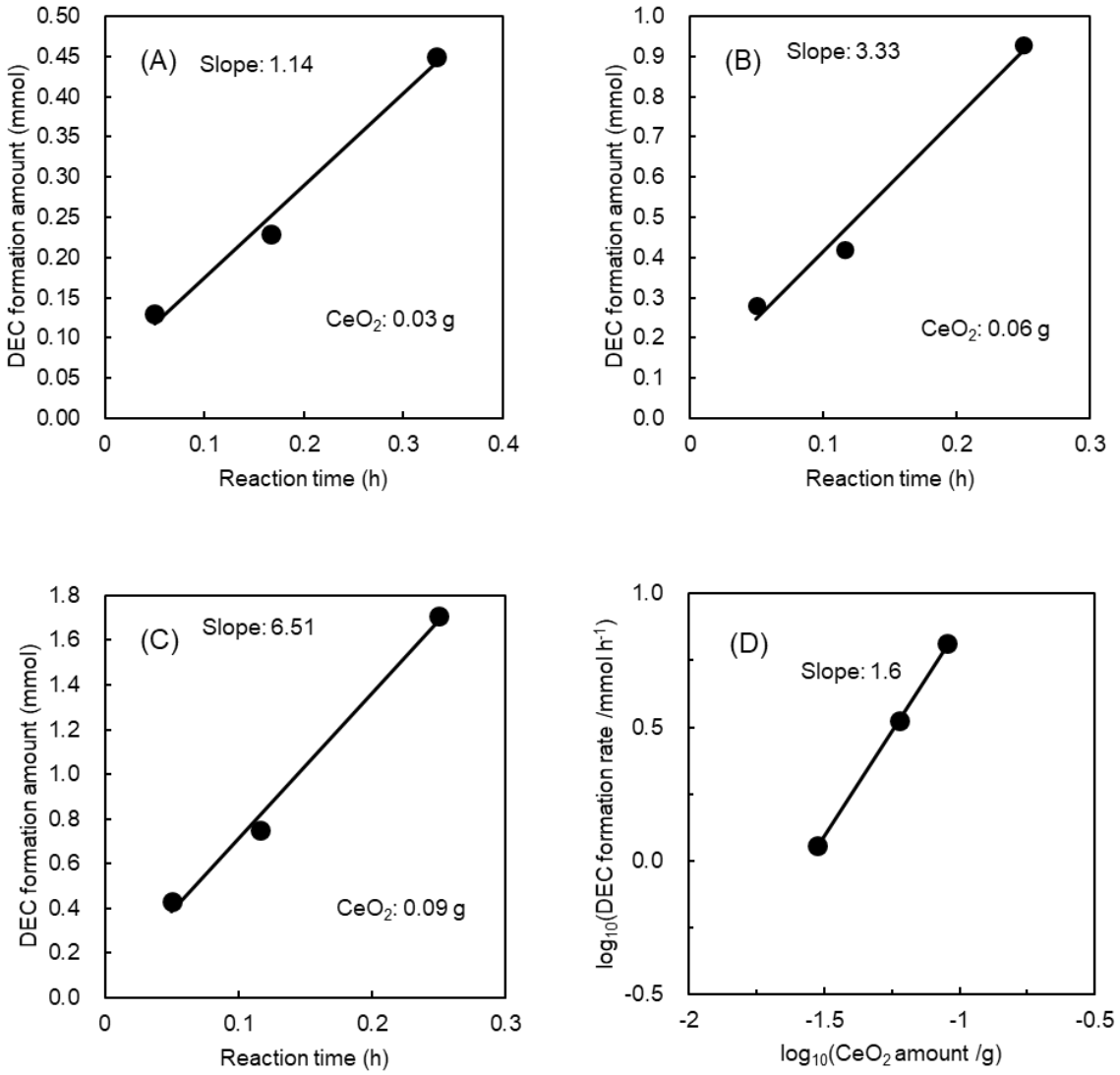

Figure S8. Effect of the amounts of CeO_2 and H-FAU at their constant weight ratio on time courses for the DEC formation over CeO_2 in the presence of DEP and H-FAU. CeO_2/H-FAU amount = (A) 0.03/0.01 g; (B) 0.06/0.02 g; (C) 0.09/0.03 g. (D) Double logarithmic plot of DEC formation rate as a function of CeO_2 amount at constant CeO_2/H-FAU weight ratio of 3 (same figure as Fig. 2C). The detailed data are summarized in Table S7.
Reaction conditions: CeO_2 0.03–0.09 g; H-FAU 0.01–0.03 g (CeO_2/H-FAU weight ratio = 3); EtOH 6.5 g; DEP 2.8 g; toluene 20 g; CO_2 5 MPa (at 393 K); 393 K; 3–20 min.

