Supporting Information

Comparative study on heterogeneous CeO_2 and homogeneous diazabicyclo[5.4.0]-7-undecene catalysts for conversion of CO_2 and monoethanolamine/ethylenediamine into cyclic compounds

Hiroki Sato,[a] Mizuho Yabushita,[a,]* Yingai Li,[a] Yoshinao Nakagawa,[a] Keiichi Tomishige[a,b,]*

[a]*Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan*
[b]*Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan*

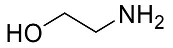
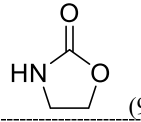
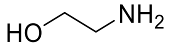
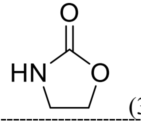
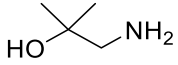
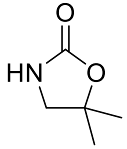
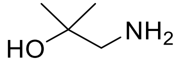
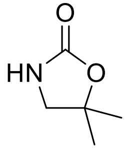
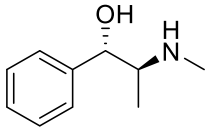
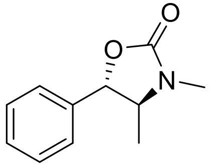
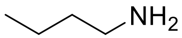
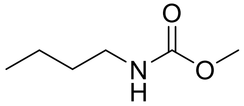
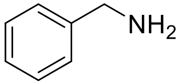
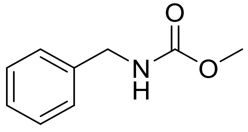
**Corresponding authors: m.yabushita@tohoku.ac.jp (M.Y.); tomishige@tohoku.ac.jp (K.T.)*

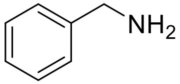
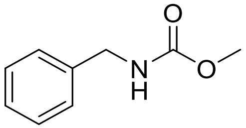
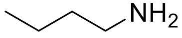
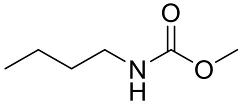
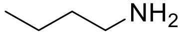
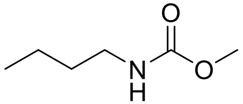
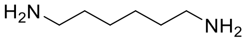
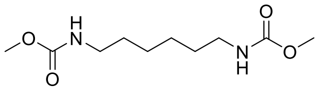
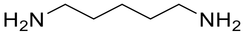
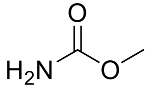
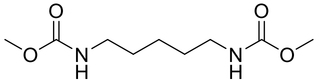
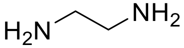
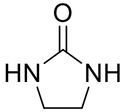
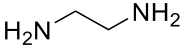
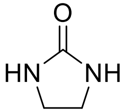
[**Calculation of the number of surface Ce atoms of CeO_2**]

In our previous report, the specific surface area for the CeO_2 sample calcined at 873 K was determined from N_2 physisorption measurement and the Brunauer-Emmett-Teller (BET) equation to be 86 m^2 g^{-1}.[S1] The crystal structure of the same sample was confirmed by powder X-ray diffraction (XRD) measurement to be a fluorite structure. According to the crystal database (ICSD card #24887), the size of unit cell of fluorite CeO_2 is 0.542 nm × 0.542 nm × 0.542 nm, and two Ce atoms are present at the surface of this unit cell. On the basis of these data, the number of surface Ce atoms of CeO_2 catalyst in this study was calculated as follows:

$$\text{Surface Ce atoms in 1 g of CeO}_2\ (\text{mmol g}^{-1}) = \frac{86\times2}{\left(0.542\times10^{-9}\right)^2\times6.02\times10^{23}}\times1000 = 0.97$$

Table S1. List of reported reaction systems for synthesizing organic carbamates and urea derivatives directly from CO_2 with either CeO_2 or DBU catalyst.[a]

Entry	Catalyst ([mmol])	Amine ([mmol])	Alcohol ([mmol])	$P(CO_2)$ [MPa]	Additive ([mmol])	Solvent ([mL])	Temp. [K]	Time [h]	Conversion [%]		Product (yield [%])	Kinetic data		Ref.
									Amine	Alcohol		Temp. [K]	v_{Product}[b] [mmol mmol^{-1} h^{-1}]	
Synthesis of organic carbamates from CO_2, amine, and alcohol														
1	CeO_2 (1.0)	 (10)	–	5	–	Acetonitrile (53)	423	4	97	–	 (97)	423	2.7	S2
2	MOF-derived CeO_2 (1.2)	 (10)	–	0.5	–	2-Propanol (15)	433	12	35	–	 (34)	n.r.	n.r.	S3
3	DBU (1.0)	 (0.5)	–	0.1	T3P[c] (0.65)	Acetonitrile (7.1)	r.t.	18	n.r.	–	 (49)	n.r.	n.r.	S4
4	DBU (0.2) + Cs_2CO_3 (3.0)	 (0.5)	–	0.1	T3P[c] (0.65)	Acetonitrile (7.1)	r.t.	18	n.r.	–	 (100)	n.r.	n.r.	S4
5	DBU (0.11)	 (0.1)	–	0.1	*n*-BuCl (0.12)	DMSO (4)	413	4	n.r.	–	 (18)	n.r.	n.r.	S5
6	MOF-derived CeO_2 (1.0)	 (5)	Methanol (900)	5.0	–	–	433	12	96	n.r.	 (88)	n.r.	n.r.	S3
7	MOF-derived CeO_2 (1.0)	 (5)	Methanol (900)	5.0	–	–	433	12	87	n.r.	 (81)	n.r.	n.r.	S3

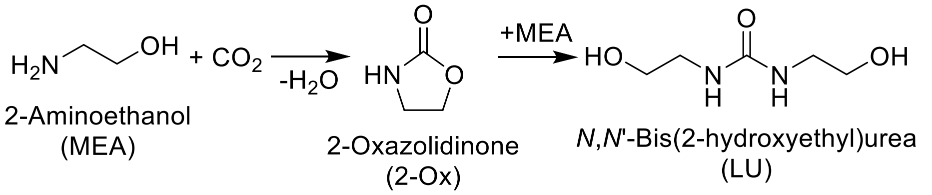
8	CeO_2 (1.0)	 (5)	Methanol (900)	5	–	–	423	12	99	n.r.	 (92)	403	0.36	S6
9	CeO_2 (1.7)	 (5)	Methanol (200)	5.0	–	–	443	8	85	n.r.	 (59)	443	0.40	S7
10	Mn-doped CeO_2 (1.7)	 (5)	Methanol (200)	5.0	–	–	443	8	87	n.r.	 (65)	443	0.45	S7
11	CeO_2 (1.2)	 (5)	Methanol (500)	5.0	–	NMP (20)	423	12	100	n.r.	 (72)	n.r.	n.r.	S8
12	CeO_2 (0.35)	 (5.9)	–	–	 (35)	Methanol (14)	453	1	100	–	 (96)	n.r.	n.r.	S9
Synthesis of urea derivatives from CO_2 and aliphatic amine														
13	CeO_2 (0.2)	 (10)	–	0.5	–	Methanol (200)	433	12	98	–	 (94)	433	4.0	S10
14	MOF-derived CeO_2 (1.2)	 (10)	–	0.5	–	2-Propanol (15)	433	12	95	–	 (94)	n.r.	n.r.	S3

[a] Abbreviations in this table: MOF = metal-organic framework; DBU = diazabicyclo[5.4.0]-7-undecene; T3P = propanephosphonic acid anhydride; *n*-Bu = *n*-butyl; DMSO = dimethyl sulfoxide; NMP = *N*-methyl-2-pyrrolidone; r.t. = room temperature; n.r. = not reported.

[b] Formation rate of target product based on the mole of CeO_2.

[c] Added into a reactor after 4 h.

Table S2. Detailed data for Fig. S11A (time courses of the conversion of MEA and CO_2 with CeO_2 and DBU catalysts).[a,b]

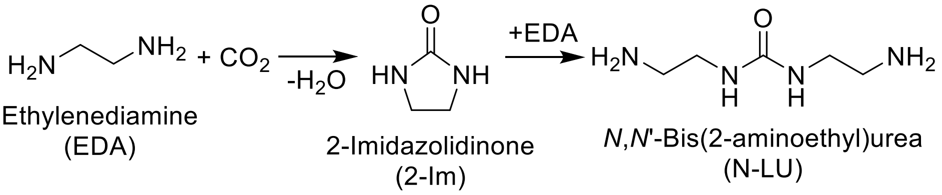


Entry	Catalyst	Time [h]	2-Ox yield [%]	Detected compounds [mmol]			Balance [%]	
				MEA	2-Ox	LU	MEA	DBU
1	CeO_2	0	15	9.0	1.5	0.10	105	–
2		1	27	6.9	2.7	0.41	95	–
3		2	32	6.4	3.2	0.47	96	–
4		4	48	4.1	4.8	0.82	89	–
5		24	83	2.1	8.4	0.045	103	–
6		48	80	2.0	8.1	0.031	100	–
8	DBU	0	0.0	13	0.0	0.0	128	130
9		4	2.0	10	0.20	0.0	104	95
10		24	40	6.6	4.1	0.0	105	102
11		72	64	3.4	6.5	0.0	98	86
12		120	86	1.2	8.7	0.19	98	73

[a] Reaction conditions: MEA 10 mmol; CeO_2 or DBU 1.0 mmol; acetonitrile 500 mmol; 403 K; CO_2 2 MPa (at r.t.); 0–120 h.

[b] Abbreviations: MEA = 2-aminoethanol; DBU = diazabicyclo[5.4.0]-7-undecene; 2-Ox = 2-oxazolidinone; LU = *N*,*N*’-bis(2-hydroxyethyl)urea.

Table S3. Detailed data for Fig. S11B (time courses of the conversion of EDA and CO_2 with CeO_2 and DBU catalysts).[a,b]

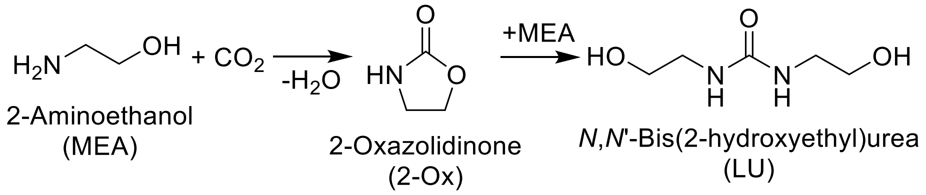


Entry	Catalyst	Time [h]	2-Im yield [%]	Detected compounds [mmol]			Balance [%]	
				EDA	2-Im	N-LU	EDA	DBU
1	CeO_2	0	1.3	10	0.13	0.0	101	–
2		1	2.1	9.8	0.21	0.0	100	–
3		2	2.4	9.7	0.24	0.0	99	–
4		4	3.3	9.6	0.33	0.0	98	–
5		24	18	7.3	1.8	0.0	90	–
6		48	30	5.8	3.0	0.0	87	–
7		72	34	6.0	3.4	0.0	94	–
8		96	45	5.1	4.5	0.0	96	–
9	DBU	0	0.81	10	0.082	0.0	101	94
10		1	2.5	9.8	0.25	0.0	99	82
11		2	3.4	10	0.35	0.0	103	78
12		4	4.6	9.1	0.47	0.0	95	69
13		24	30	6.2	3.0	0.0	91	72
14		48	51	4.5	5.1	0.0	96	62
15		72	72	2.4	7.3	0.0	96	61
16		96	94	0.41	9.5	0.0	98	55

[a] Reaction conditions: EDA 10 mmol; CeO_2 or DBU 1.0 mmol; acetonitrile 500 mmol; 403 K; CO_2 2 MPa (at r.t.); 0–96 h.

[b] Abbreviations: EDA = ethylenediamine; DBU = diazabicyclo[5.4.0]-7-undecene; 2-Im = 2-imidazolidinone; N-LU = *N*,*N*'-bis(2-aminoethyl)urea.

