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Selective Conversion of 5-Hydroxymethylfuraldehyde Using Cp*Ir Catalysts in Aqueous Formate Buffer Solution

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The highly selective hydrogenation/hydrolytic ring-opening reaction of 5-hydroxymethylfuraldehyde (5-HMF) was catalyzed by homogeneous Cp*Ir^{III} half-sandwich complexes to produce 1-hydroxy-2,5-hexanedione (HHD). Adjustment of pH was found to regulate the distribution of products and reaction selectivity, and full conversion of 5-HMF to HHD with 99% selectivity was achieved at pH 2.5. A mechanistic study revealed that the hydrolysis/ring-opening reaction of 2,5-bis-(hydroxymethyl)furan is the important intermediate reaction step. In addition, an isolated yield of 85% for HHD was obtained in a 10 g-scale experiment, and the reaction with fructose as the starting material also led to a 98% GC yield (71.9% to fructose) of HHD owing to the excellent tolerance of the catalyst under acidic conditions.

Introduction

Rapid depletion of fossil resources becomes an inevitable issue for the development of the chemical industry, which relies heavily on unrenewable resources. To pursue sustainable development, research on biomass refining, which is a promising replacement for petroleum-derived chemicals, has grown in popularity.[1] Biomass is considered to be the sole renewable organic carbon source,[2] and lignocellulose is the most abundant biomass resource.[3] To achieve the effective utilization of biomass, it is necessary to transform lignocellulose into fundamental organic molecules, known as platform molecules.[4]

The hydrolysis product of lignocellulose-based hexoses (glucose and mannose) is 5-hydroxymethylfuraldehyde (5-HMF), a promising platform molecule.[4,5] 5-HMF has the potential to be upgraded into many important bio-derived chemicals including 2,5-dimethylfuran (biofuel molecule),[6] 2,5-bis-(hydroxymethyl)furan (BHMF, organic synthesis building block),[7] 2,5-furandicarboxylicacid(polymer monomer),[8] levulinic acid[9] and 1-hydroxy-2,5-hexanedione (HHD).[10] As 5-HMF is obtained from the acidic catalytic dehydration of hexoses, in situ further transformation process for 5-HMF seem more cost-effective and environment-friendly than those following a separation process from acidic aqueous phase. Also, water is the primary solvent in many biorefinery processes,[11] and the Brønsted amphoteric property of water makes it possible to control the rate and selectivity of aqueous reactions by simply regulating pH values.[12] Therefore, looking into the role of pH in the transformation of 5-HMF in the aqueous phase has significant meaning for both theoretical and practical studies.

The hydrolytic ring opening of furan-containing 5-HMF leads to the formation of many important building block molecules. Typically, this process is carried out under acidic conditions.[5b] A common ring-opened product of 5-HMF is levulinic acid. Recently, increasing attention is paid to another ring-opened product, 1-hydroxy-2,5-hexanedione (HHD). Mentech and coworkers[10] reported the synthesis of HHD in 60% yield by reducing 5-HMF in oxalic acid solution using Pt/C as catalyst at 140 °C under 3 MPa H_2. Heeres and coworkers[13] reported a two-step process in which an aqueous solution of 5-HMF was reduced under 10 bar H_2 for 1 h using 10 mol% of Rh–Re/SiO_2 catalyst at 120 °C, followed by 80 bar H_2 for 17 h, led to full conversion of 5-HMF and the formation of HHD with 81% selectivity. Jérôme and coworkers[14] reported the conversion of fructose to HHD, which was performed in 0.3 wt% DMSO and THF solvent under 20 bar H_2, with a combined catalyst of Pd/C and Amberlyst-15; HHD in 55% yield was obtained. Later, Jérôme and coworkers[15] reported that inulin, fructose, and 5-HMF can be converted to HHD in water under CO_2 pressure over Pd/C in a one-pot process, and a 70% average yield for each step was obtained in the conversion of inulin to HHD. Satsuma and coworkers[16] reported a procedure for the production of HHD in a yield of 60% starting from 0.067 M 5-HMF aqueous solution in the presence of 8.5 mM H_3PO_4, Au/Nb_2O_5

