Electronic Supplementary Information

Direct Self-Condensation of Bio-Alcohols in Aqueous Phase

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1 Reaction mechanism.



Scheme S1. The hydrogen auto-transfer mechanism.

As suggested in Scheme S1, a general reaction mechanism is as follows: the alcohol is initially dehydrogenated to produce aldehyde, then the aldol condensation and dehydration take place under base catalyst, at last the hydrogenation of the allylic aldehyde generates saturated alcohol product ultimately. The hydrogen generated in the initial dehydrogenation step is just consumed in the last hydrogenation step, and there is no need of additional oxidant or reductant. Therefore, such mechanism is usually named as the hydrogen auto-transfer or hydrogen-borrowing mechanism.

2 General procedure for catalysts screening.

Transition metal precursors, ligands or stabilizers, butanol and solvent were mixed together in a special tube for Anton Paar Synthos 3000 for microwave irradiation. Then the aqueous solution of base was added. After heating for some specified time, the reaction mixture was extracted with Et₂O, and then the aqueous phase and organic phase were both analyzed using GC. For the determination of yield, because the products were insoluble in water, the analysis of organic phase separately was appropriate. But for the determination of conversion, the aqueous phase should be measured because of the considerable solubility of butanol in water. Then the conversion of butanol could be calculated from the analyses of organic and aqueous phase together. For some experiments during this research, we only measured the organic phase for fast catalyst evaluation.