Table S8. Effect of EtOH amount on the DEC synthesis over CeO_2 in the presence of DEP and H-FAU (detailed data for Figs. 3 (black squares) and S9).[a]

Entry	EtOH /g	EtOH conc. /mol L^{-1}	Time /min	Product /mmol		DEC yield /%	Balance /%		r_{DEC}[c] /mmol h^{-1}	$\log_{10}(r_{DEC}$ /mmol $h^{-1})$
				DEC	Acetone		Ethoxy moiety[b]	DEP		
1	1.6	1.2	3	0.12	1.1	0.57	99	101	0.59	–0.23
2	1.6	1.2	10	0.18	1.1	0.86	100	104		
3	1.6	1.2	15	0.24	1.2	1.1	96	100		
4	2.4	1.7	3	0.16	1.2	0.76	98	101	0.79	–0.15
5	2.4	1.7	10	0.23	1.2	1.1	98	102		
6	2.4	1.7	15	0.30	1.2	1.4	100	103		
7	3.2	2.3	3	0.14	0.92	0.67	94	99	0.97	–0.10
8	3.2	2.3	10	0.20	1.1	0.95	94	98		
9	3.2	2.3	20	0.36	1.3	1.7	93	96		
10	4.0	2.7	3	0.13	0.93	0.62	93	100	1.0	–0.013
11	4.0	2.7	10	0.20	1.1	0.95	92	98		
12	4.0	2.7	20	0.40	1.4	1.9	91	95		
13	4.5	3.0	3	0.13	0.92	0.62	93	100	1.0	0.010
14	4.5	3.0	10	0.25	1.1	1.2	93	98		
15	4.5	3.0	20	0.42	1.3	2.0	93	98		
16	5.0	3.3	3	0.14	0.97	0.67	93	100	1.1	0.025
17	5.0	3.3	10	0.26	1.0	1.2	93	98		
18	5.0	3.3	20	0.44	1.4	2.1	92	97		
19	6.5	4.0	3	0.13	0.68	0.62	101	106	1.1	0.058
20	6.5	4.0	10	0.23	0.88	1.1	101	105		
21	6.5	4.0	20	0.45	1.2	2.1	97	101		

[a]Reaction conditions: CeO_2 0.03 g; H-FAU 0.01 g; EtOH 1.6–6.5 g; DEP 2.8 g; toluene 20 g; CO_2 5 MPa (at 393 K); 393 K; 3–20 min.
[b]Balance of ethoxy moiety involved in DEC, DEP, and EtOH. [c]Formation rate of DEC, estimated from each slope in Fig. S9.

