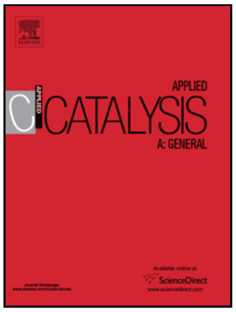

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Effect of Cp*Iridium(III) Complex and acid co-catalyst on conversion of furfural compounds to cyclopentanones or straight chain ketones

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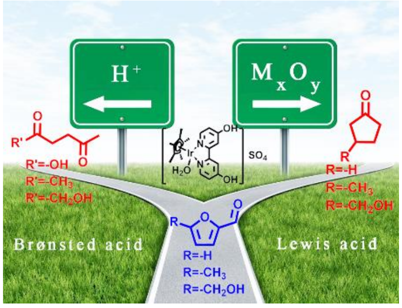
Graphical Abstracts



By using Cp*Ir , Brønsted acid and Lewis acid can promote conversion of furfural compounds to straight chain ketones and cyclopentanone derivatives, respectively.

Highlights

- A highly efficient Cp*Ir (III) Complex and acid co-catalyst system to conversion of furfural compounds to cyclopentanones or straight chain ketones.
- Mechanism of conversion of 5-HMF to HCPN proposed by our predecessors was revised and supplemented. We found that HHD condensed via Aldol reaction to produce MCP instead of HCPN.
- Brønsted acid can promote conversion of furfural compounds to straight chain ketones and Lewis acid can promote rearrangement of furfural compounds to cyclopentanones.

Abstract: In this paper, Cp*Ir (III) Complex and acid co-catalyst system was developed. By using Cp*Ir and γ-Al_2O_3 (Lewis acid), 5-hydroxymethylfurfural (5-HMF) can be converted efficiently to 3-hydroxymethyl cyclopentanone (HCPN). Meanwhile, Cp*Ir and Brønsted acid can promote conversion of 5-HMF to 1-Hydroxy-2,5-hexanedione (HHD). The effect of Lewis acid and Brønsted acid on the hydrogenation of furan derivatives was studied. Mechanism of conversion of 5-HMF to HCPN was discussed in detail and mechanism proposed by our predecessors was revised. Instead of being an intermediate for the formation of HCPN, it is believed that, HHD is a product of another reaction pathway. HHD condensed via Aldol reaction to produce 3-methylcyclopenten-2-ol-1-one (MCP) instead of HCPN. Under the promotion of Lewis acid, 5-HMF firstly convert to the precursor of HHD. After that, the reaction is through 4 π-electrocyclic ring closure process and HCPN was formed ultimately. Furthermore, we found that our Cp*Ir and acid co-catalyst system is suitable for a variety of furfural compounds. By using Cp*Ir, Brønsted acid can promote conversion of furfural compounds to straight chain ketones and Lewis acid can promote the rearrangement of furfural compounds to cyclopentanone derivatives.

Keywords: furfural compounds, Lewis acid, Brønsted acid, reaction mechanism, ketones

1. Introduction

The depletion of fossil resources has severely restricted the development of chemical industry that relies on non-renewable resources. Thus, for the sake of sustainable development, attention has been drawn to biorefinery. Lignocellulose, as the most abundant renewable organic carbon source, is an important raw material for biorefinery.[1]

5-hydroxymethylfurfural (5-HMF), as one of the most promising biomass-based platform molecules, can be synthesized from the downstream products of lignocellulose, such as glucose and fructose.[2] 5-HMF can be converted to many valuable bio-derived chemicals, including 2,5-furan dicarboxylic acid,[3] 2,5-furan carboxaldehyde,[4] 2,5-dimethyl furan,[5] 2,5-dihydroxymethyllfuran (BHMF),[6] 2,5-dimethyl tetrahydrofuran,[7] 1-hydroxy-2,5-hexanedione (HHD)[8] and 3-hydroxymethyl cyclopentanone (HCPN).[9]

3-hydroxymethylcyclopentanone (HCPN) is a valuable raw material for fine chemicals, which can be used to prepare pharmaceuticals, polymers, spices, and fuels, such as methyl jasmonate[10] and carbocyclic nucleoside[11] (Figure 1). Thus, studying the synthesis of HCPN has important scientific and economic value.

The reaction of HCPN from 5-HMF resembles a widespread concerned reaction, furfural rearrangement to cyclopentanone.[12] They both follow the mechanism of Piancatelli rearrangement reaction, which is mainly experienced by a cascade sequence that terminates with a 4 π-electrocyclic ring closure to give a pentadienyl cation, a step that is analogous to the Nazarov reaction.[13] The substitution at 5-position of the furan ring blocks Piancatelli rearrangement.[12a-12b,13c] So even though HCPN is a potential biomass-based platform molecule, the transformation of 5-HMF hydrogenation to HCPN has been rarely reported.

In 2014 and 2015, Satsuma developed Au/Nb_2O_5[9a] and Pt/SiO_2 with Ta_2O_5[9b] catalyst system to achieve the conversion of HCPN from 5-HMF. Recently, Rosseinsky obtained HCPN from 5-HMF by using Ni/Al_2O_3 metal hydrate[9c] and Cu/Al_2O_3 metal hydrate[9d] as catalyst. However, these studies all required long reaction time and showed low catalyst activity according to calculated turnover frequency (TOF)[8g] based on the reported results (Table 1). They all did not discuss the mechanism in detail and thought that 1-hydroxy-2,5-hexanedione (HHD) may be an important intermediate in the reaction. The effect of Lewis acid on the reaction was discussed.

Our study reported half-sandwich Ir complexes[8a,14] have shown excellent hydrogenation activity, selectivity and acid resistance for hydrogenation of furan ring derivatives. Recently, we discussed the effect of Brønsted acid on conversion of 5-HMF to HHD and 2,5-dihydroxymethylfuran (BHMF)[8a]. To research the effect of Lewis acid on the reaction and to further develop half-sandwich Ir complexes and acid co-catalyst system, we chose the most efficient and acid-resistant half-sandwiched Ir complex, [Cp*Ir(4,4'-$(OH)_2$-bpy)(OH_2)]SO_4 (Figure 2, Table 2, hereinafter referred to as Cp*Ir)[8a,14b] and metal oxides (Lewis acid) as catalyst in hydrogenation of 5-HMF. γ-Al_2O_3 showed the highest catalytic activity in all metal oxides used in the reaction.

Herein, we used Cp*Ir and γ-Al_2O_3 as the catalyst in hydrogenation of 5-HMF to HCPN. The yield of HCPN can reach 82% at 130 °C and 3 MPa H_2 for 4 h (TOF reach 205 h^{-1}, Table 1). The effect of Brønsted acid and Lewis acid on the hydrogenation of furfural compounds was studied. Under the catalysis of Brønsted acid and Lewis acid, HHD and HCPN can be obtained with high selectivity respectively. In our catalytic system, this rule is applicable to many furfural compounds (Scheme 1). In the article, the mechanism of the reaction was discussed in detail and mechanism proposed by our predecessors was revised and supplemented.

