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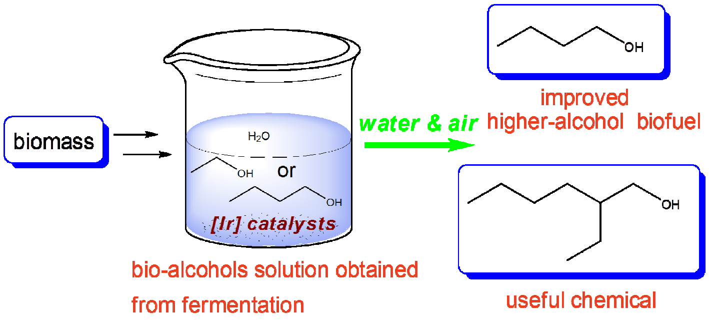

Recyclable iridium catalysts have been developed rationally for the direct self-condensation of ethanol and butanol in water and air.

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Direct Self-Condensation of Bio-Alcohols in Aqueous Phase

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Bio-alcohols (*e.g.* ethanol, butanol) are primarily obtained as diluted aqueous solutions from biomass fermentation, and thus the subsequent isolation is a very costly process. So the direct transformation of bio-alcohols in water will exhibit great advantage. This study describes the development of catalysts used for the self-condensation of bio-alcohols in water (mimic the primary fermentation solutions). Efficient iridium catalysts have been developed rationally from homogeneous to heterogeneous, and the immobilized catalysts could be reused without loss of activity, which is very important for the development of practical processes. The expected self-condensation could be realized with 80-90% selectivity in water and air. Such protocol might be used in producing butanol from ethanol solution directly, which is improved higher-alcohol biofuel. Other useful chemicals, such as 2-ethylhexanol, could also be obtained from renewable resources through this condensation reaction.

Introduction

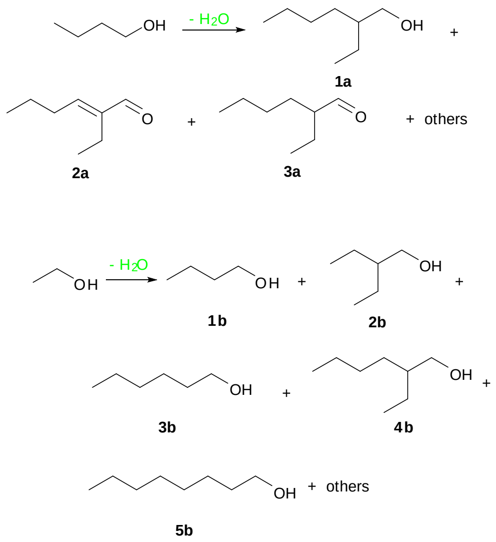
Bio-alcohols, such as ethanol and butanol, can be used as sustainable biofuels and future feedstocks for the chemical industry.[1] Currently, they are produced in increasing amounts from renewable biomass resources. However, the primarily obtained crude bio-alcohols after fermentation are diluted aqueous solutions, and thus the subsequent purification is a very costly process. The polar nature of ethanol and butanol makes it difficult to be separated from water.[2] As in the production of 1st-generation fuel ethanol, usually more than half of the energy is consumed in the distillation and dehydration steps. Therefore, the direct upgrading of aqueous ethanol or butanol solutions corresponding to those obtained after fermentation will exhibit great advantages.[3]

Alcohol condensation, which is also named as the Guerbet reaction, is an important method to produce a dimeric alcohol. The process can be conducted on a scale suitable for commercial application when the starting-alcohols contain 6 or more carbon atoms and the products are mainly used as raw materials for cosmetics, emulsifying agents, *etc.*[4] Condensation of bio-alcohols with low carbon atoms has also drawn much attention from both industrial and academic community, which might be used in manufacturing improved higher-alcohol biofuels or other useful chemicals from renewable resources.[1] Based on a general hydrogen auto-transfer mechanism (Scheme S1, ESI), the alcohol condensation process is composed of dehydrogenation, condensation and hydrogenation steps, but could be carried out in one pot.[5] Although other reaction pathways such as bimolecular condensation are possible under specific conditions,[1c] theoretically water is the sole byproduct. So, a water tolerant catalyst is intrinsically desired considering its inevitable formation.

