# One-Pot Conversion of Cellulose into *n*-Hexane over the Ir-ReO$_x$/SiO$_2$ Catalyst Combined with HZSM-5

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**S** *Supporting Information*

**ABSTRACT:** One-pot conversion of cellulose to *n*-hexane was carried out over the Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) catalyst combined with HZSM-5 as cocatalyst in a biphasic reaction system (*n*-dodecane + H$_2$O). The yield of *n*-hexane reached 83% from ball-milled cellulose and 78% from microcrystalline cellulose. Even using a high weight ratio of cellulose to water (1:1), a 71% yield of *n*-hexane could be obtained from ball-milled cellulose. The yield of *n*-hexane was almost maintained during three repeated tests when the catalyst was calcined again. The transformation of cellulose to *n*-hexane consists of the hydrolysis of cellulose to glucose via water-soluble oligosaccharides, hydrogenation of glucose to sorbitol, and successive hydrogenolysis of sorbitol to *n*-hexane. The Ir-ReO$_x$/SiO$_2$ catalyst promotes a hydrogenation and hydrogenolysis step. HZSM-5 enhanced the hydrolysis of cellulose in hot water and C−O bond hydrogenolysis activity of the Ir-ReO$_x$/SiO$_2$ catalyst.

**KEYWORDS:** *Hydrogenolysis, Cellulose, n-Hexane, Iridium, Zeolite*
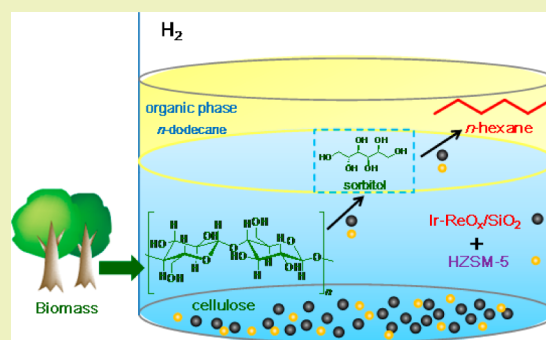
## INTRODUCTION

Conversion of renewable biomass resources into transportation fuels and value-added chemical products is drawing more and more attentions because of the shortage of fossil resources and an increasing energy demand.[1−10] Among various biomass resources, nonedible lignocellulosic biomass is the most abundant, which is composed of three parts: 40−50% cellulose, 20−40% hemicellulose, and 20−30% lignin. It is obvious that efficient transformation of cellulose, the major constituent of lignocellulosic biomass, into fuels and chemicals will play a crucial role in the sustainable production of liquid fuels and chemicals.[11−13] Cellulose is a kind of natural polymer that has a robust crystalline structure composed of β-1,4-glycosidic bonds of D-glucose. It contains a lot of hydrogen bonds between the hydroxyl groups on the glucose units of one chain and another chain. Cellulose is not soluble in water or other common organic solvents at mild temperature. Such an intrinsically robust feature makes the efficient transformation of cellulose much difficult.

In 2006, Fukuoka and Dhepe reported a pioneering approach for the direct catalytic conversion of cellulose to small organic molecules with hydrogen. They used Pt/Al$_2$O$_3$ without mineral acids, and a 31% yield of hexitols was obtained.[14] Since then, there have been numerous efforts focused on converting cellulose into polyols such as hexitols,[15−23] isosorbide,[24−26] ethylene glycol,[27−31] and propylene glycol.[32,33] These polyols can be used as sweeteners, pharmaceutical intermediates, monomers of polymers, or promising platform molecules for production of other valuable chemcials and fuels. However,

direct conversion of cellulose into other products such as *n*-hexane is also necessary in the biorefinery scheme.

Some researches on the direct conversion of lignocellulose or cellulose into alkanes were also reported. Huber et al.[34] demonstrated an integrated process for the production of alkanes from maple wood by hydrolysis into aqueous carbohydrate solutions with dilute acids (H$_2$SO$_4$, oxalic acid) followed by hydrogenation and hydrodeoxygenation of the sugar solutions over Ru/C and Pt/ZrP catalysts, respectively. Though the carbon yield of products in the gasoline range was up to 57%, the selectivity of hexane was very low (<3%). Sekine et al.[35] investigated one-pot direct catalytic conversion of cellulose to hydrocarbon by using the Pt/H-beta zeolite catalyst. The main products were C3 and C4, but no hexane was formed. Takahara et al.[36] reported hydrocracking of cellulose with Pt/HZSM-5 as the catalyst. The cellulose was pretreated in 1-hexanol, and an 89% yield of C2−C9 alkanes was produced with low selectivity to C6 ones. On the basis of the above works, the yield of *n*-hexane from cellulose was very low, and the reaction conditions were very severe. Therefore, it is a challenge to perform one-pot direct conversion of cellulose into *n*-hexane with a high yield in mild reaction conditions.