Table S4. Detailed data for Fig. S12 (initial time courses for the conversion of MEA and CO_2 at various temperatures with CeO_2 and DBU catalysts).[a,b]



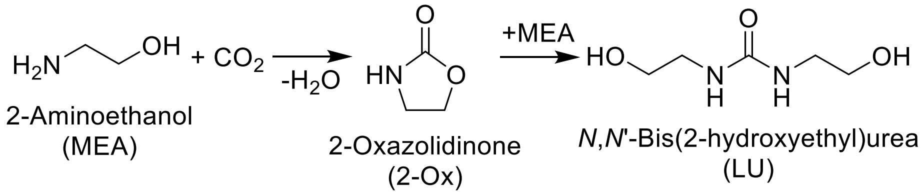
Entry	Catalyst	Catalyst amount [mmol]	Temp. [K]	Time [h]	2-Ox yield [%]	Detected compounds [mmol]			Balance [%]		$v_{\text{2-Ox}}$[c] [mmol mmol^{-1} h^{-1}]
						MEA	2-Ox	LU	MEA	DBU	
1	CeO_2	0.25	393	0	0.061	10	0.0061	0.00	103	–	0.50
2				1.5	2.7	10	0.27	0.015	102	–	
3				3	3.8	9.5	0.38	0.022	98	–	
4		0.25	403	0	0.47	11	0.048	0.0	105	–	0.80
5				2	4.4	9.4	0.45	0.088	98	–	
6				4	8.4	8.9	0.84	0.21	97	–	
7		0.25	413	0	0.93	9.9	0.093	0.0	100	–	1.3
8				0.5	2.4	10	0.24	0.033	102	–	
9				1	4.1	9.6	0.41	0.068	100	–	
10		0.25	423	0	0.17	10	0.017	0.0	105	–	2.0
11				0.33	1.9	9.7	0.19	0.017	98	–	
12				0.5	2.7	9.8	0.27	0.041	100	–	
13	DBU	5.0	393	0	0.0	11	0.0	0.0	104	101	0.020
14				2	2.0	9.8	0.20	0.0	99	91	
15				3	3.0	9.8	0.30	0.0	101	95	
16		3.0	403	0	0.0	10	0.0	0.0	102	97	0.047
17				1	1.7	10	0.20	0.0	102	94	
18				2	2.8	10	0.30	0.071	107	105	
19		2.0	413	0	0.0	11	0.0	0.0	103	106	0.069
20				1	1.6	10	0.16	0.049	100	102	
21				2	2.7	10	0.28	0.10	96	103	
22		1.0	423	0	0.0	11	0.0	0.015	109	104	0.16
23				1	1.6	11	0.17	0.051	106	103	
24				2	3.2	10	0.32	0.10	104	100	

[a] Reaction conditions: MEA 10 mmol; CeO_2 0.25 mmol or DBU 1.0–5.0 mmol; acetonitrile 500 mmol; 393–423 K; Ar 1 MPa (at r.t.) + CO_2 2 MPa (at each target temperature); 0–4 h.

[b] Abbreviations: MEA = 2-aminoethanol; DBU = diazabicyclo[5.4.0]-7-undecene; 2-Ox = 2-oxazolidinone; LU = *N*,*N*'-bis(2-hydroxyethyl)urea.

[c] Formation rate of 2-oxazolidinone per catalyst amount.

Table S5. Detailed data for Fig. S13 (effect of partial pressure of CO_2 on the initial time course for the conversion of MEA and CO_2 with CeO_2 and DBU catalysts).[a,b]



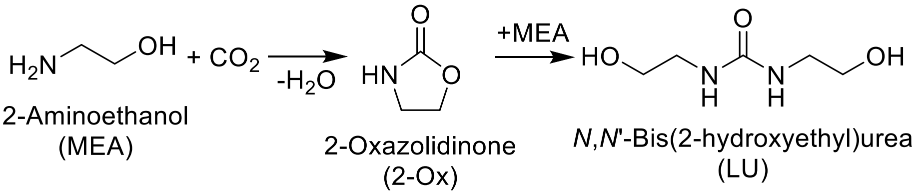
Entry	Catalyst	Catalyst amount [mmol]	$P(CO_2)$ [MPa]	Time [h]	2-Ox yield [%]	Detected compounds [mmol]			Balance [%]		$v_{2\text{-Ox}}$[c] [mmol mmol^{-1} h^{-1}]
						MEA	2-Ox	LU	MEA	DBU	
1	CeO_2	1.0	1	0	1.0	10	0.10	0.0	105	–	1.8
2				0.25	7.9	9.3	0.79	0.049	100	–	
3				0.5	10	9.4	1.0	0.096	104	–	
4		1.0	2	0	1.1	10	0.11	0.0	100	–	1.9
5				0.25	6.3	9.9	0.64	0.051	104	–	
6				0.5	10	9.4	1.0	0.11	103	–	
7		1.0	3	0	1.2	10	0.12	0.0070	103	–	1.9
8				0.25	8.3	9.4	0.84	0.063	101	–	
9				0.5	11	9.2	1.1	0.080	102	–	
10	DBU	3.0	2	0	0.0	10	0.0	0.0	102	97	0.047
11				1	1.7	10	0.17	0.0	102	94	
12				2	2.8	10	0.28	0.071	107	105	
13		3.0	3	0	0.0	10	0.0	0.0	104	102	0.054
14				2	3.8	9.6	0.38	0.092	100	100	
15				4	6.5	9.0	0.65	0.21	96	96	
16		3.0	4	0	0.0	11	0.0	0.0	107	100	0.059
17				2	3.8	9.9	0.38	0.065	102	99	
18				4	7.1	8.3	0.70	0.17	90	94	

[a] Reaction conditions: MEA 10 mmol; CeO_2 1.0 mmol or DBU 3.0 mmol; acetonitrile 500 mmol; 403 K; Ar 1 MPa (at r.t.) + CO_2 1–4 MPa (at 403 K); 0–4 h.

[b] Abbreviations: MEA = 2-aminoethanol; DBU = diazabicyclo[5.4.0]-7-undecene; 2-Ox = 2-oxazolidinone; LU = *N*,*N*'-bis(2-hydroxyethyl)urea.

[c] Formation rate of 2-oxazolidinone per catalyst amount.

Table S6. Detailed data for Fig. S14 (effect of MEA concentration on the initial time course for the conversion of MEA and CO_2 with CeO_2 and DBU catalysts).[a,b]



Entry	Catalyst	Catalyst amount [mmol]	Conc.[c] [mM]	Time [h]	2-Ox yield [%]	Detected compounds [mmol]			Balance [%]		$v_{2\text{-Ox}}$[d] [mmol mmol^{-1} h^{-1}]
						MEA	2-Ox	LU	MEA	DBU	
1	CeO_2	0.10	272	0	0.25	10	0.026	0.0	101	–	1.1
2				3	3.6	9.9	0.36	0.047	102	–	
3				4	4.5	9.5	0.45	0.081	99	–	
4		0.10	317	0	0.10	10	0.010	0.0	103	–	1.1
5				3	3.5	9.7	0.35	0.068	100	–	
6				4	4.4	9.6	0.45	0.081	99	–	
7		0.10	380	0	0.0	10	0.0	0.0	102	–	1.1
8				3	3.1	9.8	0.32	0.068	100	–	
9				4	4.2	9.5	0.43	0.099	99	–	
10		0.10	476	0	0.19	10	0.020	0.0	103	–	1.1
11				1.5	1.9	10	0.20	0.035	102	–	
12				4	4.6	9.4	0.46	0.10	99	–	
13	DBU	3.0	257	0	0.0	10	0.0	0.0	103	97	0.031
14				2	2.7	9.9	0.27	0.041	101	93	
15				4	3.7	9.6	0.37	0.082	100	93	
16		3.0	317	0	0.0	10	0.0	0.0	103	96	0.038
17				2	1.9	9.6	0.19	0.036	97	90	
18				4	4.5	9.1	0.46	0.085	95	90	
19		3.0	380	0	0.0	10	0.0	0.0	102	97	0.047
20				1	1.7	10	0.17	0.0	102	94	
21				2	2.8	10	0.28	0.071	107	105	

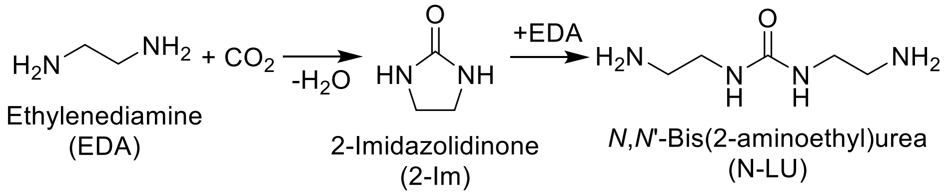
[a] Reaction conditions: MEA 10 mmol; CeO_2 0.10 mmol or DBU 3.0 mmol; acetonitrile 400–1000 mmol; 403 K; Ar 1 MPa (at r.t.) + CO_2 2 MPa (at 403 K); 0–4 h.

[b] Abbreviations: MEA = 2-aminoethanol; DBU = diazabicyclo[5.4.0]-7-undecene; 2-Ox = 2-oxazolidinone; LU = *N*,*N*'-bis(2-hydroxyethyl)urea.

[c] Initial concentration of MEA.

[d] Formation rate of 2-oxazolidinone per catalyst amount.

Table S7. Detailed data for Fig. S16 (initial time courses for the conversion of EDA and CO_2 at various temperatures with CeO_2 and DBU catalysts).[a,b]



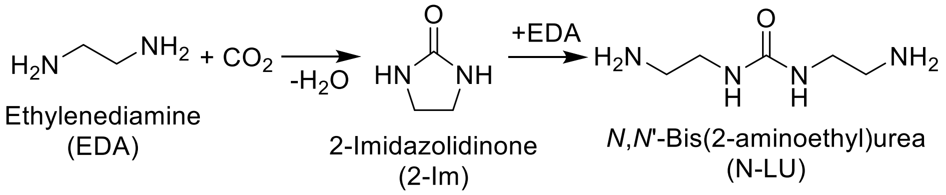
Entry	Catalyst	Catalyst amount [mmol]	Temp. [K]	Time [h]	2-Im yield [%]	Detected compounds [mmol]			Balance [%]		$v_{2\text{-Im}}$[c] [mmol mmol^{-1} h^{-1}]
						EDA	2-Im	N-LU	EDA	DBU	
1	CeO_2	3.0	403	0	0.84	8.2	0.084	0.0	82	–	0.11
2				2	11	6.9	1.1	0.0	79	–	
3				4	14	6.8	1.4	0.0	81	–	
4		2.0	413	0	1.2	8.5	0.12	0.0	86	–	0.25
5				1.5	13	6.9	1.3	0.0	82	–	
6				3	16	6.5	1.6	0.0	80	–	
7		1.0	423	0	1.6	8.6	0.16	0.0	88	–	0.59
8				1	9.1	7.6	0.91	0.0	85	–	
9				2	13	7.2	1.3	0.0	85	–	
10	DBU	3.0	403	0	0.091	9.8	0.0092	0.0	97	109	0.11
11				2	7.4	8.9	0.75	0.0	95	103	
12				4	13	8.3	1.3	0.0	94	101	
13		2.0	413	0	0.10	10	0.011	0.0	102	110	0.25
14				1.5	7.3	8.7	0.73	0.0	94	98	
15				3	15	8.1	1.5	0.0	96	96	
16		1.0	423	0	0.073	10	0.0073	0.0	102	105	0.40
17				1	4.8	8.9	0.49	0.0	94	93	
18				2	8.1	9.0	0.81	0.0	97	93	

[a] Reaction conditions: EDA 10 mmol; CeO_2 or DBU 1.0–3.0 mmol; acetonitrile 500 mmol; 403–423 K; Ar 1 MPa (at r.t.) + CO_2 2 MPa (at each target temperature); 0–4 h.

[b] Abbreviations: EDA = ethylenediamine; DBU = diazabicyclo[5.4.0]-7-undecene; 2-Im = 2-imidazolidinone; N-LU = *N*,*N*'-bis(2-aminoethyl)urea.

[c] Formation rate of 2-imidazolidinone per catalyst amount.

Table S8. Detailed data for Fig. S17 (effect of partial pressure of CO_2 on the initial time course for the conversion of EDA and CO_2 with CeO_2 and DBU catalysts).[a,b]



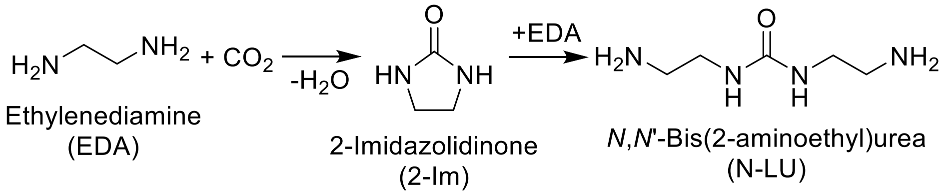
Entry	Catalyst	Catalyst amount [mmol]	$P(CO_2)$ [MPa]	Time [h]	2-Im yield [%]	Detected compounds [mmol]			Balance [%]		$v_{2\text{-Im}}$[c] [mmol mmol^{-1} h^{-1}]
						EDA	2-Im	N-LU	EDA	DBU	
1	CeO_2	3.0	1	0	1.4	8.6	0.14	0.0	86	–	0.31
2				1	13	6.6	1.3	0.0	79	–	
3				2	20	6.4	2.0	0.0	83	–	
4		3.0	2	0	0.84	8.2	0.084	0.0	82	–	0.25
5				1	9.7	6.7	0.98	0.0	76	–	
6				1.5	12	6.4	1.2	0.0	76	–	
7		3.0	4	0	1.4	7.9	0.14	0.0	80	–	0.16
8				0.5	4.5	7.4	0.45	0.0	77	–	
9				1	6.0	7.3	0.60	0.0	78	–	
10	DBU	3.0	2	0	0.091	9.8	0.0092	0.0	97	109	0.12
11				1	3.6	8.6	0.37	0.0	89	97	
12				2	7.4	8.9	0.75	0.0	95	103	
13		3.0	3	0	0.10	11	0.011	0.0	108	127	0.16
14				1	4.4	8.8	0.44	0.0	92	102	
15				2	9.5	8.9	0.96	0.0	98	107	
16		3.0	4	0	0.15	10	0.015	0.0	103	113	0.17
17				1	5.9	8.9	0.60	0.0	95	104	
18				4	21	7.6	2.1	0.0	97	89	

[a] Reaction conditions: EDA 10 mmol; CeO_2 or DBU 3.0 mmol; acetonitrile 500 mmol; 403 K; Ar 1 MPa (at r.t.) + CO_2 1–4 MPa (at 403 K); 0–4 h.