2. Experimental Section

2.1 Materials and reagents

5-hydroxymethylfurfural, 5-methyl furfural, furfural and fructose were generously gifted by Hefei Leaf Energy Biotechnology Co., Ltd (www. leafresource. com). 3-methly-2-cyclopenten-1-one (97.0%), 2-cyclopenten-1-one (> 98.0%) were purchased from Adamas Reagent Co., Ltd. 3-methylcyclopentanone (99.0%) was purchased from Shanghai yuanye Bio-Technology Co., Ltd. $IrCl_3·nH_2O$ (Ir ≥ 60.0%) was purchased from Shaanxi Kaida Chemical Engineering Co. Ltd. Pentamethylcyclopentadiene was purchased from Energy Chemical. 4,4'-dicarboxy-2,2'-bipyridine were purchased from TCI. γ-Al_2O_3-1 (99.9%, 30nm) was purchased from Xiya Reagent Co., Ltd. TiO_2 (99.8%, Anatase, 5-10nm), ZrO_2 (> 99.9%, 50 nm), WO_3 (99.9%, 50 nm), γ-Al_2O_3-2 (99.9%, 10 nm), α-Al_2O_3 (99.9%, 200 nm) were purchased from Aladdin Chemistry Co., Ltd. Ta_2O_5 (> 99.9%), $Al_2(SO_4)_3$ (98%),Ag_2SO_4 (99.7 %), ethyl acetate (99.5 %), petroleum ether (60-90ºC), methanol (99.5 %), acetonitrile (99.0%), dichloromethane (99.5%), $Na_2HPO_4·12\ H_2O$ (99.0 %), and $NaH_2PO_4·2\ H_2O$ (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. All of the metal oxides were calcined at 500 ℃ for 4 h before used.

2.2 Typical Catalyst preparation

Iridium trichloride hydrate (10 g, 0.026 mol) and pentamethylcyclopentadiene (5.0 g, 0.036 mol) were added to 300 mL methanol in a 500mL round-bottom flask, purged with nitrogen for 5 min. Then the mixture reacted under nitrogen for 48 h at room temperature. Recrystallization of the product from chloroform-hexane obtained $[IrCp^*Cl_2]_2$, an orange microcrystalline solid.[15]

$[Cp^*IrCl_2]_2$ (480 mg, 0.60 mmol) and Ag_2SO_4 (374 mg, 1.20 mmol) were added to 4 mL of water under argon atmosphere. The solution was stirred at room temperature for 12 h and then filtered to remove AgCl. The filtrate was evaporated and dried in vacuum to get yellow powder $[Cp^*Ir(H_2O)_3]SO_4$. $[Cp^*Ir(H_2O)_3]SO_4$ (48 mg, 0.10 mmol) was dissolved in 12.5 mL of water under argon and 0.10 mmol of 4,4'-dihydroxy-2,2'-bipyridine was added. The solution was stirred under reflux for 12 h. After the reaction, the aqueous solution was then distilled under reduced pressure to remove water and got a pale yellow powder. The solid was dried under vacuum at 55 °C for 12 h and got [Cp*Ir(4,4'-$(OH)_2$-bpy)(OH_2)]SO_4. The catalyst was analyzed by NMR (supporting information part 12). The catalyst can be further purified by recrystallization from water.

2.3 Catalyst characterization

The acidity of the samples was measured by NH_3-TPD. A gas chromatograph (GC-SP6890, Shandong Lu-nan Ruihong Chemical Instrument Co., Ltd., Tengzhou China) was used with an inline thermal conductivity detector (TCD). Before testing, about 80 mg of sample was heated up to 500 °C for 2 h in a flow of argon to remove adsorbed water or organic species. For NH_3-TPD, the sample was adsorbed with NH_3 until saturated at 80 °C for 1 h. After the catalyst surface became saturated, the sample was kept at 80 °C for 1 h in argon to remove the excess base. NH_3 was thermally desorbed by rising the temperature with a linear heating rate of approximately 10 $°C·min^{-1}$ from 80 °C to 800 °C. Then temperature was kept for 2 min. The total number of acid sites was calculated based on the TCD signal of NH_3.

The pyridine adsorption infrared was measured by Bruker Vertex 70 FT-IR spectrometer. The catalyst was pressed and placed in an infrared spectroscopy cell at 300 °C for 1 h, vacuum of $< 1 \times 10^{-2}$ MPa. The temperature was reduced to 30 °C, the pyridine vapor was adsorbed for 30 min and then heated to 150 °C and 250 °C. Infrared spectra were recorded.

2.4 Typical experiment and product analysis

5-HMF (25.2 mg, 0.2 mmol), Cp*Ir catalyst (dissolved in H_2O, 5 $mmol·L^{-1}$, 0.04 mL, 0.1 mol%), γ-Al_2O_3-1 (10 mg) and H_2O (3 mL) were loaded into a 10 mL stainless steel autoclave and stirred at a rate of 1000 rpm. The mixture was heated to 130 °C under 3 MPa H_2 for 4 h. The liquid products were diluted with acetonitrile and analyzed by GC. Dimethyl phthalate was used as an internal standard (The typical GC charts were showed in supporting information Figure S2 and Figure S3).

The liquid products were diluted with acetonitrile and analyzed by 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 250 °C and the detection temperature was 280 °C. An initial oven temperature of 60 °C was kept for 2 min, and the temperature increased to 240 °C in steps of 10 $°C·min^{-1}$. The column flow was 2.7 $mL·min^{-1}$. The carrier gas was nitrogen and the split ratio was 50.

3. Results and Discussion

3.1. Effect of Lewis acid and Brønsted acid on conversion of 5-HMF to HCPN and HHD

Firstly, we investigated the effect of different Lewis acid on the reaction (Figure 3). Ta_2O_5, ZrO_2, TiO_2, Nb_2O_5, Al_2O_3 were selected because of their good catalysis effect on the hydrogenation of HMF to HCPN, according to previous reports.[9] The highest yield of HCPN reached *ca.* 80% when γ-Al_2O_3 was added as Lewis acid. TiO_2 and Ta_2O_5 can also promote the reaction to HCPN with the yield of 60%, while Nb_2O_5 has weak effect on the reaction. In addition, 3-methylcyclopenten-2-ol-1-one (MCP), 1-hydroxy-2,5-hexanedione (HHD) and 3-hydroxymethylcyclopentenone (HCPEN) were also detected.