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catalyst, and 8 MPa H_2 at 140 °C. Singh and coworkers[17] performed the catalytic reaction under the following conditions: 1.0 mmol 5-HMF, 1 mol% [(η^6-p-cymene)RuCl(8-aminoquinoline)]Cl catalyst, 12 equivalents formic acid, and 10 mL water, which achieved a yield of 54% HHD at 80 °C. Zhang and coworkers[18] studied the hydrogenation/hydrolytic ring-opening reaction of 5-HMF with [Cp*-Ir(2,2′-bipyridine)(H_2O)]$^{2+}$ catalyst to produce HHD under H_2, and a yield of 85.5% was obtained. The above works show that so far the hydrogenation/ring-opening reaction of 5-HMF to HHD has not obtained a satisfied selectivity. Moreover, the mechanism of acid facilitating 5-HMF ring opening have not yet been studied in detail. Therefore, it is necessary to study the mechanism and modulating factors of the conversion of 5-HMF to achieve high selectivity for HHD, and develop the hydrogenation/hydrolytic ring-opening reaction of 5-HMF with high selectivity and excellent compatibility with the acidic aqueous phase system.

The transformation of 5-HMF to HHD contains a double-bond saturation process and furan ring-opening process. Therefore, the catalytic system should have excellent reduction ability as well as acidity. We hve previously reported[19] that Cp*Ir^{III} half-sandwich catalysts could bring about outstanding catalytic efficiency for hydrogenation of furan derivatives and withstand the acidity of the hydrolysis system. Hence, Cp*Ir^{III} half-sandwich catalysts are appropriate candidates for the catalytic selective conversion of 5-HMF to HHD.

Herein, we investigated homogeneous Cp*Ir^{III} half-sandwich complexes for the highly selective hydrogenation/hydrolytic ring-opening reaction of 5-HMF to HHD in aqueous formate buffer solution (FBS) under mild reaction conditions. We found that system acidity is a very important factor that could affect catalytic efficiency and regulate distribution of products for a better selectivity. Also, our reaction system shows an excellent tolerance to the acidic aqueous phase system, which makes it suitable for the conversion of the hydrolysis reaction solution of fructose. Mechanistic studies revealed the transformation path of 5-HMF and the effect of acidity on the reaction, and provided a new research idea for effective and selective hydrolysis of 5-HMF.

Results and Discussion

We evaluated the catalytic efficiency of a series of Cp*Ir^{III} catalysts with different electronic effect and steric effect of substituent group on the dipyridine ligand. The catalysts mentioned in this work (**1**–**7**) are shown in Figure 1. Typically, 5-HMF (1 mmol) and the catalyst (0.01 mol%) were dissolved in FBS (5 mL, 1 M) and reacted at 120 °C for 2 h (Scheme 1, condition a). The pH of buffer solution, which varied from 0.0 to 7.0, was found to have a notable effect on the product distribution. The major product was HHD at pH 1.5–3.5 (Figure 2, top). The yield of HHD increases with increasing pH value from 0.5, to a peak at pH 2.5, and then decreased at higher pH values. HHD was not observed when pH > 4.5 and the major product was BHMF at pH 4.0–6.5 (Figure 2, bottom). BHMF was observed starting at pH > 3.0, to a peak at pH 4.5, and then decreased at higher pH values. The yield of HHD using different catalysts (i.e., catalytic efficiency of different catalyst) at pH 2.5

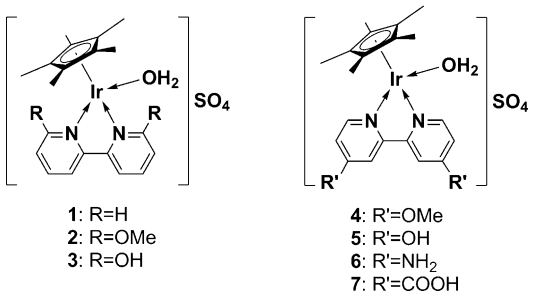
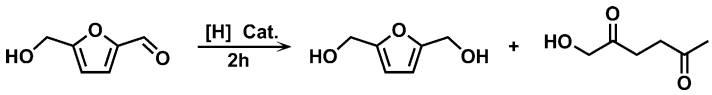


Figure 1. Cp*Ir^{III} half-sandwich complexes used in this work.