Table S1. Catal	yst screening	for butanol	condensation	using Ru	, Rh, Ir,	Cu, Pd, A	Ag. ^[a]
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Entry	[M] precursor	Ligand/stabilizer	Base (eq.)	Solvent	<i>T</i> [°C]- <i>t</i> [h]] Yield [%		6]	
	(mol%)	(mol%)				1a	2a	3a	
1	CuBr (0.5)	\	NaOH (0.2)	toluene	130-1	0	0	0	
2	CuBr (0.5)	1	NaOH (0.2)	THF	130-1	0	0	0	
3	CuBr (0.5)	\	KO ^t Bu (0.2)	THF	130-1	20	0	0	
4	RhCl ₃ -3H ₂ O (0.2)	\	NaOH (1.0)	toluene	130-1	30	1	trace	
5	RhCl ₃ -3H ₂ O (0.2)	/	NaOH (1.0)	toluene	140 ^b -4	20	1	trace	
6	RhCl ₃ -3H ₂ O (0.2)	/	NaOH (1.0)	toluene	140 ^b -30	60	trace	trace	
7	RhCl ₃ ·3H ₂ O (0.2)	١	NaOH (1.0)	toluene-H ₂ O ^c	140 ^b -12	19	trace	trace	
8	RhCl ₃ ·3H ₂ O (0.2)	١	NaOH (1.0)	toluene-H ₂ O ^d	140 ^b -12	0	0	0	
9	RhCl ₃ ·3H ₂ O (0.2)	PPh ₃ (1)	NaOAc (0.6)	toluene-H ₂ O	130-1	0	0	0	
10	RhCl ₃ ·3H ₂ O (0.2)	PPh ₃ (1)	K ₂ CO ₃ (0.6)	THF-H ₂ O	130-1	0	0	0	
11	RhCl ₃ ·3H ₂ O (0.2)	PPh ₃ (1)	NEt ₃ (0.6)	toluene-H ₂ O	130-1	0	0	0	
12	RhCl ₃ ·3H ₂ O (0.2)	PPh₃ (1)	NaOH (0.6)	toluene-H ₂ O	130-1	0	0	0	
13	RhCl ₃ ·3H ₂ O (0.2)	PPh ₃ (1)	K ₂ CO ₃ (0.6)	toluene-H ₂ O	130-1	trace	0	0	
14	RhCl ₃ ·3H ₂ O (0.2)	TPPTS (1)	K ₂ CO ₃ (0.6)	toluene-H ₂ O	140-1	0	0	0	
15	RhCl ₃ .3H ₂ O (0.2)	Bi-Py (1.5)	NaOAc (0.6)	toluene-H ₂ O	130-1	trace	0	0	
16	RhCl ₃ .3H ₂ O (0.2)	Bi-Py (1.5)	K ₂ CO ₃ (0.6)	toluene-H ₂ O	130-1	0	0	0	
17	RhCl ₃ .3H ₂ O (0.2)	Phen (1.5)	NaOAc (0.6)	toluene-H ₂ O	130-1	trace	0	0	
18	RhCl ₃ -3H ₂ O (0.2)	Phen (1.5)	K ₂ CO ₃ (0.6)	toluene-H ₂ O	130-1	trace	0	0	
19	RuCl ₃ -3H ₂ O (0.2)	PPh₃ (1)	LiOH (0.6)	hexane- H ₂ O	150-2	trace	0	0	
20	RuCl ₃ ·3H ₂ O (0.2)	DPPF (0.5)	LiOH (0.6)	hexane- H ₂ O	150-2	0	0	0	
21	RuCl ₃ ·3H ₂ O (0.2)	TPPTS (1)	LiOH (0.6)	hexane- H ₂ O	140-2	0	0	0	
22	RuCl ₃ ·3H ₂ O (0.2)	Phen (0.8)	LiOH (0.8)	H ₂ O	120-2	0	trace	trace	
23	RuCl ₃ ·3H ₂ O (0.2)	Phen (0.8)	KOH (0.8)	H ₂ O	125-1.5	0	trace	trace	
24	RuCl ₃ ·3H ₂ O (0.2)	Phen (1.5)	Cs ₂ CO ₃ (0.2)	hexane-H ₂ O	115-1	0	0	0	
25	RuCl ₃ ·3H ₂ O (0.2)	IPr (0.8)	LiOH (0.6)	hexane-H ₂ O	115-1	0	trace	trace	
26	RuCl ₃ -3H ₂ O (0.2)	IMes (0.8)	LiOH (0.6)	hexane-H ₂ O	115-1	0	0	0	
27	RuCl ₃ -3H ₂ O (0.2)	IPr (0.8)	LiOH (0.6)	hexane-H ₂ O	140-2	0	trace	trace	
28	Ru(acac) ₃ (0.2)	Bi-Py (1.5)	LiOH (0.6)	hexane-H ₂ O	120-1	0	0	0	
29	Ru(acac) ₃ (0.2)	Phen (1.5)	LiOH (0.6)	hexane-H ₂ O	120-1	0	trace	trace	
30	Ru(acac) ₃ (0.2)	IPr (0.8)	LiOH (0.5)	hexane-H ₂ O	115-1	trace	1	1	
31	RuCl ₃ -3H ₂ O (0.2)	PVP (3)	LiOH (0.6)	hexane-H ₂ O	120-1	0	trace	trace	
32	RuCl ₃ -3H ₂ O (0.2)	PVP (3) + NH_2NH_2	LiOH (0.6)	hexane-H ₂ O	125-1	0	trace	trace	
33	RuCl ₃ ·3H ₂ O (0.2)	PVP (5)	LiOH (0.6)	H ₂ O	120-1	0	0	trace	
		[H ₂ reduced]							
34	RuCl ₃ ·3H ₂ O (0.2)	SDS (3)	LiOH (0.6)	hexane-H ₂ O	120-1	0	0	0	
35	RuCl ₃ ·3H ₂ O (0.2)	PEG-400 (10)	LiOH (0.6)	H ₂ O	115-1	0	0	0	
36	RuCl ₃ ·3H ₂ O (0.2)	CTAB (2)	LiOH (0.6)	hexane-H ₂ O	120-1	0	0	0	
37	Ir(acac) ₃ (0.15)	Phen (1.5)	LiOH (0.3)	hexane-H ₂ O	115-1	0	0	0	
38	Ir(acac) ₃ (0.15)	PPh ₃ (1)	LiOH (0.3)	hexane-H ₂ O	115-1	0	0	0	
39	$Ir(acac)_3 (0.15)$	IPr (0.8)	LIOH (0.3)	hexane-H ₂ O	115-2	0	0	0	
40	$IrCl_{3} \cdot 3H_{2}O(0.2)$	IPr (0.8)	LIOH (0.5)	hexane-H ₂ O	110-2	0	1	trace	
41	IrCl ₃ ·3H ₂ O (0.2)	IPr (0.8)		H ₂ O	120-2	0	0.5	trace	
42	IrCl ₃ ·3H ₂ O (0.2)			H ₂ O	120-2	0.5	1	0.5	
43					120-2	U	0.5	trace	
44	IrCI ₃ ·3H ₂ O (0.2)	$PVP(3) + NH_2NH_2$		H ₂ O	120-2	trace	0	0	
40	$(acaC)_3 (0.15)$	$\Gamma V \Gamma (3) + INH_2INH_2$			120-2	0	0	0	
40	$Pd(OA_{0}) = (0, 2)$	$\Gamma V \Gamma (3) + IN \Pi 2 IN \Pi 2$			120-1	0	0	trace	
47	$Pd(OAc)_2(0.2)$				120-2	0	0	trace	
40	$PdCl_{2}(0.2)$	IFT (0.0)			120-2	0	0	nace 0	
49 50			KOH (0.6)	H ₂ O	120-2	0	0	0	
51	CuBr (0.35)	PPh ₂ (1)	KOH (0.0)	H ₂ O	120-2	0	0	0	
52		P\/P (5) ± NIU-NIU-		heyane-H-O	120-2	0	0	0	
53	Cu(OAc) ₂ (0.5)	PVP (5) + NH ₂ NH ₂	LiOH (0.6)	hexane-H ₂ O	120-1	0	0	0	

