Electronic Supplementary Information

Highly Efficient Sulfurized Re-Ir Catalysts for Multiple *N*-Methylation of Ethylenediamine and Its Homologous Series with CO_2 and H_2 in Water Solvent

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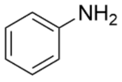
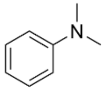
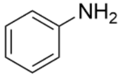
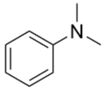
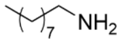
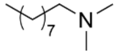
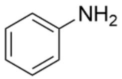
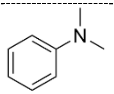
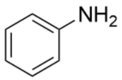
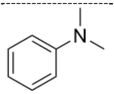
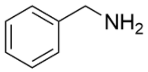
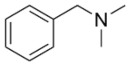
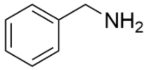
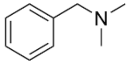
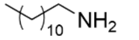
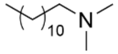
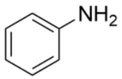
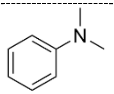
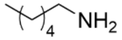
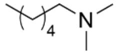
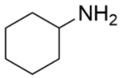
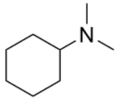
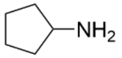
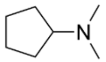
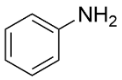
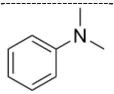
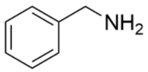
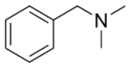
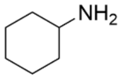
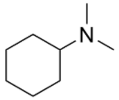
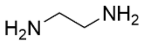
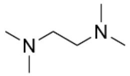
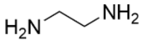
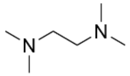
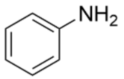
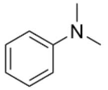
Table S1. Summary of previous reports on double and quadruple *N*-methylation of primary (di)amines with CO_2 and H_2.[a]

Entry	Catalyst	Metal[b] [mol%]	Substrate [mmol]		Temp. [K]	Time [h]	$P(CO_2)$ [MPa]	$P(H_2)$ [MPa]	Solvent ([mL])	Conv. [%]	Target product		TOF[c] $[h^{-1}]$	Ref.
											Structure	Yield [%]		
1	[Ru(triphos)(tmm)][d]	2.5		1.0	423	15	2.0	6.0	THF (2)	n.r.		94	5.0	S1
2	$Ru(acac)_3$[e]	1		0.5	413	16	2.0	6.0	THF (2)	100		96	12	S2
		5		0.5	413	24	2.0	6.0	THF (2)	n.r.		87	1.4	
3	$Co(OAc)_2 \cdot 4H_2O$[f]	5		1.0	423	24	2.0	7.0	Methanol (2.0)	n.r.		98	1.6	S3
4	$CuAlO_x$	38		1.0	433	48	3.0	7.0	Hexane (2)	n.r.		83	0.2	S4
		38		1.0	433	48	3.0	7.0	Hexane (2)	100		81	0.2	
5	2 wt% $Pd/CuZrO_x$	0.75		1.0	423	30	1.0	2.5	Octane (2)	n.r.		54	4.8	S5
		0.75		1.0	423	48	1.0	2.5	Octane (2)	n.r.		68[h]	6.0	
6	0.7 wt% $Au/\gamma\text{-}Al_2O_3$	0.5		1	413	7	2	6	Hexane (10)	100		92	52	S6
		0.5		1	443	7	2	6	Hexane (10)	n.r.		95	54	
		0.5		1	443	7	2	6	Hexane (10)	n.r.		93	52	
		0.5		1	443	7	2	6	Hexane (10)	n.r.		92	52	
7	2 wt% Au/MIL-101(Cr) $@SiO_2@Fe_3O_4$	1.5		1.0	473	10	1.0	3.0	Cyclohexane (3.0)	44.0		12.1	1.8	S7
		1.5		1.0	473	10	1.0	3.0	Cyclohexane (3.0)	99.1		96.0	13	

		1.5		1.0	473	10	1.0	3.0	Cyclohexane (3.0)	60.1		17.6	2.3	
8	5 wt% Re/C-BP	2.0		4.0	403	120	1.0	4.0	H_2O (5.0)	98		84	3.3[i]	S8
9	Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5)	0.53[g]		4.0	413	96	1.0	4.0	H_2O (5.0)	100		79	21[i]	This work
		0.53[g]		2.0	413	48	1.0	4.0	*n*-Octane (5.0)	12		1.6	0.2	

[a] Abbreviations: triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane; tmm = trimethylene methane; acac = acetylacetonate; OAc = acetate; C-BP = carbon black (Black Pearls 2000, supplied from Cabot); THF = tetrahydrofuran.

[b] The molar percent of active metal against substrate.

[c] Turnover frequency, calculated from the mole of *N*-methyl groups involved in the product divided by the mole of active metal and reaction time (the values of mole and reaction time listed in this table were used for this calculation, except for entries 8 and 9). In the cases of supported metal catalysts, the mole of supported metal(s) was used for the calculation.

[d] 5 mol% of trifluoromethanesulfonylimide was also added.

[e] 2 mol% of triphos and 1.5 mol% of methanesulfonic acid were also added.

[f] 10 mol% of triphos and 0.3 equiv. of $Sn(OTf)_2$ (OTf = trifluoromethanesulfonate) were also added.

[g] For calculation, the moles of both Re and Ir were involved.

[h] Isolated yield.

[i] The TOF value was calculated from the initial slope of N_{Me} in the time course for quadruple *N*-methylation of EDA (for entry 9, see Fig. 3).

Table S2. Detailed information about reagents and gases used in this study.

Reagent	Detailed information
NH_4ReO_4	Mitsuwa Chemical
$Ru(NO)(NO_3)_{3-x}(OH)_x$	Sigma-Aldrich
$Rh(NO_3)_3$	FUJIFILM Wako Pure Chemical
$[Pt(NH_3)_4](NO_3)_2$	Sigma-Aldrich
$Ir(NO_3)_4$	Furuya Metal, HNO_3 solution
$AgNO_3$	FUJIFILM Wako Pure Chemical
$HAuCl_4 \cdot 4H_2O$	FUJIFILM Wako Pure Chemical
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	FUJIFILM Wako Pure Chemical
ReS_2	Thermo Fisher Scientific
Carbon black	Cabot, Black Pearls 2000, S_{BET} = 1280 m^2 g^{-1}, denoted as C-BP
ZrO_2	FUJIFILM Wako Pure Chemical
Ethylenediamine	FUJIFILM Wako Pure Chemical
Ethanol	Kanto Chemical
1,4-Butanediol	FUJIFILM Wako Pure Chemical
2,3-Butanediol	Tokyo Chemical Industry, mixture of stereoisomers
N-Methylethylenediamine	Tokyo Chemical Industry, denoted as M-EDA
N,*N*-Dimethylethylenediamine	Tokyo Chemical Industry, denoted as N,N-DM-EDA
N,*N*’-Dimethylethylenediamine	Tokyo Chemical Industry, denoted as N,N’-DM-EDA
N,*N*,*N*’-Trimethylethylenediamine	Tokyo Chemical Industry, denoted as TriM-EDA
N,*N*,*N*’,*N*’-Tetramethylethylenediamine	Tokyo Chemical Industry, denoted as TetraM-EDA
1,2-Diaminopropane	Tokyo Chemical Industry
1,3-Diaminopropane	Tokyo Chemical Industry
1,4-Diaminobutane	Tokyo Chemical Industry
1,6-Diaminohexane	Tokyo Chemical Industry
Diethylenetriamine	Tokyo Chemical Industry
Triethylenetetramine	Kanto Chemical
2-(2-Aminoethylamino)ethanol	FUJIFILM Wako Pure Chemical
Methylamine	Tokyo Chemical Industry, *ca*. 40% in water
n-Butylamine	FUJIFILM Wako Pure Chemical
Aniline	Tokyo Chemical Industry
n-Octane	Tokyo Chemical Industry
H_2	99.9%, Taiyo Nippon Sanso
CO_2	99.995%, Taiyo Nippon Sanso
Ar	99.99%, Taiyo Nippon Sanso
N_2	99.99%, Taiyo Nippon Sanso

Table S3. Detailed data for Fig. 2A (effects of Ir/Re molar ratio at the constant Re loading of 4 wt% on the catalytic activity of Re-Ir/C-BP for *N*-methylation of EDA).[a,b]

Entry	Catalyst	Ir/Re[c]	S/(Re + Ir)[d]	Conv. [%]	Yield [%]										N_{Me}[f] [%]	Bal. [%]
					N-Methylated EDA					*N*-Formylated EDA						
					M-EDA	N,N-DM-EDA	N,N'-DM-EDA	TriM-EDA	TetraM-EDA	F-EDA	F-M-EDA	F-DM-EDA	F-TriM-EDA	Others[e]		
1	Re/C-BP	0	3.7	39	10	6.5	0.2	1.7	4.5	4.3	1.9	0.3	0.3	1.3	47	92
2	Re-Ir/C-BP	0.13	2.8	51	9.9	8.4	0.3	1.4	12	7.1	2.0	0.8	0.5	0.9	81	92
3	Re-Ir/C-BP	0.25	2.9	64	7.1	9.8	0.0	1.3	22	9.3	2.3	1.5	0.7	1.3	117	91
4	Re-Ir/C-BP	0.5	2.9	70	4.5	9.9	0.0	1.9	34	6.8	2.3	1.6	0.8	2.2	164	94
5	Re-Ir/C-BP	0.75	2.4	69	5.0	9.9	0.0	1.5	34	5.6	1.7	1.7	0.9	1.9	166	92
6	Re-Ir/C-BP	1.0	2.1	65	3.9	9.5	0.0	1.4	34	5.6	1.6	1.9	0.8	3.1	165	97
7	Ir/C-BP[g]	–	3.5	36	3.9	5.4	0.0	0.5	2.7	14	2.4	0.8	0.0	1.0	27	94

[a] Reaction conditions: EDA 4.0 mmol; catalyst (Re 4 wt%, Ir/Re = 0–1.0, reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 413 K; 16 h.

