Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

# Hydrogen Production from Cellulose Catalyzed by Iridium Complex in Ionic Liquid under Mild Conditions

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## 1. General

All reactions and manipulations were performed under argon atmosphere using standard Schlenk techniques. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded on JEOL ECX-500 spectrometers. Gas chromatograph analyses of hydrogen and carbon dioxide were performed on a GL-Sciences GC390 gas chromatograph with packed columns (Molecular Sieve 5A and Gaskuropack 54). Gas chromatograph analysis of organic product was performed on a GL-Sciences GC353B gas chromatograph with a capillary column (GL-Sciences TC-17 and InertCap 5). Fuel cell experiments were performed using reversible PEM fuel cell and motor and fan with propeller blade included in SOLAR HYDROGEN SCIENCE KIT (FCJJ-16, made by HORIZON FUEL CELL TECHNOLOGIES) and LED LAMPS (25000mcd@1.2V, Pure Green, OSG5DA5111A-1V, made by OptoSupply Limited) and Sealed Clip Kit M (ELPA PU-12NH, made by Asahi Electric Corporation). As cellulose, Avicel® PH-101 (~50 μm particle size, made by SIGMA-ALDRICH, Co.) was used. Distilled water was degassed prior to use. The catalyst, $[Cp^*IrCl_2]_2$,[1] (Cp*: η$^5$-pentamethylcyclopentadienyl) was prepared according to the literature method. Organic solvents were dried by passage through columns (either alumina or activated molecular sieves) on a Glass Contour solvent system. All other reagents are commercially available and were used as received.

## 2. General procedure for optimization of reaction conditions for hydrogen production from cellulose shown in Table 1:

In a two-neck round flask, ionic liquid was placed and dried under vacuum for 0.5 h. After the introduction of argon, cellulose (1.0 g) was added and magnetically stirred for 0.5 h at 100 ºC. Then, the catalyst (1.0 mol%metal) and water (0.50 mL) were added, and the reaction mixture was magnetically stirred for 24 h in an oil bath with its temperature of 135 ºC. The apparatus for the reactions shown in Table 1 was Figure S1. In the reactions shown in Table 1, the evolved gas was passed through a solution of 10 M $NaOH_{aq}$ to trap carbon dioxide generated by the reaction. The hydrogen gas was collected in a gas burette. The yield of hydrogen was calculated using the ideal gas law. The yields of hydrogen are indicated as follows: 100% yield corresponds to the formation of 1 mol of hydrogen from 1 mol of glucose unit in cellulose.

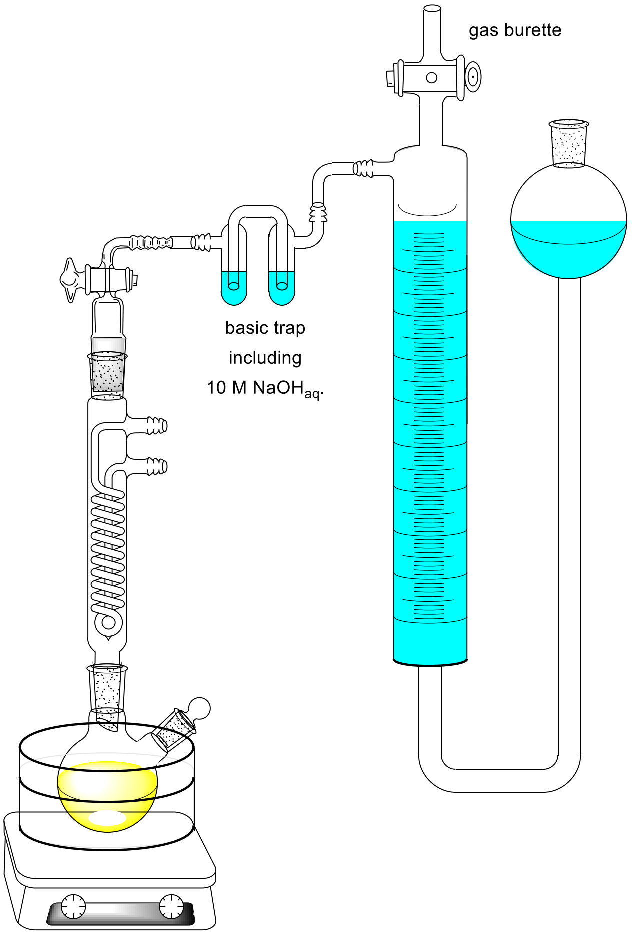
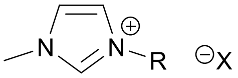