[a] Reaction conditions: Butanol (1 g, 13.5 mmol), metal precursors, ligands or stabilizers, bases and 15 mL solvent were mixed together as specified in Table S1 and microwave irradiation was used. If mixed solvent was used, the volume ratio of organic solvent to H₂O is 1:2. Phen is 1,10-phenanthroline, Bi-Py is 2,2'-bipyridine, IMes is 1,3-dimesitylimidazol-2-ylidene, IPr is 2,6-diisopropyl-phenyl imidazolium, TPPTS is tris(3-sulfonatophenyl)phosphine sodium salt, DPPF is 1,1'-bis(diphenylphosphino) ferrocene, PVP is polyvinylpyrrolidone, PEG is polyethylene glycol, CTAB is hexadecyltrimethylammonium bromide, SDS is sodium dodecyl sulphate. [b] The reactions were heated using oil bath and carried out under air. [c] 1 mL H₂O was added to 15 mL toluene after 4h. [d]. 1 mL H₂O was added to 15 mL toluene at the beginning.

3 The development of iridium catalysts.

The combination of IrCl₃ and phenanthroline was low soluble in H₂O and butanol mixtures, but when KOH solution was added, the aqueous phase turned clear and looked like homogeneous. However, the catalyst agglomerated and black precipitates formed during the reaction (Figure S1). TEM analyses also suggested that IrCl₃-phenanthroline catalyst dispersed well before the reaction, but aggregated evidently during the transformation (Figure S2).



Figure S1. Representative photos of reaction mixtures. Left: [IrCl₃, Phenanthroline, H_2O and butanol] before the reaction; Middle: [IrCl₃, Phenanthroline, H_2O , butanol and KOH] before the reaction; Right: [IrCl₃, Phenanthroline, H_2O , butanol and KOH] after the reaction and ether was added for extraction.



Figure S2. TEM images of IrCl₃-Phenanthroline catalyst before (left, scale bar: 50 nm) and after (middle, scale bar: 100 nm; right, scale bar: 2 µm) the reaction in butanol condensation.

Iridium precursors and ligand L10 formed dark-brown water soluble catalyst during the reaction (Figure S3). After extracted with ether and hexane for three times respectively to separate the organics, the water soluble catalyst could be reused for three times without obvious decrease in activity, but more black precipitates formed later. TEM analyses also suggested that water soluble catalyst dispersed well during the reaction, but some aggregation was observed after the fifth run (Figures S4).



Figure S3. Representative photos of reaction mixtures. Left: [IrCl₃, L10, H₂O, butanol and KOH] before the reaction; Right: [IrCl₃, L10, H₂O, butanol and KOH] after the reaction and ether was added for extraction.