On the other hand, the use of water as a reaction medium has received significant attention due to its many advantages from economic, environmental, and safety standpoints. However, despite various efficient catalytic systems in water have been developed to date, execution of dehydration reaction in water is still one of the most challenging research topics.[6] The alcohol condensation, including butanol and ethanol, is usually carried out in organic solvent, pure alcohol or diluted gas phase. The addition of water to the reactant mixture is usually detrimental to the catalysts. For example, Carlini and coworkers reported the application of [Pd(dppe)Cl_2] or Pd/C in combination with BuONa to catalyze the self-condensation of butanol in pure butanol phase at 180-280 ℃. The product 2-ethylhexanol could be obtained in about 60% yield with good selectivity. But the progressive hydrolysis of BuONa to the inactive NaOH would destroy the catalytic systems. In their series of related work, solid bases of Mg/Al mixed oxides derived from hydrotalcite-type (HT) precursors were developed to replace the soluble sodium alcoholate. Although such catalysts were tolerant of the co-produced water, generally the reactions were still carried out in dry alcohol mixtures.[7] Solid-bases, such as hydroxyapatites (HAP) and HT derivatives, could also be used alone to catalyze the ethanol or butanol condensation. However, the reaction temperature was up to over 300 ℃ and the pure alcohol reactant should be vaporized and diluted with inert gas first.[8] Ishii and coworkers reported the use of iridium catalysts (*e.g.* [Ir(acac)(cod)], [Cp*$IrCl_2$]$_2$) to promote the Guerbet reaction of primary alcohols. Condensation of ethanol could be obtained in about 40% conversion and over 80% selectivity to higher alcohol products. Similarly, the reactions were performed in pure alcohol or *p*-xylene solvent. And additional alkene additives (*e.g.* 1,7-octadiene) were necessary, which might function as hydrogen acceptor or as weakly coordinated ligand to stabilize the Ir intermediates.[9] Other metal catalysts of ruthenium and rhodium were also employed, and sometimes the selectivity could be up to more than 90%.[10] However, because of the detrimental effect of water, generally all reactions were carried out in organic solvent or pure alcohol. So, new catalysts are necessary considering the alcohol condensation in aqueous solvent. Here we are pleased to report our explorations in the catalyst development for butanol and ethanol self-condensation in water.

Results and discussion

According to the previous reports, the condensation of ethanol might generate butanol and other C_6 and C_8 products, which come from further condensation steps. While the products in butanol condensation are relatively simple (Scheme 1). In addition, ethanol is considered to be a more sluggish reactant.[7-9] So initially the condensation of butanol is used for the fast catalyst evaluation, and then the selected catalytic systems could be applied to ethanol condensation after some modifications.



Scheme 1 Main products in butanol and ethanol condensation

Catalyst development from butanol condensation

Initial exploration. Both microwave irradiation and conventional heating were applied, and their performance was generally similar. The reaction rate was faster under microwave irradiation, which was not curious because the energy could be delivered directly to the reacting partners and usually higher reaction rates were induced.[11] So microwave irradiation was applied for the fast catalyst screening, and then a more conventional heating method was used for further catalyst optimization.

Bifunctional catalysts comprised of transition metal precursors (Ru, Rh, Cu, Ir, Pd, Ag, *etc.*) and bases which would promote the expected dehydrogenation/hydrogenation and condensation steps were rationally screened (Table S1, ESI). Our initial results suggested that the condensation of butanol could be performed in organic solvents smoothly under basic conditions. Transition metal precursors, such as CuBr and $RhCl_3$, could effectively catalyze the reaction. But the addition of small amount of H_2O would totally destroy the catalysts, and no condensation proceeded any more (Table S1, entries 3-8, ESI). Such incompatibility with water was similar to the literature reports and clearly evidenced the challenging in realizing the alcohol condensation in aqueous phase. Although some combinations of Rh, Ru and other metal precursors generated trace amounts of products in aqueous phase, we did not obtain an acceptable transformation using these catalysts. But to our delight, we found that the combination of $IrCl_3$ and 1,10-phenanthroline (Phen) exhibited an obvious activity for butanol condensation in water (Table 1, entry 1). So the related iridium catalysts were carefully studied by variations of iridium precursors, bases, catalyst loading, reaction time, temperature, *etc.*