**Figure S1** The reaction setup for hydrogen production from cellulose shown in Table 1 and Table S2.

## 3. General procedure for optimization of reaction conditions for hydrogen production from cellulose shown in Table S1:

In a two-neck round flask, ionic liquid was placed and dried under vacuum for 0.5 h. After the introduction of argon, cellulose (1.0 g) was added and magnetically stirred for 0.5 h at 100 ºC. Then, the catalyst (1.0 mol%metal) and water (0.50 mL) were added, and the reaction mixture was magnetically stirred for 24 h in an oil bath with its temperature of 135 ºC. The apparatus for the reactions shown in Table S1 was Figure S2. In the reactions shown in Table S1, the evolved gas was directly collected in a gas burette. The ratio of hydrogen and carbon dioxide was determined by GC analysis. The yield of hydrogen was calculated using the ideal gas law. The yields of hydrogen are indicated as follows: 100% yield corresponds to the formation of 1 mol of hydrogen from 1 mol of glucose unit in cellulose.

**Table S1** Optimization of reaction conditions for hydrogen production from cellulose[a]



[BMIM][OAc]: R = *n*-Bu, X = OAc
[EMIM][OAc]: R = Et, X = OAc
[BMIM][Cl]: R = *n*-Bu, X = Cl
[BMIM][$HSO_4$]: R = *n*-Bu, X = $HSO_4$
[BMIM][$SbF_6$]: R = *n*-Bu, X = $SbF_6$

$$\underset{\substack{\text{cellulose} \\ \text{1.0 g}}}{(C_6H_{10}O_5)_n} \xrightarrow[\text{Ionic liquid (5.0 g), 135 °C, 24 h}]{\substack{\text{Ir cat. (1.0 mol\%metal)} \\ H_2O\text{ (0.50 mL)}}} H_2$$

| Entry | Catalyst | Ionic liquid | Volume of evoluted gas | Ratio of $H_2$:$CO_2$[b] | Yield of $H_2$[c] |
|---|---|---|---|---|---|
| 1 | $IrCl_3$•$5H_2O$ | [BMIM][OAc] | 107 mL | 54:46 | 39% |
| 2 | [Ir(cod)Cl]$_2$ | [BMIM][OAc] | 113 mL | 58:42 | 43% |
| 3 | [Cp*IrCl$_2$]$_2$ | [BMIM][OAc] | 133 mL | 66:34 | 59% |
| 4 | [Ru(*p*-cymene)Cl$_2$]$_2$ | [BMIM][OAc] | 121 mL | 54:46 | 44% |
| 5 | [Cp*RhCl$_2$]$_2$ | [BMIM][OAc] | 122 mL | 57:43 | 46% |
| 6 | [Cp*IrCl$_2$]$_2$ | [EMIM][OAc] | 118 mL | 70:36 | 55% |
| 7 | [Cp*IrCl$_2$]$_2$ | [BMIM][Cl] | 2 mL | 7:93 | trace |
| 8 | [Cp*IrCl$_2$]$_2$ | [BMIM][$HSO_4$] | 1 mL | 6:94 | trace |
| 9 | [Cp*IrCl$_2$]$_2$ | [BMIM][$SbF_6$] | 1 mL | 8:92 | trace |
| 10[d] | [Cp*IrCl$_2$]$_2$ | [BMIM][OAc] | 5 mL | 26:74 | trace |
| 11 | none | [BMIM][OAc] | 8 mL | 32:68 | <2% |
| 12[e] | [Cp*IrCl$_2$]$_2$ | none | 0 mL | – | 0% |
| 13[f] | [Cp*IrCl$_2$]$_2$ | [BMIM][OAc] | 96 mL | 80:20 | 52% |