Scheme 1. Reaction of 5-HMF in aqueous FBS catalyzed by different Cp*Ir^{III} half-sandwich catalysts. Reaction conditions: 5-HMF (1 mmol); catalyst (0.1 μmol, 0.01 mol% with respect to 5-HMF); and either a) FBS (1 mol L^{-1}, 5.0 mL) at 120 °C for 2.0 h, b) FBS (1 mol L^{-1}, 5.0 mL) at 130 °C for 2.0 h, or c) 1 MPa H_2 and PBS (0.1 mol L^{-1}, 5.0 mL) at 130 °C for 2.0 h.

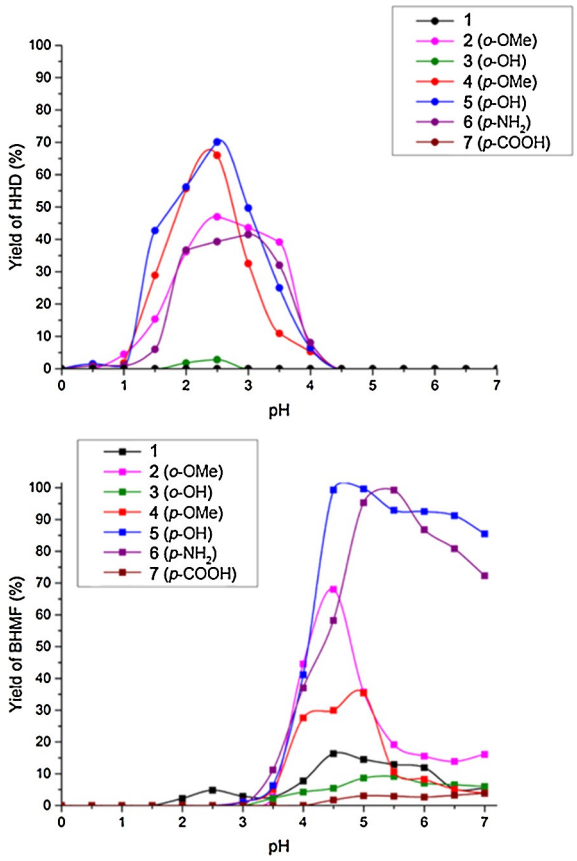


Figure 2. Yield of (top) HHD and (bottom) BHMF using different Cp*Ir^{III} half-sandwich catalysts. Reaction conditions: 5-HMF (1 mmol), catalyst (0.1 μmol, 0.01 mol% to 5-HMF), and FBS (1 M, 5.0 mL) at 120 °C for 2.0 h. GC yield, dimethyl phthalate was used as an internal standard.

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is in the order of **5** > **4** > **2** > **6** ≫ **3** > **7** ~ **1**. The yield of BHMF using different catalysts at pH 4.5 is in the order of **5** ~ **6** > **4** > **2** > **1** > **3** > **7**.

This result indicates that the position and electron donating ability of the substituent have significant effects on catalyst activity. The Hammett constants of the substituents (σ_p^+; i.e., the electron-donating ability),[20] is in the order of: $-NH_2$ ($\sigma_p^+ = -1.30$) >, $-OH$ ($\sigma_p^+ = -0.92$) >, $-OMe$ ($\sigma_p^+ = -0.78$) >, $-H$ ($\sigma_p^+ = 0.00$) >, and $-COOH$ ($\sigma_p^+ = 0.42$). Therefore, strong electron-donating groups lead to higher catalytic efficiency. The low catalytic effect of **7** is a result of the electron withdrawing ability of its 4,4-dicarboxyl substituent. The activity of **2** is lower than **4** owing to increased steric hindrance of the 2,2- versus 4,4-dimethoxy substitution. Activity of the 2,2-dihydroxy-substituted catalyst **3** is lower even than 2,2-dimethoxy-substituted catalyst **2** owing to the effect of *ortho*-hydroxyl group.[20a] 4,4-diamido-substituted catalyst **6** provides the best performance at pH 4.5. The rapid decline of catalyst activity at pH < 3.0 is a result of protonation of the amino groups. Under the same conditions, the best catalysts for selective conversion of 5-HMF to HHD are catalysts **4** and **5**.

Upon further increasing the reaction temperature to 130 °C (Scheme 1, condition b), full conversion of 5-HMF to HHD was achieved at pH 2.5 without any by-products (Figure 3). This demonstrates the excellent catalytic efficiency and selectivity of our reaction system.