Figure S4. TEM images of [Ir(acac)₃]-L10 catalyst. Left: Table 2, entry 3 (scale bar: 200 nm); Right: Table 2, entry 8 (scale bar: 200 nm).

More experiments about the development of iridium catalysts are listed in Table S2. L1-L4, L7, L10 and L11 were commercially available. L5 was prepared by the coupling between pyrazole and 2-Chloro-1,10-phenanthroline catalyzed by KOH in THF, and 2-Chloro-1,10-phenanthroline was prepared according to (*Org. Prep. Proced. Int.*, 2007, **39**, 603-608). L6 was prepared according to (*J. Org. Chem.*, 1990, **55**, 4992-4994). L8-L9 were prepared according to (*J. Organomet. Chem.*, 2009, **694**, 697-702). Representative GC spectrums of butanol condensation are depicted in Figure S5.

Table S2.	Catalysts	development	of iridium	catalyst for	butanol	condensation.[a]
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Entry	[M] precursor	Ligand/stabilizer	Base (eq.)	Solvent	<i>T</i> [°C]- <i>t</i> [h]	Conv.	Yield [%]		6]
	(mol%)	(mol%)				[%]	1a	2a	3a
1	IrCl ₃ ·3H ₂ O (0.2)	١	LiOH (1)	hexane-H ₂ O	120 ^[b] -4	n.d.	0	0	0
2	IrCl ₃ ·3H ₂ O (0.2)	Phen (1.5)	LiOH (0.8)	hexane-H₂O	120 ^[b] -3	35	5	trace	0.5
3	IrCl ₃ -3H ₂ O (0.15)	Phen (1.5)	KOH (0.3)	hexane-H ₂ O	130 ^[b] -3	40	14	trace	3
4	IrCl ₃ ·3H ₂ O (0.15)	Phen (1.5)	KOH (0.6)	hexane-H ₂ O	125 ^[b] -3	45	18	trace	3
5	IrCl ₃ ·3H ₂ O (0.15)	Phen (2)	KOH (0.6)	H ₂ O	120 ^[b] -2	40	10	trace	1
6	IrCl ₃ -3H ₂ O (0.2)	Phen (0.6)	KOH (1)	hexane-H ₂ O	140-3	13	8	trace	<1
7	IrCl ₃ ·3H ₂ O (0.2)	Phen (0.6)	KOH (1)	hexane-H ₂ O	155-9	34	22	trace	<1
8	IrCl ₃ ·3H ₂ O (0.2)	Phen (3.5)	KOH (1)	hexane-H ₂ O	140-3	2	1	0	0
9	IrCl ₃ ·3H ₂ O (0.2)	Phen (3.5)	KOH (1)	hexane-H ₂ O	155-9	35	23	trace	<1
10	IrCl ₃ ·3H ₂ O (0.2)	Phen (2)	NaOH (1)	H ₂ O	130-45	20	9	trace	3
11	IrCl ₃ ·3H ₂ O (0.2)	Phen (2)	KOH (1)	H ₂ O	130-36	27	7	trace	2
12	IrCl ₃ ·3H ₂ O (0.2)	Phen (0.7)	KOH (1)	H ₂ O	125-40	12	7	trace	1
13	IrCl ₃ ·3H ₂ O (0.2)	Phen (0.7)	KOH (1)	H ₂ O	160-6	55	43	trace	<1
14	IrCl ₃ ·3H ₂ O (0.2)	Phen (3.5)	KOH (1)	H ₂ O	160-6	51	41	trace	<1
15	IrCl ₃ ·3H ₂ O (0.2)	Phen (1.7)	KOH (0.45)	H ₂ O	160-6	30	19	trace	<1
16	IrCl ₃ ·3H ₂ O (0.2)	Phen (1)	KOH (1)	H ₂ O	150-6	39	23	trace	<1
17	IrCl ₃ ·3H ₂ O (0.2)	Phen (1.7)	KF (0.9)	H ₂ O	160-12	5	3	<1	<1