[a] The reaction was carried out with cellulose (1.0 g, 6.2 mmol), catalyst (1.0 mol%metal), and water (0.50 mL) in ionic liquid (5.0 g) at 135 ºC for 24 h. [b] Determined by GC. [c] Yield of $H_2$ is based on glucose unit, *i.e.* 100% yield corresponds to the formation of 1 mol $H_2$ from 1 mol of glucose unit. [d] No cellulose was used. [e] Water (5.0 mL) was used. [f] Water was not added.

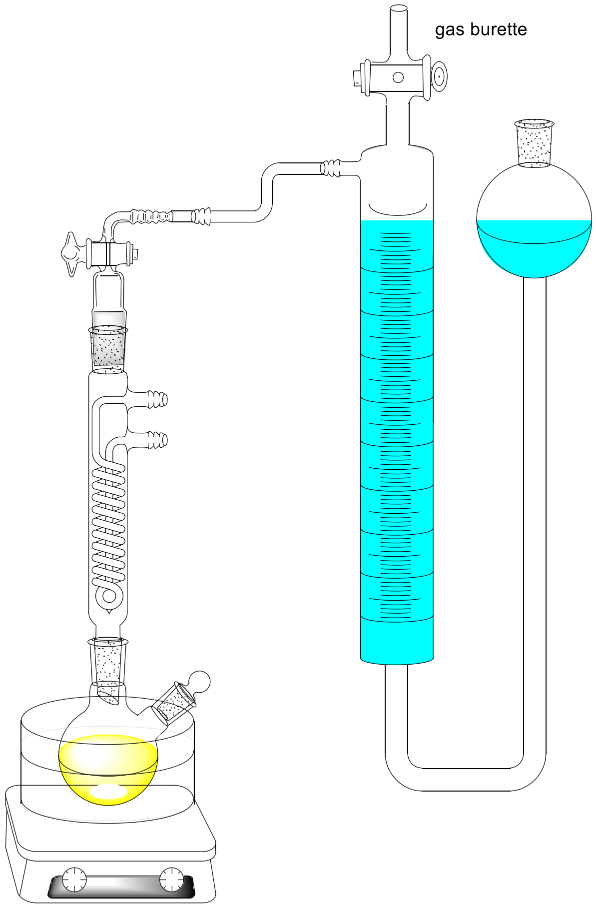
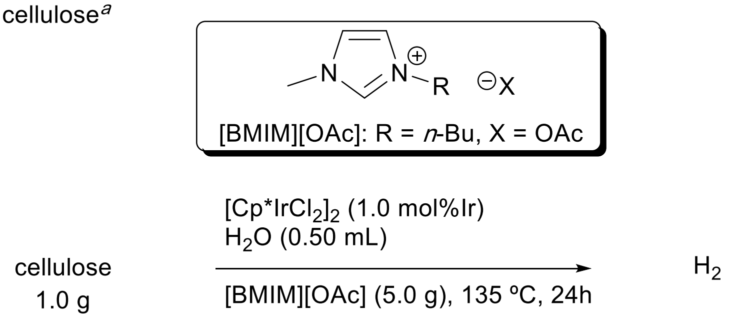


**Figure S2** The reaction setup for hydrogen production from cellulose shown in Table S1.

## 4. General procedure for optimization of the amounts of [BMIM][OAc] and water for the hydrogen production from cellulose shown in Table S2:

In a two-neck round flask, [BMIM][OAc] (0-7.0 g) was placed and dried under the vacuum for 0.5 h. After the introduction of argon, cellulose (1.0 g) was added and magnetically stirred for 0.5 h at 100 ºC. Then, the catalyst $[Cp^*IrCl_2]_2$ (1.0 mol%Ir) and water (0-0.70 mL) were added, and the reaction mixture was magnetically stirred for 24 h in an oil bath with its temperature of 135 ºC. The apparatus for the reactions shown in Table S2 was Figure S1. In the reactions shown in Table S2, the evolved gas was passed through a solution of 10 M $NaOH_{aq}$ to trap carbon dioxide generated by the reaction. The hydrogen gas was collected in a gas burette. The yield of hydrogen was calculated using the ideal gas law. The yields of hydrogen are indicated as follows: 100% yield corresponds to the formation of 1 mol of hydrogen from 1 mol of glucose unit in cellulose.