Several works about conversion of cellulose-derived materials such as sorbitol, glucose, and cellobiose into *n*-hexane through the hydrogenolysis method were reported. Dumesic and Huber

et al. have intensively investigated the production of *n*-hexane from sorbitol by using platinum-based catalysts such as Pt/SiO$_2$−Al$_2$O$_3$,[37] Pt/ZrP,[38,39] and Pt-ReO$_x$/C,[40] and the maximum yield of *n*-hexane was about 70%. Ma et al.[41,42] also reported the production of hexanes from sorbitol over the Ni/HZSM-5 catalyst combined with MCM-41, and the yield of hexanes was below 70%. In addition, the reaction conditions for both processes were harsh with reaction temperature over 500 K.

C−O hydrogenolysis of biomass-derived raw materials, such as polyols and ethers, is very important for the production of fuels and high-value chemicals. When converting sorbitol to *n*-hexane, there are six C−O bonds to remove. In our previous works, we found that the Ir-ReO$_x$/SiO$_2$ catalyst is very effective in hydrogenolysis of polyols such as glycerol into 1,3-propanediol,[43−45] erythritol into 1,4- and 1,3-butanediols,[46] and cyclic ethers with OH groups into diols such as tetrahydrofurfuryl alcohol into 1,5-pentanediol.[47] The selectivity to the target products from polyols or ethers is very high. Characterizations indicated that the surface of the Ir metal particle was partially covered with three-dimensional ReO$_x$ clusters.[44,48] We proposed that the Ir-ReO$_x$/SiO$_2$ catalyst can heterolytically dissociate H$_2$ into H$^+$ and H$^-$ on the interface between the Ir metal and ReO$_x$ species.[44,48] This kind of heterolytically dissociated hydrogen species on Ir-ReO$_x$/SiO$_2$ was effective in the selective conversion of polyols or ethers to the target products. The mechanism was similar to that of Rh-ReO$_x$/SiO$_2$ or Rh-ReO$_x$/C catalysts, which are also effective in conversion of glycerol or cyclic ethers.[49−52] The Ir-ReO$_x$/SiO$_2$ catalyst also showed high activity and selectivity in the hydrogenation of unsaturated aldehydes to unsaturated alcohols[53] and dehydrogenation of diols to the corresponding α-hydroxy ketones in water under Ar.[54] Mascal et al. have very recently used the Ir-ReO$_x$/SiO$_2$ catalyst to perform dehydrodeoxygenation of the angelica lactone dimer, which is synthesized from levulinic acid into hydrocarbons.[55] The activity of Ir-ReO$_x$/SiO$_2$ could be enhanced by the addition of various acids such as H$_2$SO$_4$, zeolites (HZSM-5, HBEA, HY), silica−alumina, or ion-exchange resin. Among them, HZSM-5 is the most suitable cocatalyst because of the stability.[56]

Recently, our group conducted conversion of sorbitol, glucose, and cellobiose into *n*-hexane over the Ir-ReO$_x$/SiO$_2$ catalyst combined with HZSM-5. Over 90% yield of *n*-hexane could be obtained at ≤443 K.[57] However, production of *n*-hexane from cellulose via these compounds needs the extra step of hydrolysis of cellulose. Direct conversion of cellulose into *n*-hexane with a heterogeneous catalyst in high yield at mild reaction conditions would be more meaningful. To the best of our knowledge, this conversion process has not yet been reported.

In this work, the binary Ir-ReO$_x$/SiO$_2$ and HZSM-5 catalyst system was applied to one-pot conversion of cellulose into *n*-hexane. High (∼80%) yield of *n*-hexane was obtained from ball-milled cellulose or even microcrystalline cellulose.