Temperature programmed desorption of ammonia (NH_3-TPD) show that the acidity of metal oxides can affect the yield of HCPN (Figure 4). There is only one weak acid site under 200 °C in each metal oxide.[16] Comparing these acid sites, we found that acid strength is ordered as follow: γ-Al_2O_3-2 > γ-Al_2O_3-1 > Ta_2O_5 > TiO_2 > α-Al_2O_3 > WO_3 > ZrO_2 > Nb_2O_5 and the order of acid amount is γ-Al_2O_3-2 > γ-Al_2O_3-1 > TiO_2 > ZrO_2 > Ta_2O_5 > WO_3 > α-Al_2O_3 > Nb_2O_5 (Figure 5). The higher acid strength, the more HCPN yield. Meanwhile, acid amount has a weak effect on the yield. Acid strength of TiO_2 is weaker than Ta_2O_5, but more likely to promote the formation of HCPN, which is due to the acid amount of TiO_2 being much larger than Ta_2O_5. The acid strength and acid amount of γ-Al_2O_3-2 are both larger than γ-Al_2O_3-1, but the yield of HCPN is slightly reduced, which showed proper Lewis acidity is important for the reaction.[9b]

Pyridine adsorption infrared (Figure 6) showed that there were no obvious Brønsted acid sites at about 1540 cm^{-1} in all kinds of metal oxides used in our reaction systems, but there were obvious Lewis acid absorption peaks at about 1450 cm^{-1}.[17] The peaks suggest that the Lewis acid sites in the metal oxides play a major role in the reaction of rearrangement from 5-HMF to HCPN. The higher wavenumber indicates the stronger Lewis acidity of the metal oxides.[9b,17] The wavenumbers of the peaks which indicates Lewis acid sites in the vicinity of 1450 cm^{-1} increase in the order of γ-Al_2O_3-2 > γ-Al_2O_3-1 > α-Al_2O_3 > ZrO_2. The peaks of Ta_2O_5、α-Al_2O_3、WO_3 and Nb_2O_5 are not obvious due to the low acid amount (supporting information Figure S11). It is consistent with the rule of NH_3-TPD. This further demonstrates that the Lewis acidity of the metal oxide promotes the formation of HCPN.

Further study showed that γ-Al_2O_3-1 can promote the formation of HCPN efficiently (Figure 7). With the increasing addition of γ-Al_2O_3-1, the selectivity of HCPN increased significantly at the beginning，followed by a slight drop. This phenomenon can be explained by the variation of acidity. Suitable Lewis acid can promote the foration of HCPN. However, when the γ-Al_2O_3-1 dosage exceeded, the system acidity increased, then the selectivity of HCPN decreased.

In water-soluble hydrogenation catalytic system, using water-soluble Lewis acids may lead to better HCPN selectivity. Based on the results above, $Al_2(SO_4)_3$ was chosen as acid catalyst and found to give the reaction a high selectivity of 1-Hydroxy-2,5-hexanedione (HHD). The selectivity of HHD reached the highest yield (77%) when using 5 wt% $Al_2(SO_4)_3$ (supporting information Figure S12). Under such condition, the pH of the reaction system was 3.84. According to our previous study,[8a] proton acid can promote the hydrogenation of 5-HMF to HHD. $Al_2(SO_4)_3$ in aqueous solution will generate H^+ and promote the formation of HHD.

BET analysis and x-ray diffraction (XRD) showed that the specific surface area, pore volume, pore size and particle size of the metal oxides have a weak effect on the reaction of rearrangement from 5-HMF to HCPN (Supporting information part 6 and part 7).

3.2. Effect of half-sandwich complex catalysts on conversion of 5-HMF to HCPN

We evaluated the catalytic efficiency of a series of half-sandwich complex catalysts by discussing the effects of substitutes, hydrogenation activity metals and ligands (Table 2). Half-sandwich catalyst exhibited hydrogenation activity by forming a metal hydride intermidates, which can be promoted by high hydrogenation pressure.[14b,18a] Comparing catalyst 1, 2 and 3, iridium showed better activity than rhodium and ruthenium, though rhodium and ruthenium were reported to show a high activity towards the hydrogenation of ketones.[18a-18b] It may be explained by the fact that iridium hydride intermidate was more stable and showed high activity in lower hydrogenation pressure illuminated by saturation kinetic.[18a] The hydroxyl-substituted catalyst activity is greater than the methoxy-substituted catalyst, which can be explained by Hammett constants of the substituents (-OH ($\sigma_p^+ = -0.92$) >, -OMe ($\sigma_p^+ =-0.78$) >, -H ($\sigma_p^+ = 0.00$)).[8a] Strong electron-donating groups lead to higher catalytic activity. Ortho-substituent Cp*Ir was reported to exhibit good performance in the hydrogenation of carbon dioxide to formic acid[17c]. However, according to previous reports[18d-18e] and our study[18f], compared with para-substituents, ortho-substituents showed dehydrogenation activity to carbonyl compounds. Activity of catalyst 4-OH is lower than 4-OMe due to the high dehydrogenation activity of 4-OH[18d-18f]. Moreover, steric effect showed an important influence of catalyst activity. Ortho-substituents may hinder the formation of metal hydride intermediates and weaken the effect of active intermediates on substrates. Thus, catalyst 1 had higher catalytic activity than catalyst 4 and 5.

3.3. Reaction mechanism of 5-HMF to HCPN and HHD

Through the discussion of the effect of various Brønsted acids and Lewis acids, we have found that Brønsted acid is not effective in promoting the hydrogenation of 5-HMF to 3-hydroxymethylcyclopentanone (HCPN). Meanwhile, Lewis acid can greatly promote the formation of HCPN. Previous studies[9] suggested that Brønsted acid inhibited further cyclization of HHD. The studies also claimed that HHD was an important reaction intermediate in the transformation from 5-HMF to HCPN. However, their conjectures were not well supported by concrete evidence. HHD was hydrogenated in our catalytic system (supporting information part 2 and Figure S4). HCPN and HCPEN were almost undetected after the reaction. HHD is not a reaction intermediate for formation of HCPN in our catalytic system. Furthermore, we found that Brønsted acid can promote hydrogenation ring-opening of 5-HMF to HHD[8a] and Lewis acid can promote the rearrangement of 5-HMF to HCPN.

In addition, we detected a small amount of methylcyclopenten-2-ol-1-one (MCP) in the reaction, which was generated from Aldol condensation of HHD. HHD condensed via Aldol reaction to produce MCP instead of

HCPN (Scheme 2). We found that strong base and Lewis acid can promote the Aldol condensation reaction of HHD to MCP (supporting information part 1 and part 2).

On the basis of previous reports[9,13] and our speculation, the reaction is more likely to undergo Piancatelli rearrangement reaction to produce 4-hydroxy-4-(hydroxymethyl)cyclopent-2-en-1-one (HHCPEN) and then hydrogenate to HCPN. However, we almost did not detect HHCPEN in conversion to HCPN from 5-HMF. HHCPEN was unstable in our catalytic system due to hydrogenation reaction. Therefore, we tried the reaction of BHMF over metal oxide under $N_{2.}$ As expected, we had a high selectivity to get HHCPEN. In our catalytic system, HHCPEN was almost completely hydrogenated to HCPN (supporting information part 4, Figure S7 and Figure S8).