**Table S2** Optimization of the reaction conditions for the hydrogen production from cellulose[a]



| Entry | [BMIM][OAc] (g) | $H_2O$ (mL) | Volume of evolved $H_2$[b] | Yield of $H_2$[c] |
|---|---|---|---|---|
| 1 | 7.0 | 0.50 | 86 mL | 58% |
| 2 | 5.0 | 0.50 | 90 mL | 60% |
| 3 | 3.0 | 0.50 | 77 mL | 52% |
| 4[d] | none | 0.50 | 0 mL | 0% |
| 5 | 5.0 | 0.70 | 90 mL | 60% |
| 6 | 5.0 | 0.30 | 87 mL | 58% |
| 7 | 5.0 | none | 78 mL | 52% |

[a] The reaction was carried out with cellulose (1.0 g, 6.2 mmol), catalyst (1.0 mol%metal), and water (0.50 mL) in ionic liquid (5.0 g) at 135 ºC for 24 h. [b] $CO_2$ was absorbed by a basic trap. [c] Yield of $H_2$ is based on glucose unit, *i.e.* 100% yield corresponds to the formation of 1 mol $H_2$ from 1 mol of glucose unit. [d] Water (5.0 mL) was used.

## 5. Qualitative and quantitative analysis of evolved gas by the hydrogen production from cellulose shown in Table 1 and Table S1:

Firstly, evolved gas under optimal condition (Table 1, entry 3) was qualitatively analyzed by GC.
The chromatogram of the evolved gas by the reaction of entry 3 in Table 1 is shown as Figure S3(a). The chromatogram of the standard pure hydrogen gas is shown as Figure S3(b). By the comparison of Figure S3(a) and S3(b), it was confirmed that pure hydrogen was obtained by the reaction of entry 3 in Table 1.
Additionally, the chromatogram of the evolved gas by the reaction without basic trap of entry 3 in Table S1 is shown as Figure S3(c). The chromatogram of the standard gas composed of hydrogen (75%) and carbon dioxide (25%) is shown as Figure S3(d). From these results, it was revealed that the gas directly collected in the gas burette by the reaction of entry 3 in Table S1 contained hydrogen and carbon dioxide in the ratio of 66:34.
Furthermore, time-resolved quantitative analysis under optimal condition (Table 1, entry 3) was also performed. The generated gas was collected in a gas burette and its volume was measured during the course of reaction. A plot of the yield of hydrogen is shown in Figure S4.