## ■ EXPERIMENTAL SECTION

**Catalyst Preparation.** The SiO$_2$ (G-6, BET surface area 535 m$^2$/g) supplied by Fuji Silysia Chemical, Ltd. was used as a support of the catalysts. Ir-ReO$_x$/SiO$_2$ catalysts were prepared by the sequential incipient wetness impregnation method as described previously.[43,44] First, Ir/SiO$_2$ was prepared by impregnating (1.69−1.90 g of SiO$_2$) with an aqueous solution of H$_2$IrCl$_6$ (Furuya Metals Co., Ltd.; 0.821 g of 9.74 wt % solution + 4 g of H$_2$O). After evaporating the solvent and

drying at 383 K for 12 h, it were impregnated with an aqueous solution of NH$_4$ReO$_4$ (Soekawa Chemical Co., Ltd.; 0−0.334 g in 6 g of H$_2$O). These catalysts were calcined in air at 773 K for 3 h after drying at 383 K for 12 h. The loading amount of Ir was 4.0 wt %, and the Re/Ir molar ratio was 0−3. All the catalysts were used in powdered form with a granule size of <100 mesh. HZSM-5 [JRC-Z5-90H(1), Süd-Chemie Catalysts and Catalysis Society of Japan, Si/Al$_2$ = 90] was used as received.

**Pretreatment of Cellulose.** Pretreatment of cellulose was conducted by using a ball-mill (Fritsch planetary mono mill "classic line"-Pulverisette 6). Cellulose (Merck, Avicel microcrystalline, 6 g) was charged in a 250 mL ZrO$_2$ pot with 108 ZrO$_2$ balls (about 360 g, diameter 10 mm). Then the pot was rotated at a speed of 300 rpm for 0.5−4 h (0.5 h cool down after every hour). The ball-milled cellulose was characterized by XRD (Rigaku MiniFlex 600). The crystallinity indices (CrIs) were determined using the commonly used XRD peak height method developed by Segal et al.[58]

$$CrI\ (\%) = (I_{002} - I_{AM})/I_{002} \times 100$$

where $I_{002}$ represents the maximal intensity of the (002) reflection, and $I_{AM}$ represents the minimal intensity between the (002) and (101) reflection. The amount of physically adsorbed water was determined by using thermogravimetric analysis (TGA) under an inert N$_2$ atmosphere using a Rigaku TG 8120 Thermo plus EVO II/TG-DTG. The experiment indicated that the water content was about 6 ± 1 wt % in the ball-milled cellulose. Weight correction was applied for the calculation of conversion in the activity tests.

**Activity Tests.** Activity tests were performed in a 190 mL stainless steel autoclave with an inserted round-bottomed glass vessel. The Ir-ReO$_x$/SiO$_2$ catalyst (0.15 or 0.3 g) was put into an autoclave together with a spinner and an appropriate amount of water (1.0−9.5 g) and heated at 473 K with 8 MPa H$_2$ for 1 h for the reduction pretreatment. The stirring rate was 250 rpm. After the pretreatment, the autoclave was cooled, and hydrogen was removed. Ball-milled cellulose (0.5 or 1.0 g) or microcrystalline cellulose (0.5 g), HZSM-5 (0.06 or 0.12 g), and *n*-dodecane (4 mL; Tokyo Chemical Industry Co., Ltd., 99%) were put into the autoclave. A picture of the glass vessel after feeding is shown in Figure S1 of the Supporting Information. *n*-Dodecane was added to trap the produced *n*-hexane. After sealing the reactor, the air content was purged by flushing three times with H$_2$ (1 MPa, 99.99%; Nippon Peroxide Co., Ltd.). The reactor was pressurized with H$_2$ to 2.0−8.0 MPa and then heated to a set temperature (433−493 K). The heating took about 0.6 h. After the temperature reached the set one, the temperature was kept for appropriate reaction time. The stirring rate was 500 rpm. After the reaction, the reactor was cooled by using an ice bath, and the gases were collected in a gas bag. The reaction mixture was separated into organic and aqueous phases. The autoclave contents were transferred to a vial, and the catalyst was separated by centrifugation and filtration. The products in the aqueous phase were analyzed by using HPLC (Shimadzu LC-10A) with a refractive index detector (RID) and a Sugar SH1011 column (diameter 8 mm, 300 mm) or an Aminex HPX-87C column (diameter 7.8 mm, 300 mm) and gas chromatograph (Shimadzu GC-2014) equipped with TC-WAX capillary column (diameter 0.25 mm, 30 m) and FID. The products in the organic phase were analyzed by gas chromatograph (Shimadzu GC-2014) equipped with a CP-Sil5 capillary column (diameter 0.25 mm, 50 m) and FID. The products in the gas phase were analyzed by gas chromatograph (Shimadzu GC-2014) equipped with an Rtx-1-PONA capillary column (diameter 0.25 mm, 100 m) and FID. The volume of gases was calculated by the ideal gas equation. The products were hexanes such as *n*-hexane, 2-methylpentane, and 3-methylpentane; hexanols such as 1-hexanol, 2-hexanol ,and 3-hexanol; cyclic ethers such as 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran; C−C cracking products such as *n*-pentane, *n*-butane, propane, ethane, and methane; sugar alcohols such as sorbitol and glucose; and other products that could not be identified. The weight of cellulose after reaction was determined by subtracting the weight of charged catalyst from the weight of the remaining solid. The conversion and yield were calculated on the carbon basis and defined as follows