According to the research above, we proposed the following reaction mechanism (Scheme 2), which is different from previous reports.[9] Instead of being an intermediate for the formation of HCPN, we believe, HHD is a product of another reaction pathway. HHD and HCPN are in a competitive relationship, Brønsted acid is added to promote the formation of HHD, rather than inhibition of HHD continue cyclization. When Lewis acid was used as the catalyst, the reaction firstly formed 4π-electrocyclic ring. According to frontier molecular orbital theory, the highest occupied molecular orbital (HOMO) of the 4π intermediate undergoes conrotatory motion under heating and closes ring to form a five-membered ring structure.[19] This five-membered ring structure loses a hydrogen ion to form a cyclopentanone structure and finally generate HCPN via hydrogenation.

3.4. Effect of reaction conditions on conversion of 5-HMF to HCPN

Hydrogen pressure, reaction time, half-sandwich Ir complex concentration and temperature of the reaction system were investigated (Figure 8). Hydrogen pressure was found to be nearly unrelated to the yield of HCPN. When H_2 was greater than 2 MPa, the yield of HCPN was basically stabilized. As reaction proceeded, the yield of intermediate products such as BHMF and HCPEN decreased, then transformed into HCPN. After 4 h, the yield of HCPN did not increased. When the dosage of Cp*Ir was more than 0.1%, the yield of HCPN was almost stable, the decrease of Cp*Ir could affect the selectivity of HCPN. When Cp*Ir was not used, almost no HCPN was detected. Temperature changes show that the increase of temperature within a certain range can promote the reaction. When reaction temperature was low, the main reaction product was 2,5-dihydroxymethylfuran. It indicated that the reaction was not complete. As temperature rose up to 130 °C, the yield of HCPN increased to 80% or more. Then, as temperature increased, the yield of HCPN tended to be stable.

3.5. Effect of Lewis acid and Brønsted acid on conversion of furfural compounds to ketones

In addition to 5-HMF, other furfural derivatives can also rearrangement to cyclopentanone derivatives in our catalyst systems. Interestingly, they are in line with the rule that Brønsted acid promotes the conversion to straight chain ketones and Lewis acid promotes rearrangement to cyclopentanone derivative (Table 3). 5-methyl furfural can be hydrogenated to 3-methyl-cyclopentanone and 3-methyl-cyclopent-2-en-1-ketone in the Lewis acid catalysis, to 2,5-hexanedione under the Brønsted acid catalysis. Furfural can be hydrogenated to 2-cyclopentenone and cyclopentanone under Lewis acid catalysis, to levulinic acid and γ-valerolactone under Brønsted acid catalysis.

3.6. Conversion of fructose to HCPN

5-HMF can be obtained from hydrolysis of fructose in industry. In order to show the potential of our catalyst system, we studied the reaction of producing HCPN with fructose as raw material (supporting information part 11). The yield of HCPN can reach 80% (59.2% to fructose). These results prove that our catalyst system can convert crude 5-HMF from fructose hydrolysis to HCPN, with good yield.[2i]

4. Conclusions

In summary, a highly efficient Cp*Ir (III) Complex and acid co-catalyst system was developed. By using Cp*Ir and γ-Al_2O_3 (Lewis acid), the hydrogenation of 5-HMF to HCPN can get the highest TOF reported. Meanwhile, Cp*Ir and Brønsted acid can promote conversion of 5-HMF to HHD. More important, different from previous reports, we find that HHD is not a reaction intermediate for the formation of HCPN in our catalytic system. HHD condensed via Aldol reaction to produce MCP instead of HCPN. Furthermore, we found that our Cp*Ir and acid co-catalyst system is suitable for various furfural compounds. Brønsted acid and Lewis acid can promote conversion of furfural compounds to straight chain ketones and cyclopentanones respectively.

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Reference

[1] a) A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411-2502; b) D. M. Alonso, S. G. Wettstein, J. A. Dumesic, Chem. Soc. Rev. 41(2012) 8075-8098.

[2] a) M. Watanabe, Y. Aizawa, T. Iida, R. Nishimura, H. Inomata, Appl. Catal. A 295 (2005) 150-156; b) Y. Román-Leshkov, J. N. Chheda, J. A. Dumesic, Science 312 (2006) 1933-1937; c) H. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, Science 316 (2007)1597-1600; d) G. Yong, Y. Zhang, Y. Ying, Angew. Chem. Int. Ed. 120 (2008) 9485-9488; e) F. H. Richter, K. Pupovac, R. Palkovits, F. Schüth, ACS Catal. 3 (2012)123-127; f) V. Choudhary, S. H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N. S. Marinkovic, A. I. Frenkel, S. I. Sandler, D. G. Vlachos, J. Am. Chem. Soc. 135 (2013)3997-4006; g) R. J. van Putten, J. C. van der Waal, E. D. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, Chem. Rev. 113 (2013) 1499-1597; h) Q. Xu, Z. Zhu, Y. Tian, J. Deng, J. Shi, Y. Fu, BioResources 9 (2014) 303-315; i) G. Yi, S. P. Teong, X. Li, Y. Zhang, ChemSusChem **7** (2014) 2131-2135; j) L. Qi, Y. F. Mui, S. W. Lo, M. Y. Lui, G. R. Akien I. T. Horvath, ACS Catal. 4 (2014)1470-1477; k) X. Cao, S. P. Teong, D. Wu, G. Yi, H. Su, Y. Zhang, Green Chem. 17 (2015) 2348-2352; l) A. Osatiashtiani, A. F. Lee, M. Granollers, D. R. Brown, L. Olivi, G. Morales, J. A. Melero, K. Wilson, ACS Catal. 5 (2015)4345-4352.

[3] a) P. Verdeguer, N. Merat, A. Gaset, J. Mol. Catal. 85 (1993) 327-344; b) O. Casanova, S. Iborra, A. Corma, ChemSusChem 2 (2009) 1138-1144; c) S. E. Davis, L. R. Houk, E. C. Tamargo, A. K. Datye, R. J. Davis, Catal. Today 160 (2011) 55-60; d) J. M. R. Gallo, D. M. Alonso, M. A. Mellmer, J. A. Dumesic, Green Chem. 15 (2013) 85-90; e) J. Cai, H. Ma, J. Zhang, Q. Song, Z. Du, Y. Huang, J. Xu, Chem. -Eur. J. 19 (2013) 14215-14223; f) J. Deng, H. J. Song, M. S. Cui, Y. P. Du, Y. Fu, ChemSusChem **7** (2014) 3334-3340; g) G. Yi, S. P. Teong, X. Li, Y. Zhang, ChemSusChem **7** (2014) 2131-2135; h) X. Wan, C. Zhou, J. Chen, W. Deng, Q. Zhang, Y. Yang, Y. Wang, ACS Catal. 4 (2014) 2175-2185; i) X. Han, L. Geng, Y. Guo, R. Jia, X. Liu, Y. Zhang, Y. Wang, Green Chem. 18 (2016)1597-1604.

