

pH-Regulated Aqueous Catalytic Hydrogenation of Biomass Carbohydrate Derivatives by Using Semi-sandwich Iridium Complexes

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Abstract: Semi-sandwich Ir complexes [Cp*Ir-(di-OMebpy)(OH₂)][SO₄] (di-OMe-bpy = 4,4'-dimethoxyl-2,2'-bipyridine) and $[Cp*Ir-(di-OH-bpy)(OH_2)][SO_4]$ (di-OH-bpy = 4,4'-dihydroxyl-2,2'bipyridine) are excellent efficient catalysts for the aqueous hydrogenation reactions of biomass carbohydrate derivatives. We show that pH value plays an important role in the hydrogenation reaction. By adjusting pH value of solvent, we can improve the catalytic efficiency and control the product distribution. The turnover frequencies (TOF) of hydrogenation of furfural up to 13877 h⁻¹ and TOF of hydrogenation of levulinic acid up to 12200h⁻¹ at 120 °C. Converting furfural into GVL in one step is observed at strong acidic aqueous system, which makes it easy to achieve a product distribution-controlled by pH adjustment.

Introduction

Nowadays, the rapid development of human society is at the expense of great consumption of the non-renewable resources. The gradual depletion of fossil resources have attracted global attention to the research of exploring alternatives to organic carbon sources ^[1]. Biomass is the sole readily-available renewable carbon source to produce liquid fuels and fine chemicals ^[2-3]. The major component of lignocellulosic biomass is carbohydrate polymers ^[4], which contain pentose monomer and hexose monomer ^[5]. Both carbohydrates and their derivatives have rich oxygenated functional groups ^[6-7]. Considering efficient utilization of biomass, it is necessary to remove oxygenated functional groups efficiently and selectively ^[8-9]. Hydrogenation is the preferred method for biomass processing owing to its atom economy. Normally, the raw biomass is rich in water and its

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derivatives are water-soluble, highly-reactive and low volatile ^[10]. In addition, water plays an important role as the solvent or reactant in biomass treatment process ^[2, 11]. Therefore, carbohydrates derivatives are suitable for aqueous reaction ^[10]. Considering the advantages of hydrogenation and aqueous reaction, the aqueous hydrogenation reaction is an essential method to convert biomass into fuels and fine chemicals ^[12].

Among the hydrogenation products of carbohydrates derivatives, furfuryl alcohol and y-valerolactone (GVL) are drawing ever more attention. Furfuryl alcohol, the selective reduction product of furfural ^[13], is mainly used for synthesizing widely-adopted furfuryl alcohol resins and the production of polyurethane foams and polyesters ^[14]. GVL, known as platform molecules ^[15], can be used the synthesis of 2-methyl-tetrahydrofuran ^[16], 1,4-pentanediol ^[17], liquid alkanes ^[18], ionic liquids ^[19-21] and polymers ^[22]. Also, GVL was suggested as a fuel additive ^[23] and a green solvent ^[24-28] due to distinctive physical chemistry properties.

As a cheap and abundant solvent for organic reactions, water attracts particular attention due to its superior physicochemical properties over traditional organic solvents like non-toxic, non-carcinogenic, non-combustible and non-explosive ^[29]. Moreover, water has the Brønsted amphoteric behaviour, hence the reaction rates and selectivity can be regulated by the adjusting of pH value [30]. Recently, various homogeneous catalytic systems used in aqueous hydrogenation reaction of biomass carbohydrate derivatives have been reported. Typically, Ru complexes [18,31,32] and Ir complexes [33,34] performed well in homogeneous catalysis. In particular, iridium complexes have drawn considerable attentions in homogeneous catalytic hydrogenation because of their robustness and highly activity in respect of turnover frequencies (TOFs) and turnover numbers (TONs).^[35,36] However, researchers found the inorganic acid such as sulphuric acid, which is necessary in biomass hydrolysis system, would weaken the catalytic efficiency [37]. Thus, the tolerance of catalysts to acidity is very important in biomass treatment process.