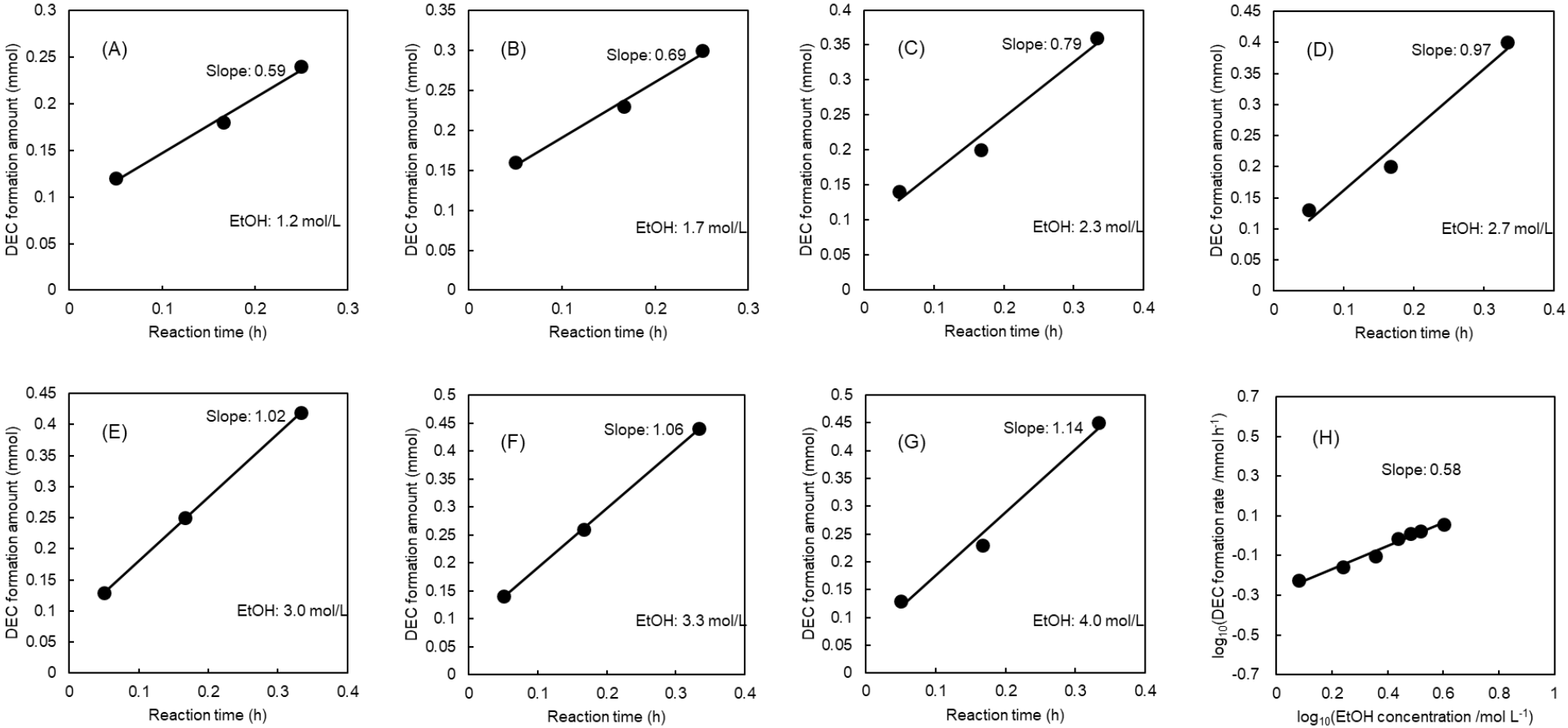

Figure S9. Effect of EtOH amount on time courses for the DEC formation over CeO_2 in the presence of DEP and H-FAU. EtOH amount = (A) 1.6 g (1.3 M); (B) 2.4 g (2.0 M); (C) 3.2 g (2.7 M); (D) 4.0 g (3.3 M); (E) 4.5 g (3.7 M); (F) 5.0 g (4.2 M); (G) 6.5 g (5.4 M). (H) Double logarithmic plot of DEC formation rate as a function of EtOH concentration (same figure as Fig. 3 (black squares)). The detailed data are summarized in Table S8.
Reaction conditions: CeO_2 0.03 g; H-FAU 0.01 g; EtOH 1.6–6.5 g; DEP 2.8 g; toluene 20 g; CO_2 5 MPa (at 393 K); 393 K; 3–20 min.

Table S9. Effect of EtOH amount on the DEC synthesis over CeO_2 without DEP or H-FAU (detailed data for Figs. 3 (red circles) and S10).[a]

Entry	EtOH /g	Toluene /g	EtOH conc. /mol L^{-1}	Time /min	Product /mmol	DEC yield /%	Balance /%	r_{DEC}[c] /mmol h^{-1}	$\log_{10}(r_{DEC}$ /mmol $h^{-1})$
					DEC		Ethoxy moiety[b]		
1	3.2	20	2.5	3	0.0066	<1	87	0.076	–1.1
2	3.2	20	2.5	10	0.012	<1	84		
3	3.2	20	2.5	20	0.028	<1	92		
4	1.6	8.2	2.9	3	0.0071	<1	95	0.095	–1.0
5	1.6	8.2	2.9	5	0.010	<1	95		
6	1.6	8.2	2.9	10	0.018	<1	93		
7	4.8	20	3.5	3	0.0080	<1	93	0.066	–1.2
8	4.8	20	3.5	7	0.011	<1	93		
9	4.8	20	3.5	15	0.021	<1	90		
10	6.5	20	4.4	3	0.0078	<1	96	0.072	–1.1
11	6.5	20	4.4	7	0.011	<1	92		
12	6.5	20	4.4	15	0.022	<1	95		
13	3.2	6.3	5.6	3	0.012	<1	89	0.066	–1.2
14	3.2	6.3	5.6	10	0.022	<1	91		
15	3.2	6.3	5.6	20	0.031	<1	90		
16	6.5	2.9	11	3	0.019	<1	95	0.062	–1.2
17	6.5	2.9	11	7	0.021	<1	94		
18	6.5	2.9	11	15	0.031	<1	95		
19	6.5	0	17	3	0.016	<1	92	0.081	–1.1
20	6.5	0	17	10	0.025	<1	92		
21	6.5	0	17	20	0.039	<1	92		

[a]Reaction conditions: CeO_2 0.03 g; EtOH 1.6–6.5 g; toluene 0–20 g; CO_2 5 MPa (at 393 K); 393 K; 3–20 min. [b]Balance of ethoxy moiety involved in DEC and EtOH. [c]Formation rate of DEC, estimated from each slope in Fig. S10.