[b] Abbreviations: M-EDA = *N*-methylethylenediamine; N,N-DM-EDA = *N*,*N*-dimethylethylenediamine; N,N'-DM-EDA = *N*,*N*'-dimethylethylenediamine; TriM-EDA = *N*,*N*,*N*'-trimethylethylenediamine; TetraM-EDA = *N*,*N*,*N*',*N*'-tetramethylethylenediamine; F-EDA = *N*-(2-aminoethyl)formamide; F-M-EDA = *N*-(2-aminoethyl)-*N*-methylformamide; F-DM-EDA = *N*-(2-(dimethylamino)ethyl)formamide; F-TriM-EDA = *N*-(2-(dimethylamino)ethyl)-*N*-methylformamide.

[c] Ir/Re molar ratio based on the amounts of metal precursors used in the catalyst preparation.

[d] Molar ratio of S to the sum of Re and Ir, determined by XRF.

[e] Including piperazine, 2-imidazolidinone, methylamine, and their corresponding *N*-methylated compounds.

[f] Degree of *N*-methylation calculated using eqn. 4.

[g] Ir 4 wt%.

Table S4. Detailed data for Fig. 2B (effects of Re loading at the constant Ir/Re molar ratio of 0.5 on the catalytic activity of Re-Ir/C-BP for *N*-methylation of EDA).[a,b]

Entry	Catalyst	Re[c] [wt%]	S/(Re + Ir)[d]	Conv. [%]	Yield [%]										N_{Me}[f] [%]	Bal. [%]
					N-Methylated EDA					*N*-Formylated EDA						
					M-EDA	N,N-DM-EDA	N,N’-DM-EDA	TriM-EDA	TetraM-EDA	F-EDA	F-M-EDA	F-DM-EDA	F-TriM-EDA	Others[e]		
1	Re-Ir/C-BP	2	6.7	45	10	9.7	0.0	1.5	13	5.2	1.8	0.6	0.6	0.2	85	95
2	Re-Ir/C-BP	4	2.9	70	4.5	9.9	0.0	1.9	34	6.8	2.3	1.6	0.8	2.2	164	94
3	Re-Ir/C-BP	6	1.7	70	3.7	10	0.0	1.4	34	6.8	1.7	2.5	0.9	3.6	163	92
4	Re-Ir/C-BP	8	1.0	71	4.2	10	0.0	1.4	32	6.7	1.7	2.5	0.8	3.8	158	90

[a] Reaction conditions: EDA 4.0 mmol; catalyst (Re 2–8 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 413 K; 16 h.

[b] Abbreviations: M-EDA = *N*-methylethylenediamine; N,N-DM-EDA = *N*,*N*-dimethylethylenediamine; N,N’-DM-EDA = *N*,*N*’-dimethylethylenediamine; TriM-EDA = *N*,*N*,*N*’-trimethylethylenediamine; TetraM-EDA = *N*,*N*,*N*’,*N*’-tetramethylethylenediamine; F-EDA = *N*-(2-aminoethyl)formamide; F-M-EDA = *N*-(2-aminoethyl)-*N*-methylformamide; F-DM-EDA = *N*-(2-(dimethylamino)ethyl)formamide; F-TriM-EDA = *N*-(2-(dimethylamino)ethyl)-*N*-methylformamide.

[c] Re molar ratio based on the amounts of metal precursors used in the catalyst preparation.

[d] Molar ratio of S to the sum of Re and Ir, determined by XRF.

[e] Including piperazine, 2-imidazolidinone, methylamine, and their corresponding *N*-methylated compounds.

[f] Degree of *N*-methylation calculated using eqn. 4.

Table S5. Pressure effect of *N*-methylation of EDA over Re-Ir/C-BP catalyst at 413 K.[a,b]

Entry	$P(CO_2)$[c] [MPa]	$P(H_2)$[c] [MPa]	$P(CO_2)/P(H_2)$	Conv. [%]	Yield [%]										N_{Me}[e] [%]	Bal. [%]
					N-Methylated EDA					*N*-Formylated EDA						
					M-EDA	N,N-DM-EDA	N,N’-DM-EDA	TriM-EDA	TetraM-EDA	F-EDA	F-M-EDA	F-DM-EDA	F-TriM-EDA	Others[d]		
1	1.0	4.0	0.25	61	6.4	11	0.0	2.0	22	6.4	1.9	1.5	0.7	1.9	123	93
2	2.0	3.0	0.67	71	7.2	11	0.0	3.0	35	4.0	1.3	0.8	0.9	2.4	180	96
3	3.0	2.0	1.5	60	7.7	10	0.2	1.1	20	12	2.6	2.1	0.9	1.6	112	100
4	4.0	1.0	4.0	53	10	11	0.4	2.1	14	4.6	1.5	0.5	0.5	2.2	94	94
5	0.2	0.8	0.25	16	7.6	3.3	0.0	0.5	1.0	3.1	0.5	0.0	0.0	1.1	20	101
6	0.6	2.4	0.25	30	11	8.2	0.2	1.5	7.0	3.0	0.7	0.3	0.2	1.0	60	103

[a] Reaction conditions: EDA 4.0 mmol; Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.10 g; water 5.0 g; 413 K; 12 h.

[b] Abbreviations: M-EDA = *N*-methylethylenediamine; N,N-DM-EDA = *N*,*N*-dimethylethylenediamine; N,N’-DM-EDA = *N*,*N*’-dimethylethylenediamine; TriM-EDA = *N*,*N*,*N*’-trimethylethylenediamine; TetraM-EDA = *N*,*N*,*N*’,*N*’-tetramethylethylenediamine; F-EDA = *N*-(2-aminoethyl)formamide; F-M-EDA = *N*-(2-aminoethyl)-*N*-methylformamide; F-DM-EDA = *N*-(2-(dimethylamino)ethyl)formamide; F-TriM-EDA = *N*-(2-(dimethylamino)ethyl)-*N*-methylformamide.

[c] Pressure at r.t.

[d] Including piperazine, 2-imidazolidinone, methylamine, and their corresponding *N*-methylated compounds.

[e] Degree of *N*-methylation calculated using eqn. 4.

Table S6. Effect of reaction temperature on *N*-methylation of EDA over Re-Ir/C-BP catalyst.[a,b]

Entry	Temp. [K]	Conv. [%]	Yield [%]										N_{Me}[d] [%]	Bal. [%]
			N-Methylated EDA					*N*-Formylated EDA						
			M-EDA	N,N-DM-EDA	N,N’-DM-EDA	TriM-EDA	TetraM-EDA	F-EDA	F-M-EDA	F-DM-EDA	F-TriM-EDA	Others[c]		
1	373	20	2.1	0.6	0.0	0.5	0.4	13	0.6	0.0	0.0	0.0	7	98
2	393	46	5.9	6.9	0.0	0.6	7.2	14	2.2	1.8	0.6	0.0	50	94
3	403	56	7.1	10	0.0	1.1	17	10	2.4	1.8	0.7	0.5	98	94
4	413	70	4.5	9.9	0.0	1.9	34	6.8	2.3	1.6	0.8	2.2	164	94
5	433	87	2.3	6.2	0.0	2.0	42	2.0	1.0	0.7	1.3	18	189	89
6	453	100	0.7	4.4	0.0	3.4	27	0.0	0.4	0.2	0.6	55	127	91
7[e]	433	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.4	0	101
8[e]	453	22	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	23	0	101

[a] Reaction conditions: EDA 4.0 mmol; Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 373–453 K; 16 h.

[b] Abbreviations: M-EDA = *N*-methylethylenediamine; N,N-DM-EDA = *N*,*N*-dimethylethylenediamine; N,N’-DM-EDA = *N*,*N*’-dimethylethylenediamine; TriM-EDA = *N*,*N*,*N*’-trimethylethylenediamine; TetraM-EDA = *N*,*N*,*N*’,*N*’-tetramethylethylenediamine; F-EDA = *N*-(2-aminoethyl)formamide; F-M-EDA = *N*-(2-aminoethyl)-*N*-methylformamide; F-DM-EDA = *N*-(2-(dimethylamino)ethyl)formamide; F-TriM-EDA = *N*-(2-(dimethylamino)ethyl)-*N*-methylformamide.

[c] The detailed composition is shown in Table S6.

[d] Degree of *N*-methylation calculated using eqn. 4.

[e] Without catalyst.