The use of other organic solvent such as hexane was intended to promote the transformation by phase separation, but experimental results suggested that it was unnecessary. The condensation performed well in pure water. An interesting phenomenon was that large amounts of $IrCl_3$ and phenanthroline mixtures were insoluble in water initially, but when base was added, the aqueous phase turned clear and looked like homogeneous. Phenanthroline might function as bidentate ligand or stabilizer, and possibly active Ir intermediates formed. However, the catalyst agglomerated and black precipitates formed during the reaction, even at 125 ℃. TEM analyses also suggested that $IrCl_3$-phenanthroline catalyst dispersed well before the reaction, but aggregated evidently during the transformation (Figures S1-S2, ESI). Similar phenomenon had been reported by Cadierno and coworkers.[12] They investigated palladium and bipyridine catalyst in the reaction of arylboronic acids with unsaturated carbonyl compounds in aqueous medium. Under strongly basic conditions, the catalyst solubility increased and aqueous nano-dispersed solutions could be prepared, but extensive aggregation was observed during the reaction. Such aggregates of nanoparticles were still active to catalyze the condensation, as with the reaction time prolonged, more products formed, but it was not surprising that their activity would be reduced inevitably (Table 1, entries 5-6).

Table 1 Catalyst development for butanol condensation in water[a]

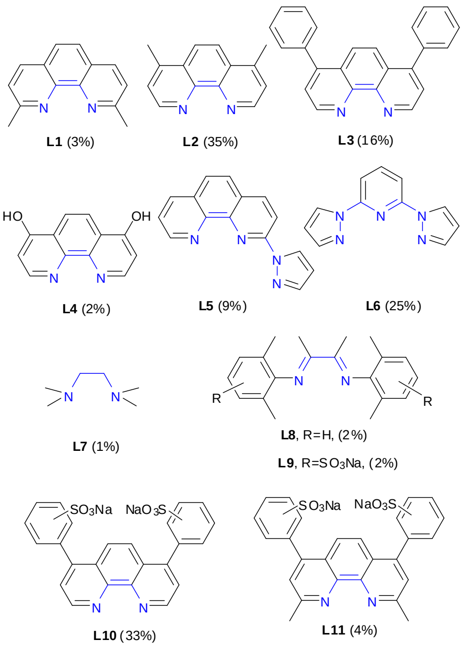
Entry	Catalyst [M]-base	Condition solvent-T [°C]-t [h]	Yield (Sele.) of 1a [%]
1	$IrCl_3$/Phen-LiOH	hexane/H_2O-120-2	6
2	$IrCl_3$/Phen-LiOH	hexane/H_2O-140-2	12
3	$IrCl_3$/Phen-KOH	hexane/H_2O-140-2	14
4	$IrCl_3$/Phen-KOH	H_2O-125[b]-40	6
5	$IrCl_3$/Phen-KOH	H_2O-160[b]-6	45 (82)
6	$IrCl_3$/Phen-KOH	H_2O-160[b]-24	55 (81)
7[c]	$IrCl_3$/Phen-KOH	H_2O-160[b]-6	31 (78)
8	$IrCl_3$/Phen-KOH/NaOAc	H_2O-160[b]-6	48 (87)
9	$IrCl_3$/Phen-KOH/NaOAc	H_2O-170[b]-6	45 (81)
10[d]	$IrCl_3$/Phen-KOH/NaOAc	H_2O-160[b]-24	59 (88)
11[e]	$IrCl_3$/Phen-KOH	H_2O-160[b]-6	27 (72)

[a] Reaction conditions: 1 g butanol, 0.2 mol% metal chloride hydrates (abbreviated as metal chlorides), 0.05 g Phen if used, 1 equiv of base (for mixed bases, 0.8 equiv of NaOAc was added), 15 mL solvent (for mixed solvents, the volume ratio of organic solvent to H_2O is 1:2 except for entry 4 and 5). Microwave irradiation was used unless otherwise stated. [b] The reactions were heated using oil bath and carried out under air. [c] 0.4 mol% $IrCl_3{\cdot}3H_2O$ was used. [d] 2 Equiv of KOH was used. [e] The reaction was carried out under N_2.