Himeda and coworkers ^[30,38-43] and Fukuzumi and coworkers ^[44] have developed a series of semi-sandwich iridium complexes catalysts, which show good water-solubility and acid resistance. Also, our group have reported that water-soluble semi-sandwich iridium complexes can efficiently convert levulinic acid (LA) into GVL under mild conditions (120 °C and 1.01 MPa) in pure aqueous system ^[34]. In addition, pH was recently demonstrated to effectively regulate the catalytic efficiency and distribution of products of hydrogenation/ring-opening reaction of 5-HMF catalyzed by semi-sandwich iridium catalyst ^[45]. **FULL PAPER**

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Reaction conditions: **a**) Furfural (0.60 mmol), aqueous solution of catalyst (0.5 mmol/L, 100 μ L), phosphate buffer solution (2 mL), 1.0 MPa H₂, 120 °C, 1 hour. The catalyst/substrate molar ratio of highest TOF (7340 h⁻¹) is 0.0017% (A fifth of the general reaction condition). **b**) LA (0.49 mmol), aqueous solution of catalyst (0.5 mmol/L, 50 μ L), phosphate buffer solution (2 mL), 1.0 MPa H₂, 120 °C, 1 hour. **c)** Furfural (0.60 mmol), aqueous solution of catalyst (0.5 mmol/L, 100 μ L), formate buffer solution (1mol/L, 2 mL), 1.0 MPa H₂, 120 °C, 1 hour. **c)** Furfural (0.60 mmol), aqueous solution of catalyst (0.5 mmol/L, 100 μ L), formate buffer solution (1mol/L, 2 mL), 1.0 MPa H₂, 120 °C, 1 hour. The catalyst/substrate molar ratio of highest TOF (13800h⁻¹) is 0.0017% (A fifth of the general reaction condition). **d)** LA (0.49 mmol), aqueous solution of catalyst (0.5 mmol/L, 50 μ L), formate buffer solution (1mol/L, 2 mL), 1.0 MPa H₂, 120 °C, 1 hour. The catalyst (0.5 mmol/L, 50 μ L), formate buffer solution (1mol/L, 2 mL), 1.0 MPa H₂, 120 °C, 1 hour. The catalyst (0.5 mmol/L, 50 μ L), formate buffer solution (1mol/L, 2 mL), 1.0 MPa H₂, 120 °C, 1 hour. The catalyst (0.5 mmol/L, 50 μ L), formate buffer solution (1mol/L, 2 mL), 1.0 MPa H₂, 120 °C, 1 hour.

Herein, we developed the pH-regulated aqueous hydrogenation of biomass-derived molecules over semi-sandwich iridium complexes. By adjusting pH value of solvent and electronic density of substituent on ligand, we can improve the catalytic efficiency and control the product distribution. Full conversion of furfural to furfuryl alcohol (TOF up to 13877 h⁻¹) and full conversion of LA to GVL (TOF up to 12200 h⁻¹) were achieved respectively. In addition, under strong acidic aqueous conditions, the hydrogenation product of furfural, furfuryl alcohol, could be hydrolyzed into LA, and LA could be further converted into GVL. Hence to achieve the one-pot conversion of GVL from furfural.

Results and Discussion

Initially, we investigated the influence of electronic effect of substituents on TOF under different pH values. Two of the most active catalysts in our previous work $^{[34,45]}$, $[Cp*Ir-(di-OMe-bpy)(OH_2)][SO_4]$ (di-OMe-bpy = 4,4'-dimethoxyl-2,2'-bipyridine) (catalyst 1) and $[Cp*Ir-(di-OH-bpy)(OH_2)][SO_4]$ (di-OH-bpy = 4,4'-

dihydroxyl-2,2'-bipyridine) (catalyst 2), were used to perform our experiments. Furfural, which is the typical product of dehydration of pentose, is hydrogenated under 1MPa H₂ at 120 °C for one hour over 0.0083mol% catalyst 1. And the pH value from 0.5 to 7.0 was regulated with H₂SO₄/H₃PO₄ or phosphate buffer solution (PBS). Under above reaction conditions, the TOFs versus reaction pH value are shown in Chart a) of Fig. 1, Table s1-s2. The results showed that, under pH of 3.5, we obtained the highest yield of furfuryl alcohol and the maximum TOF of 1600h⁻¹. When we use hydroxyl as the substitute (catalyst 2), the highest TOF is 7340 h⁻¹ under pH of 5.0. Our previous research found that the electron-donating group on catalysts would promote catalytic activity significantly [34,45]. A small amount of GVL was observed when pH<1.5. And soluble furfuryl alcohol resins and insoluble humins were formed at pH 2-4. As pH value raises above 3, the hydroxyl group of 4,4'-dihydroxyl-2,2'-bipyridine ionizes into aryl oxygen anion (Figure 2, species 2), which results in a remarkable improvement in electron-donating ability. Thus, the activity of catalyst 2 is more highly than catalyst 1. Goldberg and coworkers suggested that there are [Cp*Ir-(di-OMe-bpy)(H)]+ intermediate in **FULL PAPER**

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the reaction process, which would react with protonized carboxylic compounds ^[46]. At higher pH values, the concentration of protonated carbonyl compound in the system is decreasing, while proton characteristics of intermediate is increasing. This causes the decrease of the catalytic activity ^[47].