Table S7. Detailed information about “Others” in Table S6.[a,b]

Entry	Temp. [K]	Conv. [%]	Yield [%]							Bal. [%]
			PM-DETA	M-PZ	DM-PZ	MA[c]	DMA[c]	TMA[c]	EU	
1	373	20	0.0	0.0	0.0	0.0	0.0	0.0	0.0	98
2	393	46	0.0	0.0	0.0	0.0	0.0	0.0	0.0	94
3	403	56	0.5	0.0	0.0	0.0	0.0	0.0	0.0	94
4	413	70	0.4	0.0	0.5	0.0	0.3	0.4	0.6	94
5	433	87	1.3	0.8	8.0	0.0	2.2	4.2	1.7	89
6	453	100	1.1	1.0	23	2.0	7.0	10	11	91
7[d]	433	2.5	0.0	0.1[e]	0.0	0.0	0.0	0.0	3.3	101
8[d]	453	22	0.0	0.3[e]	0.0	0.0	0.0	0.0	23	101

[a] Reaction conditions: EDA 4.0 mmol; Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 373–453 K; 16 h.

[b] Abbreviations: PM-DETA = *N*,*N*,*N*’,*N*’’,*N*’’-pentamethyldiethylenetriamine; M-PZ = *N*-methylpiperazine; DM-PZ = *N*,*N*’-dimethylpiperazine; MA = methylamine; DMA = dimethylamine; TMA = trimethylamine; EU = 2-imidazolidinone (*i.e.*, ethylene urea).

[c] Yield [%] = (Product [mol]) / (2 × (EDA [mol])) × 100.

[d] Without catalyst.

[e] Piperazine. M-PZ was not detected.

Table S8. Detailed data for Fig. 4A (time course of *N*-methylation of EDA over Re-Ir/C-BP catalyst at 403 K.[a,b]

Entry	Time [h]	Conv. [%]	Yield [%]										N_{Me}[d] [%]	Bal. [%]
			N-Methylated EDA					*N*-Formylated EDA						
			M-EDA	N,N-DM-EDA	N,N'-DM-EDA	TriM-EDA	TetraM-EDA	F-EDA	F-M-EDA	F-DM-EDA	F-TriM-EDA	Others[c]		
1	4	18	4.5	1.8	0.0	0.0	0.5	10	0.7	0.0	0.0	0.0	10	100
2	8	30	7.1	5.1	0.0	0.5	3.3	10	1.4	0.7	0.3	0.0	32	96
3	12	42	8.2	8.0	0.0	0.8	7.5	11	1.7	1.0	0.4	0.3	57	97
4	16	56	7.1	10	0.0	1.1	17	10	2.4	1.8	0.7	0.5	98	94
5	24	62	8.0	9.5	0.0	1.4	23	9.0	2.1	1.5	0.8	0.5	121	94
6	48	87	2.7	5.5	0.0	1.8	54	4.7	1.5	1.7	1.3	2.5	236	93
7	72	94	1.9	3.1	0.0	1.3	69	2.8	0.9	1.3	1.0	5.8	287	93
8	96	98	1.9	1.2	0.0	1.0	76	1.3	0.5	0.7	0.7	11	310	96
9	120	99	0.0	0.9	0.0	0.9	82	0.7	0.0	0.5	0.6	12	331	97

[a] Reaction conditions: EDA 4.0 mmol; Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 403 K; 4–120 h.

[b] Abbreviations: M-EDA = *N*-methylethylenediamine; N,N-DM-EDA = *N*,*N*-dimethylethylenediamine; N,N'-DM-EDA = *N*,*N*'-dimethylethylenediamine; TriM-EDA = *N*,*N*,*N*'-trimethylethylenediamine; TetraM-EDA = *N*,*N*,*N*',*N*'-tetramethylethylenediamine; F-EDA = *N*-(2-aminoethyl)formamide; F-M-EDA = *N*-(2-aminoethyl)-*N*-methylformamide; F-DM-EDA = *N*-(2-(dimethylamino)ethyl)formamide; F-TriM-EDA = *N*-(2-(dimethylamino)ethyl)-*N*-methylformamide.

[c] Including piperazine, 2-imidazolidinone, methylamine, and their corresponding *N*-methylated compounds.

[d] Degree of *N*-methylation calculated using eqn. 4.

Table S9. Detailed data for Fig. 4B (time course of *N*-methylation of EDA over Re-Ir/C-BP catalyst at 413 K).[a,b]

Entry	Time [h]	Conv. [%]	Yield [%]										N_{Me}[d] [%]	Bal. [%]
			N-Methylated EDA					*N*-Formylated EDA				Others[c]		
			M-EDA	N,N-DM-EDA	N,N’-DM-EDA	TriM-EDA	TetraM-EDA	F-EDA	F-M-EDA	F-DM-EDA	F-TriM-EDA			
1	4	34	7.3	6.0	0.0	0.6	3.8	7.8	1.4	0.7	0.3	0.0	36	93
2	8	52	7.4	10	0.0	1.3	15	6.7	1.9	1.1	0.6	1.3	93	94
3	12	61	6.4	11	0.0	2.0	22	6.4	1.9	1.5	0.7	1.9	123	93
4	16	70	4.5	9.9	0.0	1.9	34	6.8	2.3	1.6	0.8	2.2	164	94
5	24	83	2.4	7.3	0.0	2.1	51	2.7	1.2	1.1	0.7	4.2	227	91
6	48	91	1.5	4.2	0.0	1.7	62	2.5	1.0	0.9	0.7	5.7	264	92
7	72	100	0.0	0.7	0.0	1.8	72	0.0	0.0	0.0	0.4	9.9	293	90
8	96	100	0.0	0.0	0.0	1.1	79	0.0	0.0	0.0	0.5	18	320	100

[a] Reaction conditions: EDA 4.0 mmol; Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 413 K; 4–96 h.

[b] Abbreviations: M-EDA = *N*-methylethylenediamine; N,N-DM-EDA = *N*,*N*-dimethylethylenediamine; N,N’-DM-EDA = *N*,*N*’-dimethylethylenediamine; TriM-EDA = *N*,*N*,*N*’-trimethylethylenediamine; TetraM-EDA = *N*,*N*,*N*’,*N*’-tetramethylethylenediamine; F-EDA = *N*-(2-aminoethyl)formamide; F-M-EDA = *N*-(2-aminoethyl)-*N*-methylformamide; F-DM-EDA = *N*-(2-(dimethylamino)ethyl)formamide; F-TriM-EDA = *N*-(2-(dimethylamino)ethyl)-*N*-methylformamide.

[c] Including piperazine, 2-imidazolidinone, methylamine, and their corresponding *N*-methylated compounds.

[d] Degree of *N*-methylation calculated using eqn. 4.

Table S10. Time course of *N*-methylation of EDA over Re-Ir/C-BP catalyst at 393 K.[a,b]

Entry	Time [h]	Catalyst amount [g]	Conv. [%]	Yield [%]										N_{Me}[d] [%]	Bal. [%]
				N-Methylated EDA					*N*-Formylated EDA						
				M-EDA	N,N-DM-EDA	N,N’-DM-EDA	TriM-EDA	TetraM-EDA	F-EDA	F-M-EDA	F-DM-EDA	F-TriM-EDA	Others[c]		
1	8	0.10	28	6.0	4.8	0.0	0.3	2.5	13	2.1	1.5	0.3	0.0	26	102
2	16	0.10	46	5.9	6.9	0.0	0.6	7.2	14	2.2	1.8	0.6	0.0	50	94
3	24	0.10	54	6.3	9.6	0.0	1.1	16	11	2.9	3.0	1.0	0.0	92	94
4	48	0.10	72	4.0	8.8	0.0	1.3	34	9.1	2.3	3.3	1.3	1.0	162	91
5	48	0.30	91	2.9	6.1	0.0	1.5	62	3.0	0.7	2.0	2.4	3.1	266	92
6	72	0.30	93	2.0	4.8	0.0	1.0	70	3.1	0.6	2.2	1.5	5.4	293	97
7	96	0.30	95	1.2	3.2	0.0	1.0	74	1.7	0.4	1.4	1.2	6.5	307	96
8	120	0.30	100	0.0	0.8	0.0	1.0	82	0.0	0.0	0.5	1.0	9.7	332	95

[a] Reaction conditions: EDA 4.0 mmol; Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.10 or 0.30 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 393 K; 8–120 h.

[b] Abbreviations: M-EDA = *N*-methylethylenediamine; N,N-DM-EDA = *N*,*N*-dimethylethylenediamine; N,N’-DM-EDA = *N*,*N*’-dimethylethylenediamine; TriM-EDA = *N*,*N*,*N*’-trimethylethylenediamine; TetraM-EDA = *N*,*N*,*N*’,*N*’-tetramethylethylenediamine; F-EDA = *N*-(2-aminoethyl)formamide; F-M-EDA = *N*-(2-aminoethyl)-*N*-methylformamide; F-DM-EDA = *N*-(2-(dimethylamino)ethyl)formamide; F-TriM-EDA = *N*-(2-(dimethylamino)ethyl)-*N*-methylformamide.

[c] Including piperazine, 2-imidazolidinone, methylamine, and their corresponding *N*-methylated compounds.

[d] Degree of *N*-methylation calculated using eqn. 4.

Table S11. Detailed data for Fig. 5 (reuse test of Re-Ir/C-BP catalyst for *N*-methylation of EDA).[a,b]

Entry	Run	Conv. [%]	Yield [%]										N_{Me}[d] [%]	Bal. [%]	Ratio of leached metal against original metal loading[e] [%]	
			N-Methylated EDA					*N*-Formylated EDA				Others[c]				
			M-EDA	N,N-DM-EDA	N,N’-DM-EDA	TriM-EDA	TetraM-EDA	F-EDA	F-M-EDA	F-DM-EDA	F-TriM-EDA				Re	Ir
1	1st	70	4.5	9.9	0.0	1.9	34	6.8	2.3	1.6	0.8	2.2	164	94	<0.1	<0.1
2	2nd	68	5.1	10	0.0	2.0	34	5.8	2.1	1.5	0.7	1.6	168	95	<0.1	<0.1
3	3rd	68	5.8	10	0.0	2.7	33	3.5	1.6	1.1	0.8	1.7	166	92	<0.1	<0.1
4	4th	67	4.9	10	0.0	1.9	33	4.7	1.4	1.3	1.0	2.1	160	92	<0.1	<0.1

[a] Reaction conditions: EDA 4.0 mmol; Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 413 K; 16 h. The spent catalyst was reused after washing with water and ethanol, drying at room temperature, and reduction in H_2 at 773 K.