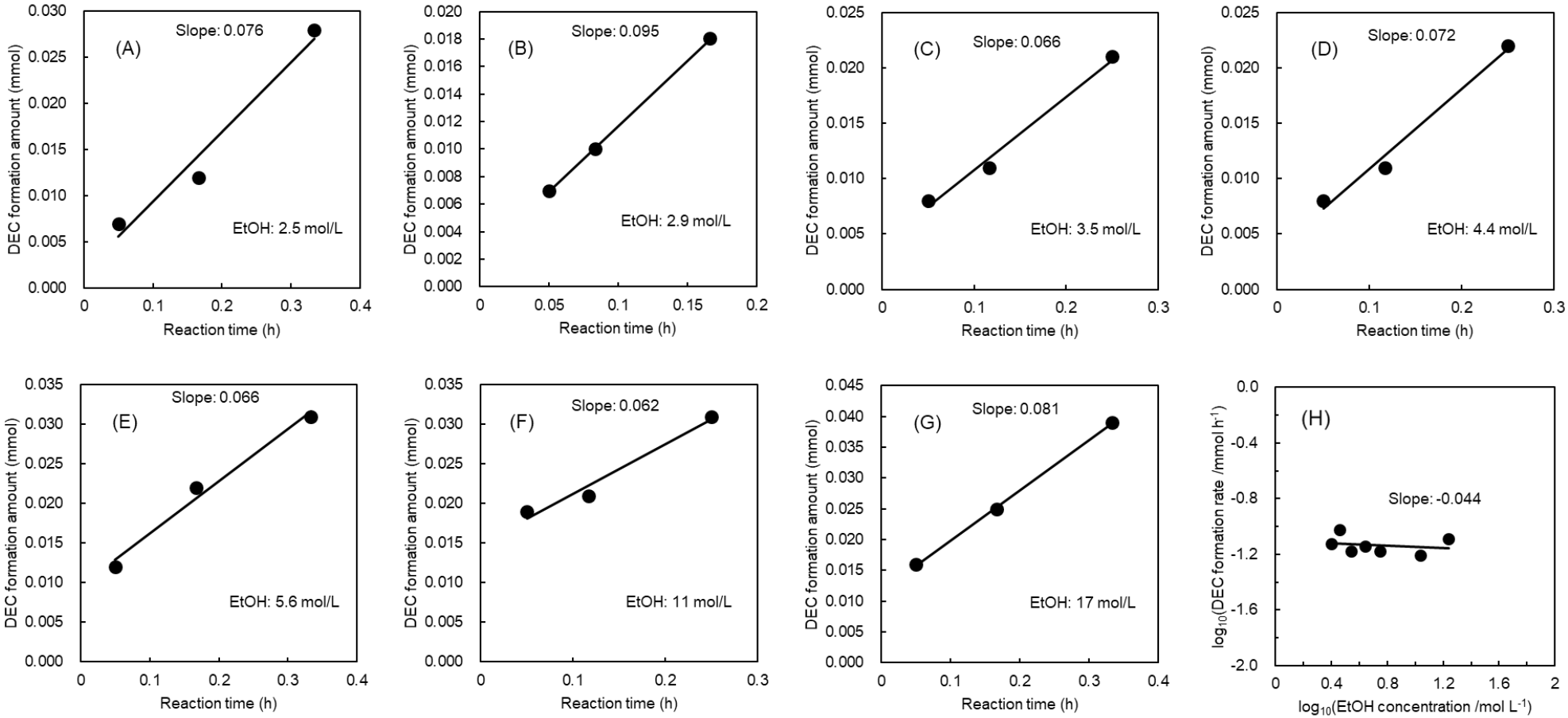

Figure S10. Effect of EtOH amount on time courses for the DEC formation over CeO_2. EtOH/toluene amount (EtOH concentration) = (A) 3.2 g/20 g (2.5 M); (B) 1.6 g/8.2 g (2.9 M); (C) 4.8 g/20 g (3.5 M); (D) 6.5 g/20 g (4.4 M); (E) 3.2 g/6.3 g (5.6 M); (F) 6.5 g/2.9 g (11 M); (G) 6.5 g/0 g (17 M). (H) Double logarithmic plot of DEC formation rate as a function of EtOH concentration (same figure as Figure 3 (red squares)). The detailed data are summarized in Table S9. Reaction conditions: CeO_2 0.03 g; EtOH 1.6–6.5 g; toluene 0–20 g; CO_2 5 MPa (at 393 K); 393 K; 3–20 min.

Table S10. Effect of DEP amount on the DEC synthesis over CeO_2 in the presence of DEP and H-FAU (detailed data for Figs. 4 and S11).[a]

Entry	DEP /mmol	DEP conc. /mol L^{-1}	Time /min	Product /mmol		DEC yield /%	Balance /%		r_{DEC}[c] /mmol h^{-1}	$\log_{10}(r_{DEC}$ /mmol $h^{-1})$
				DEC	Acetone		Ethoxy moiety[b]	DEP		
1	7.0	0.21	3	0.13	1.2	1.9	96	103	1.1	0.032
2	7.0	0.21	10	0.21	1.1	3.0	96	97		
3	7.0	0.21	20	0.43	1.4	6.1	94	94		
4	14	0.41	3	0.13	0.85	0.92	95	97	1.2	0.061
5	14	0.41	10	0.21	0.99	1.5	94	97		
6	14	0.41	20	0.45	1.3	3.2	95	95		
7	21	0.60	3	0.13	0.68	0.62	101	106	1.1	0.058
8	21	0.60	10	0.23	0.88	1.1	101	105		
9	21	0.60	20	0.45	1.2	2.1	97	101		
10	28	0.77	3	0.13	1.1	0.46	95	99	1.2	0.083
11	28	0.77	7	0.20	1.6	0.71	95	100		
12	28	0.77	15	0.37	1.7	1.3	96	99		