LA is the typical dehydration product of hexose. Under identical conditions (0.0083 mol% catalyst, 1.0 MPa H₂, 120 °C, 1 hour), TOF of hydrogenation of LA is 2864 h⁻¹ (pH=1.5) by using catalyst 1 and 4326 h⁻¹ (pH=2.5) by using catalyst 2 (see Chart b) of Fig. 1, Table s3-s4). The TOF change trend of hydrogenation of LA is same as the hydrogenation of furfural. This result confirms the above speculation.

It has been reported that semi-sandwich iridium complexes can catalyse the decomposition of formic acid (FA) ^[48], which is the by-product of acidic hydrolysis of biomass raw material. Thus, it is economical to use formic acid as a hydrogen source in the reduction of carbohydrate derivatives. Furfural is hydrogenated at 120 °C for 1 hour in 1mol/L FA buffer solution (pH value ranges from 2.0 to 7.0). The TOFs versus reaction pH value are shown in Chart c) of Fig. 1, Table s5-s6. TOF of catalyst 2 is higher than that of catalyst 1. The value is 13877 h⁻¹, which is higher than the reported TOF we have known [13,49-54] (see Table s9). Under the same conditions, the efficiency of catalyst 2 (TOF=12200 h⁻¹) in the hydrogenation of levulinic acid is higher than catalyst 1 (TOF= 6800 h⁻¹), which is better than the highest value that we previously reported [17,18,31,33,34,55-60] (see Table s10). The TOFs versus reaction pH value are shown in Chart c) of Fig. 1, Table s7-s8. In our reaction system, catalyst is mainly in the form of the partial deprotonated species (Figure 2, species 2). As formic acid ionizes into formate, the electrostatic attraction makes it easier to combine with the catalyst in homogeneous phase than hydrogen in biphasic system. This results in a higher reaction efficiency using formic acid as hydrogen source.

The ratios of the highest TOFs between Cat.2 and Cat.1 show the correlation between substrates reactivity and reaction

rates. Using furfural as substrate, the ratios of the highest TOFs between Cat.2 and Cat.1 are 4.4 (PBS) and 3.8 (FBS) respectively. While the ratios of the highest TOFs are 1.5 (PBS) and 1.8 (FBS) respectively with LA as substrate. The values of furfural are higher than the values of LA under different buffer solutions. Therefore, hydrogenation of furfural is more influenced by electronic effect of the substituents than hydrogenation of LA, and the aldehydic carbonyl group of furfural is more active than the ketone carbonyl of LA.

Table 1. Product distribution in strong acidic system. vield, % (TOF) hydrogen entry Cat. c(Ir) source furfuryl GVL LA alcoho 0.0083 mol% 1 mol/l 0 14 0 1^[a] 1 4.8 ppm HCOOH (0) (422)(0) 0.0083 mol% 0 0 1 mol/l 2^[a] (30) 4.8 ppm HCOOH (0) (0) 0.083 mol% 1 mol/L 0 **3**[a] (21) 48 ppm HCOOH (0) (12)0.083 mol% 1 mol/L 2 3 6 **∆**[a] HCOOH (6) (18) (9) 48 ppm 0.0083 mol% 24 35 0 5^[b] 1 MPa H₂ 4.8 ppm (0) (724) (1056)0.0083 mol% 6^[b] 1 MPa H₂ 2 (1237) (272) 4.8 ppm (0) 0.083 mol% 0 55 **7**[b] 1 MPa H₂ (3) (166) 48 ppm (0) 0.083 mol% 47 0 8^[b] 1 MPa H₂ 2 48 ppm (0) (3) (142)

Reaction Conditions: Furfural (0.60 mmol), aqueous solution of catalyst (0.5 mmol/L or 5 mmol/L, 100 μ L), 1.0 MPa H₂, 120 °C, 4 hour. **[a]** formate buffer solution (pH=1.0, 1mol/L, 2 mL), **[b]** phosphate buffer solution (pH=1.0, 0.1mol/L, 2 mL)