[b] Abbreviations: M-EDA = *N*-methylethylenediamine; N,N-DM-EDA = *N*,*N*-dimethylethylenediamine; N,N’-DM-EDA = *N*,*N*’-dimethylethylenediamine; TriM-EDA = *N*,*N*,*N*’-trimethylethylenediamine; TetraM-EDA = *N*,*N*,*N*’,*N*’-tetramethylethylenediamine; F-EDA = *N*-(2-aminoethyl)formamide; F-M-EDA = *N*-(2-aminoethyl)-*N*-methylformamide; F-DM-EDA = *N*-(2-(dimethylamino)ethyl)formamide; F-TriM-EDA = *N*-(2-(dimethylamino)ethyl)-*N*-methylformamide.

[c] Including piperazine, 2-imidazolidinone, methylamine, and their corresponding *N*-methylated compounds.

[d] Degree of *N*-methylation calculated using eqn. 4.

[e] Quantified by ICP-OES.

Table S12. Results of H_2-TPR for Re-Ir/C-BP and Ir/C-BP catalysts shown in Fig. S6.

Entry	Catalyst	Ir/Re	Re		Ir		H_2 consumption amount[a]
			[wt%]	[mmol g^{-1}][a]	[wt%]	[mmol g^{-1}][a]	[mmol g^{-1}]
1	Re/C-BP	0	4.0	0.22	–	–	0.44
2	Re-Ir/C-BP	0.13	4.0	0.22	0.5	0.027	0.49
3	Re-Ir/C-BP	0.25	4.0	0.22	1.0	0.053	0.59
4	Re-Ir/C-BP	0.5	4.0	0.22	2.1	0.11	0.66
5	Re-Ir/C-BP	1.0	4.0	0.22	4.1	0.22	1.02
6	Ir/C-BP	–	–	–	4.0	0.21	1.02

[a] Normalized by catalyst amount.

Table S13. Results of CO chemisorption for Re-Ir/C-BP, Ir/C-BP, and ReS_2.[a]

Entry	Catalyst	Ir/Re	Re [wt%]	Ir [wt%]	CO uptake[b] [mmol g^{-1}]	CO/(Re + Ir) [mol/mol]
1	Re/C-BP	0	4.0	–	8.4	0.039
2	Re-Ir/C-BP	0.13	4.0	0.5	13	0.055
3	Re-Ir/C-BP	0.25	4.0	1.0	16	0.061
4	Re-Ir/C-BP	0.5	4.0	2.1	37	0.12
5	Re-Ir/C-BP	0.75	4.0	3.1	44	0.12
6	Re-Ir/C-BP	1.0	4.0	4.1	42	0.10
7	Ir/C-BP	–	–	4.0	42	0.20
8	ReS_2	–	74	–	0.0	0.0

[a] Each catalyst was reduced under a H_2 flow (30 mL min^{-1}) at 773 K for 1 h prior to CO adsorption. ReS_2 was analyzed as-is without reduction treatment.

[b] CO uptake normalized by catalyst amount.

Table S14. Detailed data for Fig. 7A (double logarithmic plot of EDA conversion rate as a function of concentration of EDA in *N*-methylation of EDA over Re-Ir/C-BP at 413 K).[a,b]

Entry	EDA[c] [mmol]	Time [h]	Conv. [%]	v_{EDA}[d] [mmol g^{-1} h^{-1}]	Yield [%]										Bal. [%]
					N-Methylated EDA					*N*-Formylated EDA					
					M-EDA	N,N-DM-EDA	N,N'-DM-EDA	TriM-EDA	TetraM-EDA	F-EDA	F-M-EDA	F-DM-EDA	F-TriM-EDA	Others[e]	
1	4.0	0.5	3.3	4.8	0.0	0.0	0.0	0.0	0.0	3.6	0.0	0.0	0.0	0.0	100
2	(0.75)	1	11		1.9	0.3	0.0	0.0	0.0	5.4	0.0	0.0	0.0	0.0	97
3		2	21		4.6	1.9	0.0	0.1	0.5	7.7	0.6	0.2	0.0	0.0	94
4	6.0	1	6.5	5.5	1.6	0.2	0.0	0.0	0.0	5.3	0.5	0.0	0.0	0.0	101
5	(1.1)	2	11		4.0	0.9	0.0	0.0	0.1	6.5	0.5	0.0	0.0	0.0	101
6		3	25		6.3	2.6	0.0	0.3	0.8	7.1	0.8	0.2	0.0	0.0	93
7	8.0	1	5.3	4.6	1.3	0.2	0.0	0.0	0.0	4.5	0.3	0.0	0.0	0.0	101
8	(1.4)	2	14		3.5	0.5	0.0	0.0	0.1	5.9	0.3	0.0	0.0	0.0	97
9		3	23		5.2	1.7	0.0	0.2	0.4	6.6	0.6	0.0	0.0	0.0	92
10	10	1	7.7	4.9	0.8	0.0	0.0	0.0	0.0	4.7	0.0	0.0	0.0	0.0	98
11	(1.8)	2	13		2.3	0.3	0.0	0.0	0.0	5.6	0.2	0.0	0.0	0.0	96
12		3	17		4.1	1.0	0.0	0.0	0.2	6.3	0.5	0.0	0.0	0.0	96

[a] Reaction conditions: EDA 4.0–10 mmol; Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 413 K; 0–3 h.

[b] Abbreviations: M-EDA = *N*-methylethylenediamine; N,N-DM-EDA = *N*,*N*-dimethylethylenediamine; N,N'-DM-EDA = *N*,*N*'-dimethylethylenediamine; TriM-EDA = *N*,*N*,*N*'-trimethylethylenediamine; TetraM-EDA = *N*,*N*,*N*',*N*'-tetramethylethylenediamine; F-EDA = *N*-(2-aminoethyl)formamide; F-M-EDA = *N*-(2-aminoethyl)-*N*-methylformamide; F-DM-EDA = *N*-(2-(dimethylamino)ethyl)formamide; F-TriM-EDA = *N*-(2-(dimethylamino)ethyl)-*N*-methylformamide.

[c] The values in parentheses represent the concentration of EDA (unit: M).

[d] Conversion rate of EDA based on the mass of catalyst used.

[e] Including piperazine, 2-imidazolidinone, methylamine, and their corresponding *N*-methylated compounds.

Table S15. Detailed data for Fig. 7B (double logarithmic plot of EDA conversion rate as a function of partial pressure of H_2 in *N*-methylation of EDA over Re-Ir/C-BP at 413 K).[a,b]

Entry	$P(H_2)$ [MPa]	Time [h]	Conv. [%]	v_{EDA}[c] [mmol g^{-1} h^{-1}]	Yield [%]										Bal. [%]
					N-Methylated EDA					*N*-Formylated EDA					
					M-EDA	N,N-DM-EDA	N,N'-DM-EDA	TriM-EDA	TetraM-EDA	F-EDA	F-M-EDA	F-DM-EDA	F-TriM-EDA	Others[d]	
1	1.0	2	8.0	1.1	1.5	0.0	0.0	0.0	0.0	4.3	0.0	0.0	0.0	0.0	98
2		4	12		4.5	1.5	0.0	0.0	0.3	5.2	0.4	0.0	0.0	0.0	100
3		6	18		6.2	2.5	0.0	0.2	0.7	5.2	0.5	0.0	0.0	0.0	97
4	2.0	1	3.5	2.1	0.6	0.0	0.0	0.0	0.0	3.9	0.0	0.0	0.0	0.0	101
5		2	8.9		2.5	0.4	0.0	0.0	0.0	5.5	0.0	0.0	0.0	0.0	100
6		3	13		5.0	1.7	0.0	0.1	0.3	6.0	0.5	0.0	0.0	0.0	101
7	3.0	1	7.3	2.7	1.1	0.0	0.0	0.0	0.0	4.9	0.0	0.0	0.0	0.0	99
8		2	14		3.7	1.1	0.0	0.0	0.2	6.8	0.4	0.0	0.0	0.0	98
9		3	20		5.2	2.1	0.0	0.2	0.5	7.1	0.0	0.0	0.0	0.0	98
10	4.0	0.5	3.3	4.8	0.0	0.0	0.0	0.0	0.0	3.6	0.0	0.0	0.0	0.0	100
11		1	11		1.9	0.3	0.0	0.0	0.0	5.4	0.0	0.0	0.0	0.0	97
12		2	21		4.6	1.9	0.0	0.1	0.5	7.7	0.6	0.2	0.0	0.0	94

[a] Reaction conditions: EDA 4.0 mmol; Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 1.0–4.0 MPa + Ar (4 – $P(H_2)$) MPa (r.t.); 413 K; 0–3 h.