[b] Abbreviations: EDA = ethylenediamine; DBU = diazabicyclo[5.4.0]-7-undecene; 2-Im = 2-imidazolidinone; N-LU = *N*,*N*'-bis(2-aminoethyl)urea.

[c] Formation rate of 2-imidazolidinone per catalyst amount.

Table S9. Detailed data for Fig. S18 (initial time courses for the conversion of EDA and CO_2 over CeO_2 catalyst at CO_2 pressure of 0.2 MPa).[a,b]



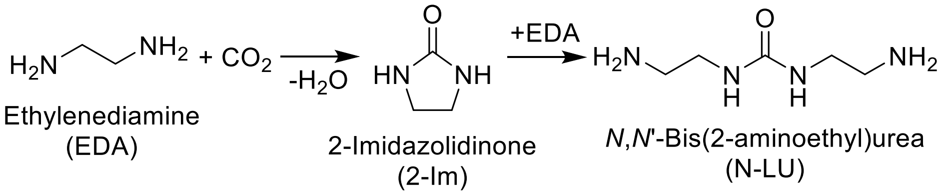
Entry	Catalyst	Catalyst amount [mmol]	Temp. [K]	Time [h]	2-Im yield [%]	Detected compounds [mmol]			Bal. [%]	$v_{2\text{-Im}}$[c] [mmol mmol^{-1} h^{-1}]
						EDA	2-Im	N-LU		
1	CeO_2	1.0	403	0	2.1	8.1	0.21	0.0	83	0.54
2				0.66	15	6.7	1.5	0.0	81	
3				2	35	5.4	3.5	0.0	88	
4		2.0	413	0	1.7	8.5	0.17	0.0	86	1.1
5				0.33	14	7.4	1.34	0.0	88	
6				0.66	16	6.5	1.6	0.0	81	
7		1.0	423	0	1.1	9.0	0.11	0.0	90	1.6
8				0.33	5.1	8.5	0.51	0.0	89	
9				0.5	9.3	7.3	0.93	0.0	82	

[a] Reaction conditions: EDA 10 mmol; CeO_2 1.0–2.0 mmol; acetonitrile 500 mmol; 403–423 K; Ar 1 MPa (at r.t.) + CO_2 0.2 MPa (at each target temperature); 0–2 h.

[b] Abbreviations: EDA = ethylenediamine; 2-Im = 2-imidazolidinone; N-LU = *N*,*N*'-bis(2-aminoethyl)urea.

[c] Formation rate of 2-imidazolidinone per catalyst amount.

Table S10. Detailed data for Fig. S19 (effect of EDA concentration on the initial time course for the conversion of EDA and CO_2 with CeO_2 and DBU catalysts).[a,b]



Entry	Catalyst	Catalyst amount [mmol]	Conc.[c] [mM]	Time [h]	2-Im yield [%]	Detected compounds [mmol]			Balance [%]		$v_{2\text{-Im}}$[c] [mmol mmol^{-1} h^{-1}]
						EDA	2-Im	N-LU	EDA	DBU	
1	CeO_2	3.0	190	0	0.85	9.2	0.086	0.0	93	–	0.12
2				2	7.9	8.4	0.79	0.0	91	–	
3				4	16	6.9	1.6	0.0	84	–	
4		3.0	257	0	1.1	8.7	0.12	0.0	86	–	0.14
5				1.5	8.9	8.2	0.91	0.0	90	–	
6				3	13	7.3	1.3	0.0	86	–	
7		3.0	380	0	0.84	8.2	0.084	0.0	82	–	0.11
8				2	11	6.9	1.1	0.0	79	–	
9				4	14	6.8	1.4	0.0	81	–	
10	DBU	3.0	190	0	0.0	10	0.0	0.0	100	118	0.084
11				2	5.0	9.3	0.51	0.0	97	114	
12				4	10	8.5	1.0	0.0	95	108	
13		3.0	257	0	0.12	9.9	0.012	0.0	98	117	0.10
14				1.5	4.4	9.3	0.45	0.0	97	111	
15				3	9.3	8.6	0.94	0.0	95	107	
16		3.0	380	0	0.091	9.8	0.0092	0.0	97	109	0.11
17				2	7.4	8.9	0.75	0.0	95	103	
18				4	13	8.3	1.3	0.0	94	101	

[a] Reaction conditions: EDA 10 mmol; CeO_2 or DBU 3.0 mmol; acetonitrile 500–1000 mmol; 403 K; Ar 1 MPa (at r.t.) + CO_2 2 MPa (at 403 K); 0–4 h.

[b] Abbreviations: EDA = ethylenediamine; DBU = diazabicyclo[5.4.0]-7-undecene; 2-Im = 2-imidazolidinone; N-LU = *N*,*N*'-bis(2-aminoethyl)urea.

[c] Formation rate of 2-imidazolidinone per catalyst amount.

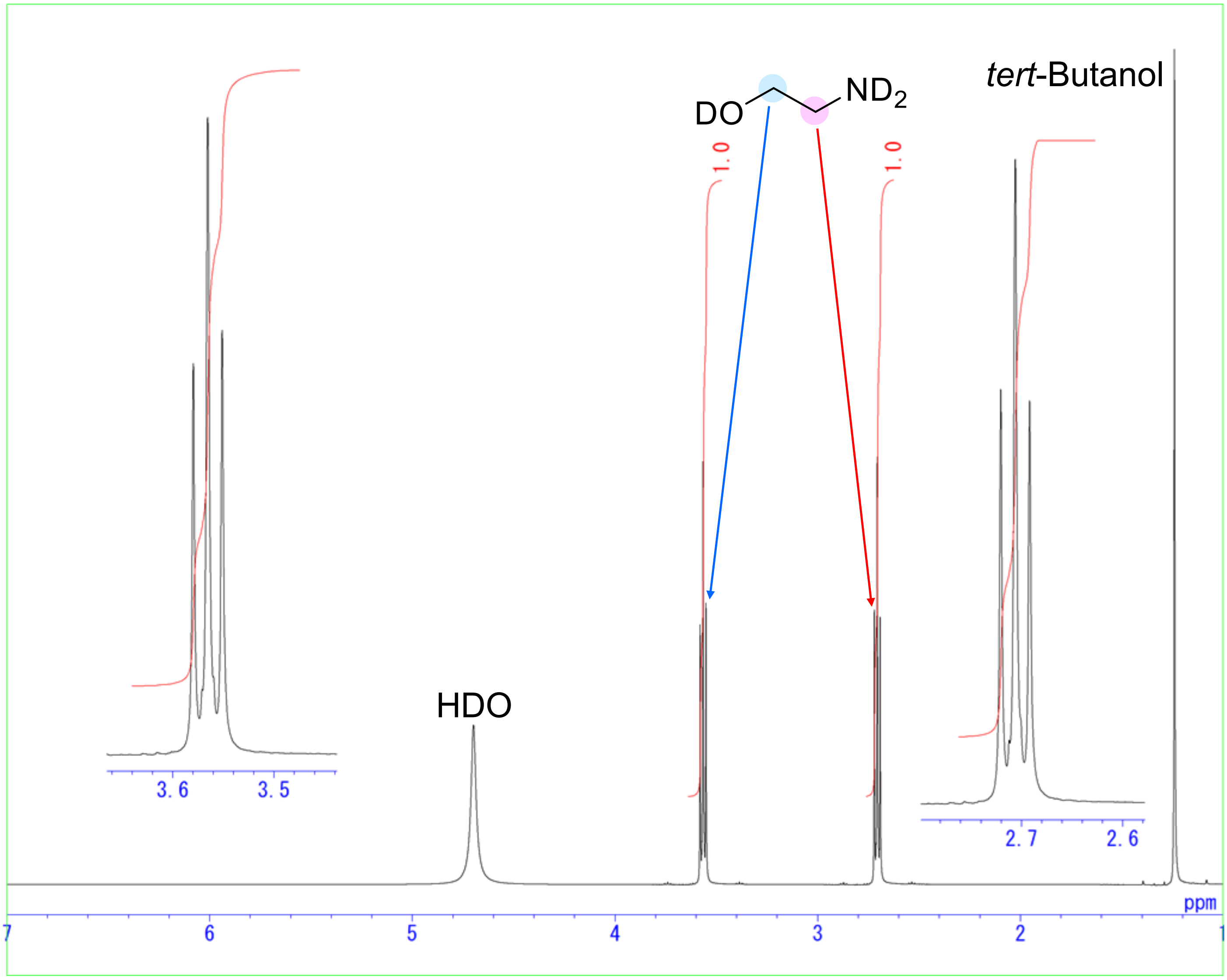


Fig. S1. ^{1}H NMR spectrum of commercially available MEA.
Deuterated solvent = D_2O; internal standard = *tert*-butyl alcohol.

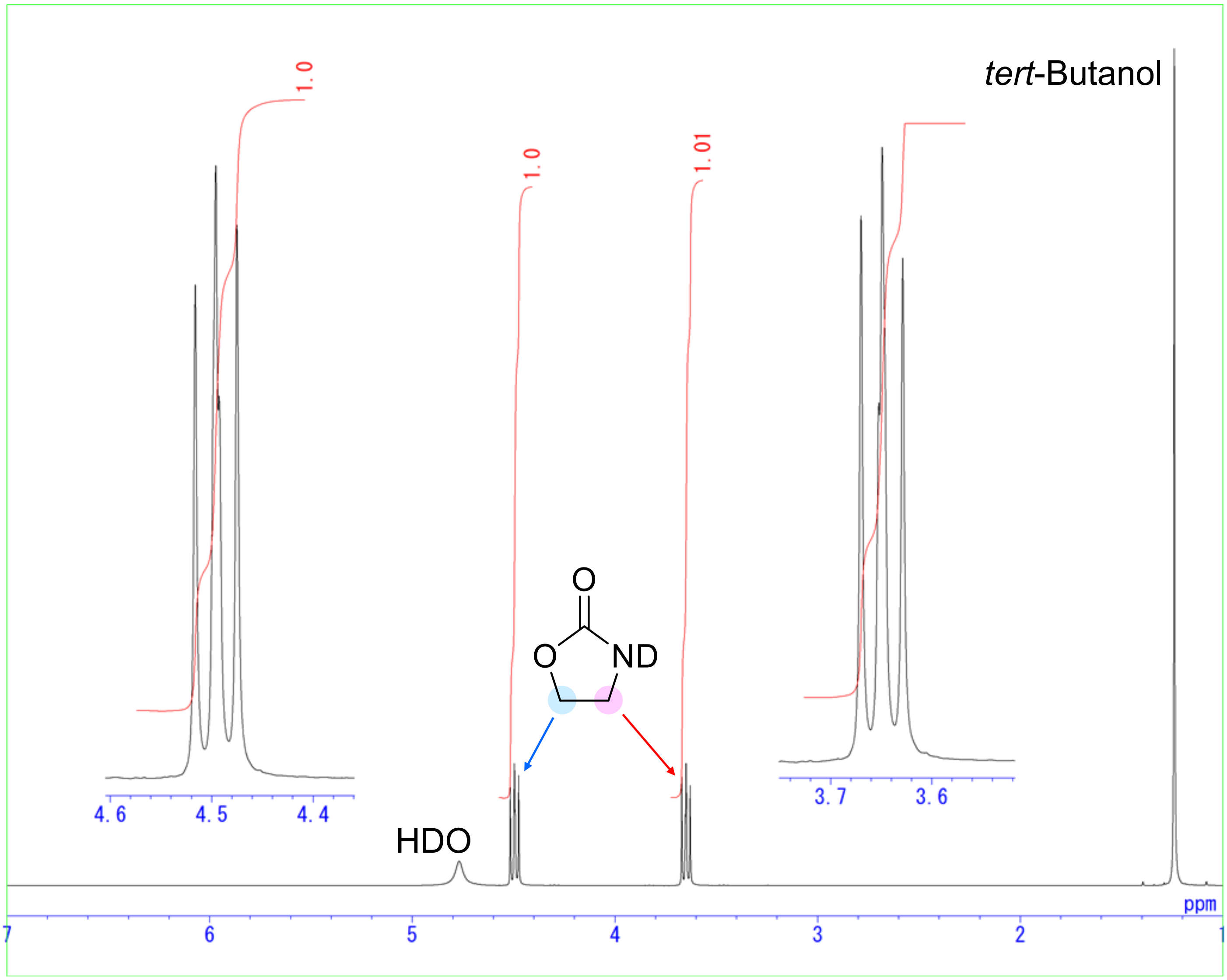


Fig. S2. ^{1}H NMR spectrum of commercially available 2-oxazolidinone.
Deuterated solvent = D_2O; internal standard = *tert*-butyl alcohol.