**Table 1. Conversion of Ball-Milled Cellulose to *n*-Hexane over Ir-ReO$_x$/SiO$_2$ Catalyst with Different Re/Ir Molar Ratio + HZSM-5[a]**

| | | | yield (%) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| entry | Re/Ir | conv. (%) | *n*-hexane | HxOHs | *iso*-hexanes | cyclic ethers | C5 | C4 | C3 | C2 | C1 | sorbitol | glucose | loss of carbon balance (%) |
| 1 | 0 | 40 | 0.6 | 0.0 | 0.0 | 0.9 | 0.1 | 0.0 | 0.0 | 0.0 | 0.0 | 17 | 0.9 | 21 |
| 2 | 0.25 | 43 | 15 | 1.3 | 0.5 | 1.2 | 2.2 | 0.1 | 0.1 | 0.0 | 0.1 | 0.0 | 0.0 | 22 |
| 3 | 0.5 | 46 | 17 | 1.2 | 0.5 | 1.4 | 2.1 | 0.2 | 0.6 | 0.0 | 0.1 | 0.0 | 0.0 | 23 |
| 4 | 1 | 49 | 26 | 0.6 | 1.0 | 1.6 | 3.0 | 0.2 | 0.2 | 0.1 | 0.1 | 0.0 | 0.0 | 16 |
| 5 | 2 | 53 | 35 | 0.1 | 1.1 | 1.1 | 3.2 | 0.3 | 0.3 | 0.1 | 0.1 | 0.1 | 0.0 | 11 |
| 6 | 3 | 52 | 33 | 0.2 | 1.0 | 1.2 | 3.3 | 0.3 | 0.2 | 0.1 | 0.1 | 0.0 | 0.0 | 12 |
| 7[a] | 0 | 94 | 7.2 | 1.8 | 0.2 | 4.3 | 0.4 | 0.1 | 0.0 | 0.0 | 0.0 | 24 | 0.0 | 59 |

[a]HxOH: hexanol. *iso*-Hexanes: 2-methylpentane and 3-methylpentane. Cyclic ethers: 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran. C1, methane; C2, ethane; C3, propane; C4, butane; and C5, pentane. Reaction conditions: Cellulose (0.5 g; ball-milling time 2 h), H$_2$O (9.5 g), *n*-dodecane (4 mL), catalyst (0.15 g), HZSM-5 (Si/Al$_2$ = 90) (0.06 g), initial H$_2$ (6 MPa), 463 K, 2 h, and 7[a] is 12 h.

Conversion (%)

$$= \frac{\text{weight of reactant charged} - \text{weight of reactant after reaction}}{\text{weight of reactant charged}}$$

$$\times\ 100$$

Yield of detected products (% − C)

$$= \frac{\text{mol}_{\text{product}} \times \text{C atoms in product}}{\text{mol}_{\text{reactant charged}} \times \text{C atoms in reactant}} \times 100$$

Loss of carbon balance (% − C)

$$= (\text{Conversion} - \text{sum of yield of detected products}) \times 100$$

The loss of carbon balance also included experimental errors in the activity tests. We conducted the repeated tests in the reaction conditions where the highest *n*-hexane yield was obtained five times (Table S1, Supporting Information). The standard deviations were small (~ ±2%) in conversion of cellulose, yields of products, and loss of carbon balance. The difference between the highest and lowest values of loss of carbon balance in the repeated tests was 5%. In addition, the experimental errors may be estimated from the results with high conversion. In fact, at high conversion, the loss of carbon balance was always small, suggesting that the experimental errors were small (e.g., ≤5%). The total organic carbon (TOC) analysis was conducted with Shimadzu TOC-L CSN analyzer. The used catalysts including Ir-ReO$_x$/SiO$_2$ and HZSM-5 were washed together with excess water and dried in air at 383 K and then calcined at 773 K for 3 h. A slight loss (<8% in weight) was observed during the recovery process and was compensated with fresh catalysts in each reuse experiment. The ratio of the amount of compensated fresh catalysts to initial amount was set to the same for both Ir-ReO$_x$/SiO$_2$ and HZSM-5. Before the activity test, the reduction pretreatment was carried out in the same way as for the fresh catalyst. The amount of eluted metal during the reaction was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Scientific iCAP 6500).