The effect of hydrogen sources on the reaction at 130 °C was investigated by using H_2 as hydrogen source, for comparison with HCOOH, and by varying the pH from 0.0 to 7.0 (Scheme 1, condition c). Dissolving 5-HMF (1 mmol) and catalyst (0.01 mol%) in phosphoric acid/sodium phosphate buffer solution (PBS, 5 mL, 0.1 M, pH 0.0–7.0) under 1 MPa H_2 for 2 h (Figure 4), we found that the highest yield of HHD is lower than half of that value when H_2 was used as the source of hydrogen. As H_2 is poorly water soluble, we improved the H_2 pressure in the system. The results show that the yield can be

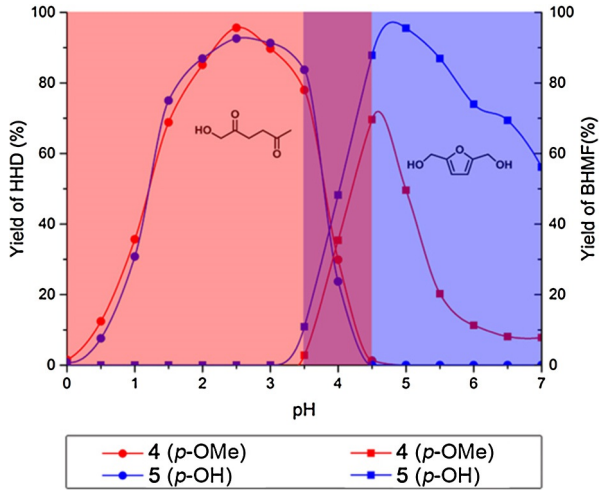

Figure 3. Reaction of 5-HMF in aqueous FBS catalyzed by **4** and **5**. Reaction conditions: 5-HMF (1 mmol), catalyst (0.1 μmol, 0.01 mol% to 5-HMF), and FBS (1 M, 5.0 mL) at 130 °C for 2.0 h. GC yield, dimethyl phthalate was used as an internal standard.

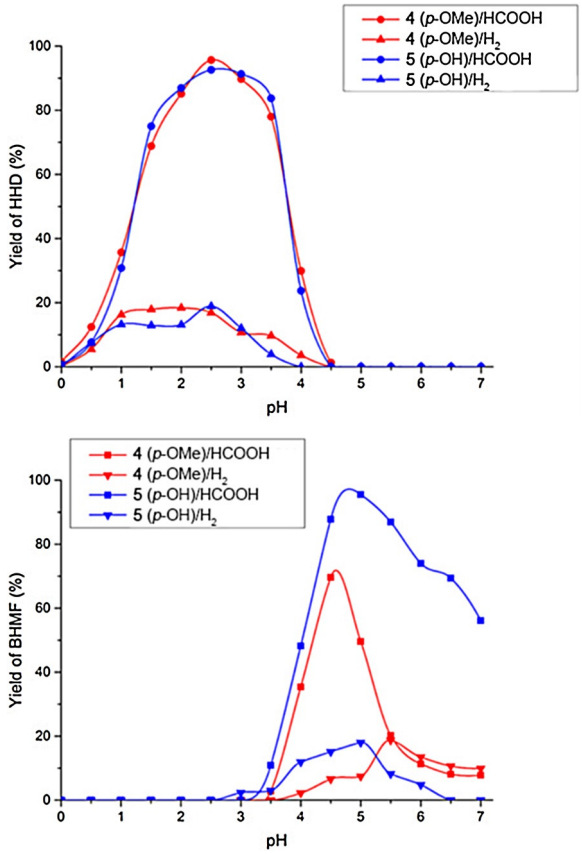

Figure 4. Reaction of 5-HMF to (top) HHD and (bottom) BHMF catalyzed by **4** and **5**. Reaction conditions: 5-HMF (1 mmol); catalyst (0.1 μmol, 0.01 mol% to 5-HMF); and either a) FBS (1 M, 5.0 mL) or b) under 1 MPa H_2 and PBS (0.1 M, 5.0 mL) at 130 °C for 2.0 h. GC yield, dimethyl phthalate was used as an internal standard.

improved to some extent, but it is still unsatisfactory. Considering HCOOH is decomposed to produce CO_2 in a FBS, and the high pressure CO_2 was reported to promote the hydrogenation/hydrolysis reaction and restrain humin in the acid hydrolysis system,[15,21] we tried to improve the yield of HHD by introducing CO_2 (partial pressure of CO_2 equal to H_2) in this system, but the results were not significantly improved (Figure S6 and S7).