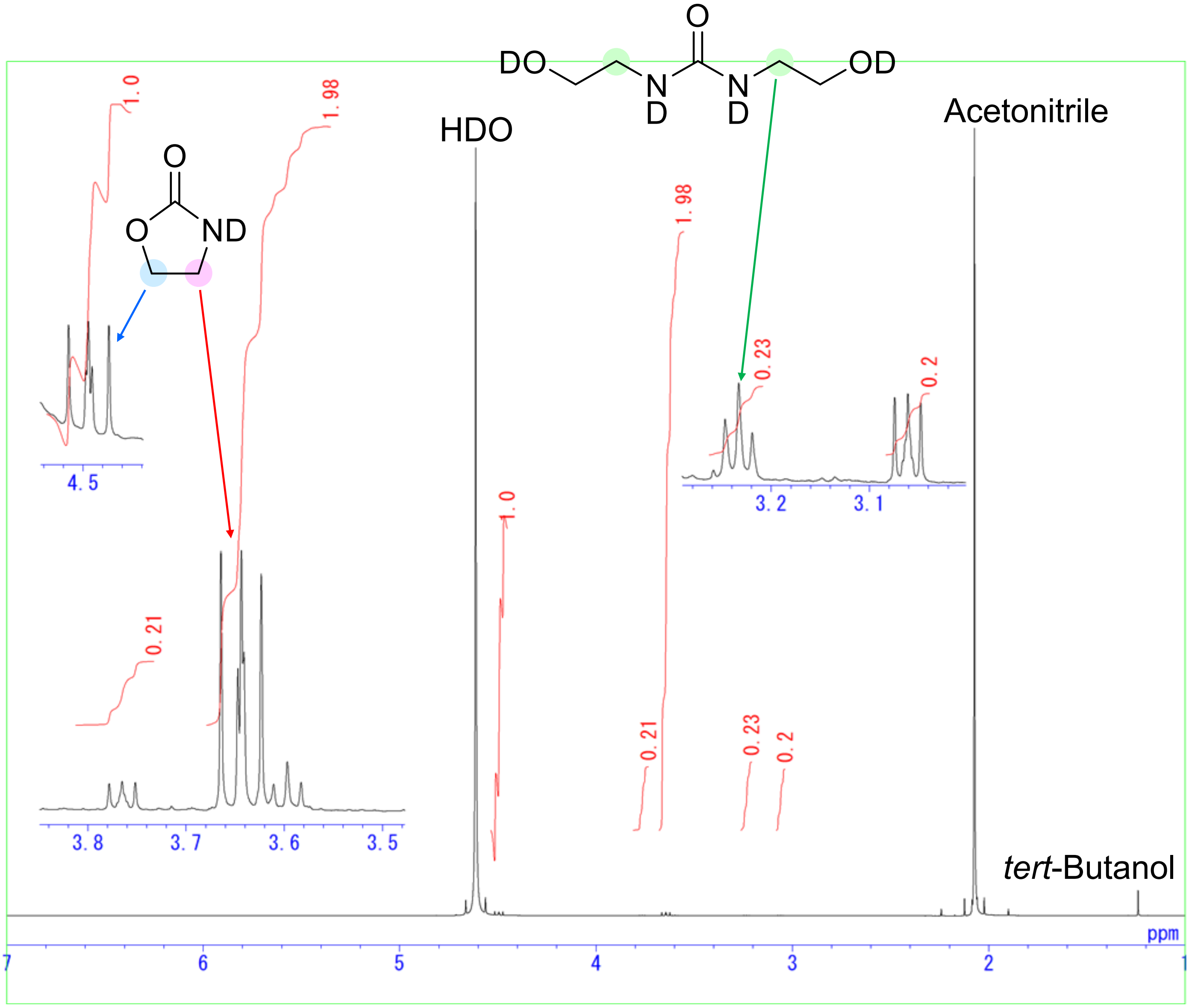


Fig. S3. ^{1}H NMR spectrum of typical reaction mixture in the conversion of MEA and CO_2 over the CeO_2 catalyst.

Deuterated solvent = D_2O; internal standard = *tert*-butyl alcohol.

Reaction conditions: MEA 10 mmol; CeO_2 1.0 mmol; acetonitrile 500 mmol; 403 K; CO_2 2 MPa (at r.t.); 48 h.

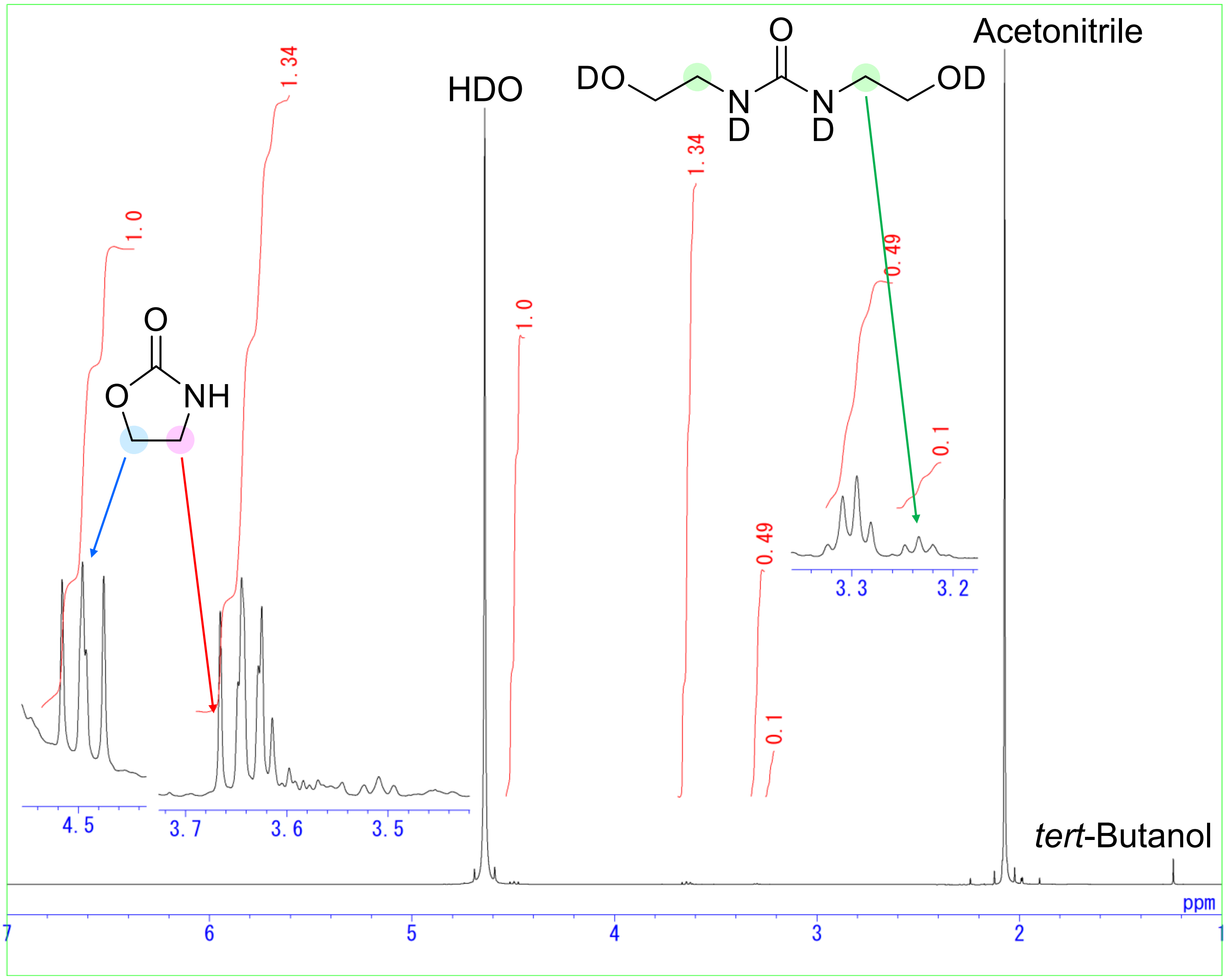


Fig. S4. ^{1}H NMR spectrum of typical reaction mixture in the conversion of MEA and CO_2 in the presence of the DBU catalyst.

Deuterated solvent = D_2O; internal standard = *tert*-butyl alcohol.

Reaction conditions: MEA 10 mmol; DBU 1.0 mmol; acetonitrile 500 mmol; 403 K; CO_2 2 MPa (at r.t.); 20 h.

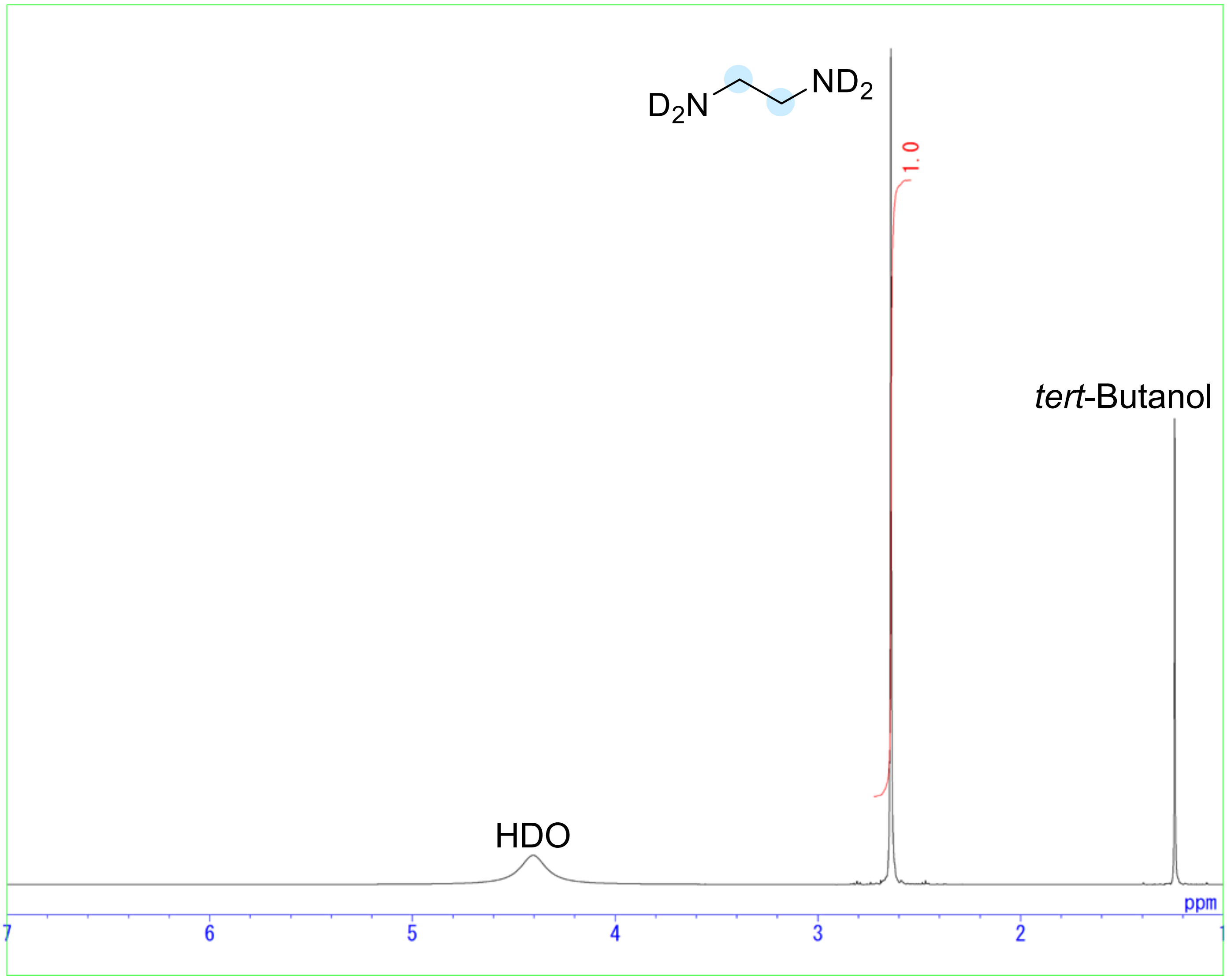


Fig. S5. ^{1}H NMR spectrum of commercially available EDA.
Deuterated solvent = D_2O; internal standard = *tert*-butyl alcohol.