[4] a) W. Partenheimer, V. V. Grushin, Adv. Synth. Catal. 343 (2001) 102-111; b) C. Carlini, P. Patrono, A. M. R. Galletti, G. Sbrana V. Zima, Appl. Catal. A 289 (2005) 197-204; c) A. Takagaki, M. Takahashi, S. Nishimura, K. Ebitani, ACS Catal. 1 (2011) 1562-1565; d) Z.-Z. Yang, J. Deng, T. Pan, Q.-X. Guo, Y. Fu, Green Chem. 14 (2012) 2986-2989; e) Z. Zhang, Z. Yuan, D. Tang, Y. Ren, K. Lv, B. Liu, ChemSusChem **7** (2014) 3496-3504; f) J. Nie, H. J. Liu, J. Catal. 316 (2014) 57-66; g) C. Fang, J.-J. Dai, H.-J. Xu, Q.-X. Guo, Y. Fu, Chin. Chem. Lett. 26 (2015) 1265-1268; h) G. Lv, H. Wang, Y. Yang, T. Deng, C. Chen, Y. Zhu, X. Hou, ACS Catal. 5 (2015) 5636-5646; i) B. Liu, Y. Ren, Z. Zhang, Green Chem. 17 (2015) 1610-1617; j) M. Chatterjee, T. Ishizaka, A. Chatterjee, H. Kawanami, Green Chem. 2017.

[5] a) Y. R. Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, Nature 447 (2007) 982-985; b) M. Chidambaram, A. T. Bell, Green Chem. 12 (2010) 1253-1262; c) T. Thananatthanachon, T. B. Rauchfuss, Angew. Chem. Int. Ed. 49 (2010) 6616-6618; d) Y. B. Huang, M. Y. Chen, L. Yan, Q. X. Guo, Y. Fu, ChemSusChem 7 (2014) 1068-1072; e) M.-Y. Chen, C.-B. Chen, B. Zada, Y. Fu, Green Chem. 18 (2016) 3858-3866.

[6] a) R. Alamillo, M. Tucker, M. Chia, Y. P. Torres, J. A. Dumesic, Green Chem. 14 (2012) 1413-1419; b) J. Ohyama, A. Esaki, Y. Yamamoto, S. Arai, A. Satsuma, RSC Adv. 3 (2013) 1033-1036; c) S. Subbiah, S. P. Simeonov, J. M. S. S. Esperanca, L. P. N. Rebelo, C. A. M. Afonso, Green Chem. 15 (2013) 2849-2853; d) H. Cai, C. Li, A. Wang, T. Zhang, Catal. Today 234 (2014) 59-65; e) Y. Nakagawa, K. Takada, M. Tamura, K. Tomishige, ACS Catal. 4 (2014) 2718-2726; f) A. J. Kumalaputri, G. Bottari, P. M. Erne, H. J. Heeres, K. Barta, ChemSusChem 7 (2014) 2266-2275; g) W. Hao, W. Li, X. Tang, X. Zeng, Y. Sun, S. Liu, L. Lin, Green Chem. 18 (2016) 1080-1088.

[7] a) T. S. Hansen, K. Barta, P. T. Anastas, P. C. Ford, A. Riisager, *Green Chem.* 2012, 14, 2457-2461; b) X. Kong, Y. Zhu, H. Zheng, F. Dong, Y. Zhu, Y.-W. Li, *RSC Adv.* 2014, 4, 60467-60472; c) Y. Zhu, X. Kong, H. Zheng, G. Ding, Y. Zhu, Y.-W. Li, *Catal. Sci. Technol.* 2015, 5, 4208-4271; d) X. Kong, R. Zheng, Y. Zhu, G. Ding, Y. Zhu, Y.-W. Li, *Green Chem.* 2015, 17, 2504-2514; e) X. Kong, Y. Zhu, H. Zheng, X. Li, Y. Zhu, Y.-W. Li, *ACS Catal.* 2015, 5, 5914-5920; f) A. B. Gawade, M. S. Tiwari, G. D. Yadav, *ACS Sustainable Chem. Eng.* 2016, 4, 4113-4123.

[8] a) W. P. Wu, Y. J. Xu, R. Zhu, M. S. Cui, X. L. Li, J. Deng, Y. Fu, ChemSusChem 9 (2016) 1209-1215; b) G. C. A. Luijkx, N. P. M. Huck, F. van Rantwijk, L. Maat, H. van Bekkum, Heterocycles 77 (2009) 1037-1044; c) F. liu, M. Audemar, K. V. De Oliveira, J. M. Clacens, F. De Campo, F. Jerome, Green Chem. 16 (2014) 4110-4114; d) F. Liu, M. Audemar, K. V. De Oliveira J. M. Clacens, F. De Campo, F. Jerome, ChemSusChem 7 (2014) 2089-2093; e) Y. Yang, Z. Du, J. Ma, F. Lu, J. Zhang, J. Xu, ChemSusChem 7 (2014) 1352-1356; f) Z. Xu, P. Yan, W. Xu, X. Liu, Z. Xia, B. Chung, S. Jia, Z. C. Zhang, ACS Catal. 5 (2015) 788-792; g) Z. Xu, P. Yan, H. Li, K. Liu, X. Liu, X. Jia, Z. C. Zhang, ACS Catal. 6 (2016) 3784-3788; h) Z. Xu, P. Yan, Z. C. Zhang, Chin. J. Org. Chem. 37 (2017) 40-46.

[9] a) J. Ohyama, R. Kanao, A. Esaki, A. Satsuma, Chem. Commun. 50 (2014) 5633-5636; b) J. Ohyama, R. Kanao, Y. Ohira, A. Satsuma, Green Chem. 18 (2016) 676-680; c) N. Perret, A. Grigoropoulos, M. Zanella, D. T. Manning, J. B. Claridge, M. J. Rosseinsky, ChemSusChem 9 (2016) 521-531; d) R. Ramos, A. Grigoropoulos, N. Perret, M. Zanella, A. P. Katsoulidis, T. D. Manning, J. B. Claridge, M. J. Rosseinsky. Green Chem. 19 (2017)1701-1713.

[10] T. Kitahara, Y. Warita, M. Abe, M. Seya, Y. Takagi, K. Mori, *Agric. Biol. Chem.* 55 (1991) 1013-1017.

[11] P. Marcé, Y. Díaz, M. I. Matheu, S. Castillón, *Org. Lett.* 10 (2008) 4735-4738.