[a]Reaction conditions: CeO_2 0.03 g; H-FAU 0.01 g; EtOH 6.5 g; DEP 7.0–28 mmol; toluene 20 g; CO_2 5 MPa (at 393 K); 393 K; 3–15 min.
[b]Balance of ethoxy moiety involved in DEC, DEP, and EtOH. [c]Formation rate of DEC, estimated from each slope in Fig. S11.

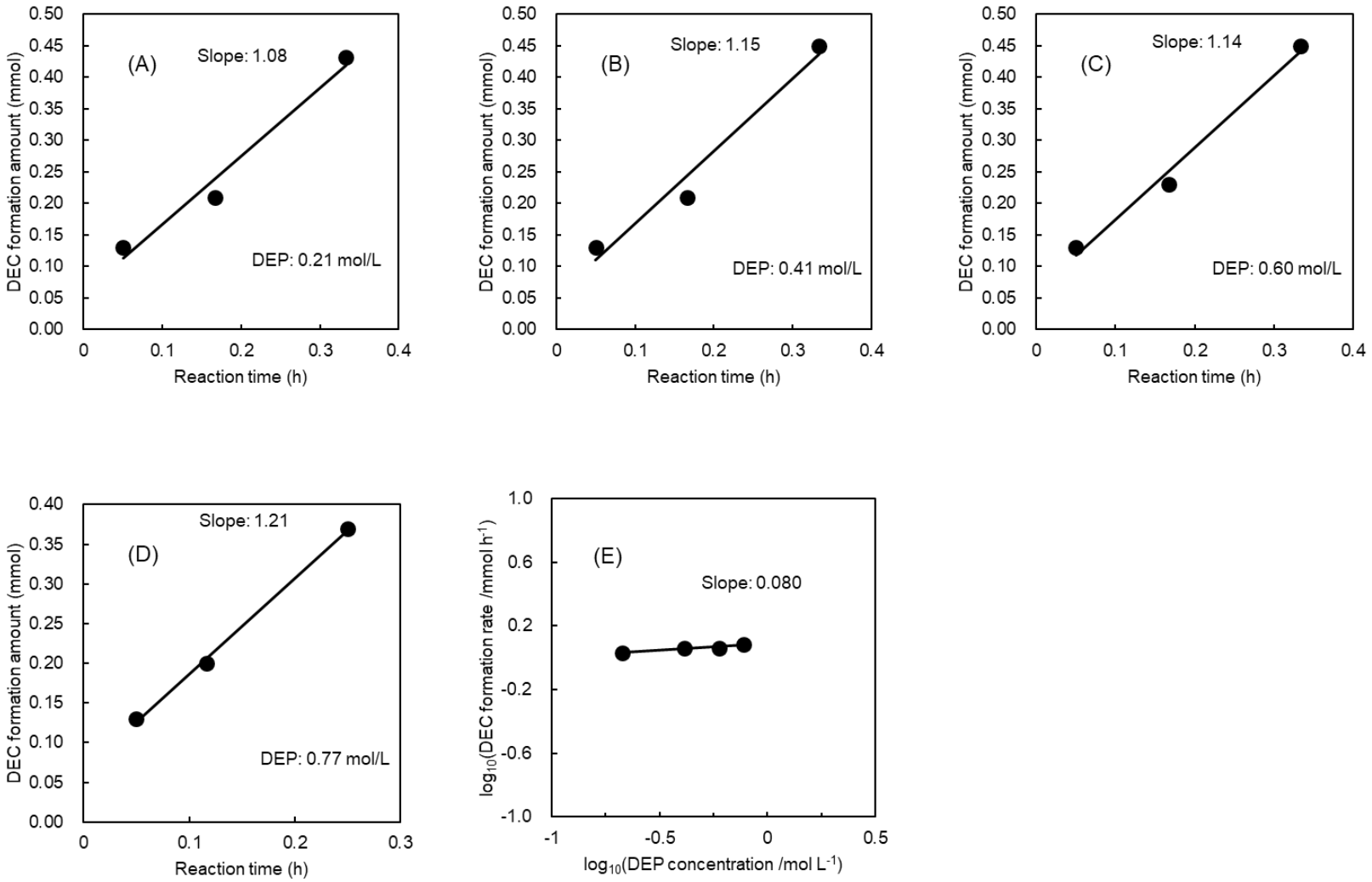

Figure S11. Effect of DEP amount on time courses for the DEC formation over CeO_2 in the presence of DEP and H-FAU. DEP amount = (A) 7 mmol (0.21 M); (B) 14 mmol (0.41 M); (C) 21 mmol (0.60 M); (D) 28 mmol (0.77 M). (E) Double logarithmic plot of DEC formation rate as a function of DEP concentration (same figure as Fig. 4). The detailed data are summarized in Table S10.
Reaction conditions: CeO_2 0.03 g; H-FAU 0.01 g; EtOH 6.5 g; DEP 7–28 mmol; toluene 20 g; CO_2 5 MPa (at 393 K); 393 K; 3–15 min.