Later, we investigated the reason that leads to low yield of HHD in PBS by detecting the change of pH with different hydrogen sources. When using HCOOH as hydrogen source, the pH raised from 2.5 to 6.5 owing to the reaction of HCOOH at 130 °C for 2 h. When using H_2 as hydrogen source, the buffer solution is PBS and the pH value shows no change after reaction. We investigated the stability of HHD and BHMF in different buffer solutions. Degradation rates of BHMF are higher than degradation rates of HHD under the same conditions, and both degradation rates in PBS are higher than degradation rates in FBS. The results show that the continuously increased pH slows down the degradation of BHMF and results in a better yield when using HCOOH as hydrogen source (Table S1).

To investigate the ring-opening mechanism of 5-HMF under acidic conditions, we proposed a possible reaction mechanism

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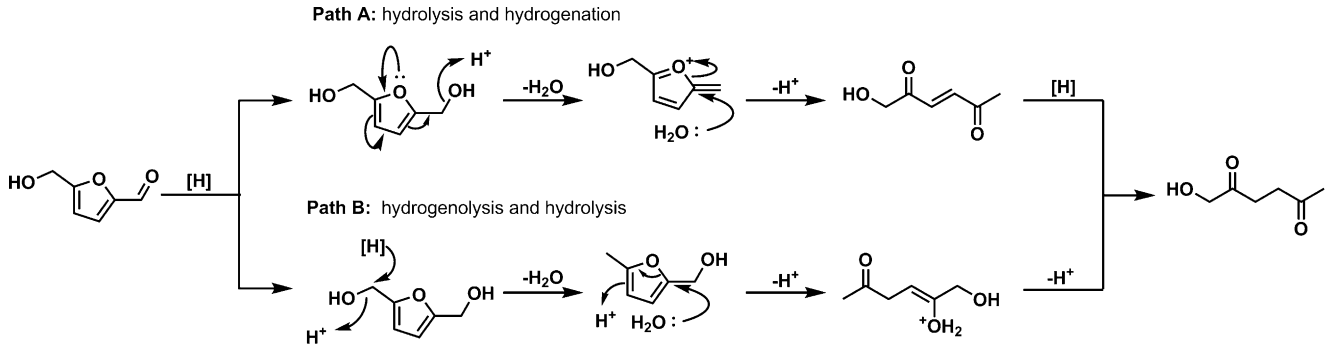
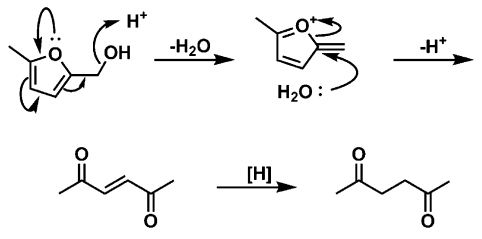


Scheme 2. Possible reaction paths for the ring-opening of 5-HMF under acidic conditions.

(Scheme 2). The aldehyde group of 5-HMF was first saturated to obtain BHMF. Then BHMF had two possible reaction paths: (A) BHMF was hydrolyzed/ring opened to produce 1-hydroxyl-3-en-2,5-hexanedione, then the C=C was saturated to obtain HHD; or (B) BHMF underwent hydrogenolysis to produce 5-methylfurfuryl alcohol, and then ring opening to generate HHD.[22]