Reaction temperature exhibited important influence on the transformation. The conversion was improved evidently at 160 ℃, but higher temperature was ineffective (Table 1, entry 9). Increasing the iridium loading exhibited no improvement (Table 1, entry 7), possibly because of the catalyst aggregation. High ligand to iridium ratio would suppress the activity at 140 ℃, but little difference was found at 155-160 ℃. Common inorganic bases, such as KOH, could promote the condensation effectively. More expensive and water sensitive bases (*e.g.* KO^{t}Bu, NaOEt) could be avoided. About 1.0 equivalent of base relative to the amount of butanol was needed to obtain a good conversion (Table S2, ESI). NaOAc could not promote the condensation alone, but the combination of NaOAc with KOH would increase the reaction rate, especially at low temperatures.[13] However, little difference was found at 160 ℃, except the selectivity was a little improved (Table 1, entries 5, 8). The reaction could be performed under air, and more interestingly, the reaction rate was even faster than inert conditions (Table 1, entry 11).[14] Very small amounts of condensation products with unsaturated C=C and C=O bonds were formed under both nitrogen and air atmosphere (less than 1%). Another unwanted byproduct which could usually be observed was butyric acid.[1c] The oxidation of alcohol to acid had been investigated before and transition metal catalysts such as Pt could promote the transformation.[15] Sometimes ethanol was also formed, which should come from the retro-aldol reaction. However, these byproducts could be suppressed to less than 1% after optimization (Figure S5, ESI).

With regard to butanol condensation in diluted aqueous solution, nearly 60% yield and 90% selectivity to the desired 2-ethylhexanol could be obtained within 24 h (Table 1, entry 10), which clearly evidenced the feasibility of our original design. Such results are comparable with literature reports,[7,9] while the direct transformation in water is a significant advantage. 2-Ethylhexanol is an important product which is usually used as precursor to plasticizers. It is now produced industrially not from butanol but from butanal derived from propene. One major drawback of the present $IrCl_3$-phenanthroline catalyst is that it is unstable and agglomerated during the reaction. Such aggregation makes the catalyst difficult to be recycled, and in addition, further improvement of activity is possible if the aggregation could be avoided. Therefore it would be advantageous to find a way to stabilize and reuse the precious metal catalyst.

Ligands development. The modification of ligands from steric and electronic aspects was usually employed to get a more suitable catalyst. N-N multi-coordinated structure in phenanthroline was speculated to be critical in creating an active catalyst, so more ligands with this key function were investigated in order to improve the catalyst stability and activity (Scheme 2). All reactions were performed under similar conditions as specified in Table S2 in ESI.



Scheme 2 Modification of ligands (Yields of 2-ethylhexanol in brackets)

Very small amounts of products were generated using $IrCl_3$ alone or in combination with other phosphine ligands. Such results clearly indicated the crucial role played by a suitable ligand. Methyl substitutes in phenanthroline nearby the N-atoms would sharply decrease the catalyst activity (L1 in Scheme 2), which implied that sterically crowded coordination structure would block the active center. Substitutes away from the N-atoms did not decrease the activity obviously, however, this change did not generate a more active catalyst (L2 in Scheme 2). Although there is one more N-coordinate site in L5 and L6 compared to phenanthroline, the catalyst formed also exhibited very low activity, and iridium black formed yet. The imine ligands were not active possibly because of the similar steric reason and low solubility in water (L8 and L9 in Scheme 2). With regard to electronic modification of the ligands, electron donating hydroxide group decreased the activity evidently (L4 in Scheme 2), while the electron withdrawing sulfo-group increased the activity (L3 and L10 in Scheme 2). Possibly a higher electron density in iridium center would make the alcohol dehydrogenation step difficult. Aliphatic amine ligand was ineffective (L7 in Scheme 3) because of the lack of the π-back-bonding between iridium and aromatic N-N ligands, which would ensure tighter coordination.[13]

Table 2 Butanol condensation using water-soluble ligand L10[a]

Entry	Catalyst [Ir]-ligand (molar ratio)	Condition *T* [°C]-*t* [h]	Conv. [%]	Yield (Sele.) of 1a [%]
1	$IrCl_3$-L10 (1:3)	150-12	45	35 (78)
2	$IrCl_3$-L10 (1:3)	170-12	40	20
3	$[Ir(acac)_3]$-L10 (1:3)	150-12	55	40 (73)
4	reuse entry 3 for 2nd	150-24	51	34
5[b]	reuse entry 3 for 2nd	150-24	49	35
6	reuse entry 3 for 3rd	150-24	51	38
7	reuse entry 3 for 4th	150-24	36	26
8	reuse entry 3 for 5th	150-24	21	12
9	$[Ir(acac)_3]$-L10 (1:3)	140-24	21	16 (76)
10	$[Ir(OAc)_3]$-L10 (1:3)	150-12	57	42 (74)
11	$[Ir(OAc)_3]$-L10 (1:8)	150-12	54	49 (91)
12	reuse entry 11 for 2nd	150-24	55	46 (84)
13	reuse entry 11 for 3rd	150-24	50	42