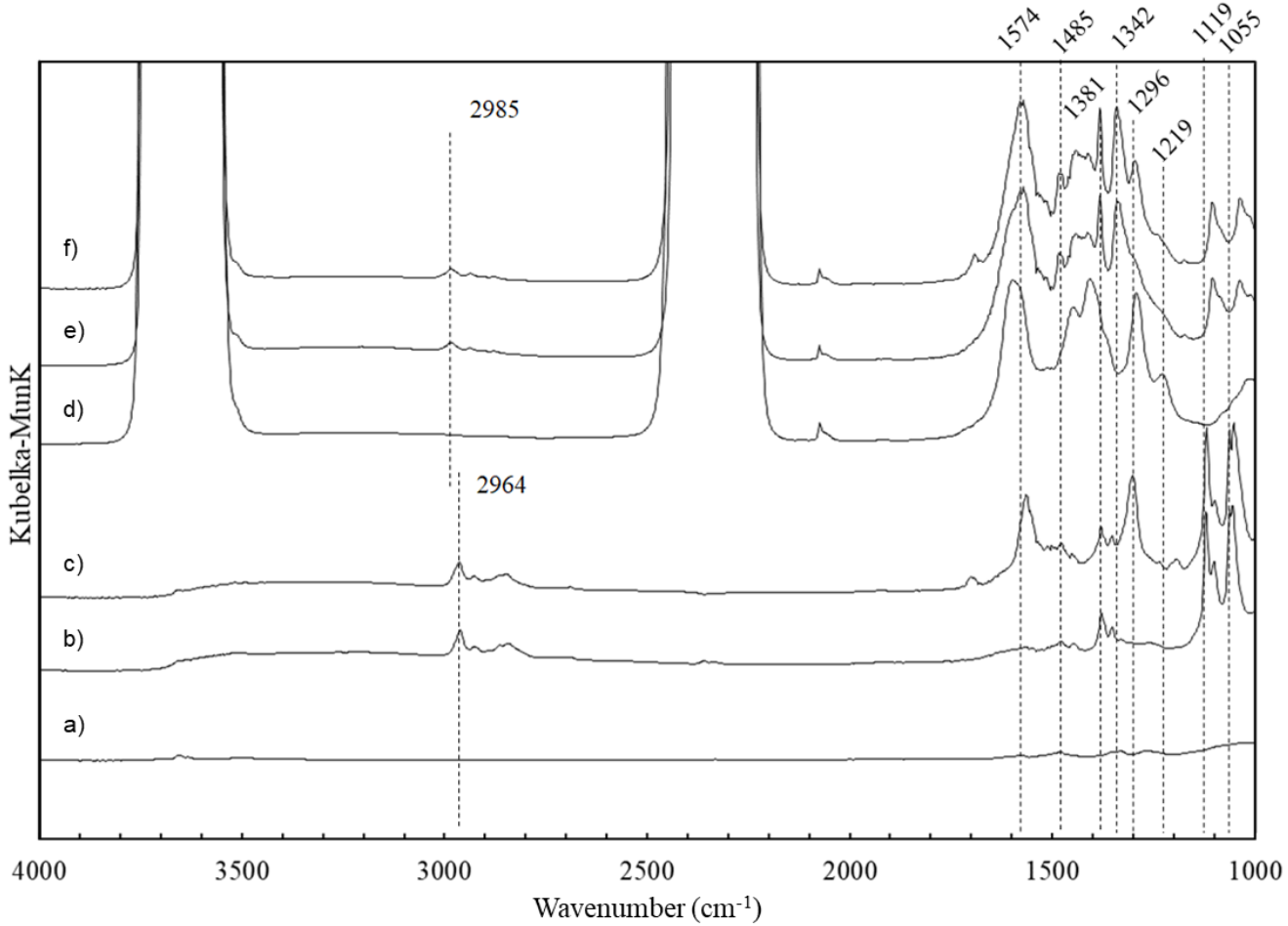

Figure S12. Full-scale DRIFT spectra of CeO_2 with different treatment(s): (a) after treatment at 873 K for 3 h in 20 vol% O_2/N_2 flow (50 mL min^{-1}); (b) after injection of EtOH in N_2 flow (30 mL min^{-1}) at 0.1 MPa; (c) after injection of DEP in N_2 flow (30 mL min^{-1}) at 0.1 MPa; (d) after pressurization by CO_2 at 4 MPa; (e) after injection of EtOH in N_2 flow (30 mL min^{-1}) at 0.1 MPa, purging with CO_2, and pressurization by CO_2 at 4 MPa; (f) after injection of DEP in N_2 flow (30 mL min^{-1}) at 0.1 MPa, purging with CO_2, and pressurization by CO_2 at 4 MPa. The whole procedure except for (a) was operated at room temperature. The spectra (a–c) were recorded in N_2 flow (30 mL min^{-1}) at room temperature, and the spectra (d–f) were done in CO_2 (4 MPa) at room temperature. All the spectra were recorded after the CeO_2 surface was saturated by each compound (*i.e.*, EtOH, DEP, or CO_2). All the spectra were normalized on the basis of the spectrum of CeO_2 itself before each treatment.

The expanded spectra are shown in Fig. 5. The detailed assignments are listed in Table S11.

Table S11. Assignment of absorption peaks observed in DRIFT spectra of CeO_2 with different treatments (Fig. 5).

Wavenumber /cm^{-1}	Assignment	Similar band in other works[a]	Ref(s)
2985	$\nu_{as}(CH_3)$ of ethyl moiety in ethyl carbonate		
2964	$\nu_{as}(CH_3)$ of ethyl moiety in ethoxy species	$\nu_{as}(CH_3)$ of ethyl moiety (2970)	S2, S3
2929	$\nu_{as}(CH_2)$ of ethyl moiety	$\nu_{as}(CH_2)$ of ethyl moiety (2933–2930)	S2, S3