An important distinction between the two reaction paths is the generation of 5-methylfurfuryl alcohol as an intermediate. Therefore, we carried out the reaction using 5-methylfurfuryl alcohol as the starting material to check our reaction path. If 5-methylfurfuryl alcohol reacted to form 2,5-hexanedione through the hydrolytic ring-opening reaction followed by hydrogenation, it indicates that path B is our reaction path., whereas if 5-methylfurfuryl alcohol reacts to form HHD via ring-opening reaction, it indicates that path A is our reaction path. Analysis of the product solution of 5-methylfurfuryl alcohol by GC–MS revealed the only product was 2,5-hexanedione (Scheme 3). Hence, path A is our reaction mechanism. Moreover, to confirm that BHMF is the intermediate, the hydrolysis/ring-opening reaction of BHMF was carried out under the optimal conditions for HHD (130 °C, 1 M, pH 2.5 FBS, catalyst **5**, 2 h). A red solid that is insoluble in water and methanol was formed. The detection of 24.5% yield of HHD in the GC spectrum supports that BHMF is the intermediate of reaction. Dumesic and coworkers[7a] reported that BHMF can polymerize easily under acidic conditions. Generation of BHMF polymers leads to a poor yield of HHD. Higher HHD yields (66.4%) were obtained at lower temperature (100 °C) owing to inhibition of BHMF polymerization. Jérôme and coworkers[15] and Zhang and coworkers[18] pointed out that BHMF and exocyclic double-bond species are generated as intermediates in the reduction process of 5-HMF, which confirm our conclusion.



Scheme 3. Mechanism for the conversion of 5-methylfurfuryl alcohol to 2,5-hexanedione.

There are three main steps in the reaction process: 1) reduction of 5-HMF to BHMF, 2) hydrolysis/ring-opening reaction of BHMF, and 3) reduction of the ketene intermediate. The major competitive reactions are polymerization of BHMF, decomposition reaction of HHD, and decomposition reaction of HCOOH. Reduction of the aldehyde group, hydrolysis/ring opening of BHMF, and polymerization of BHMF are promoted by strong acidity, whereas catalyst **4** and **5** are more active in weakly acidic media. At pH 4.5–7.0, reduction of the aldehyde groups can be carried out smoothly, which is different from hydrolysis/ring-opening reaction of the furan ring, hence leading to the generation of BHMF as the major product. At pH $<$ 4.0, BHMF can further react to open the furan ring, thus PBS can catalyze the hydrolysis of furan ring with sustained strong acidity (pH 2.5), and also lead to the decomposition of BHMF, whereas for FBS, the pH is rising with the continuous decomposition of HCOOH. The strong acidity in prophase of reaction facilitates the hydrolysis/ring-opening reaction of BHMF, reducing the concentration of BHMF and avoiding polymerization. The hydrogenation process was accelerated by the increase in the catalytic activity with the increase in pH. The weak acidity in the later stage of reaction also avoids the decomposition reaction of BHMF. This balance is the key to transfer 5-HMF to HHD in high efficiency and selectivity in FBS.

To test the recyclability and stability of the catalyst, a large-scale experiment was performed in a 1 L autoclave (Figure 5). 5-HMF (12.6 g, 0.1 mol) and catalyst **5** (6.3 mg, 0.01 mol%) were dissolved in FBS (500 mL, 1 M, pH 2.5) to react for 2 h at 130 °C. After the system dropped to room temperature, the gas produced by the reaction system was carefully released. A 92% GC yield of HHD was obtained. By adjusting the pH of cooled solution to 2.5 with pure HCOOH, and then extracting with dichloromethane, an isolated yield of 85% for HHD (11.0 g) was obtained by silica-gel column chromatography (Figure S1). The next cycle was performed by adding fresh 5-HMF (12.6 g, 0.1 mol) to the extracted solution for 2 h at 130 °C. The treatment procedure of the second cycle was the same as the first cycle, with an isolated yield of 70% for HHD. To investigate what causes the decrease in yield, the organic phase and aqueous phase were characterized by inductively coupled plasma atomic emission spectrometry (ICP-AES). Ac-

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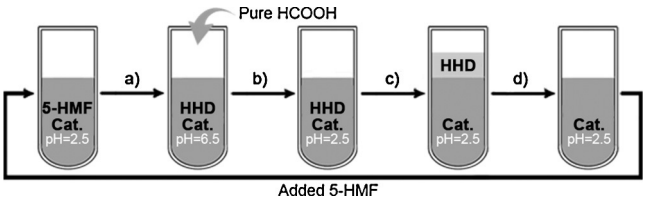


Figure 5. Catalyst recycling process for the hydrogenation of 5-HMF in aqueous FBS using phase separation: a) 130 °C, 2 h; b) acidification; c) extract with CH_2Cl_2; d) phase separation.

cording to the results of ICP-AES detection, the concentration of Ir fell from 3.84 to 2.36 mg L^{-1}, whereas the TON rose from 9200 to 11388 (Table 1). This indicates that there is no loss in activity of the catalyst and a slight loss in the extraction process causes the decrease of HHD yield.