[12] a) Y. Yang, Z. Du, Y. Huang, F. Lu, F. Wang, J. Gao, J. Xu, Green Chem. 15 (2013) 1932-1940; b) G. S. Zhang, M. M. Zhu, Q. Zhang, Y. M. Liu, H. Y. He, Y. Cao, Green Chem. 18 (2016) 2155-2164; c) M. Hronec, K. Fulajtarová, Catal. Commun. 24 (2012) 100-104; d) M. Hronec, K. Fulajtárova, M. Mičušík, Appl. Catal. A 468 (2013) 426-431; e) M. Hronec, K. Fulajtárova, T. Soták. Appl. Catal. B 154 (2014) 294-300; f) M. Hronec, K. Fulajtárova, T. Liptaj, M. Stolcová, N. Prónayová, T. Soták, Biomass Bioenergy 63 (2014) 291-299; g) M. Hronec, K. Fulajtárová, I. Vávra, T. Soták, E. Dobročkab, M. Mičušík, *Appl. Catal. B* 181 (2016) 210-219; h) D. C. Elliott, T. R. Hart, Energy Fuels 23 (2009) 631-637; i) V. V. Ordomsky, J. C. Schouten, J. van der Schaaf, T. A. Nijhuis, Appl. Catal. A 451 (2013) 6-13; j) J. Guo, G. Xu, Z. Han, Y. Zhang, Y. Fu, Q. Guo, Acs Sustain. Chem. Eng. 2 (2014) 2259-2266; k) X. L. Li, J. Deng, J. Shi, T. Pan, C. G. Yu, H. J. Xu, Y. Fu, Green Chem. 17 (2015) 1038-1046; l) R. Fang, H. Liu, R. Luque, Y. Li, Green Chem. 17 (2015) 4183-4188; m) X. Hu, R. J. M. Westerhof, L. Wu, D. Dong, C. Z. Li, Green Chem. 17 (2015) 219-224; n) Y. Xu, S. Qiu, J. Long, C. Wang, J. Chang, J. Tan, Q. Liu, L. Ma, T. Wang, Q. Zhang, RSC Adv. 5 (2015) 91190-91195.

[13] a) G. Piancatelli, A. Scettri, S. Barbadoro, Tetrahedron Lett. 17 (1976) 3555-3558; b) G. Piancatelli, D. M. Auria, D. F. Onofrio, Synthesis 9 (1994) 867-889; c) O. N. Faza, C. S. López, R. Álvarez, A. R. de Lera, Chem. -Eur. J. 10 (2004) 4324-4333; d) G. K. Veits, D. R. Wenz, J. R. de Alaniz, Angew. Chem. Int. Ed. 49 (2010) 9484-9487; e) L. I. Palmer, R. J. de Alaniz, Angew. Chem. Int. Ed. 50 (2011) 7167-7170; f) R. Chung, D. Yu, V. T. Thai, A. F. Jones, G. K. Veits, J. R. de Alaniz, J. E. Hein, ACS Catal. 5 (2015) 4579-4585.

[14] a) J. Deng, Y. Wang, T. Pan, Q. Xu, Q. X. Guo, Y. Fu, ChemSusChem 6 (2013) 1163-1167; b) W. P. Wu, Y. J. Xu, S. W. Chang, J. Deng, Y. Fu, ChemCatChem 8 (2016) 3375-3380.

[15] C. White, A. Yates, P. M. Maitlis, Inorg. Synth 29 (1992) 228-234.

[16] a) N. Y. Topsøe, K. Pedersen. E. G. Derouane, J. Catal. 70 (1981) 41-52; b) C. V. Hidalgo, H. Itoh, T. Hattori, M. Niwa, Y. Murakami, J. Catal. 85 (1984) 362-369.

[17] a) E. P. Parry, J. Catal 2 (1963) 371-379; b) C. Emeis, J. Catal. 141 (1993) 347-354; c) A. Corma, Chem. Rev. 95 (1995) 559-614; d) A. Corma, M. J. D. Cabanas, J. M. Triguero, F. Rey, J. Rius, Nature 418 (2002) 514-517; e) V. Santacroce, F. Bigi, A. Casnati, R. Maggi, L. Storaro, E. Moretti, L. Vaccaro, G. Maestri, Green Chem. 18 (2016) 5764-5768; f) V. V. Kumar, G. Naresh, S. Deepa, P. G. Bhavani, M. Nagaraju, M. Sudhakar, K. V. R. Chary, J. Tardio, S. K. Bhargava, A. Venugopal, Appl. Catal. A 531 (2017)169-176.

[18] a) T. P. Brewster, A. J. M. Miller, D. M. Heinekey, K. I. Goldberg, J. Am. Chem. Soc. 135 (2013)16022-16025; b) J. S. M. Samec, J. E. Bäckvall, P. G. Andersson, P. Brandtb, Chem. Soc. Rev. 35 (2006) 237-248; c) W. H. Wang, J. T. Muckerman, E. Fujita, Y. Himeda, ACS Catal. 3 (2013) 856-860; d) R. Kawahara, K. Fujita, R. Yamaguchi, J. Am. Chem. Soc. 134 (2012) 3643-3646; e) R. Kawahara, K. Fujita, R. Yamaguchi. Angew. Chem. Int. Ed., 51 (2012) 12790-12794; f) R. Zhu, B. Wang, M. Cui, J Deng, X. Li, Y. Ma, Y. Fu, Green Chem. 18 (2016) 2029-2036.

[19] W. Kirmse, N. G. Rondan, K. N. Houk, J. Am. Chem. Soc. 106 (1984) 7989-7991.

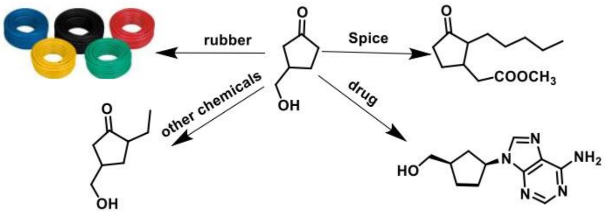


Figure 1. Application of 3-hydroxymethyl cyclopentanone.

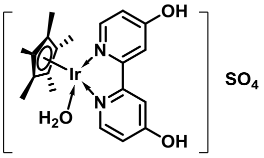


Figure 2. $[CP^*Ir(4,4'-(OH)_2-bpy)(OH_2)]SO_4$.

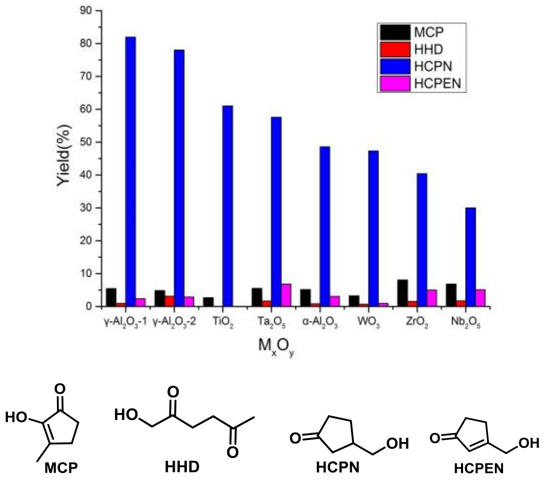


Figure 3. Product distributions obtained by the reaction using CP*Ir with various metal oxides. Reaction condition: HMF aq. (0.067 M, 3 mL); Cp*Ir (0.1 mol%); a metal oxide (10 mg); H_2 3 MPa; 130 °C; 4 h. γ-Al_2O_3-1: 30 nm, γ-Al_2O_3-2: 10 nm.