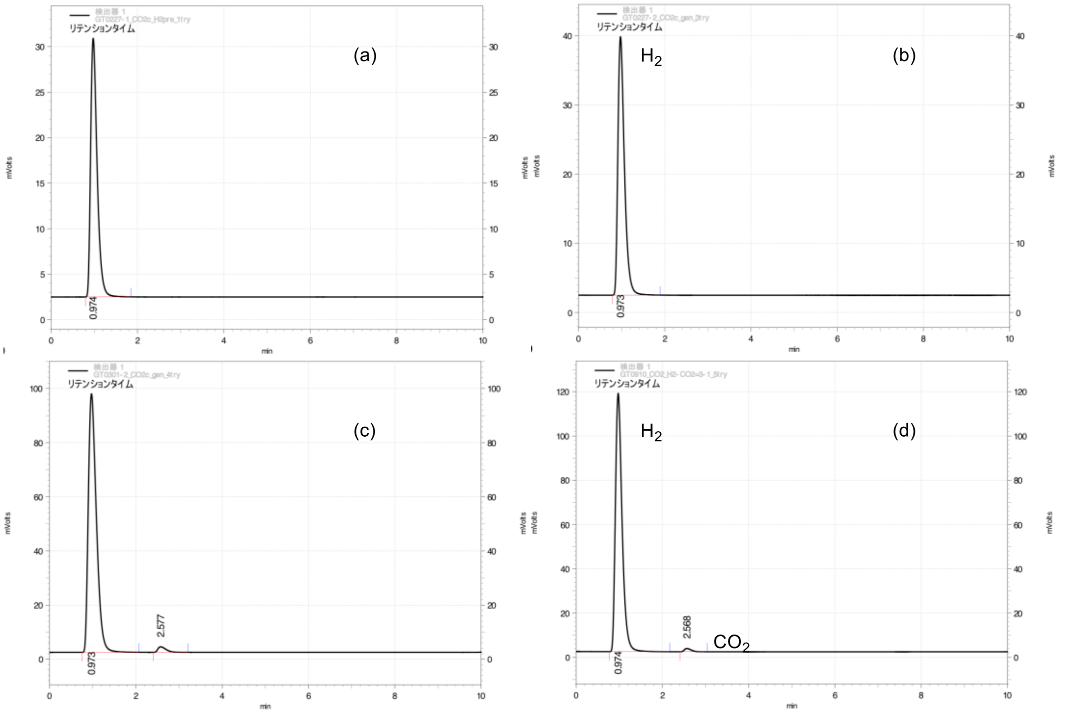


**Figure S3.** Results of GC analyses. (a) The chromatogram of the evolved gas by hydrogen production from cellulose under optimal condition with basic trap (Table 1, entry 3). (b) The chromatgarm of the standard gas of pure hydrogen. (c) The chromatogram of the evolved gas by hydrogen production from cellulose under optimal condition without basic trap (Table S1, entry 3). (d) The chromatgarm of the standard gas composed of hydrogen (75%) and carbon dioxide (25%).

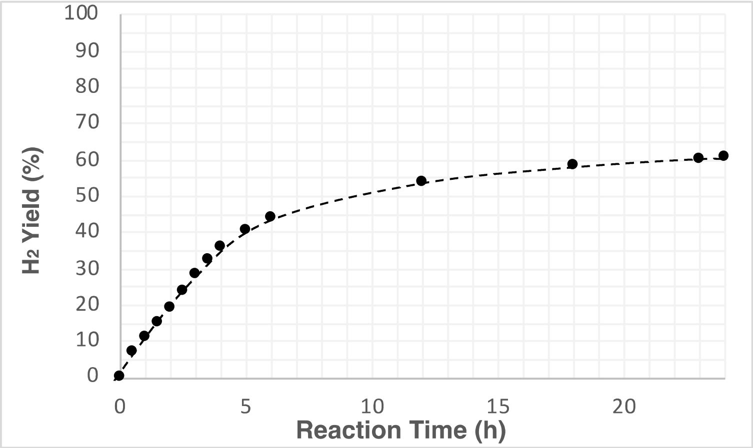


**Figure S4** A plot of the yield of hydrogen in the dehydrogenation of cellulose under optimal condition (Table 1, entry 3).

## 6. Rhodium-catalyzed hydrogenation of 1-decence by hydrogen evolved from cellulose shown in Scheme 2:

In a two-neck round flask **I**, [BMIM][OAc] (5.0 g) was placed and dried under the vacuum for 0.5 h. After the introduction of argon, cellulose (1.0 g) was added and magnetically stirred for 0.5 h at 100 ºC. Then, the catalyst $[Cp^*IrCl_2]_2$ (1.0 mol%Ir) and water (0.50 mL) were added. Another two-neck round flask **II**, in which 1-decene (1.40 g, 10.0 mmol) and $Rh(PPh_3)_3Cl$ (0.463 g, 0.500 mmol) and benzene (5.0 mL) were placed under an atmosphere of argon, was prepared. The flask **I** was connected to the flask **II** with a syringe as a pressure regulator (Figure S5). The flask **I** was magnetically stirred for 24 h under reflux condition (bath temperature was 135 ºC) and simultaneously the flask **II** was magnetically stirred for 24 h at 60 ºC. The yield of decane was determined by GC analysis using undecane as an internal standard. The formation of 3.5 mmol decane was confirmed and it corresponds to 95% yield based on the hydrogen generated in the flask **I**, which is estimated to be 3.7 mmol at this optimal conditions.