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In a strong acidic phosphate buffer system with pH of 1.0 (0.0083 mol% catalyst, 1.0 MPa H₂, 120 °C, 1 hour), we found that furfural can be converted into y-valerolactone directly in onepot without any intermediate product separation step. While GVL was not detected in formate buffer system. As mentioned above, a loss of catalytic activity was detected at strong acidic solution, hence we carried out the cascade reaction from furfural to GVL with an increase in catalyst concentration to 0.083 mol% and an increase in reaction time to 4 hour. When hydrogenation of furfural was performed in formate buffer solution (pH=1.0) with 0.0083mol% catalyst for 4 hour, only LA was obtained (Table 1, entry 1 and 2). A GVL yield less than 10% was achieved by increasing the catalyst concentration to 0.083 mol% in formate buffer solution (Table 1, entry 3 and 4). When furfural was reduced under 1 MPa H₂ for 4 h using 0.0083 mol% of catalyst 1 at 120 °C, a LA yield of 24% and a GVL yield of 35% was obtained (Table 1, entry 5). While LA in 41% yield and GVL in 9% yield was obtained using 0.0083 mol% of catalyst 2 (Table 1, entry 6). In the case of 0.083 mol% catalyst use in phosphate buffer solution at pH 1.0, a 55% yield of GVL and a 3% yield of 2methyltetrahydrofuran with catalyst 1, and a 47% yield of GVL with catalyst 2 were obtained respectively (Table 1, entry 7 and 8). These results are consistent with our previous work [34], catalyst 1 performed slightly better than catalyst 2 in strong acidic system.

From the above results, H₂ is better hydrogen source than formic acid for the one-pot conversion of furfural to GVL in strong acid aqueous system (a) of Scheme 1). However, in our previous work ^[45], formate buffer solution performed better than phosphate catalvtic buffer solution in conversion of 5hydroxymethylfuraldehyde (5-HMF) to 1-hydroxy-2,5hexanedione (HHD, b) of Scheme 1). This is a result of pH rise with HCOOH decomposition during the hydrogenation/hydrolysis reaction of 5-HMF in formate buffer solution, which avoid the degradation of 2,5-bis-(hydroxymethyl)furan (BHMF) and HHD. Moreover, acid-catalyzed hydrolysis of BHMF could still occur with a mild acidity in the pH change process. In contrast, hydrolysis of furfuryl alcohol to LA requires a sustained strong acidity, and then LA could be reduced to GVL. Besides, GVL is stable in strong acidic solution. Furthermore, furfuryl alcohol can easily polymerize to soluble furfuryl alcohol resins and insoluble humins in the range of pH 2-4. Hence, it is necessary to keep





Figure 3. The competition of FA decomposition with the hydrogenation reaction.

strong acidity (pH<1.5) using phosphate buffer solution. Since the species 5 (Figure 4) is instable at such acidity, it tends to combine with hydron. That causes the competition of FA decomposition with the hydrogenation reaction. The system cannot provide enough hydride when FA is used as hydrogen source. In order to improve the yield of GVL, we enhance H₂ pressure up to 1.5 MPa. But no improvement had been detected (Figure s3). Previous studies ^[61-62] indicated that hydrolysis of furfuryl alcohol competed with its polymerization, and humins was observed in our reaction, both of which caused the decreasing of GVL yield. And humins increase with the substrate concentration (Figure s4).

Goldberg and coworkers ^[46-63] have pointed out that 2methyltetrafuran could be obtained by hydrogenation of LA and deep hydrogenation of GVL over semi-sandwich iridium complexes catalysts. We carried out the hydrogenation reaction of GVL under our optimum experimental conditions (0.083 mol% Cat.1, 1 MPa H₂, 120 °C, and 4 hour). Less than 1% yield of 2methyltetrafuran was obtained. Since our reaction conditions (1 MPa and 4 hour) are milder than Goldberg's work (30bar and 18 hour), hydrogenation reaction of GVL was difficult to process. Xu and coworkers ^[64] and Zhu and coworkers ^[65] showed the direct hydrogenolysis of furfuryl alcohol with subsequent hydrogenation into 2-methyltetrafuran under hydrogen atmosphere. Thus, the 2methyltetrafuran in our reaction system came from hydrogenolysis of furfuryl alcohol.