18	IrCl ₃ ·3H ₂ O (0.2)	Phen (1.7)	CsF (0.9)	H ₂ O	160-12	5	3	<1	<1
19	IrCl ₃ ·3H ₂ O (0.2)	Phen (1.7)	K ₂ CO ₃ (0.9)	H ₂ O	160-12	27	22	trace	<1
20	IrCl ₃ ·3H ₂ O (0.2)	Phen (1.7)	K ₃ PO ₄ (0.9)	H ₂ O	160-6	40	28	trace	<1
21	IrCl ₃ ·3H ₂ O (0.2)	Phen (1.7)	NaOAc (1)	H ₂ O	160-12	1	0	0	0
22	IrCl ₃ ·3H ₂ O (0.2)	Phen (1.7)	KOH (2) + NaOAc (0.8)	H₂O	160-6	55	49	<1	<1
23	IrCl ₃ -3H ₂ O (0.6)	Phen (3.5)	KOH (1)	H ₂ O	160-12	50	40	<1	<1
24 ^[c]	IrCl ₃ -3H ₂ O (0.2)	Phen (1)	KOH (1)	H ₂ O	160-12	26	18	<1	<1
25	ICl ₃ ·3H ₂ O (0.2)	PPh3 (2)	KOH (1)	H ₂ O	160-12	n.d.	2	1	<1
26	ICl ₃ ·3H ₂ O (0.2)	TPPTS (1)	KOH (1)	H ₂ O	160-12	n.d.	3	<1	<1
27	IrCl ₃ ·3H ₂ O (0.2)	L1 (2)	KOH (1)	H ₂ O	160-12	25	3	<1	<1
28	IrCl ₃ ·3H ₂ O (0.2)	L2 (2)	KOH (1)	H ₂ O	160-12	42	35	<1	<1
29	IrCl ₃ ·3H ₂ O (0.2)	L3 (1.6)	KOH (1)	H ₂ O	160-12	30	16	<1	<1
30	IrCl ₃ ·3H ₂ O (0.2)	L4 (2)	KOH (1)	H ₂ O	160-12	15	2	<1	trace
31	IrCl ₃ -3H ₂ O (0.2)	L5 (2)	KOH (1)	H ₂ O	160-12	15	9	trace	trace
32	IrCl ₃ ·3H ₂ O (0.2)	L6 (2)	KOH (1)	H ₂ O	160-12	35	25	trace	trace
33	IrCl ₃ ·3H ₂ O (0.2)	L7 (3)	KOH (1)	H ₂ O	160-12	n.d.	1	0	0
34	IrCl ₃ -3H ₂ O (0.2)	L8 (1.5)	KOH (1)	H ₂ O	160-12	30	2	0	0
35	IrCl ₃ .3H ₂ O (0.2)	L9 (0.6)	KOH (1) + NaOAc (0.8)	H ₂ O	150-12	n.d.	2	0	0
36	IrCl ₃ ·3H ₂ O (0.2)	L10 (0.6)	KOH (0.8)	hexane-H ₂ O	135-2	n.d.	1	0	0
37	IrCl ₃ ·3H ₂ O (0.2)	L10 (0.6)	KOH (0.8)	hexane-H ₂ O	150-5	n.d.	10	0	0
38	IrCl ₃ -3H ₂ O (0.2)	L10 (0.6)	KOH (0.8)	hexane-H ₂ O	150-10	42	23	trace	0
39	IrCl ₃ ·3H ₂ O (0.2)	L10 (0.6)	KOH (1)	H ₂ O	160-12	43	33	trace	trace
40	IrCl ₃ .3H ₂ O (0.2)	L11 (0.6)	KOH (1) + NaOAc (0.8)	H ₂ O	150-12	20	4	trace	trace
41	Ir(acac) ₃ (0.17)	Phen (1.7)	KOH (1)	H ₂ O	160-6	47	32	trace	trace
42	[Cp*lrCl ₂] ₂ (0.17)	Phen (1.7)	KOH (1)	H ₂ O	160-6	40	33	trace	trace
43	IrCl ₃ ·3H ₂ O (0.2)	Phen (0.7)	KOH (1) +	H ₂ O	125-40	25	14	trace	<1
			NaOAc (0.8)						
44	Ir/C (15 wt%)	Phen (2)	KOH (1.5)	H ₂ O	180-12	27	22	trace	trace
45	Ir/C (15 wt%)	Phen (2)	KOH (1.5)	H ₂ O	140-12	33	24	trace	trace
46	Ir/C (15 wt%)	L10 (0.5)	KOH (1.5)	H ₂ O	160-12	50	40	trace	trace
47	Ir/C (15 wt%)	L11 (0.5)	KOH (1.5)	H ₂ O	160-12	19	14	0	0
48	Ir/C (15 wt%)	PPh ₃ (2)	KOH (1.5)	H ₂ O	160-12	12	2	0	0
49	Ir/C (15 wt%)	Pyridine (2)	KOH (1.5)	H ₂ O	160-12	13	3	0	0