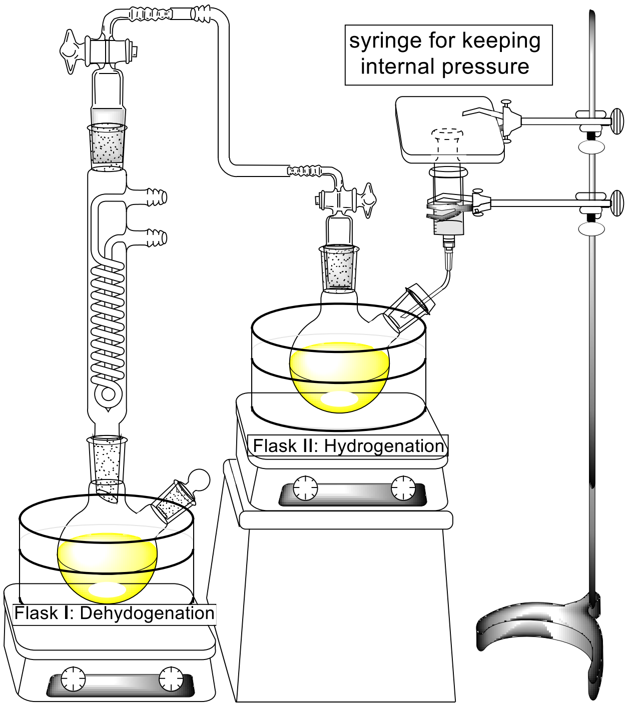
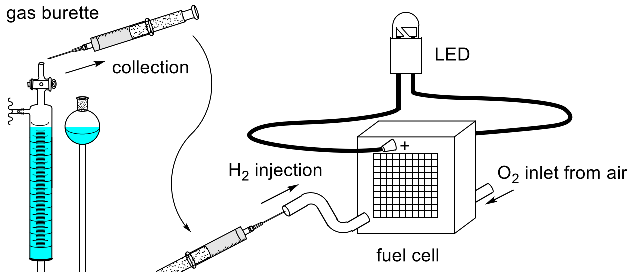


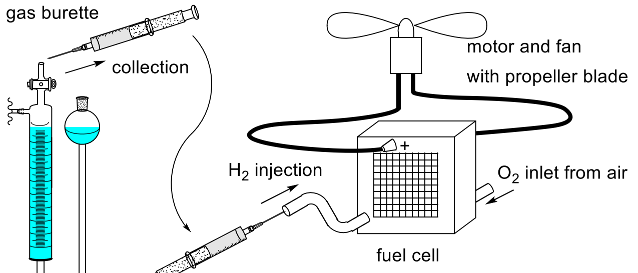
**Figure S5** The reaction setup for rhodium-catalyzed hydrogenation of 1-decence by hydrogen evolved from cellulose shown in Scheme 2.

## 7. Application of the produced hydrogen to generation of electricity in a fuel cell:

In a two-neck round flask, [BMIM][OAc] (5.0 g) was placed and dried under the vacuum for 0.5 h. After the introduction of argon, cellulose (1.0 g) was added and magnetically stirred for 0.5 h at 100 ºC. Then, the catalyst (1.0 mol%metal) and water (0.50 mL) were added, and the reaction mixture was magnetically stirred for 24 h in an oil bath with its temperature of 135 ºC. The setup shown in Figure S2 was used. Evolved gas composed of hydrogen and carbon dioxide was directly collected in a gas burette.
The circuit to emit an LED was set up shown in Figure S6a. In this circuit, a fuel cell is connected to LED via connecting leads and hydrogen inlet and oxygen inlet are at anode side and cathode side, respectively. When the collected gas in the gas burette after the reaction was injected into the fuel cell, the emission of LED was observed (Figure 1).
Similarly, the circuit to drive a motor was also set up shown in Figure S6b. In this circuit, the motor and fan with propeller blade was used instead of LED of the above circuit. When the collected gas in the gas burette after the reaction was injected into the fuel cell, the move of propeller blade was obsedved.
A video files of the light emission of the LED and the rotation of the motor are provided as other supporting information files.



a) The circuit connecting to LED



b) The circuit connecting to motor

**Figure S6** Schematic view of circuit for application of the produced hydrogen to generation of electricity in a fuel cell.