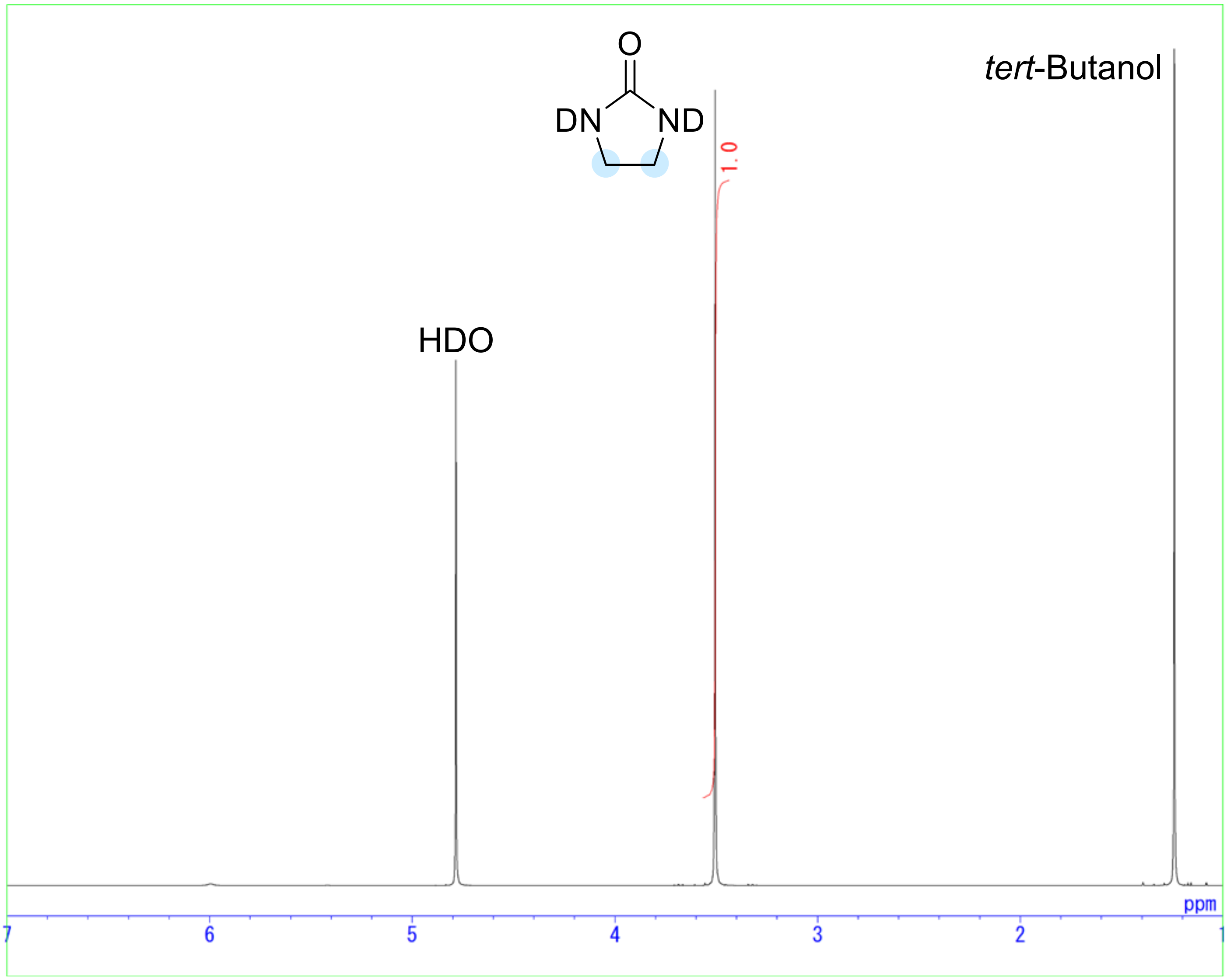


Fig. S6. ^{1}H NMR spectrum of commercially available 2-imidazolidinone.
Deuterated solvent = D_2O; internal standard = *tert*-butyl alcohol.

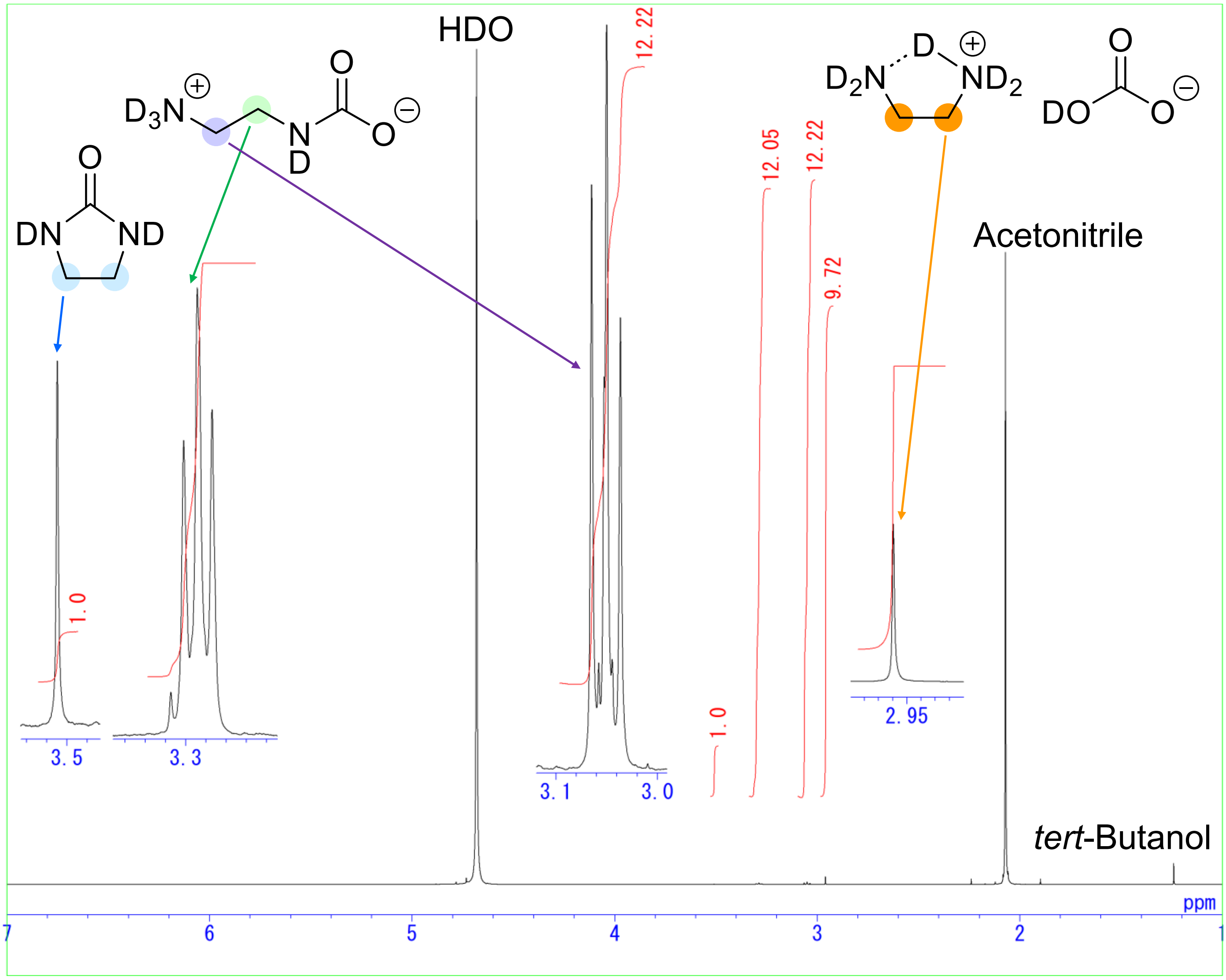


Fig. S7. ^{1}H NMR spectrum of typical reaction mixture in the conversion of EDA and CO_2 over the CeO_2 catalyst.

Deuterated solvent = D_2O; internal standard = *tert*-butyl alcohol.

Reaction conditions: EDA 10 mmol; CeO_2 1.0 mmol; acetonitrile 500 mmol; 403 K; CO_2 2 MPa (at r.t.); 4 h.

The peak assignments are based on previous reports[S11,S12] with consideration of solvent effect.

The unreacted EDA was observed as ethylenediamine carbamic salt (EDA-CA) and counter cation of hydrogencarbonate because of spontaneous capture of CO_2 in the reactor. Meanwhile, these EDA-derived species undergo thermal decomposition in a GC chamber and are detected as EDA.[S12]

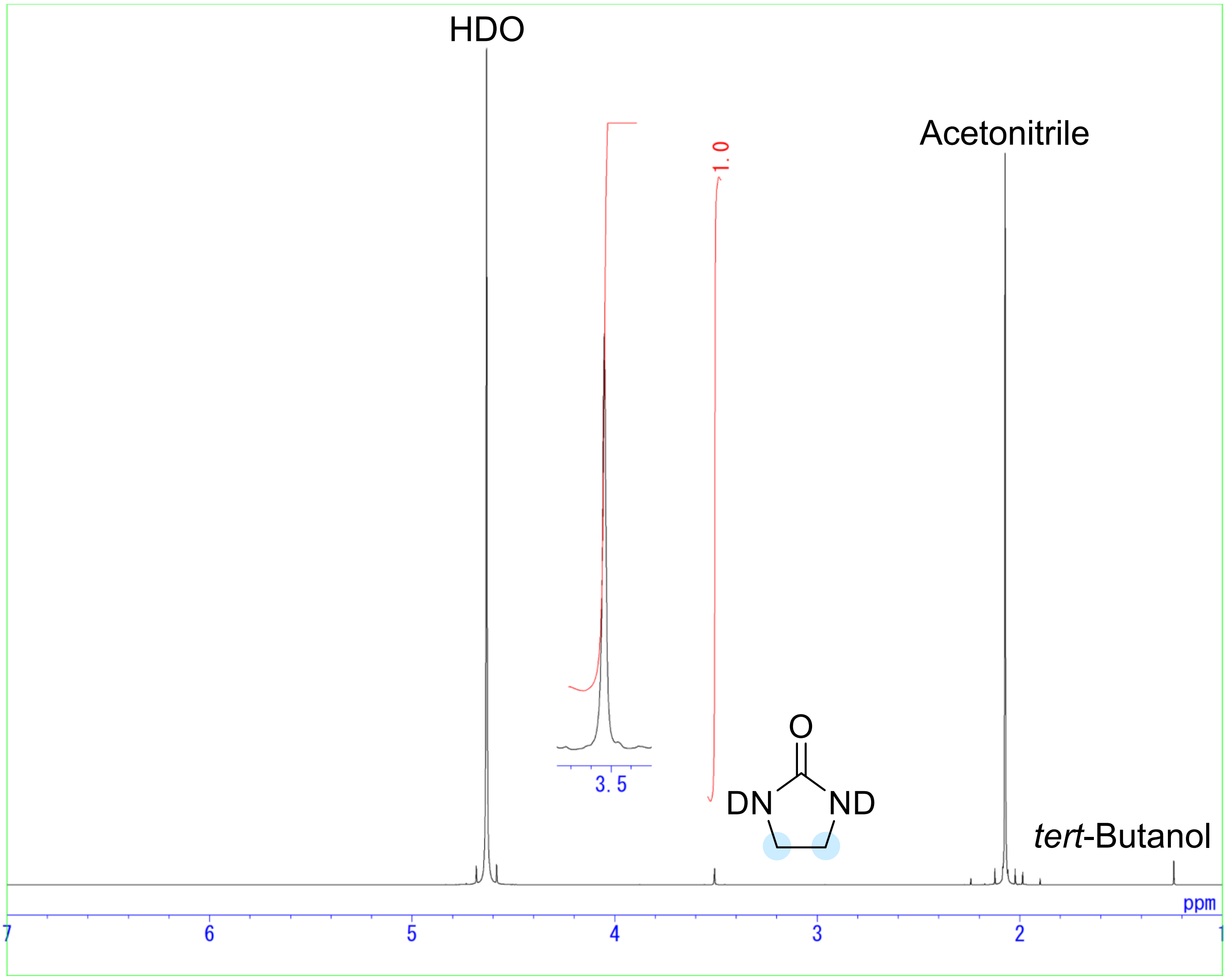


Fig. S8. ^{1}H NMR spectrum of typical reaction mixture in the conversion of EDA and CO_2 in the presence of the DBU catalyst.

Deuterated solvent = D_2O; internal standard = *tert*-butyl alcohol.

Reaction conditions: EDA 10 mmol; DBU 1.0 mmol; acetonitrile 500 mmol; 403 K; CO_2 2 MPa (at r.t.); 96 h.