[b] Abbreviations: M-EDA = *N*-methylethylenediamine; N,N-DM-EDA = *N*,*N*-dimethylethylenediamine; N,N'-DM-EDA = *N*,*N*'-dimethylethylenediamine; TriM-EDA = *N*,*N*,*N*'-trimethylethylenediamine; TetraM-EDA = *N*,*N*,*N*',*N*'-tetramethylethylenediamine; F-EDA = *N*-(2-aminoethyl)formamide; F-M-EDA = *N*-(2-aminoethyl)-*N*-methylformamide; F-DM-EDA = *N*-(2-(dimethylamino)ethyl)formamide; F-TriM-EDA = *N*-(2-(dimethylamino)ethyl)-*N*-methylformamide.

[c] Conversion rate of EDA based on the mass of catalyst used.

[d] Including piperazine, 2-imidazolidinone, methylamine, and their corresponding *N*-methylated compounds.

Table S16. Detailed data for Fig. 7C (double logarithmic plot of EDA conversion rate as a function of partial pressure of CO_2 in the *N*-methylation of EDA over Re-Ir/C-BP at 413 K).[a,b]

Entry	$P(CO_2)$ [MPa]	Time [h]	Conv. [%]	v_{EDA}[c] [mmol g^{-1} h^{-1}]	Yield [%]										Bal. [%]
					N-Methylated EDA					*N*-Formylated EDA					
					M-EDA	N,N-DM-EDA	N,N'-DM-EDA	TriM-EDA	TetraM-EDA	F-EDA	F-M-EDA	F-DM-EDA	F-TriM-EDA	Others[d]	
1	0.3	2	7.7	1.8	2.9	0.6	0.0	0.0	0.0	3.5	0.0	0.0	0.0	0.0	99
2		4	15		6.0	2.6	0.0	0.3	0.6	4.2	0.5	0.0	0.0	0.0	99
3		6	28		8.2	5.1	0.0	0.7	2.3	3.4	0.5	0.2	0.0	0.0	92
4	0.5	1	3.4	2.6	1.0	0.0	0.0	0.0	0.0	3.7	0.0	0.0	0.0	0.0	101
5		1.5	8.8		3.1	0.6	0.0	0.0	0.0	4.7	0.0	0.0	0.0	0.0	100
6		3	16		5.7	2.3	0.0	0.2	0.5	5.2	0.4	0.0	0.0	0.0	96
7	0.7	1	6.3	2.8	1.2	0.0	0.0	0.0	0.0	4.3	0.0	0.0	0.0	0.0	99
8		2	16		4.4	1.5	0.0	0.0	0.3	6.3	0.4	0.0	0.0	0.0	97
9		3	20		5.6	2.5	0.0	0.2	0.7	6.8	0.6	0.0	0.0	0.0	97
10	1.0	0.5	3.3	4.8	0.0	0.0	0.0	0.0	0.0	3.6	0.0	0.0	0.0	0.0	100
11		1	11		1.9	0.3	0.0	0.0	0.0	5.4	0.0	0.0	0.0	0.0	97
12		2	21		4.6	1.9	0.0	0.1	0.5	7.7	0.6	0.2	0.0	0.0	94

[a] Reaction conditions: EDA 4.0 mmol; Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 0.3–1.0 MPa + H_2 4.0 MPa + Ar $(1 - P(CO_2))$ MPa (r.t.); 413 K; 0–6 h.

[b] Abbreviations: M-EDA = *N*-methylethylenediamine; N,N-DM-EDA = *N*,*N*-dimethylethylenediamine; N,N'-DM-EDA = *N*,*N*'-dimethylethylenediamine; TriM-EDA = *N*,*N*,*N*'-trimethylethylenediamine; TetraM-EDA = *N*,*N*,*N*',*N*'-tetramethylethylenediamine; F-EDA = *N*-(2-aminoethyl)formamide; F-M-EDA = *N*-(2-aminoethyl)-*N*-methylformamide; F-DM-EDA = *N*-(2-(dimethylamino)ethyl)formamide; F-TriM-EDA = *N*-(2-(dimethylamino)ethyl)-*N*-methylformamide.

[c] Conversion rate of EDA based on the mass of catalyst used.

[d] Including piperazine, 2-imidazolidinone, methylamine, and their corresponding *N*-methylated compounds.

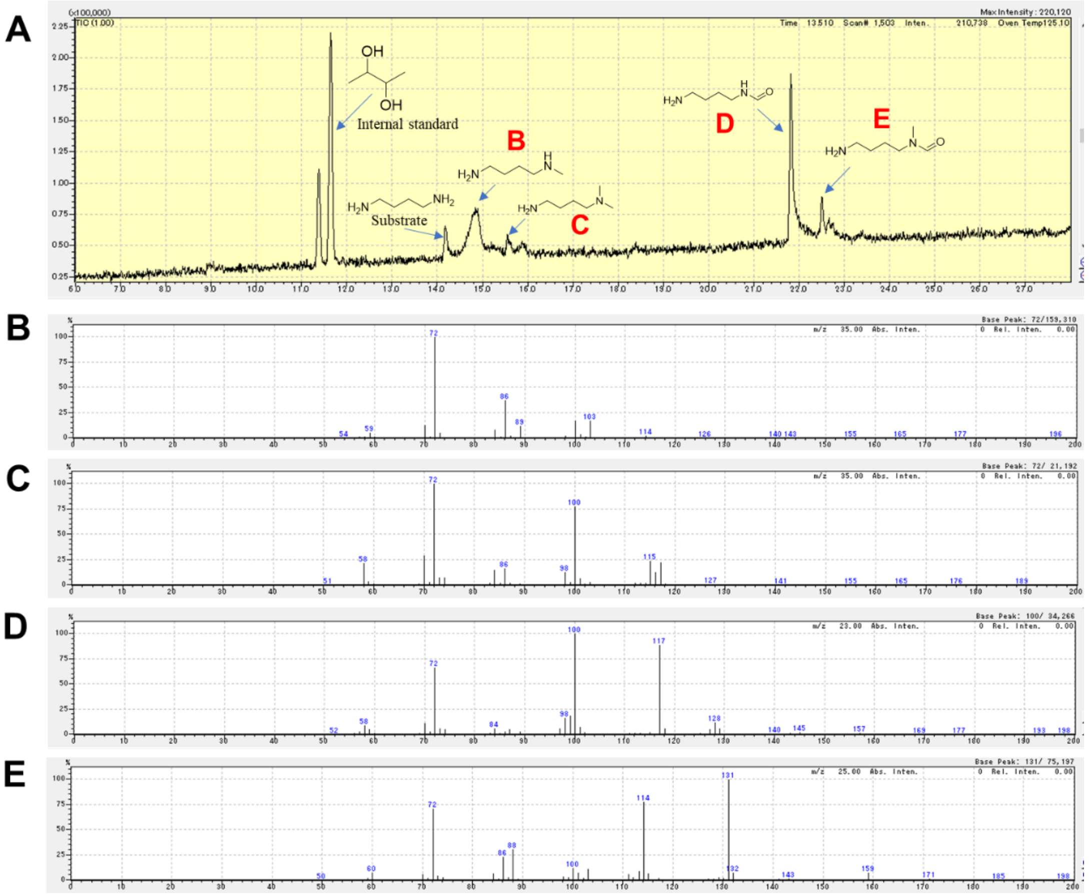


Fig. S1 (A) Total ion chromatogram recorded by GC-MS (CI) for the reaction mixture of *N*-methylation of 1,4-diaminobutane, and mass spectra of the peaks at (B) 14.9 min, (C) 15.3 min, (D) 21.8 min, and (E) 22.5 min.

Reaction conditions: 1,4-diaminobutane 2.0 mmol; Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.30 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 413 K; 24 h.

Column for GC-MS: InertCap for Amines capillary column (ø0.32 mm × 30 m).

Assignments for mass spectra in Fig. S1

[Fig. S1B] *N*-Methylbutane-1,4-diamine (M = 102 g mol^{-1}): 72 ($[M + H - CH_3NH_2]^+$), 86 ($[M + H - NH_3]^+$), 103 ($[M + H]^+$).

[Fig. S1C] *N*,*N*-Dimethylbutane-1,4-diamine (M = 116 g mol^{-1}): 58 ($[M + H - (CH_3)_3N]^+$), 72 ($[M + H - (CH_3)_2NH]^+$), 100 ($[M + H - NH_3]^+$) , 117 ($[M + H]^+$).

[Figure S1D] *N*-(4-Aminobutyl)formamide (M = 116 g mol^{-1}): 72 ($[M + H - HCONH_2]^+$), 100 ($[M + H - NH_3]^+$), 117 ($[M + H]^+$).

[Fig. S1E] *N*-(4-Aminobutyl)-*N*-methylformamide (M = 130 g mol^{-1}): 72 ($[M + H - HCONHCH_3]^+$), 86 ($[M + H - HCONH_2]^+$), 114 ($[M + H - NH_3]^+$) , 131 ($[M + H]^+$).