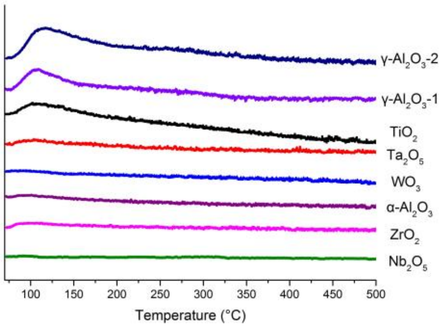


Figure 4. NH_3-TPD profiles of metal oxides used in the reaction.

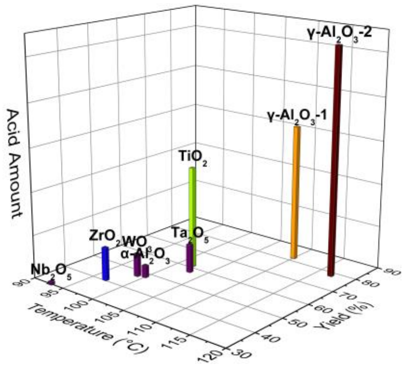


Figure 5. The relation of desorption temperature of NH_3, acid amount and yield of HCPN for metal oxides used in the reaction.

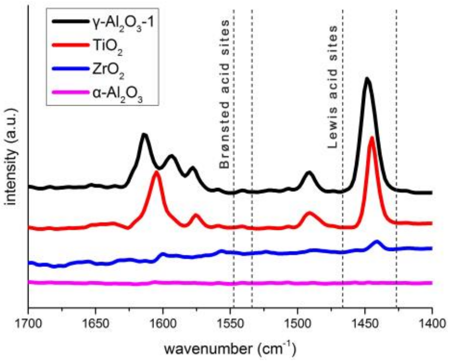


Figure 6. The pyridine adsorption infrared in 150 °C of metal oxides used in the reaction.

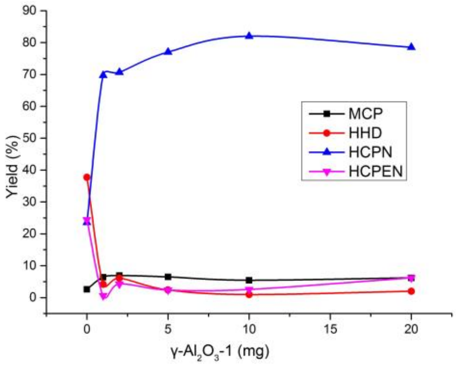


Figure 7. Product distributions obtained by the reaction using Cp*Ir with increasing γ-Al_2O_3-1. Reaction condition: HMF aq. (0.067 M, 3 mL); Cp*Ir (0.1 mol%); H_2 3 MPa; 130 °C; 4 h.

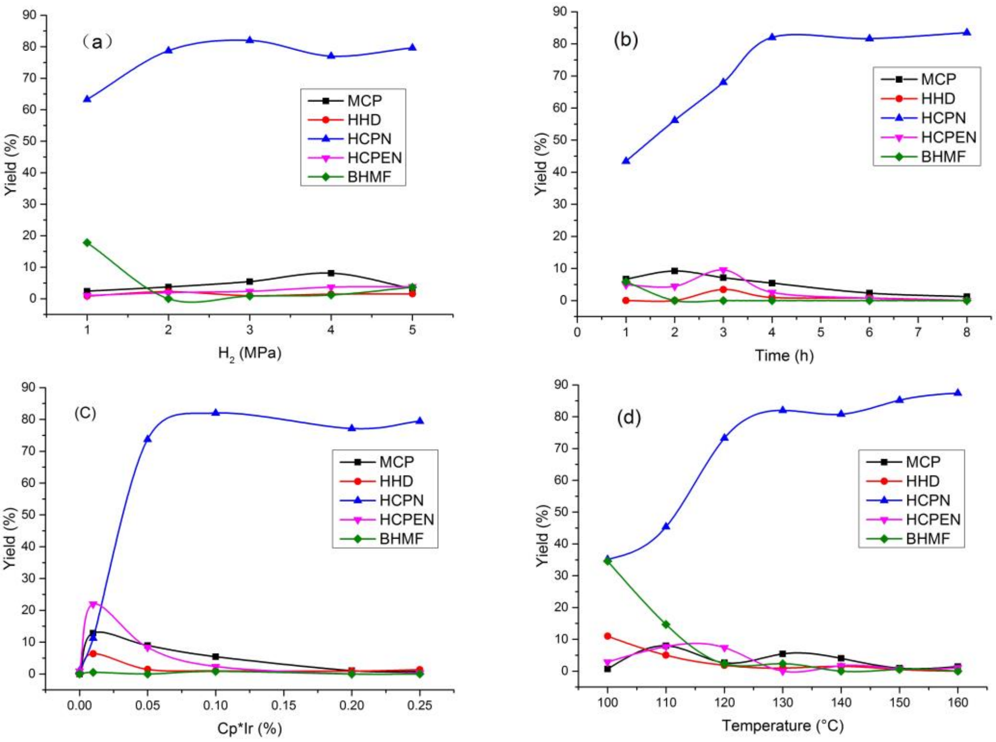
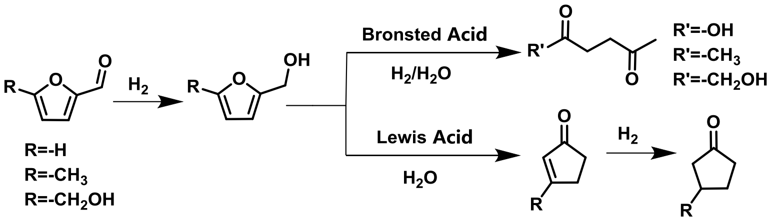
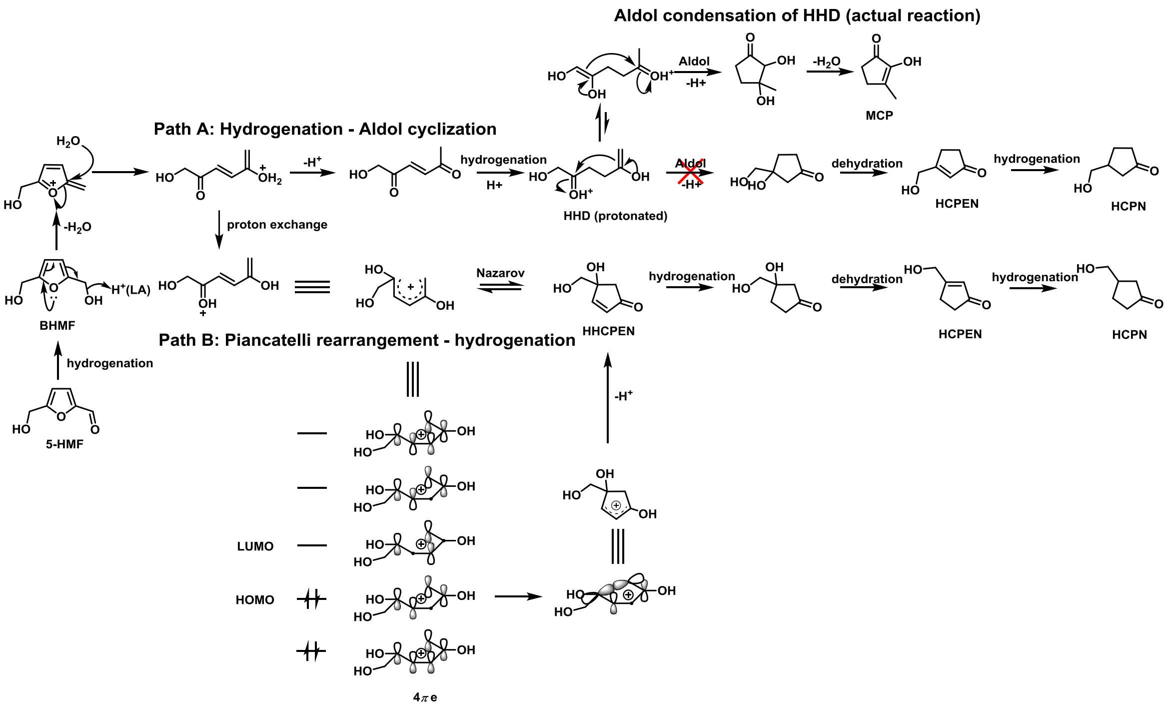