Li and coworkers ^[66] found that the reduction efficiency of furfural and levulinic acid in methanol system is better than reactions in water. Dumesic and coworkers ^[67] pointed out that GVL solubilized humins during cellulose deconstruction process. We performed the hydrogenation loading organic solvents as additive in phosphate buffer solution. The formation of humins significantly decreased by adding organic solvents while GVL yield was not improved (Figure s2) due to the selectivity decreased.

Conclusions

In conclusion, we report a pH-regulated aqueous catalytic hydrogenation of biomass carbohydrate derivatives by using semi-sandwich iridium complexes. We observed the best catalytic efficiency and TOF so far under mild conditions. Moreover, by simply regulating the pH values, we can control the product distribution and achieve the one-pot aqueous reaction for the preparation of γ -valerolactone from furfural. Our system is compatible with pure water system and low concentration of substrate, which shows a robustness of semi-sandwich Ir complexes for acidic aqueous system and a remarkable viability for practical hydrolysis system.

Experimental Section

Materials. All catalysts and chemicals are commercially available. LA (99%), FA (98%), and GVL (98%) were purchased from Aladdin Reagent Co. Ltd. Furfural was generous gifts from Hefei Leaf Energy Biotechnology Co., Ltd. and used with purification by distillation. (Pentamethylcyclopentadienyl) iridium (III) chloride dimer [(Cp*IrCl₂)₂,

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98%] was purchased from Suzhou Sinocompound Technology Co., Ltd. 4,4'-dimethoxy-2,2'-bipyridine were purchased from TCI. 4,4'-dihydroxy-2,2'-bipyridine, were synthesized according to the previously reported procedures[68]

Preparation of 0.1 mol/L phosphate buffer solution. pH range from 0.5 to 1.5. Dripping concentrated sulphuric acid into the solution of phosphoric acid (0.1 mol/L) while measuring the pH with a pH meter. pH range from 2.0 to 7.0. Making a solution of monosodium orthophosphate (0.1 mol/L) with the same concentration as the orthophosphoric acid or disodium hydro-gen phosphate and mixing while measuring the pH with a pH meter.

Preparation of 1 mol/L formate buffer solution. pH range from 0.5 to 1.5. Dripping concentrated sulphuric acid into the formic acid solution (1 mol/L) while measuring the pH with a pH meter. pH range from 2.0 to 7.0. Mixing the solution of formic acid (1 mol/L) with the same concentration as formate while measuring the pH with a pH meter.

General catalytic hydrogenation of LA or furfural with H₂. LA (0.49 mmol) or furfural (0.60 mmol), aqueous solution of catalyst (0.5 mmol/L, 50µL for LA, 100 µL for furfural), and phosphate buffer solution (2 mL) were added to a 10 mL zirconium alloy high-pressure reaction tube, and stirred at a rate of 900 rpm under 1.0 MPa H₂, The mixture was heated to 120 °C for 1 hour. The mixture of substrates and catalyst were heated to the desired temperature in 10 min and cooled down in water to room temperature after the reaction. The liquid products were diluted with acetonitrile and analysed by using GC on a Shimadzu GC-2014 gas chromatograph equipped with a DB-FFAP capillary column (30 m×0.320 mm×0.25µm) and a flame ionization detector. An internal standard (1methyl-2-pyrrolidone) was used to determine the amount of product. The typical GC chart of the internal standard was showed in Figure s1

General catalytic hydrogenation of LA or furfural with FA. LA (0.49 mmol) or furfural (0.60 mmol), formate buffer solution (2mL), aqueous solution of catalyst (0.5 mmol/L, 50µL for LA, 100 µL for furfural) were loaded in sealed glass tube. The catalytic conversion proceeded as de-scribed above, but in the absence of hydrogen.

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Full conversion of furfural to furfuryl alcohol (TOF up to 13877 h^{-1}) and full conversion of levulinic acid to γ -valerolactone (TOF up to 12200 h^{-1}) were reached respectively. In addition, the one-pot aqueous reaction of furfural for the preparation of γ -valerolactone was achieved.

Wei-Peng Wu, Yong-Jian Xu, Shang-Wei Chang, Jin Deng,* and Yao Fu*

Page No. – Page No. pH-Regulated Aqueous Catalytic Hydrogenation of Biomass Carbohydrate Derivatives by Using Semi-sandwich Iridium Complexes