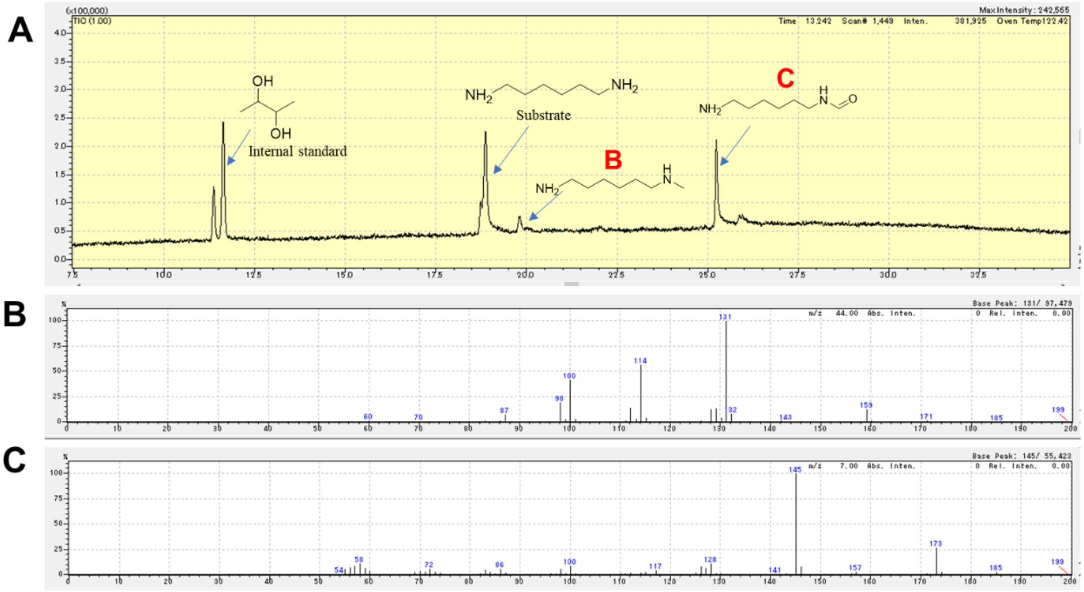


Fig. S2 (A) Total ion chromatogram recorded by GC-MS (CI) for the reaction mixture of *N*-methylation of 1,6-diaminohexane, and mass spectra of the peaks at (B) 19.8 min and (C) 25.2 min.
Reaction conditions: 1,6-diaminohexane 2.0 mmol; Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.30 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 413 K; 24 h.
Column for GC-MS: InertCap for Amines capillary column (ø0.32 mm × 30 m).

Assignments for mass spectra in Fig. S2
[Fig. S2B] *N*-Methylhexane-1,6-diamine (M = 130 g mol^{-1}): 100 ($[M + H - CH_3NH_2]^+$), 114 ($[M + H - NH_3]^+$), 131 ($[M + H]^+$), 158 ($[M + C_2H_5]^+$).
[Fig. S2C] *N*-(6-Aminohexyl)formamide (M = 144 g mol^{-1}): 100 ($[M + H - HCONH_2]^+$), 117 ($[M + H - CO]^+$), 128 ($[M + H - NH_3]^+$) , 145 ($[M + H]^+$), 173 ($[M + C_2H_5]^+$).

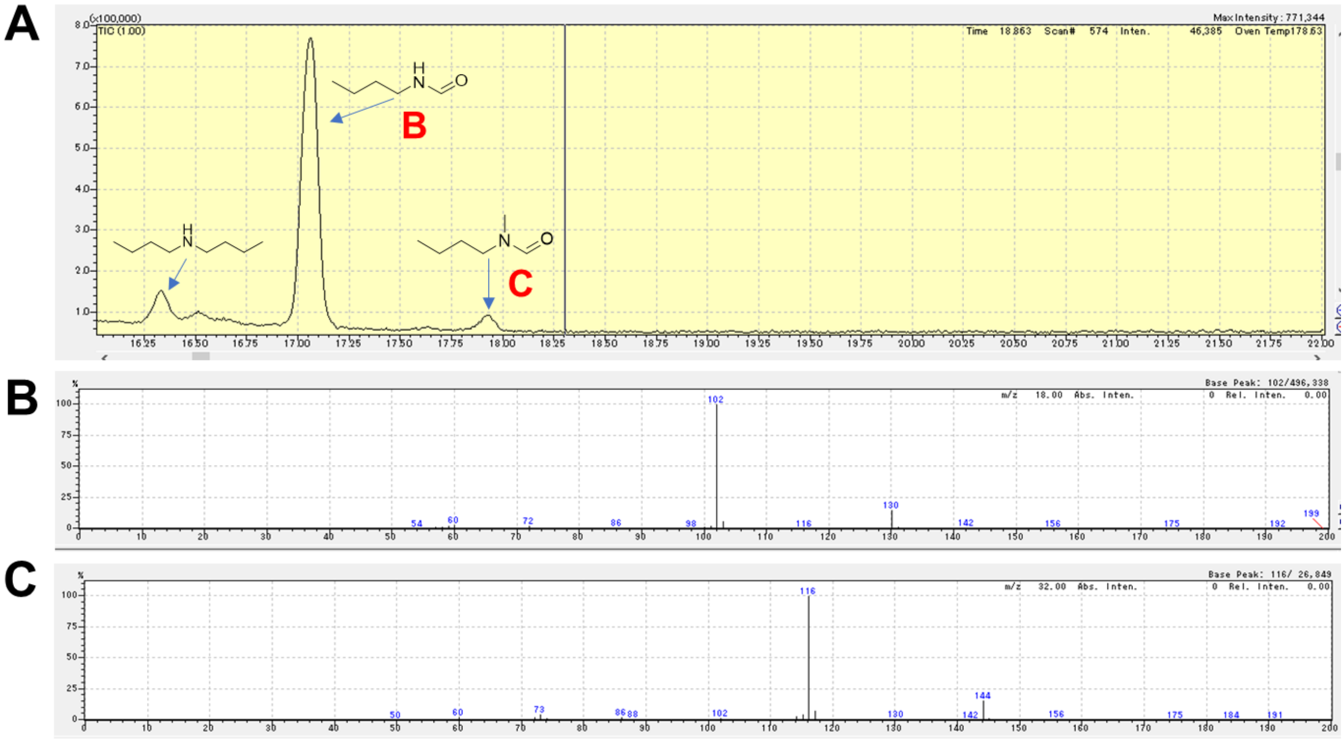


Fig. S3 (A) Total ion chromatogram recorded by GC-MS (CI) for the reaction mixture of *N*-methylation of *n*-butylamine, and mass spectra of the peaks at (B) 17.1 min and (C) 17.8 min.
Reaction conditions: *n*-butylamine 2.0 mmol; Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduced in H_2 at 773 K) 0.30 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 413 K; 24 h.
Column for GC-MS: InertCap for Amines capillary column (ø0.32 mm × 30 m).

Assignments for mass spectra in Fig. S3
[Fig. S3B] *N*-Butylformamide (M = 101 g mol^{-1}): 102 ($[M + H]^+$), 130 ($[M + C_2H_5]^+$).
[Fig. S3C] *N*-Butyl-*N*-methylformamide (M = 115 g mol^{-1}): 116 ($[M + H]^+$), 144 ($[M + C_2H_5]^+$).

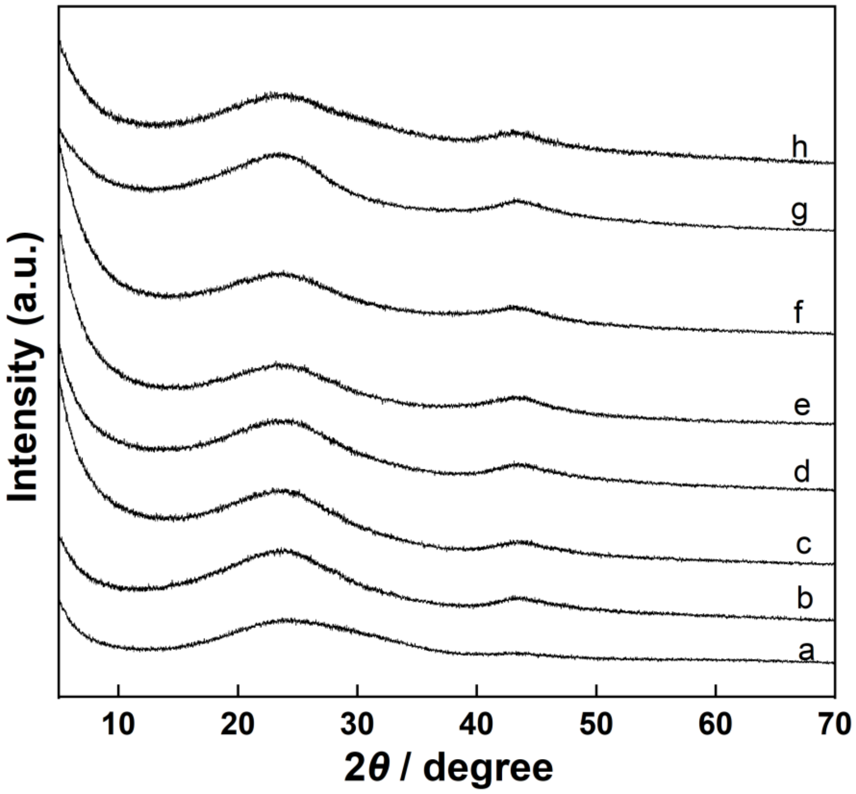


Fig. S4 XRD patterns of catalysts after either reduction (H_2, 773 K) + passivation or reaction: (a) C-BP; (b) Ir/C-BP (Ir 4 wt%); (c) Re/C-BP (Re 4 wt%); (d) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.13); (e) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.25); (f) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5); (g) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, after 4 times use); (h) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 1.0).
Reaction conditions: EDA 4.0 mmol; Re-Ir/C-BP (reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 413 K; 16 h.