[a] Reaction conditions: 1 g butanol, 0.01 g iridium precursors, 1.0 equiv of KOH and 0.8 equiv of NaOAc, 18 mL H_2O. The reactions were carried out under air and heated using oil bath. The aqueous solution containing iridium catalyst and base was reused after extraction with ether and hexane. [b] Fresh 0.3 equiv of KOH and NaOAc were added.

Water soluble ligand L10 (Bathophenanthroline disulfonic acid disodium salt) exhibited very interesting characteristics. The catalyst stayed in aqueous phase and dispersed well after the reaction, and the product yield was considerable. Reaction temperature was also important (Table 2, entry 9), but the temperature could be about 10 ℃ lower than $IrCl_3$-phenanthroline catalyst. At 150 ℃, the water soluble catalyst was stable and there was no black precipitate. But at 160 ℃, small precipitates formed. At 170 ℃, more precipitates formed and the activity was destroyed (Table 2, entry 2). Different iridium precursors such as $[Ir(acac)_3]$ and $[Ir(OAc)_3]$ exhibited similar activity. After extraction, the water soluble catalyst could be reused for three times without obvious decrease in activity (Table 2, entries 4-8). The base solubilized in aqueous solution could also be reused. It could be anticipated from the reaction mechanism, which suggested base would not be consumed during the transformation. However, more precipitates formed later. TEM analyses also suggested that the water soluble catalyst dispersed well during the reaction, but some aggregation was observed after the fifth run (Figures S3-S4, ESI).

It is possible to find more suitable water soluble ligands or reaction conditions after further optimization. For example, higher molar ratio of ligand to metal exhibited better results, and the expected selectivity could be up to 91% (Table 2, entry 11). However, it should be noted that the water soluble catalyst possibly will not be the best choice for the condensation of butanol or ethanol in water from a practical viewpoint. Because bio-ethanol or bio-butanol is primarily accessed as diluted aqueous solution from biomass fermentation, and our design is to carry out the condensation directly in water. The catalyst solubilized in the aqueous phase is difficult to be isolated from water, so practically its reuse is still difficult. Heterogeneous catalyst might be better considering the ultimate practical application.

Catalyst immobilization. Based on the above explorations, Ir is the most suitable candidate to be immobilized and its properties should be modified in the immobilized catalyst. Ir/C (5 wt% iridium content) was not a very active catalyst when used separately, and only 6% yield was obtained (Table 3, entry 1). However, when Ir/C was used in combination with some N-containing ligands, the transformation could be promoted and the activity was comparable with $IrCl_3$-phenanthroline catalyst. Phenanthroline and its water soluble counterpart L10 were still the most active ligands (Table 3, entry 2, and Table S2 in ESI). Upon the reuse of Ir/C, its activity decreased (Table 3, entry 4). The iridium concentration was determined to be about 5×10^{-5} g mL^{-1} in aqueous solution after the reaction, which implied that about 10% iridium in Ir/C leached into the aqueous solvent. Consequently the color of aqueous solvent changed into brownish-yellow (Figure S6, ESI). Ir/C might act as the iridium source to afford the real active intermediate.[16] Another interesting aspect was the activity at low temperatures. Ir/C-phenanthroline was more active than $IrCl_3$-phenanthroline at 125 ℃ (Table 3, entry 3), although the reaction rate was still slow. That improvement could be attributed to the avoidance of iridium aggregation. Activated carbon was added to $IrCl_3$-phenanthroline system for the immobilization of active iridium catalyst.[17] Such combination did not generate negative impact (Table 3, entry 5), but the reuse of this solid exhibited sharply decreased activity (Table 3, entry 6). The interaction between iridium catalyst and carbon support was not tight enough and possibly the active catalyst was lost during isolation.