## 8. Procedures for reactions associated with hydrogen production from cellulose shown in Scheme 3:

(Scheme 3a and b) In a two-neck round flask, [BMIM][OAc] (5.0 g) was placed and dried under the vacuum for 0.5 h. After the introduction of argon, substarte (1.0 g) was added and magnetically stirred for 0.5 h at 100 ºC. Then, the catalyst $[Cp^*IrCl_2]_2$ (1.0 mol%Ir) and water (0.50 mL) were added, and the reaction mixture was magnetically stirred for 24 h in an oil bath with its temperature of 135 ºC using the setup shown in Figure S1. The evolved gas was passed through a solution of 10 M $NaOH_{aq}$ to trap carbon dioxide generated by the reaction. The hydrogen gas was collected in a gas burette. The yield of hydrogen was calculated using the ideal gas law. The results are shown in Scheme 3a and b.
(Scheme 3c) In a two-neck round flask, [BMIM][OAc] (15 g) was placed and dried under the vacuum for 0.5 h. After the introduction of argon, toilet paper (1.0 g) was added and magnetically stirred for 0.5 h at 100 ºC. Then, the catalyst $[Cp^*IrCl_2]_2$ (1.0 mol%Ir) and water (0.50 mL) were added, and the reaction mixture was magnetically stirred for 24 h in an oil bath with its temperature of 135 ºC using the setup shown in Figure S2. The evolved gas was directly collected in a gas burette and the yield of hydrogen was calculated using the ideal gas law. The result is shown in Scheme 3c (47 mL of hydrogen along with 8 mL of carbon dioxide was obtained). We also performed the similar reaction using the setup shown in Figure S1 (with a basic trap), which led to the collection of 47 mL of pure hydrogen in the gas burette.

## 9. Examination of the reusability of the catalyst shown in Scheme 4:

In a two-neck round flask, [BMIM][OAc] (5.0 g) was placed and dried under vacuum for 0.5 h. After the introduction of argon, cellulose (1.0 g) was added and magnetically stirred for 0.5 h at 100 ºC. Then, the catalyst $[Cp^*IrCl_2]_2$ (1.0 mol%Ir) and water (0.50 mL) were added, and the reaction mixture was magnetically stirred for 24 h in an oil bath with its temperature of 135 ºC using the setup shown in Figure S1.

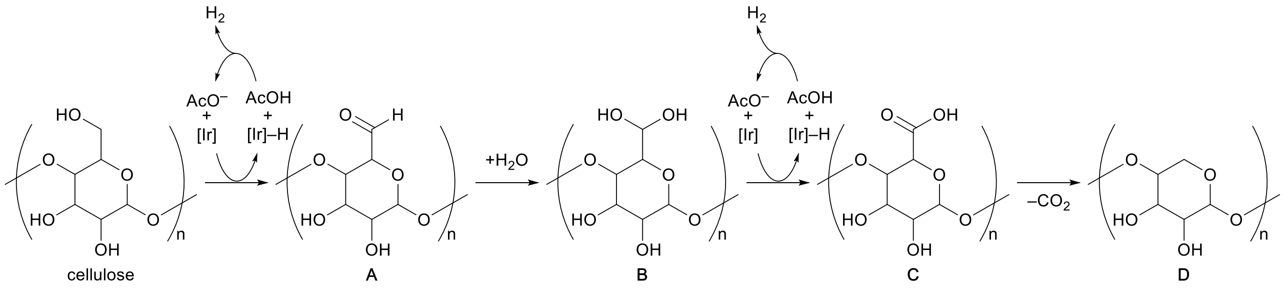
After first run and cooling to room temperature, cellulose (1.0 g) was added and magnetically stirred for 0.5 h at 100 ºC. Then, water (0.50 mL) was added, and the reaction mixture was magnetically stirred for 24 h in an oil bath with its temperature of 135 ºC (second run) using the setup shown in Figure S1 again.