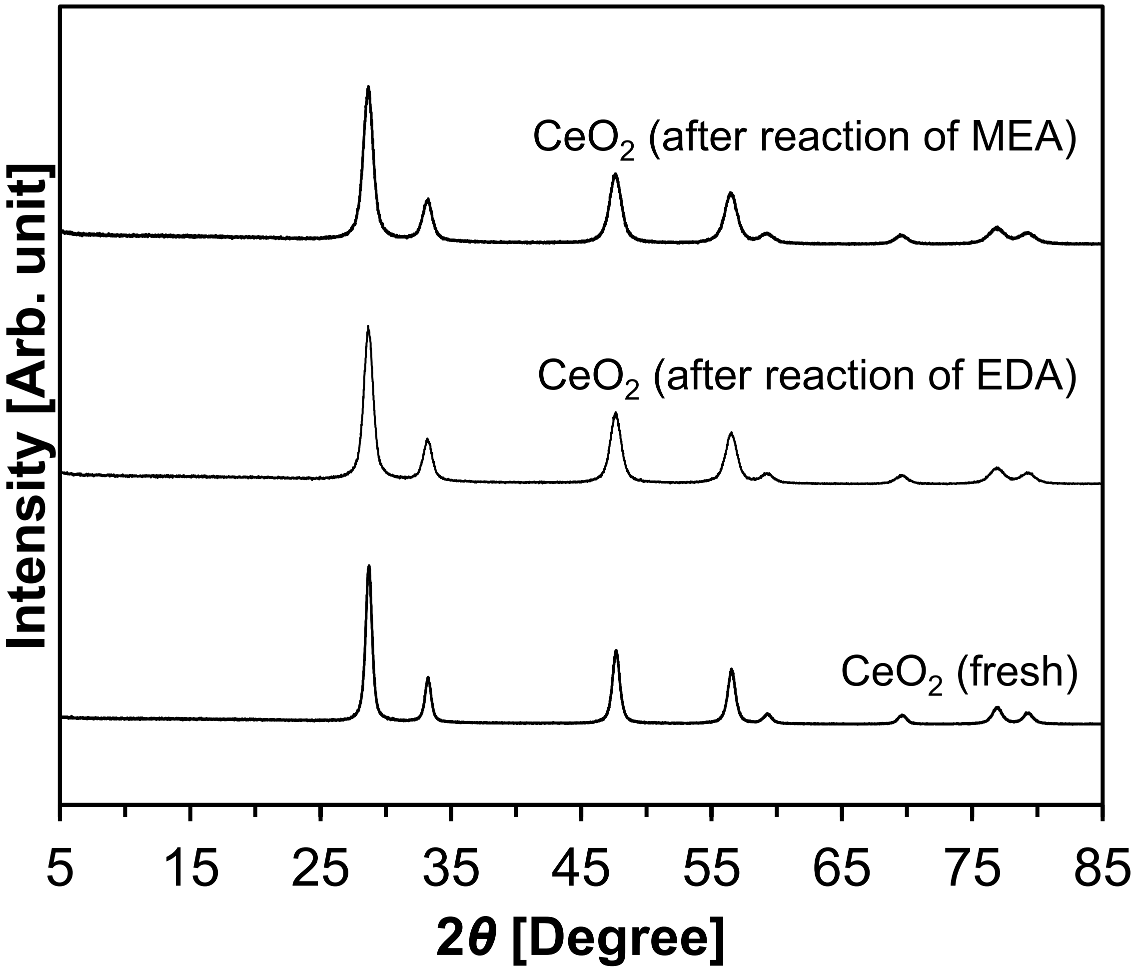
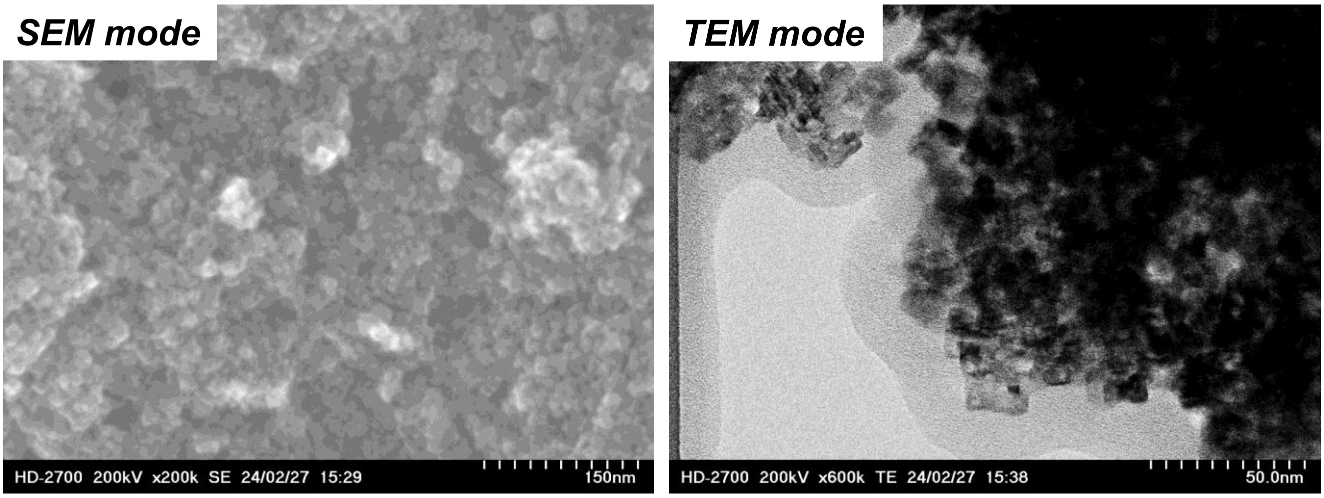


Fig. S9. XRD patterns of fresh and spent CeO_2 catalysts.

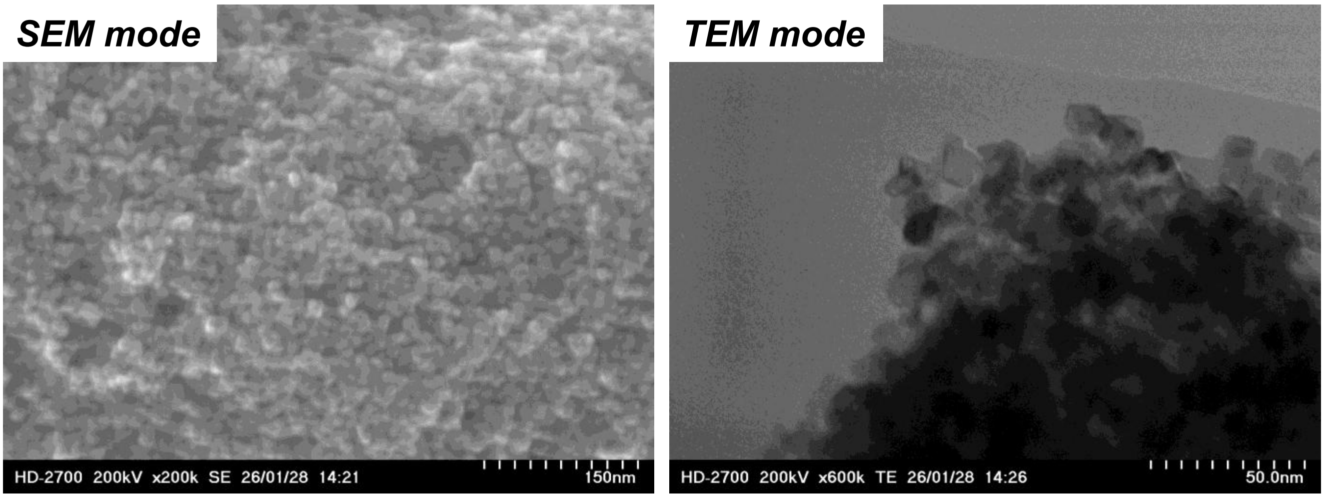
Reaction conditions for the reaction of MEA: MEA 10 mmol; CeO_2 1.0 mmol; acetonitrile 500 mmol; 403 K; CO_2 2 MPa (at r.t.); 4 h.

Reaction conditions for the reaction of EDA: EDA 10 mmol; CeO_2 1.0 mmol; acetonitrile 500 mmol; 403 K; CO_2 2 MPa (at r.t.); 24 h.

(A) CeO_2 (fresh)



(B) CeO_2 (after reaction of MEA)



(C) CeO_2 (after reaction of EDA)

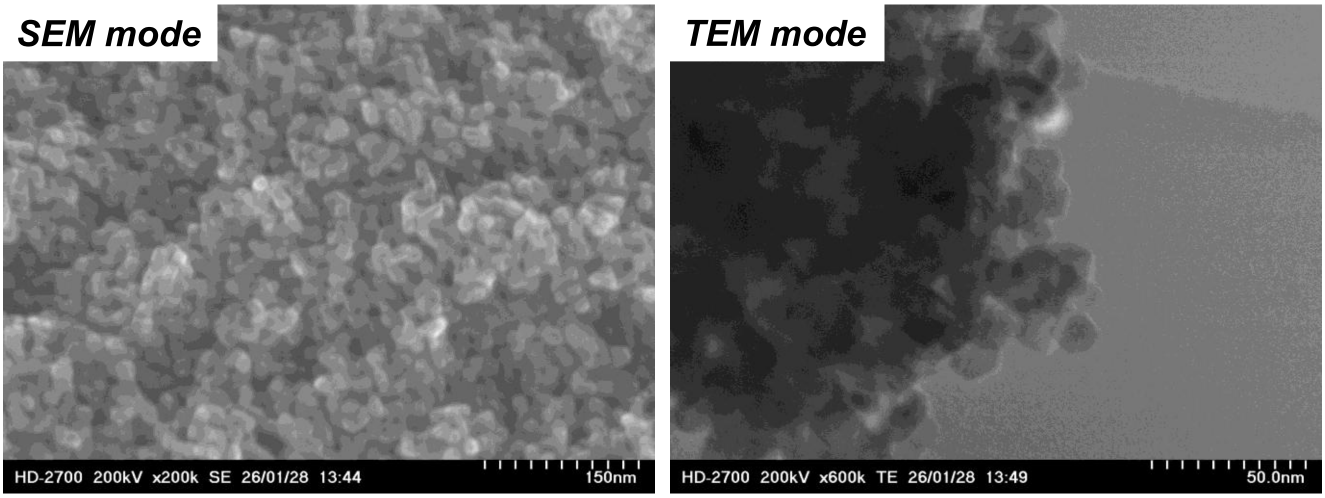


Fig. S10. STEM images of fresh and spent CeO_2 catalysts.

Reaction conditions for the reaction of MEA: MEA 10 mmol; CeO_2 1.0 mmol; acetonitrile 500 mmol; 403 K; CO_2 2 MPa (at r.t.); 4 h.

Reaction conditions for the reaction of EDA: EDA 10 mmol; CeO_2 1.0 mmol; acetonitrile 500 mmol; 403 K; CO_2 2 MPa (at r.t.); 24 h.

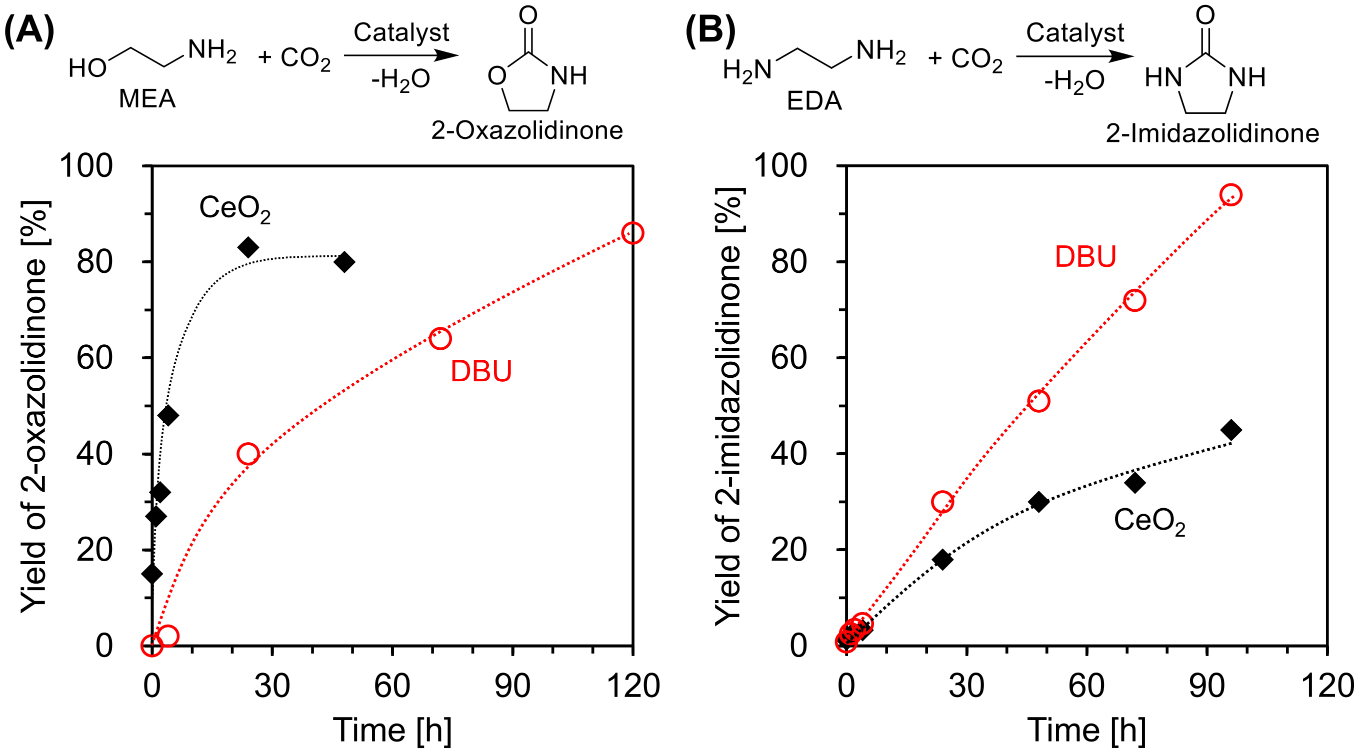


Fig. S11. Time courses of (A) conversion of MEA and CO_2 and (B) conversion of EDA and CO_2 with CeO_2 and DBU catalysts.