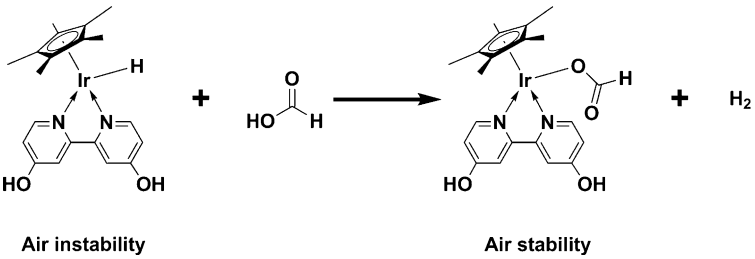
Table 1. Reuse of **5** for the hydrogenation of 5-HMF in aqueous FBS.[a]

Cycle index	Ir conc. [mg L^{-1}]	GC yield	TON	TOF [h^{-1}]
1	3.84	92%	9200	4600
2	2.36	70%	11388	5694

[a] Reaction conditions: 5-HMF (0.1 mol), catalyst (0.01 mmol, 0.01 mol% with respect to 5-HMF), and FBS (1 M, 500 mL) at 130 °C for 2 h.

To investigate whether the supplement of pure HCOOH causes loss of catalyst, we extracted the solution without adjusting pH. However, the solution exposed to air darkened in color. The pH of the separated aqueous phase was adjusted with pure HCOOH and then fresh 5-HMF was added for the next cycle. The reaction produced less than 10% HHD after 2 h. This result suggested that catalytically active [Ir–H] species in the reaction process[23] were instable towards O_2. Addition of HCOOH allowed the air-instable [Ir–H] species to transform into air-stable [Ir–OCOH] species (Scheme 4). Hence, delayed supplement of HCOOH for pH adjustment to 2.5 leads to ineffectiveness of the catalyst and hinders subsequent extraction.

5-HMF can be obtained from hydrolysis of fructose in industry. To show the application potential of our catalyst system, we studied the reaction to produce HHD with fructose as a starting material. Initially, we carried out the hydrolysis of fructose with isopropanol and HCl in water at 120 °C for 3 h.[24] After removing the isopropanol and water by reduced pressure distillation, pure water was added and the solid was removed by centrifugal separation. A light yellow solution of 5-HMF with HPLC yield of 73.4% was obtained. Pure HCOOH was added into the crude 5-HMF solution to adjust pH to 2.5. Acidified 5-HMF (5 mL) was mixed with the catalyst (0.01 mol%) and produced HHD with 98% GC yield (71.9% to fructose) at 130 °C for 2 h. These results support that our catalyst system can yield the selective transformation of crude 5-HMF, which was obtained from hydrolysis of fructose, to HHD in excellent yield.



Scheme 4. Stabilization of the Cp*Ir catalyst in FBS.

Conclusions

We developed Cp*Ir^{III} half-sandwich catalysts for selective conversion of 5-hydroxymethylfuraldehyde to 1-hydroxy-2,5-hexanedione in high yield and selectivity in aqueous formate buffer solution (FBS), which has an excellent tolerance to acidic aqueous conditions. We found that effective control of pH can increase catalytic efficiency and regulate the distribution of products. A mechanistic study demonstrated the path of 5-HMF transformation and the effect of acidity on the reaction system. We found that increasing the pH in the FBS reaction process can reduce competitive reactions and improve reaction selectivity. Our catalytic system can transform 5-HMF in the hydrolysis solution of fructose in excellent yield as well, which showed a potential for a large-scale production.