[a] Reaction conditions: Butanol (1 g, 13.5 mmol), iridium precursors, bases, 18 mL H₂O. The reactions were carried out under air conditions and heated using oil bath unless otherwise stated. [b] Microwave irradiation was used. [c] 3 g butanol was used.



Figure S5. Representative GC spectrums of butanol condensation in water.

4 General procedure for the development of immobilized iridium catalysts.

The preparation of immobilized Ir-N catalysts was slightly modified according to Beller and co-workers' series of work (Ref.18) by variations of iridium precursors, catalyst loading, activated carbon support, pyrolysis conditions et al.

Take entry 13 in Table S3 for example, $Ir(acac)_3$ (0.128 g, 0.262 mmol, 5 wt% Ir), phenanthroline hydrate (0.311g, 1.57 mmol) and carbon support (1 g) were mixed together in ethanol solvent (30 mL). The mixture was stirred at 70 °C for 24 h and then ethanol was removed by evaporation. Then the solid was pyrolyzed at different

temperature gradient and heating time under N₂. The pyrolyzed Ir-N catalysts were stable under air, and the subsequent operations were all carried out under air conditions. In recycling experiments, the immobilized catalyst was filtrated and rinsed with ethanol and water, and then dried in the oven at 110 ∞ .

The impregnation of IrCl₃-phenanthroline onto carbon support was not good because of the low solubility of IrCl₃ in ethanol, so that the activity of the corresponding pyrolyzed catalysts was slightly worse (Table S3, entries 6, 8, 11, 14). The performance of commercially available carbon Vulcan XC72R and Norit SX Ultra was similar during immobilization. The surface of Norit CAP Super carbon (produced by chemical activation using the phosphoric acid process) was modified by phosphorus, so that the corresponding catalytic activity was damaged (Table S3, entries 16-18).

Entry	Ir precursor	Carbon support	Pyrolysis condition		Conv. [%]	Yield of
	(Ir precursor-molar ratio of Ir to Phen)		Temperature gradient [°C/h]	Maximum temperature [°C]- <i>t</i> [h]		1a [%]
1	Ir(OAc)₃ (1%-1:3)	Norit SX Ultra	240	800-2	19	11
2	Ir(OAc)₃ (5%-1:3)	Norit SX Ultra	240	800-2	35	21
3	IrCl ₃ (1%-1:3)	Norit SX Ultra	240	800-2	19	11
4	Ir(OAc) ₃ (5%-1:6)	Norit SX Ultra	240	800-3	43	32
5	Ir(acac) ₃ (5%-1:6)	Norit SX Ultra	240	800-3	45	31
6	IrCl ₃ (5%-1:6)	Norit SX Ultra	240	800-3	29	14
7	Ir(OAc)₃ (5%-1:6)	Norit SX Ultra	90	800-3	45	32
8	IrCl ₃ (5%-1:6)	Norit SX Ultra	90	800-3	39	22
9	Ir(OAc)₃ (5%-1:6)	Vulcan XC72R	240	800-3	42	36
10	Ir(acac)3 (5%-1:6)	Vulcan XC72R	240	800-3	43	37
11	IrCl ₃ (5%-1:6)	Vulcan XC72R	240	800-3	33	20
12	Ir(OAc) ₃ (5%-1:6)	Vulcan XC72R	90	800-3	43	35
13	Ir(acac)3 (5%-1:6)	Vulcan XC72R	90	800-3	42	37
14	IrCl ₃ (5%-1:6)	Vulcan XC72R	90	800-3	50	29
15	Reuse of entry 13				43	37
16	Ir(OAc) ₃ (5%-1:6)	Norit CAP Super	240	800-3	9	3
17	Ir(acac) ₃ (5%-1:6)	Norit CAP Super	240	800-3	9	1
18	IrCl ₃ (5%-1:6)	Norit CAP Super	240	800-3	10	4