Reaction conditions: MEA or EDA 10 mmol; CeO_2 or DBU 1.0 mmol; acetonitrile 500 mmol; 403 K; CO_2 2 MPa (at r.t.); 0–120 h.

Detailed data are listed in Tables S2 and S3.

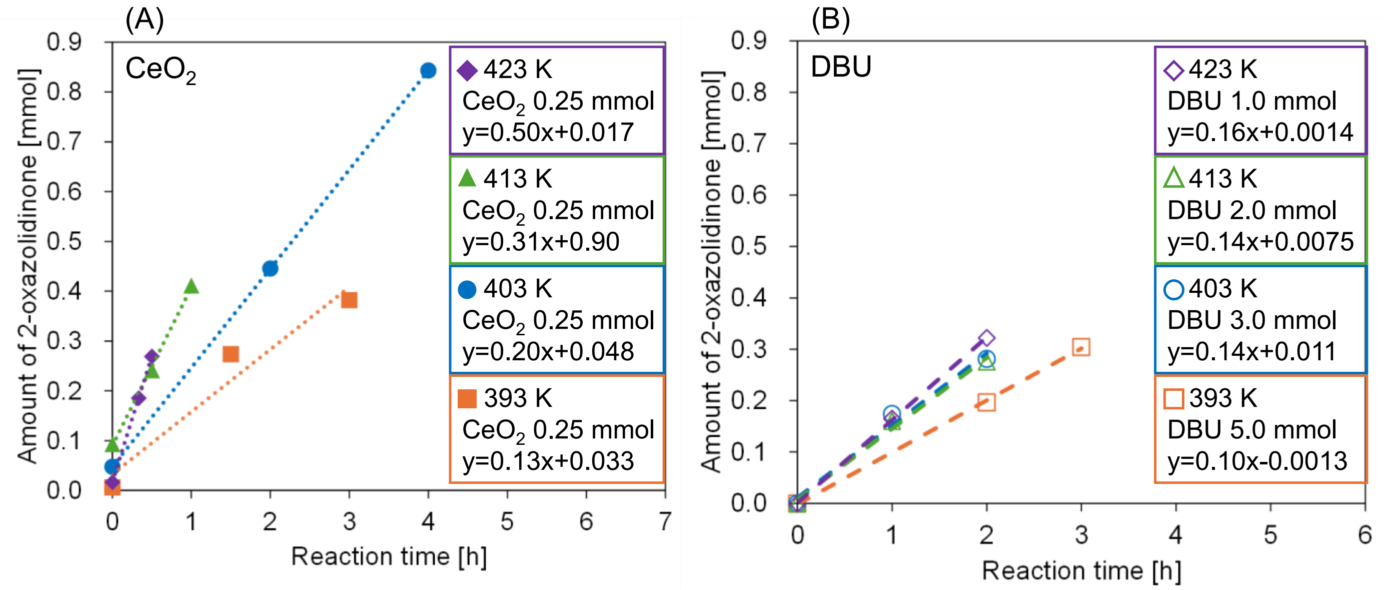


Fig. S12. Initial time courses for the conversion of MEA and CO_2 at various temperatures with (A) CeO_2 and (B) DBU catalysts.

Reaction conditions: MEA 10 mmol; CeO_2 0.25 mmol or DBU 1.0–5.0 mmol; acetonitrile 500 mmol; 393–423 K; Ar 1 MPa (at r.t.) + CO_2 2 MPa (at each target temperature); 0–4 h.

Detailed data are listed in Table S4.

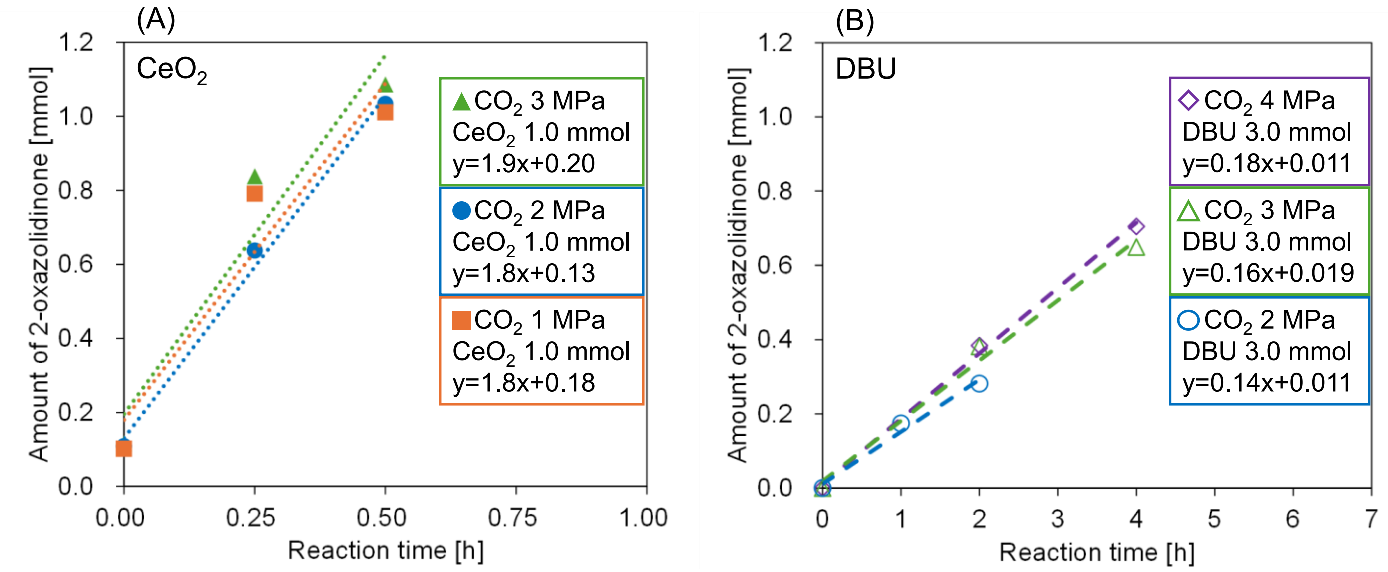


Fig. S13. Effect of partial pressure of CO_2 on the initial time course for the conversion of MEA and CO_2 with (A) CeO_2 and (B) DBU catalysts.

Reaction conditions: MEA 10 mmol; CeO_2 1.0 mmol or DBU 3.0 mmol; acetonitrile 500 mmol; 403 K; Ar 1 MPa (at r.t.) + CO_2 1–4 MPa (at 403 K); 0–4 h.

Detailed data are listed in Table S5.

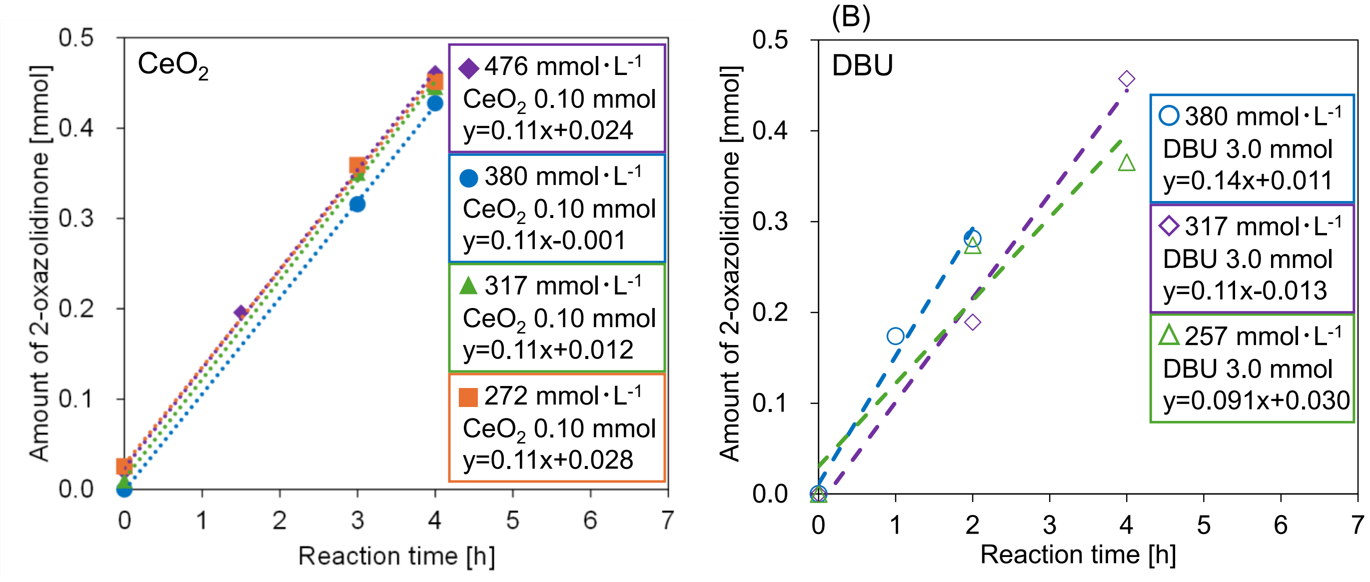


Fig. S14. Effect of MEA concentration on the initial time course for the conversion of MEA and CO_2 with (A) CeO_2 and (B) DBU catalysts.

Reaction conditions: MEA 10 mmol; CeO_2 0.10 mmol or DBU 3.0 mmol; acetonitrile 400–1000 mmol; 403 K; Ar 1 MPa (at r.t.) + CO_2 2 MPa (at 403 K); 0–4 h.

Detailed data are listed in Table S6.

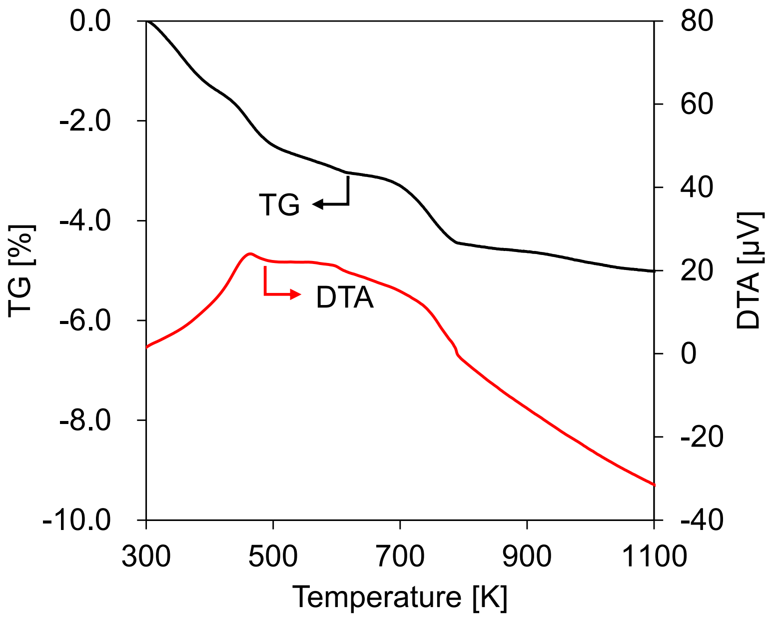


Fig. S15. TG-DTA profile for the spent CeO_2 catalyst for the conversion of EDA and CO_2 (2 MPa at r.t.) at 403 K for 96 h.

Reaction conditions: EDA 10 mmol; CeO_2 1.0 mmol; acetonitrile 500 mmol; 403 K; CO_2 2 MPa (at r.t.); 96 h.

TG-DTA conditions: spent catalyst 9.9 mg; air flow (500 mL min^{-1}); ramping from room temperature to 1173 K by 10 K min^{-1}.