The two broad peaks observed at *ca.* 24° and 44° in Fig. S4 were attributed to the (002) and (10) planes of graphitic materials, respectively.[S9]

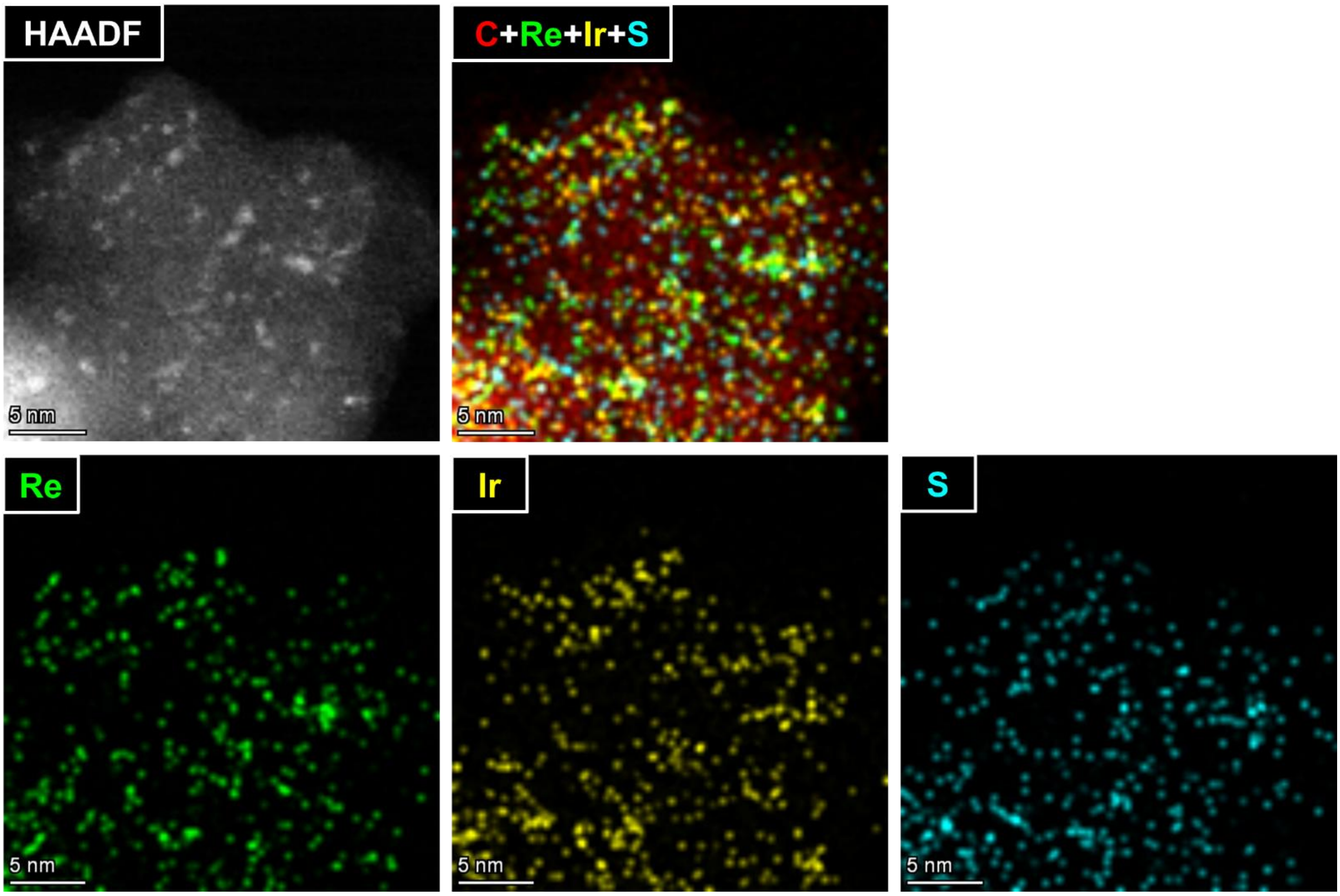


Fig. S5 HAADF-STEM image and elemental mapping of Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5) after reduction (H_2, 773 K) + passivation.

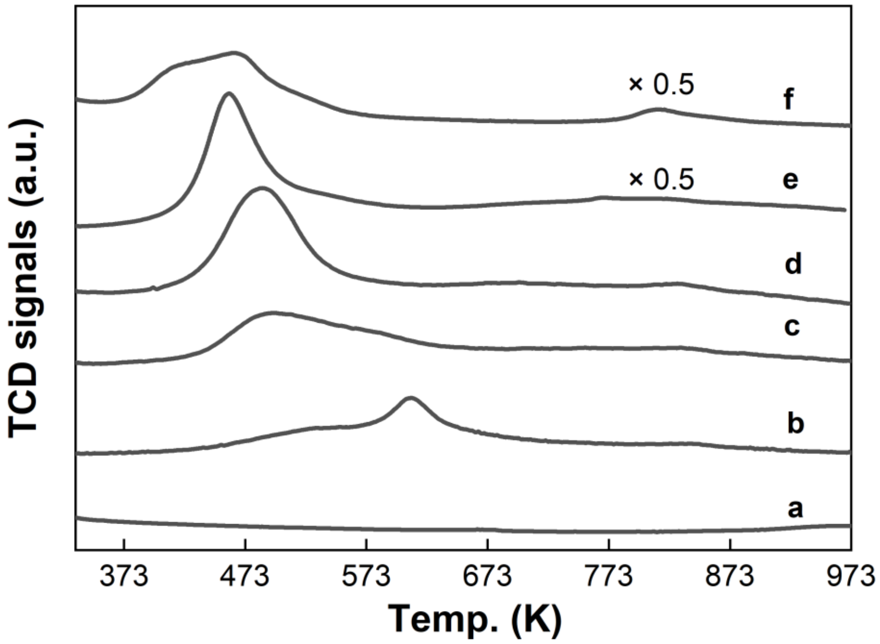


Fig. S6 H_2-TPR profiles for C-BP impregnated with different amount of Re and Ir precursors.
Sample legends: (a) C-BP; (b) Re/C-BP (4 wt%); (c) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.25); (d) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5); (e) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 1.0); (f) Ir/C-BP (Ir 4 wt%).
Measurement conditions: 10 vol% H_2/Ar (30 mL min^{-1}); 353–973 K; ramp rate 10 K min^{-1}.
TCD signals were normalized by the mass of catalysts used for each measurement.
Quantitative data are summarized in Table S12.

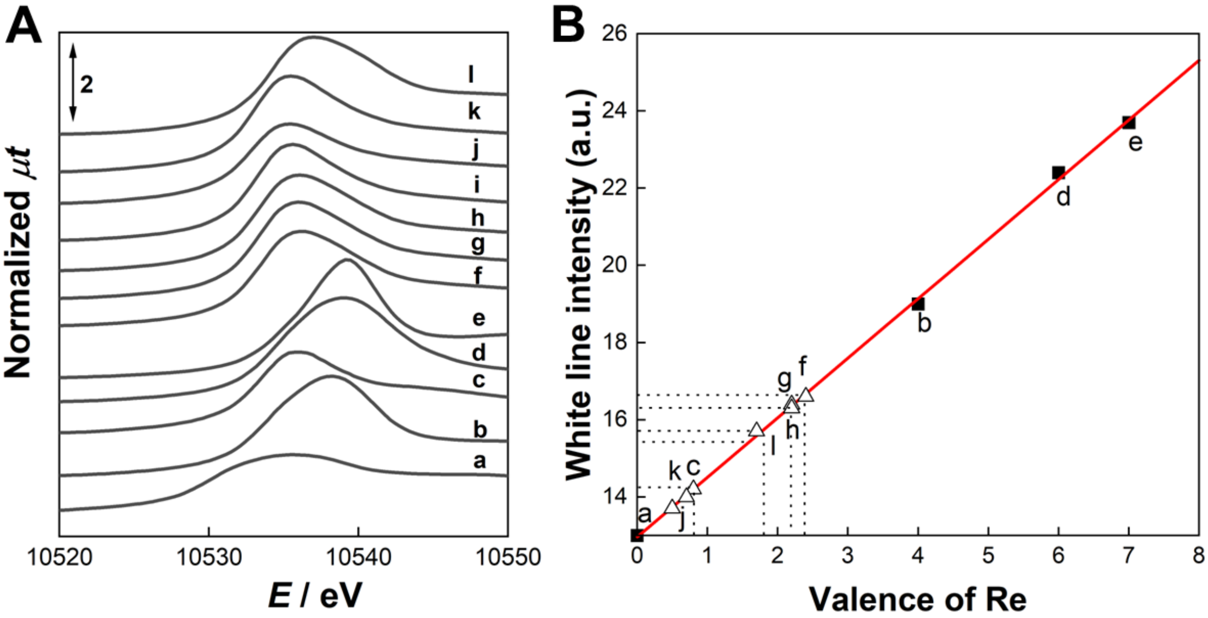


Fig. S7 (A) Re L_3-edge XANES spectra of catalysts after reduction/reaction and authentic samples and (B) parametric plot of white line area of Re L_3-edge XANES spectra *vs.* valence of Re.

Sample legends: (a) Re powder; (b) ReO_2; (c) ReS_2; (d) ReO_3; (e) NH_4ReO_4; (f) Re/C-BP (Re 4 wt%, reduction); (g) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.13, reduction); (h) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.25, reduction); (i) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduction); (j) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reaction); (k) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 1.0, reduction); (l) Re-Ir/C-BP(deS-973) (Re 4 wt%, Ir/Re = 0.5, reduction).

Reduction conditions: H_2 flow 30 mL min^{-1}; 773 K; 1 h.