Experimental Section

Materials

5-HMF, BHMF, and 5-methylfurfuryl alcohol were generously gifted by Hefei Leaf Energy Biotechnology Co., Ltd (www.leafresource.com). $IrCl_3 \cdot nH_2O$ (Ir ≥ 60%) was purchased from Shaanxi Kaida Chemical Engineering Co. Ltd. Pentamethylcyclopentadiene was purchased from Energy Chemical. Fructose (99%) was purchased from Alfa Aesar. 2,2′-Bipyridine, 4,4′-dicarboxy-2,2′-bipyridine, and 4,4′-dimethoxy-2,2′-bipyridine were purchased from TCI. Ethyl acetate (99.5%), petroleum ether (60 ~ 90 °C), methanol (99.5%), dichloromethane (99.5%), isopropanol (99.5%), hydrochloric acid (37%), silver sulfate (99.7%), formic acid (98.0%), sodium formate dihydrate (99.5%), $Na_2HPO_4 \cdot 12H_2O$ (99.0%), and $NaH_2PO_4 \cdot 2H_2O$ (99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Reagent water was purchased from Wahaha. The autoclave was provided by Anhui Kemi Machinery Technology Co., Ltd. $[Cp^*IrCl_2]_2$,[25] 4,4′-dihydroxy-2,2′-bipyridine,[26] 4,4′-diamino-2,2′-bipyridine,[27] 6,6′-dihydroxyl-2,2′-bipyridine,[28] and 6,6′-dimethoxyl-2,2′-bipyridine[29] were synthesized according to the previously reported procedures.

General catalytic reaction

5-HMF (126 mg, 1 mmol), catalyst (0.50 mmol L^{-1}, 200 μL, 0.01 mol%) and FBS (5 mL, 1 M, pH range 0.0–7.0) were loaded into a 35 mL sealed glass tube and stirred at a rate of 700 rpm. The mixture was heated to 130 °C for 2 h with an oil bath and cooled in water to room temperature after the reaction. The liquid products were di-

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luted with methanol and analyzed by GC using dimethyl phthalate as an internal standard.

GC detection method

The liquid products were diluted with methanol and analyzed by using a Shimadzu GC-2014 gas chromatograph equipped with a capillary column (DM Wax 30 m×0.25 mm) and a flame ionization detector. The vaporization temperature was 523 K and the detection temperature was 553 K. An initial oven temperature of 333 K was held for 2 min; the temperature was ramped at 10 K min^{-1} until 513 K was reached. The column flow was 2.7 mL min^{-1}. The carrier gas was nitrogen and the split ratio was 50.

Conversion of fructose to HHD by two steps process

Fructose (0.45 g, 2.5 mmol), anhydrous isopropanol (4.85 mL), water /0.15 mL), and 37% HCl (5 mol%, 10 mL) were loaded into a 15 mL sealed glass tube with filled with argon and back-released three times. The mixture was heated to 130 °C with oil bath and stirred at a rate of 700 rpm for 3 h. After cooling in an ice bath, the solution was loaded into a round flask and the solvent was removed by reduced pressure distillation at 40 °C for 30 min. A brown sticky liquid (crude 5-HMF) was obtained. Water was added into round-bottom flask and evaporated under room-temperature until deeply colored impurity precipitated. The faint yellow supernatant was separated by decantation. This procedure was repeated until the decanted supernatant was colorless. The combined supernatant fractions were centrifuged twice to remove any solids. The products were separated using a Hitachi L2000 HPLC System, Alltech C18 column at 30 °C at a wavelength of 265 nm. The mobile phase was 30% methanol and 0.1% aqueous phosphoric acid with a rate of 1 mL min^{-1}. To the resulting 5-HMF solution (concentration was detected with HPLC: 0.517 mol L^{-1}) was added pure HCOOH to adjust pH to 2.5. The mixture of this solution and 0.01 mol% catalyst **5** was heated to 130 °C for 2 h in an oil bath and cooled in water to room temperature after the reaction. The liquid products were diluted with methanol and analyzed by GC using dimethyl phthalate as an internal standard.

Recyclability tests

5-HMF (12.6 g, 0.1 mol), catalyst **5** (0.01 mol%, 6.3 mg, 0.01 mmol), and FBS (500 mL, 1 M, pH 2.5) were loaded into 1 L autoclave to react for 2 h at 130 °C and stirred at a rate of 700 rpm. After the system has dropped to room temperature by cooling water circulation, the gas produced by the reaction system is carefully released. 2 mL of this solution was diluted with methanol and analyzed by GC using dimethyl phthalate as an internal standard. The pH of cooled solution was adjusted to 2.5 using pure HCOOH, then dichloromethane was used in the extraction process. The next cycle was performed by adding fresh 5-HMF (12.6 g, 0.1 mol) into the solution and extracting for 2 h at 130 °C. The treatment procedure of the second cycle was the same as the first cycle.

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