2845	$\nu_{s}(CH_3)$ of ethyl moiety	$\nu_{s}(CH_3)$ of ethyl moiety (2880)	S2
1598	$\nu(CO_3)$ of hydrogen carbonate	$\nu(CO_3)$ of hydrogen carbonate (1613, 1599)	S4
1583	$\nu(CO_3)$ of hydrogen carbonate	$\nu(CO_3)$ of hydrogen carbonate (1599)	S4
1574	$\nu(CO_3)$ of bidentate ethyl carbonate	$\nu(CO_3)$ of bidentate carbonate (1567)	S4
1485	$\nu(CO_3)$ of monodentate ethyl carbonate	$\nu(CO_3)$ of monodentate carbonate (1504)	S4
1479	$\delta(CH_2)$ of ethyl moiety	$\delta(CH_2)$ of ethyl moiety (1473)	S3
1461	$\nu(CO_3)$ of polydentate ethyl carbonate	$\nu(CO_3)$ of polydentate carbonate (1462–1460)	S4, S5
1413	$\nu(CO_3)$ of hydrogen carbonate	$\nu(CO_3)$ of hydrogen carbonate (1413–1404)	S4, S6
1381	$\nu(CO_3)$ of polydentate and/or monodentate ethyl carbonate	$\nu(CO_3)$ of polydentate carbonate (1353) $\nu(CO_3)$ of monodentate carbonate (1351)	S4
1380	$\delta_s(CH_3)$ of ethoxy species	$\delta_s(CH_3)$ of ethoxy species	S3
1342	$\nu(CO_3)$ of monodentate ethyl carbonate	$\nu(CO_3)$ of monodentate ethyl carbonate (1351)	S4
1296	$\nu(CO_3)$ of bidentate ethyl carbonate	$\nu(CO_3)$ of bidentate carbonate (1289–1278)	S4, S5
1219	δ(OH) of hydrogen ethyl carbonate	δ(OH) of hydrogen carbonate (1218–1217)	S4, S6
1122	ν(C–O) of terminal ethoxy species	ν(C–O) of terminal alkoxy species (1110–1101)	S2, S5
1054	ν(C–O) of bridged ethoxy species	ν(C–O) of bridged alkoxy species (1050)	S5
1037	$\nu(CO_3)$ of hydrogen carbonate	$\nu(CO_3)$ of hydrogen carbonate (1025)	S4

[a]Values in parentheses represent wavenumber (unit: cm^{-1}).