Recently, Beller and coworkers reported a novel method for the preparation of heterogeneous catalysts via immobilization and pyrolysis of molecularly defined complexes. The heterogenized carbon supported cobalt- or iron-nitrogen catalysts were successfully applied in the nitroarenes reduction and alcohols selective oxidation.[18] That protocol also proved to be applicable here. Pyrolysis of the *in situ*-generated Ir-phenanthroline complexes supported on carbon led to highly active catalysts. The preparation of the catalyst material, such as iridium loading, pyrolysis temperature, different iridium precursors and carbon supports would all influence the catalyst activity (Table S3, ESI). After optimization, the transformation could be achieved comparable with the homogeneous iridium catalyst (Table 3, entries 8-9). Moreover, the resulting aqueous solvent was colorless and there was no iridium leaching according to AAS determination (Figure S6, ESI). Nitrogen-enriched carbon surface formed in this protocol, which would make the interaction between iridium and carbon support tighter.[18] Five consecutive experiments were performed in order to investigate the catalyst stability and reusability. Notably, the pyrolyzed catalyst was highly stable and could be reused without loss of activity, which was important for the development of practical processes (Table 3, entries 10-13).

Table 3 Butanol condensation using heterogeneous catalysts[a]

Entry	[Ir] Catalyst	Conv. [%]	Yield (Sele.) of 1a [%]
1	Ir/C	16	6
2	Ir/C-Phen	36	31 (86)
3[b]	Ir/C-Phen	25	19
4	reuse of Ir/C in entry 2 -Phen	25	12
5	$IrCl_3$ (0.2 mol%)-Phen-AC	53	42 (80)
6	reuse entry 5	32	7
7	$[Ir(acac)_3]$-Phen-AC pyrolyzed (1 wt% Ir)	19	11
8	$[Ir(acac)_3]$-Phen-AC pyrolyzed (5 wt% Ir)	42	37 (88)
9	$[Ir(OAc)_3]$-Phen-AC pyrolyzed (5 wt% Ir)	42	36 (86)
10	reuse entry 9 for 2nd	41	36 (88)
11	reuse entry 9 for 3rd	43	37 (86)
12	reuse entry 9 for 4th	41	36 (88)
13	reuse entry 9 for 5th	42	36 (86)

[a] Reaction conditions: 1g butanol, 0.15 g supported catalyst, 0.05 g phenanthroline hydrate if used, 1.0 equiv of KOH, 18 mL H_2O, 160 °C, 16 h. The catalysts were filtrated, rinsed with ethanol and water, and then dried in the oven for the recycling tests. Preparation details for the pyrolyzed catalysts were described in ESI. [b] The reaction was carried out at 125 °C.

Application to ethanol condensation

Bio-ethanol is produced in large amounts from renewable resources currently. Condensation of ethanol in water could be used in the production of improved higher-alcohol biofuels and other useful chemicals from the fermentation ethanol solution directly. High energy-cost dehydration and distillation steps might be eliminated because such products could be less expensive to isolate from water.[1,19] Application of the catalysts developed from butanol condensation into ethanol condensation exhibited similar tendency. It was found that the main products in ethanol condensation were butanol, hexanol and octanol (*n*- and *i*-). The unsaturated counterparts were much less. Reaction temperature also influenced the transformation evidently (Table 4, entry 3). Water soluble catalysts exhibited better activity than Ir-phenanthroline catalysts (Table 4, entries 1-2), and similarly the aqueous catalyst solution could be reused without obvious loss of activity (Table 4, entry 5). Interestingly, the distribution of products could be adjusted by the catalytic systems. $[Ir(OAc)_3]$ generated more deep condensation products than $IrCl_3$ (Table 4, entries 2, 4). High molar ratio of ligand to Ir and the addition of NaOAc were slightly better for the formation of butanol (Table 4, entries 6-8). Ir/C and the pyrolyzed iridium-nitrogen catalysts were also applicable, and butanol could be formed with more than 50% selectivity (Table 4, entries 10-11). Until now, the condensation products butanol, hexanol and octanol could be obtained in more than 40% one-way overall yield and 80% total selectivity.