## ■ RESULTS AND DISCUSSION

**Re/Ir Molar Ratio Effect on Conversion of Cellulose to *n*-Hexane over Ir-ReO$_x$/SiO$_2$ Catalyst.** First, ball-milled cellulose was used as a substrate because ball milling is known to be an efficient way to reduce the crystallinity of cellulose and improve accessibility to the catalysts' active site.[61] The amorphous part of cellulose has weak hydrogen bonds and is chemically more reactive than the crystalline one. Ir-ReO$_x$/SiO$_2$ catalysts with various Re/Ir molar ratios were applied to the conversion of cellulose in combination with HZSM-5 (Table 1). Ir/SiO$_2$ showed a very low yield of *n*-hexane after 2 h even prolonging reaction time, and a large amount of sorbitol was formed (entries 1 and 8). In contrast, the addition of Re to Ir/

SiO$_2$ exhibited a very high yield of *n*-hexane indicating that Ir-ReO$_x$/SiO$_2$ has excellent C−O hydrogenolysis activity. With an increasing amount of added Re, the conversion of cellulose increased at short reaction times up to Re/Ir = 2 (entries 2−5), and further addition of Re hardly affected the performance (entry 6). Therefore, Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) was chosen as the catalyst to optimize reaction conditions. The dependence of activity on the Re/Ir ratio was similar to that reported in the hydrogenolysis of glycerol[41] and tetrahydrofurfuryl alcohol.[47,59] The time course of the catalysis by Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) + HZSM-5 is shown in Figure 1. When the reaction time was 12
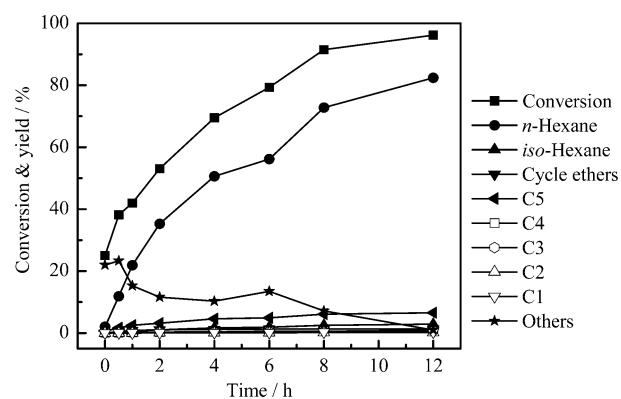


**Figure 1.** Time dependence on conversion of ball-milled cellulose to *n*-hexane over Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) catalyst + HZSM-5. *iso*-Hexanes: 2-methylpentane and 3-methylpentane. Cyclic ethers: 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran. C1, methane; C2, ethane; C3, propane; C4, butane; and C5, pentane. Others: unidentified products. Reaction conditions: Cellulose (0.5 g; ball-milling time 2 h), H$_2$O (9.5 g), *n*-dodecane (4 mL), Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) (0.15 g), HZSM-5 (Si/Al$_2$ = 90) (0.06 g), initial H$_2$ (6 MPa), 463 K.

h, cellulose was almost completely converted, and the *n*-hexane yield reached 83%. The TG-DTA of the catalyst after 12 h of reaction was conducted (Figure S2, Supporting Information). The amount of combustible species was less than 2% of used cellulose. On the other hand, the loss of mass balance was 1% of used cellulose. The difference of these values was within the experimental error. Total organic carbon (TOC) analysis of the aqueous phase after reaction was also conducted. Only about 1% C of initial cellulose was detected, agreeing with the GC result. These measurements confirmed the complete conversion of cellulose and polyols intermediates.