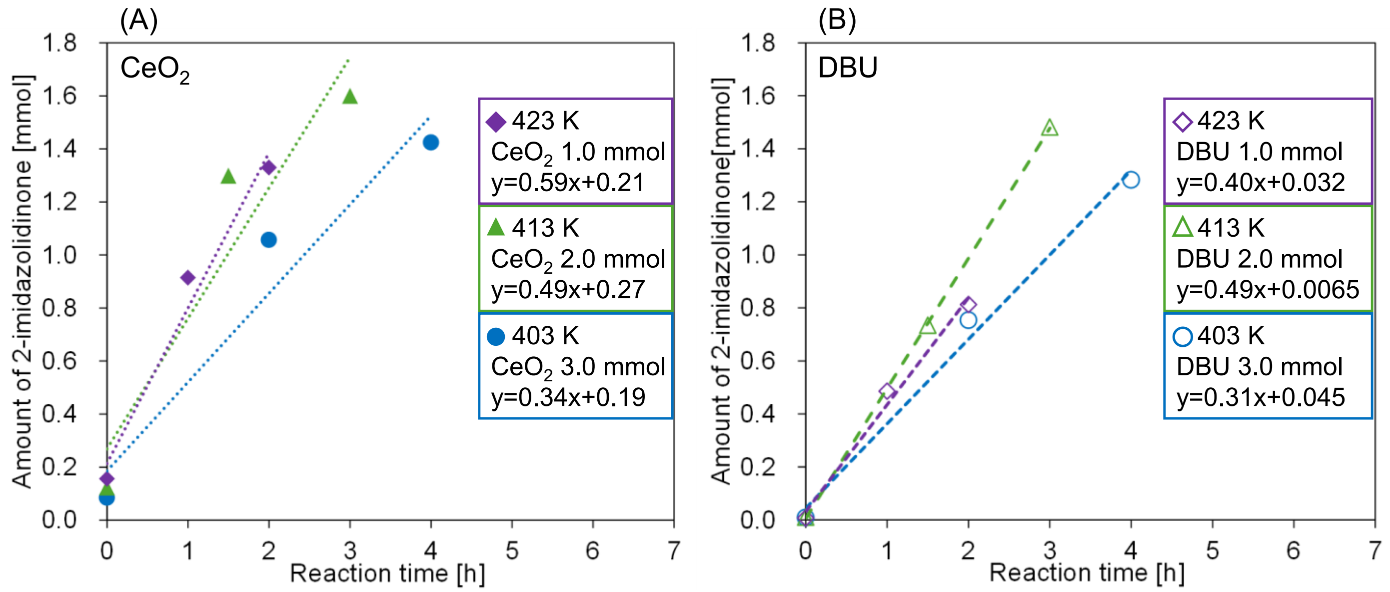


Fig. S16. Initial time courses for the conversion of EDA and CO_2 at various temperatures with (A) CeO_2 and (B) DBU catalysts.

Reaction conditions: EDA 10 mmol; CeO_2 or DBU 1.0–3.0 mmol; acetonitrile 500 mmol; 403–423 K; Ar 1 MPa (at r.t.) + CO_2 2 MPa (at each target temperature); 0–4 h.

Detailed data are listed in Table S7.

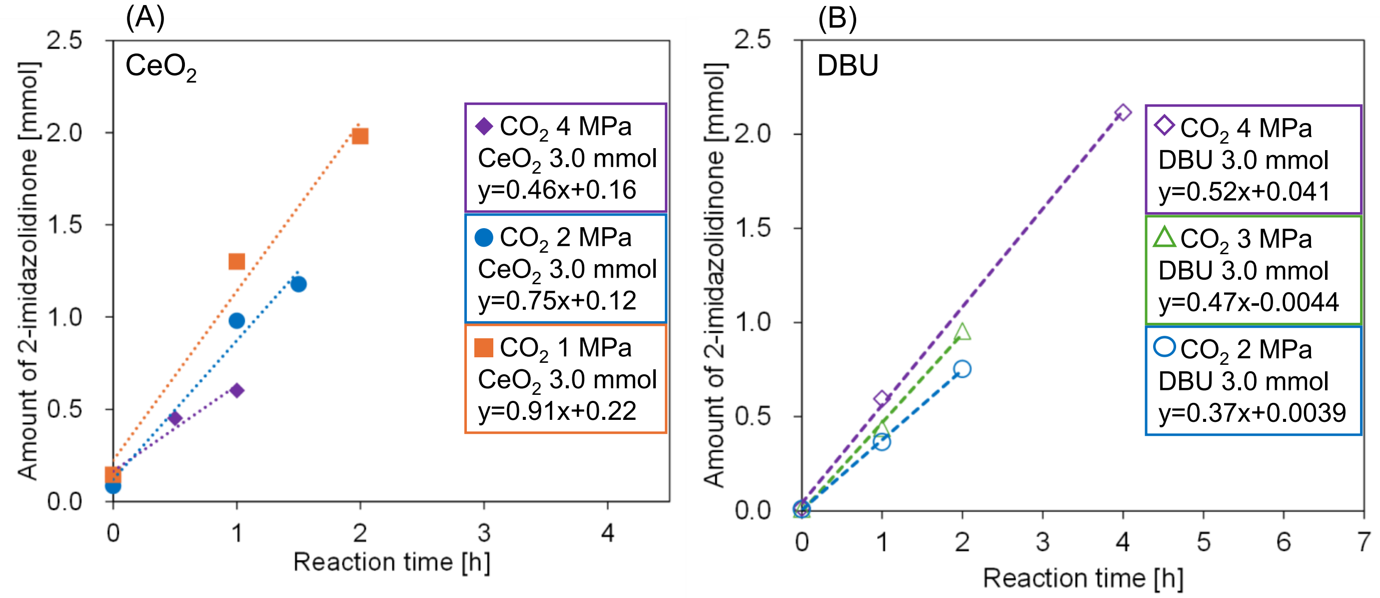


Fig. S17. Effect of partial pressure of CO_2 on the initial time course for the conversion of EDA and CO_2 with (A) CeO_2 and (B) DBU catalysts.

Reaction conditions: EDA 10 mmol; CeO_2 or DBU 3.0 mmol; acetonitrile 500 mmol; 403 K; Ar 1 MPa (at r.t.) + CO_2 1–4 MPa (at 403 K); 0–4 h.

Detailed data are listed in Table S8.

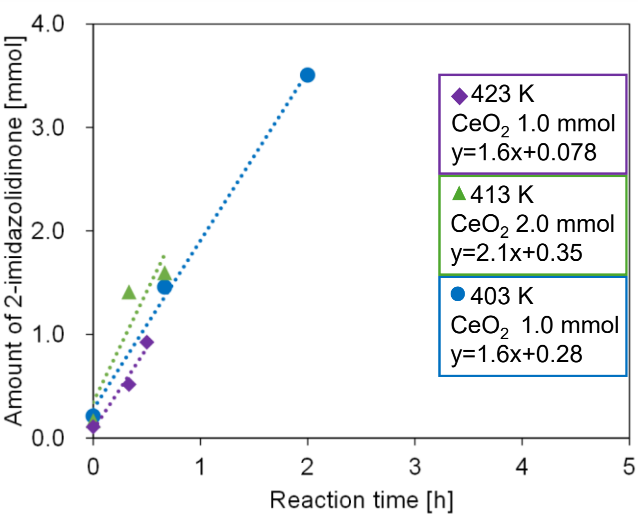


Fig. S18. Initial time courses for the conversion of EDA and CO_2 over CeO_2 catalyst at CO_2 pressure of 0.2 MPa.

Reaction conditions: EDA 10 mmol; CeO_2 1.0–2.0 mmol; acetonitrile 500 mmol; 403–423 K; Ar 1 MPa (at r.t.) + CO_2 0.2 MPa (at each target temperature); 0–2 h.

Detailed data are listed in Table S9.

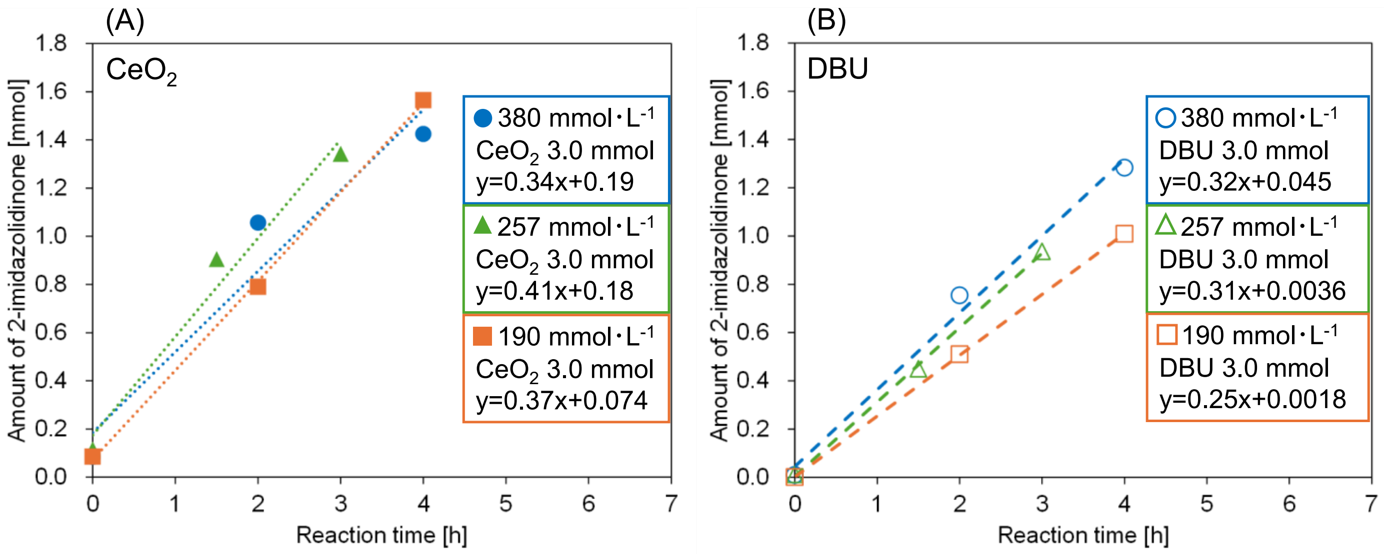


Fig. S19. Effect of EDA concentration on the initial time course for the conversion of EDA and CO_2 with (A) CeO_2 and (B) DBU catalysts.

Reaction conditions: EDA 10 mmol; CeO_2 or DBU 3.0 mmol; acetonitrile 500–1000 mmol; 403 K; Ar 1 MPa (at r.t.) + CO_2 2 MPa (at each target temperature); 0–4 h.

Detailed data are listed in Table S10.

Supplementary references

S1 R. Fujii, M. Yabushita, Y. Li, Y. Nakagawa and K. Tomishige, *ACS Catal.*, 2023, **13**, 11041–11056.

S2 M. Tamura, M. Honda, K. Noro, Y. Nakagawa and K. Tomishige, *J. Catal.*, 2013, **305**, 191–203.

S3 G. S. More and R. Srivastava, *Ind. Eng. Chem. Res.*, 2021, **60**, 12492–12504.

S4 J. K. Mannisto, J. Heikkinen, J. Puumi, A. Sahari, P. R. Veliz and T. Repo, *Org. Lett.*, 2025, **27**, 5971–5976.

S5 J. Puumi, A. Sahari, A. Žáková, J. K. Mannisto, N. M. Maier and T. Repo, *ACS Omega*, 2025, **10**, 33843–33849.

S6 M. Honda, S. Sonehara, H. Yasuda, Y. Nakagawa and K. Tomishige, *Green Chem.*, 2011, **13**, 3406–3413.

S7 R. Zhang, L. Guo, C. Chen, J. Chen, A. Chen, X. Zhao, X. Liu, Y. Xiu and Z. Hou, *Catal. Sci. Technol.*, 2015, **5**, 2959–2972.

S8 K. A. Alferov, Z. Fu, S. Ye, D. Han, S. Wang, M. Xiao and Y. Meng, *ACS Sustainable Chem. Eng.*, 2019, **7**, 10708–10715.

S9 T. Wei, L. Wang, J. Zhang, Y. Cao, X. Hui, J. Shi, S. Xu, L. Zhao, P. He and H. Li, *Ind. Eng. Chem. Res.*, 2024, **63**, 4338–4352.

S10 M. Tamura, K. Noro, M. Honda, Y. Nakagawa and K. Tomishige, *Green Chem.*, 2013, **15**, 1567–1577.

S11 H. Koizumi, K. Takeuchi, K. Matsumoto, N. Fukaya, K. Sato, M. Uchida, S. Matsumoto, S. Hamura and J.-C. Choi, *Commun. Chem.*, 2021, **4**, 66.

S12 J. Peng, M. Yabushita, Y. Li, R. Fujii, M. Tamura, Y. Nakagawa and K. Tomishige, *Appl. Catal. A: Gen.*, 2022, **643**, 118747.