Figure 8. The influence of H_2, time, Cp*Ir concentration and temperature. Reaction condition: (a) (b) (c) (d) 5-HMF aq. (0.067 M, 3 mL), γ-Al_2O_3-1 (10 mg); (a) (b) (d) Cp*Ir (0.1 mol%); (b) (c) (d) H_2 3 MPa; (a) (b) (c) 130 °C; (a) (c) (d) 4 h.



Scheme 1. The Influence of Lewis Acid and Brønsted Acid to Reaction



Sheme 2. The Mechanism of the Reaction We Proposed. LA= Lewis Acid.

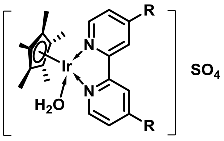
Table 1. Hydrogenation of 5-HMF to HCPN Reported by Previous Study and This Work

Entry	Catalyst	Condition	Conv. [%]	Yield [%]	TOF [h^{-1}][a]	Ref.
1	Au/Nb_2O_5	8MPa H_2/ 140 °C/ 12 h	>99	86	50	9a
2	Pt/SiO_2 and Ta_2O_5	3MPa H_2/ 140 °C/ 12 h	100	82	27	9b
3	Ni/Al_2O_3 metal hydrate	2MPa H_2/ 140 °C/ 6 h	100	81	1	9c
4	Cu/Al_2O_3 metal hydrate	2MPa H_2/ 180 °C/ 6 h	100	86	1	9d
5	Cp*Ir and γ-Al_2O_3	3MPa H_2/ 130 °C/ 4 h	100	82	205	this work

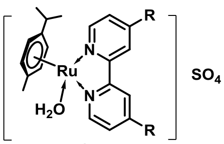
[a] TOF is calculated by molar ratio of product/catalyst. TOF is the average value of 1 h.

Table 2. The Hydrogenation of 5-HMF by Using Different Half-sandwich Complexes[a]

Cat.	Conv.	Selectivity [%]				
	[%]	MCP	HHD	HCPN	HCPEN	BHMF
1-H	60	7	0	3	34	2
1-OH	100	5	1	82	2	0
1-OMe	98	5	5	22	41	0
2-OH	99	8	1	15	48	0
2-OMe	45	2	1	0	7	0
3-OH	99	16	2	13	44	0
3-OMe	32	3	0	3	6	22
4-OH	89	9	3	2	36	0
4-OMe	93	14	2	7	51	1
5-H[b]	100	10	4	20	54	0
5-OH[b]	98	1	0	40	5	36
5-OMe[b]	99	13	2	24	48	0



1



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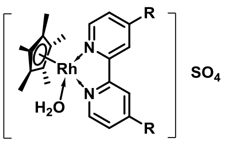

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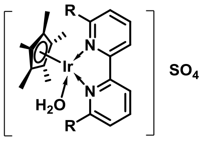

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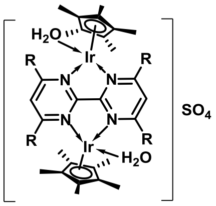
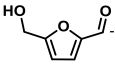
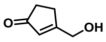
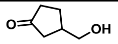
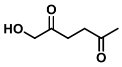
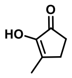
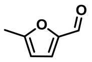
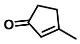
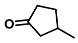
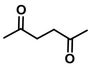
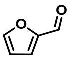
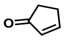
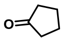
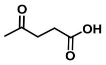
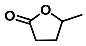


5

R = -H
= -OH
= -OMe

Reaction conditions: [a] 5-HMF, 5-methyl furfural (0.067 M, 3 mL), half-sandwich complexes (0.1 mol%), γ-Al_2O_3-1 (10 mg), 3 MPa H_2, 130 °C, 4 h; [b] half-sandwich complexes (0.05 mol%).

Table 3. Effect of acid on conversion of furfural compounds to ketones

Entry	Substrate	Acid	Conv. [%]	Yield [%]			
1		10 mg γ-Al_2O_3-1[a]	100		2		82
		5 wt% $Al_2(SO_4)_3$[b]	100		74		Trace
		pH=2.5 formic acid buffer solution[c]	100		90		Trace
2		10 mg γ-Al_2O_3-1[a]	100		30		24
		pH=1.5 phosphate buffer solution[d]	100		39		
3		10 mg γ-Al_2O_3-1[a]	100		60		Trace
		pH=1.0 phosphate buffer solution[e]	100		41		9

Reaction conditions: [a] 5-HMF, 5-methyl furfural or furfural aq. (0.067 M, 3 mL), Cp*Ir (0.1 mol%), γ-Al_2O_3-1 (10 mg), H_2 3 MPa, 130 °C, 4 h. [b] 5-HMF aq. (0.067 M, 3 mL), Cp*Ir (0.1 mol%), H_2 3 MPa, 130 ˚C, 4 h. [c] 5-HMF (0.2 M), pH = 2.5 formic acid buffer solution (1 M), Cp*Ir (0.01 mol%), 130 ˚C, 2 h.[8a] [d] 5-methyl furfural (0.067 M), 3mL pH = 1.5 phosphate buffer solution (0.1 M), Cp*Ir (0.1 mol%), H_2 3 MPa, 130 °C, 4 h. [e] Furfural (0.60 mmol), 2 mL pH = 1.0 phosphate buffer solution (0.1 M), Cp*Ir (0.0083 mol%), 1 MPa H_2, 120 °C, 4 h.[14b]