The evolved gas by these reactions was passed through a solution of 10 M $NaOH_{aq}$ to trap carbon dioxide generated by the reaction. The hydrogen gas was collected in a gas burette. The yield of hydrogen was calculated using the ideal gas law. The results are shown in Scheme 4. The yields of hydrogen are based on 1 g cellulose: 100% yield corresponds to the formation of 1 mol of hydrogen from 1 mol of glucose unit in cellulose.

## 10. A plausible reaction pathway for hydrogen production from cellulose:

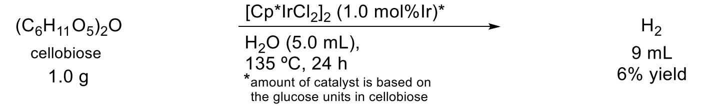
A plausible reaction pathway for hydrogen production from cellulose is shown in Scheme S1. The first step would be catalytic dehydrogenation of primary alcoholic moiety in cellulose to aldehyde intermediate **A** with release of hydrogen. Next, the intermediate **A** would be converted to the intermediate **B** having geminal diol moieties by hydration. Subsequently, catalytic dehydrogenation of the intermediate **B** would occur to give carboxylic acid intermediate **C**. Finally, transformation from **C** to **D** by decarboxylation would proceed to generate carbon dioxide.

The results that the ratio of hydrogen and carbon dioxygen was 2 to 1 under optimal condition (Table S1, entry 3) is consistent with this plausible pathway. On the other hands, short-time (for 3 h) reaction was conducted under the optimal conditions. By the analysis of evolved gas at the point of time after 3 h, the composition of gas was confirmed to be $H_2$:$CO_2$ = 75:25. Because the ratio of hydrogen was slightly higher at early stage of reaction, dehydrogenation would be prior to decarboxylation, which also supports the proposed reaction pathway.



**Scheme S1** A plausible reaction pathway for hydrogen production from cellulose

Additionally, to obtain another information related to the dehydrogenation of cellulose, the reaction of cellobiose in water was investigated. In a two-neck round flask, cellobiose (1.0 g) was placed under argon atmosphere. Water (5.0 mL) and catalyst $[Cp^*IrCl_2]_2$ (1.0 mol%Ir) were added, and the reaction mixture was magnetically stirred for 24 h in an oil bath with its temperature of 135 ºC using the setup shown in Figure S1. The evolved gas was passed through a solution of 10 M $NaOH_{aq}$ to trap carbon dioxide generated by the reaction. The hydrogen gas was collected in a gas burette. The yield of hydrogen was calculated using the ideal gas law. The results are shown in Scheme S2. This reaction gives hydrogen in 6%. Measurement of pH value of the reaction mixture was conducted before and after the reaction. As the results, acidic shift was observed (from 4.8 to 1.8). Additionally, in the $^{13}C\{1H\}$ NMR analysis, a signal at 174.6 ppm was observed, which could be assigned as a carbonyl carbon of carboxylic acid. These results supports the formation of carboxylic acid species in this catalytic system after dehydrogenation.



Reaction mixture before reaction; pH = 4.8
Reaction mixture after reaction; pH = 1.8

In $^{13}C\{^1H\}$ NMR analysis after the reaction, a signal due to a carboxylic acid moiety was observed at 174.6 ppm.

**Scheme S2** Hydrogen production from cellobiose in water

## 11. Reference

[1] R. G. Ball, W. A. G. Graham, D. M. Heinekey, J. K. Hoyano, A. D. McMaster, B. M. Mattson, S. T. Michel, *Inorg. Chem.* **1990**, *29*, 2023.