Table 4 Ethanol condensation in aqueous phase[a]

Entry	Catalyst [Ir]-base	Condition *T* [°C]-*t* [h]	Conv. [%]	Yield [%]					Overall Sele. [%]
				1b	2b	3b	4b	5b	
1	$IrCl_3$-Phen (1:10, molar ratio) -KOH/NaOAc	160-16	45	17	3	1	1	1	51
2	$IrCl_3$-L10 (1:3) -KOH	150-16	43	18	4	2	1	1	60
3	$IrCl_3$-L10 (1:3) -KOH/NaOAc	115-40	10	5	1	0.5	0.5	0.5	75
4	$[Ir(OAc)_3]$-L10 (1:3) -KOH	150-16	45	19	7	4	3	2	78
5	reuse entry 4 for 2nd	150-16	40	16	7	3	3	2	78
6	$[Ir(OAc)_3]$-L10 (1:3) -KOH/NaOAc	150-16	48	22	7	4	2	2	77
7	$[Ir(OAc)_3]$-L10 (1:8) -KOH	150-16	47	23	6	3	2	2	77
8[b]	$[Ir(OAc)_3]$-L10 (1:10) -KOH/NaOAc	150-16	52	26	7	3	3	3	81
9	Ir/C-Phen-KOH	160-24	41	20	5	2	3	2	78
10	$[Ir(OAc)_3]$-Phen-AC pyrolyzed (5 wt% Ir)-KOH	160-16	43	23	7	1	1	0.5	76
11	reuse entry 10 for 2nd	160-16	45	25	7	1	1	0.5	77

[a] Reaction conditions: 1 g ethanol, 0.01 g iridium precursors or 0.2 g supported catalysts, 1.0 equiv of KOH and 1 equiv of NaOAc if used, 18 mL H_2O. All reactions were carried out under air and heated in oil bath. Reuse and preparation of the pyrolyzed catalyst were the same as described in Table 2 and 3. [b] 0.02 g $[Ir(OAc)_3]$ and 1.5 equiv of KOH were used.

Experimental

Chemicals and equipments

Commercially available chemicals including transition metal precursors, carbon supported catalysts, inorganic bases, organic reagents and GC standards were purchased from SCRC, Alfa Aesar or TCI and used as received. Commercially unavailable ligands were prepared according to literatures in ESI. The concentration of ethanol or butanol usually varied from 5% to 15% to mimic the primary fermentation solution.

Microwave irradiation experiments were performed on Anton Paar Synthos 3000. Experiments under conventional thermal treatment were carried out in autoclave and heated using oil bath or heating plate with magnetic stirring. GC analyses were carried out on VARIAN 450-GC equipped DB-FFAP capillary column (30 m x 0.32 mm x 0.25 μm). GC-MS analyses were carried out on Agilent 7890A GC with a 5975C MS-unit. TEM (transmission electron microscopy) images were taken using a field emission H-7600 electron microscope at 120 kV. AAS (atomic absorption spectroscopy) was measured on INESA 4510F.

Quantitative GC analyses

Generally all reactions in this research were carried out in diluted aqueous solutions. Because the organic products exhibit low solubility in water, it is necessary to collect the 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. Internal standard method was used for the analyses of organic phase. Because the organic internal standards were insoluble in water, modified external standard method was applied for the analyses of aqueous phase. Known concentrations of alcohol reactants and products were analyzed using this method, and the obtained results suggested its feasibility.

General reaction procedure

Take the butanol condensation using $IrCl_3$-phenanthroline catalyst for example: Butanol (1 g, 13.5 mmol), $IrCl_3$ $3H_2O$ (0.01 g, 2.8 x 10^{-2} mmol, 0.2 mol%) and phenanthroline hydrate (0.05 g, 0.25 mmol) were mixed in H_2O (9 mL). Then KOH solution (0.76 g, 13.5 mmol in 9 mL H_2O) was added. The mixture was heated using microwave irradiation or oil bath without exclusion of air. After heating for a specified reaction time, Et_2O was added for extraction. Both the organic and aqueous phase were analyzed by GC. Products were identified by using pure chemicals and GC-MS.

Conclusions

Direct self-condensation of bio-alcohols including butanol and ethanol in water has been successfully realized. Novel iridium catalysts are rationally developed from homogeneous to heterogeneous, and the immobilized catalysts are evidenced to be stable and reusable. The reaction could be performed under air conditions and the use of other additives such as H_2 or alkene could be avoided. Considering the ultimate practical application, the catalytic activity and selectivity should be improved further, especially for ethanol condensation. In addition, nearly stoichiometric amount of KOH solution is not eco-friendly, which is also a common concern in the industrial processes catalyzed by bases.[20] Such challenges are being addressed in our lab now.

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Notes and references

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† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/c000000x/

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