Reaction conditions: EDA 4.0 mmol; catalyst (reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 413 K; 16 h.

The values of average valence of Re species in each sample determined from these data are summarized in Table 5.

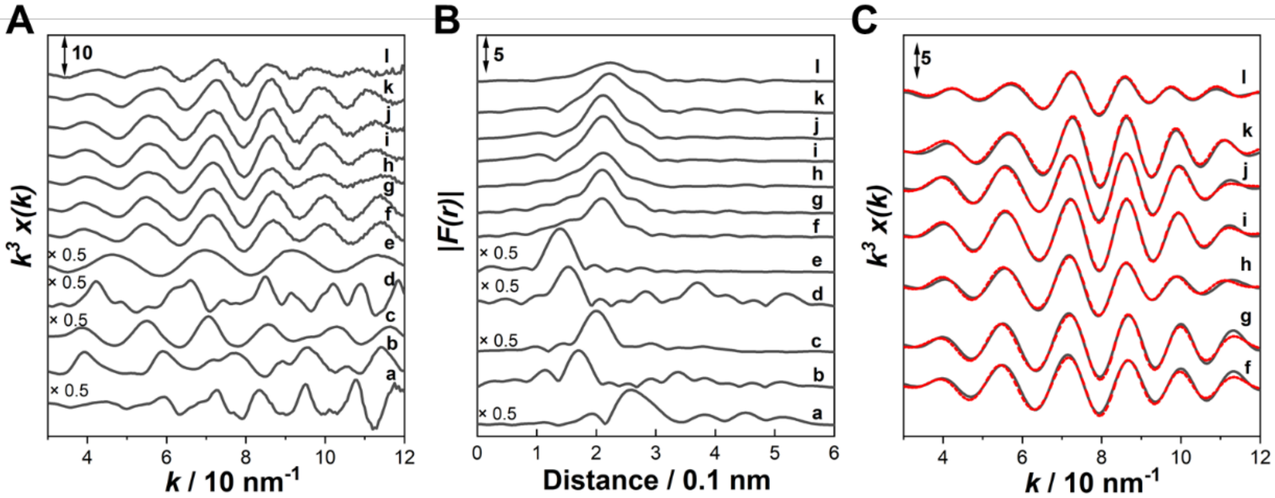


Fig. S8 Re L_3-edge EXAFS spectra of catalysts after reduction/reaction and authentic samples: (A) k^3-weighted EXAFS oscillations; (B) Fourier transform of k^3-weighted EXAFS oscillations; (C) inverse Fourier-filtered EXAFS data (black solid lines) and fitted data (red dotted lines).

Sample legends: (a) Re powder; (b) ReO_2; (c) ReS_2; (d) ReO_3; (e) NH_4ReO_4; (f) Re/C-BP (Re 4 wt%, reduction); (g) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.13, reduction); (h) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.25, reduction); (i) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduction); (j) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reaction); (k) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 1.0, reduction); (l) Re-Ir/C-BP(deS-973) (Re 4 wt%, Ir/Re = 0.5, reduction).

Reduction conditions: H_2 flow 30 mL min^{-1}; 773 K; 1 h.

Reaction conditions: EDA 4.0 mmol; catalyst (reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 413 K; 16 h.

The curve fitting results of EXAFS are listed in Table 5.

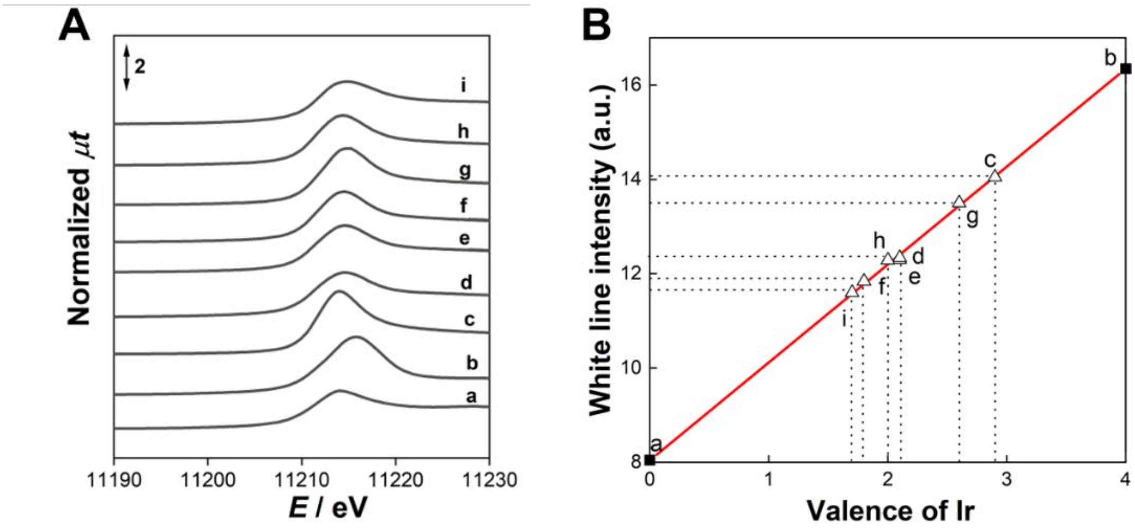


Fig. S9 (A) Ir L_3-edge XANES spectra of catalysts after reduction/reaction and authentic samples and (B) parametric plot of white line area of Ir L_3-edge XANES spectra *vs.* valence of Ir.

Sample legends: (a) Ir powder; (b) IrO_2; (c) Ir/C-BP (Ir 4 wt%, reduction); (d) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.13, reduction); (e) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.25, reduction); (f) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduction); (g) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reaction); (h) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 1.0, reduction); (i) Re-Ir/C-BP(deS-973) (Re 4 wt%, Ir/Re = 0.5, reduction).

Reduction conditions: H_2 flow 30 mL min^{-1}; 773 K; 1 h.

Reaction conditions: EDA 4.0 mmol; catalyst (reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 413 K; 16 h.

The values of average valence of Re species in each sample determined from these data are summarized in Table 6.

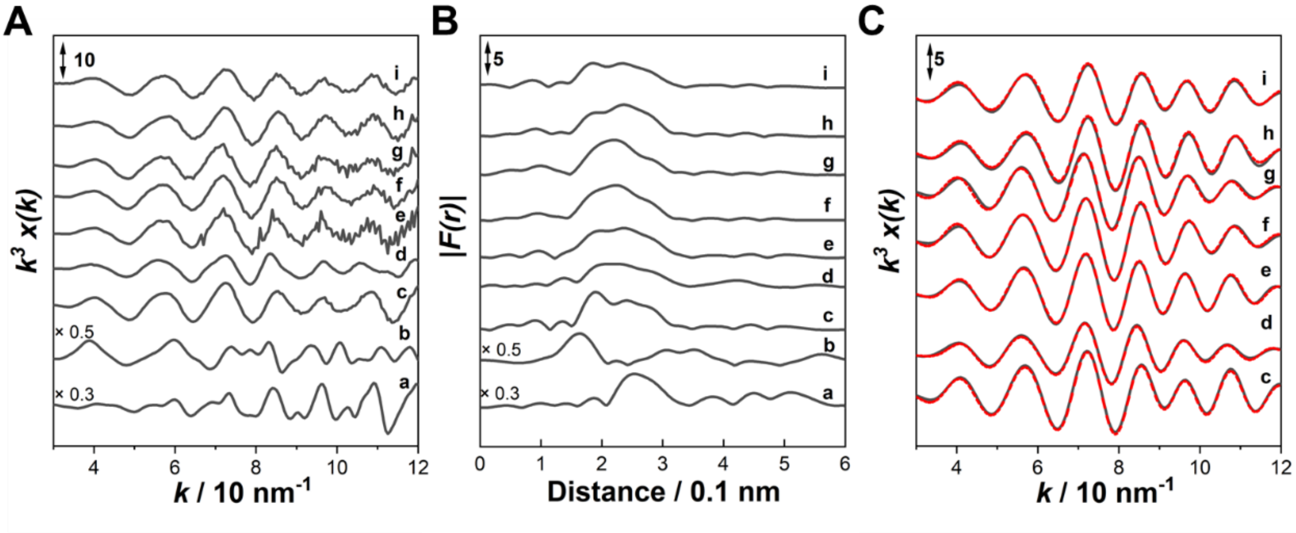


Fig. S10 Ir L_3-edge EXAFS spectra of catalysts after reduction/reaction and authentic samples: (A) k^3-weighted EXAFS oscillations; (B) Fourier transform of k^3-weighted EXAFS oscillations; (C) inverse Fourier-filtered EXAFS data (black solid lines) and fitted data (red dotted lines).

Sample legends: (a) Ir powder; (b) IrO_2; (c) Ir/C-BP (Ir 4 wt%, reduction); (d) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.13, reduction); (e) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.25, reduction); (f) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reduction); (g) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 0.5, reaction); (h) Re-Ir/C-BP (Re 4 wt%, Ir/Re = 1.0, reduction); (i) Re-Ir/C-BP(deS-973) (Re 4 wt%, Ir/Re = 0.5, reduction).

Reduction conditions: H_2 flow 30 mL min^{-1}; 773 K; 1 h.

Reaction conditions: EDA 4.0 mmol; catalyst (reduced in H_2 at 773 K) 0.10 g; water 5.0 g; CO_2 1.0 MPa + H_2 4.0 MPa (r.t.); 413 K; 16 h.

The curve fitting results of EXAFS are listed in Table 6.

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