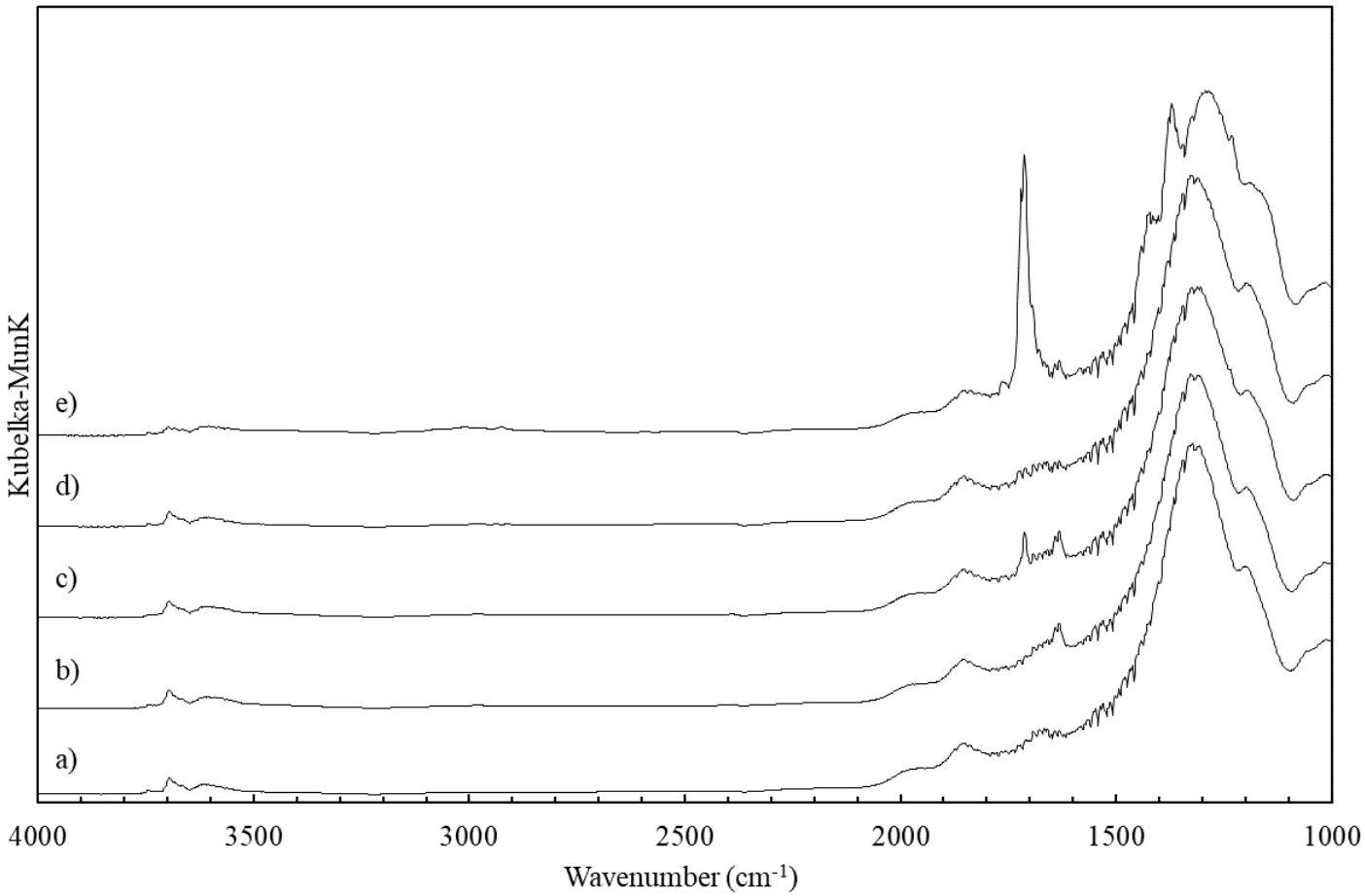

Fig. S13. DRIFT spectra of H-FAU after heat-treatment at 773 K for 1 h in 20 vol% O_2/N_2 (50 mL min^{-1}) and subsequent different treatment(s): (a) in N_2 flow (30 mL min^{-1}); (b) after injection of 1.1 μmol of EtOH in N_2 flow (30 mL min^{-1}) at 0.1 MPa; (c) after injection of 1.1 μmol of DEP in N_2 flow (30 mL min^{-1}) at 0.1 MPa; (d) after injection of 0.55 μmol of DEC in N_2 flow (30 mL min^{-1}) at 0.1 MPa; (e) after injection of 3.2 μmol of acetone in N_2 flow (30 mL min^{-1}) at 0.1 MPa. The whole treatment procedure was operated at room temperature. All the spectra were recorded in N_2 flow (30 mL min^{-1}) at room temperature and normalized on the basis of the spectrum of H-FAU itself before each treatment.

Table S12. Effect of DEP amount on the DEC synthesis over CeO_2 in the presence of DEP and H-FAU (detailed data for Fig. 6).[a]

Entry	EtOH used /mmol	EtOH detected /mmol	Product /mmol		Balance /%	
			DEC	Acetone	Ethoxy moiety (in DEP + EtOH)	DEP
1	0	6	0.26	1.2	89	96
2	18	18	1.2	2.1	84	91
3	35	33	2.3	3.9	88	97
4	52	52	2.9	5.8	94	107
5	70	68	4.1	5.7	93	101
6	105	103	4.3	5.9	97	108

[a]Reaction conditions: CeO_2 0.1 g; H-FAU 0.01 g; EtOH 0–105 mmol; DEP 21 mmol; toluene 20 g; CO_2 5 MPa (at room temperature); 393 K; 1 h.

Supplementary references

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