Table S3. Optimization of pyrolyzed catalysts.[a]

[a] Reaction conditions: Butanol (1 g, 13.5 mmol), supported catalyst (0.15 g, 15 wt%), 1.0 equivalents of KOH, 18 mL H₂O, 160 °C, 16 h. The catalysts were filtrated, rinsed with ethanol and water, and then dried in the oven for the recycling tests.

From the comparison of representative photos in butanol condensation, the colour of aqueous phase was different obviously (Figure S6). AAS determination suggested that about 10% iridium in Ir/C might leach into the aqueous solvent, while there was no iridium leaching when using the pyrolyzed iridium catalyst. Beller and co-workers had investigated the structure of carbon supported cobalt- or iron-nitrogen catalysts. The carbon surface was modified by pyridine-type nitrogen, pyrrole-type nitrogen and quaternary amine species. Such nitrogen-enriched carbon surface made the interaction between iridium and carbon support very tight.



Figure S6. Representative photos of reaction mixtures. Left: Table 3, entry 2; Right: Table 3, entry 9. Ether was added for extraction.

50 nm

5 Representative photos and spectrum in ethanol condensation.

Figure S7. TEM images of [Ir(OAc)₃]-L10 catalyst in ethanol condensation. Left: Table 4, entry 6 (scale bar: 50 nm); Right: Table 4, entry 7 (scale bar: 50 nm).



Figure S8. Representative GC spectrum of ethanol condensation in water.

6 Quantitative GC analyses.

Generally all reactions in this research were carried out in diluted aqueous solutions. Because the products exhibit low solubility in water, it is necessary to collect the organic products by extraction. In addition, butanol is partly soluble in water and ethanol is miscible with water, so that the analyses of aqueous phase are also necessary for the quantitative determination.

In the measurements of butanol condensation, internal standard method was used for the analyses of organic phase. Because the organic internal standards were insoluble in water, external standard method was applied for the analyses of aqueous phase. Direct injection of an aqueous sample was tested, but the GC response values were bad and the measurement was inaccurate. So, after the primary analyses of organic solution and phase separation, an additional 10 times of ether in volume was added to the aqueous phase for extraction. Then the resulting ether solution was used to stand for the aqueous phase in GC determination. Standard curves suggested that this method was appropriate for the quantitative determination of the butanol conversion and product yield (Figure S9).



Figure S9. Standard curve of butanol with dodecane (left) and 2-ethylhexanol with dodecane (right).

For the measurements in ethanol condensation, because of the miscibility of ethanol with water, the same analytical method as used in butanol condensation was inaccurate. So 10 times of acetone was added to the reaction mixture in order to form one solution, and then this solution was analyzed in GC. Standard curve suggested that this method was much better (Figure S10), however, small analytical errors might still exist.



Figure S10. Standard curve of ethanol with dodecane.

To avoid the inaccuracy caused by unexpected loss of components during the reaction, two internal standards (dodecane and anisole) could be added before and after the reaction respectively.

The yield in ethanol condensation (yield of butanol, hexanol or octanol) was calculated based on:

 $\frac{\text{amount of ethanol needed to produce the existed alcohol}}{\text{amount of ethanol added}}$ Take the yield of butanol for example: Yield (butanol) = $\frac{2 \text{ x moles of butanol}}{\text{moles of ethanol fed}}$

The selectivity in ethanol condensation (selectivity of butanol, hexanol or octanol) was calculated based on:

amount of ethanol needed to produce the existed alcohol amount of ethanol reacted

Take the selectivity of butanol for example: Selectivity (butanol) = $\frac{2 \text{ x moles of butanol}}{\text{moles of ethanol}}$

So, the theoretical overall yield is 100% and the total selectivity reflects the amount of desired transformation among the reacted ethanol. For example, 80% total selectivity means that 80% of the reacted ethanol has been transformed into the expected longer-chain alcohol products.