**Effect of Pretreatment.** The dependences of structure and reactivity of cellulose on ball-milling conditions were investigated. Figure 2 shows the XRD patterns of the cellulose
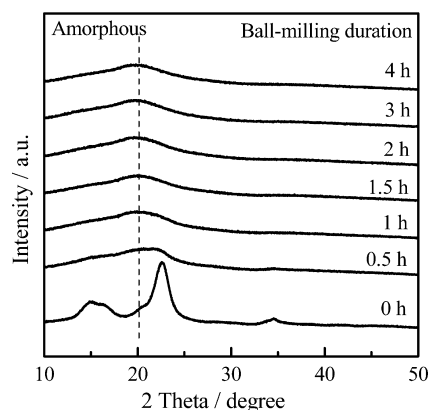


**Figure 2.** XRD patterns of cellulose after different ball-milling duration.

samples after different pretreatment. The microcrystalline cellulose without ball milling was mainly composed of crystalline regions that possessed four characteristic peaks at $2\theta = 15°$ (101), $16°$ (10$\bar{1}$), $23°$ (002), and $34°$ (040) with a small peak at $2\theta = 21°$ attributable to amorphous regions.[60] In the milled samples, the crystalline peaks of cellulose became weaker and broader with longer ball-milling time. After 2 h of ball milling, the crystalline peaks almost disappeared, and the peak at $2\theta = 21°$ became dominant. The pattern was unchanged after further milling. The crystallinity of cellulose was estimated to be 80% for fresh cellulose, 20% for the cellulose milled after 0.5 h, and below 5% for samples milled for 1 h or longer.

The dependence of the reactivity of treated cellulose is shown in Table 2. The cellulose conversion and the n-hexane yield increased quickly with longer ball-milling time up to 2 h. The effect leveled after 2 h of ball milling. Reactivity and n-hexane yield fairly corresponded with the change in crystallinity of the cellulose.

**Effect of Reaction Conditions.** Table 3 shows the effect of reaction temperature on production of n-hexane from ball-milled cellulose over Ir-ReO$_x$/SiO$_2$ + HZSM-5. The conversion of cellulose increased with higher reaction temperature. The yield of n-hexane also increased dramatically except in the case

of reaction temperatures above 463 K. The byproducts such as iso-hexane and C1−C5 yield increased, indicating that high temperature enhanced C−C bonds cracking and isomerization reactions. The selectivity of n-hexane decreased as the temperature increased when compared at similar conversion of cellulose (entries 3 and 6), but the increase in byproducts was not large. A similar increase in byproducts has been observed for conversion of cellobiose to n-hexane.[57]

Table 4 shows the effect of hydrogen pressure on conversion of ball-milled cellulose over Ir-ReO$_x$/SiO$_2$ + HZSM-5. A rapid increase in the n-hexane yield was observed when the H$_2$ pressure was elevated from 2 to 6 MPa (entries 1−3). The yield of unidentified products, possibly polyols, decreased sharply as H$_2$ pressure increased, which can be explained by the positive reaction order with respect to H$_2$ pressure in hydrogenolysis catalyzed by Ir-ReO$_x$/SiO$_2$.[44,47] In addition, at lower H$_2$ pressure, the yields of degradation products ($\leq$C5) were slightly higher. Some types of the degradation reactions such as the retro-aldol reaction may have lower reaction order with respect to hydrogen pressure. However, when H$_2$ pressure was increased further to 8 MPa, the yield of n-hexane decreased slightly (entry 4). Therefore, a moderate pressure 6 MPa was preferred to the production of n-hexane.

Table 5 shows the effect of water amount on production of n-hexane from ball-milled cellulose over Ir-ReO$_x$/SiO$_2$ + HZSM-5. Different weight ratios of cellulose to water varied from 1:19 to 1:1 were applied. The yield of n-hexane was slightly decreased with a higher ratio of cellulose to water, while the amount of unidentified products increased. The unidentified products' amount was still larger than that in the low weight ratios of cellulose to water, even with the reaction time prolonged to 24 h (entry 5). That could be attributed to the polymerization or coking of cellulose in the highly concentrated reaction solution. It is worth noting that the yield of n-hexane kept above 70%, even though the weight ratio of cellulose to water increased up to 1:1. In previously reported processes, the starting concentration of cellulose in solution is very low (about 1−3 wt %).[14−32] There are only two cases using the concentration of cellulose up to 15 wt %, but the yields of target products dropped quickly as the concentration increased.[33,61] Therefore, the cellulose/water weight ratio in our system, even considering the use of n-dodecane as cosolvent, is very high in comparison with the reported systems for cellulose conversion, showing the advantage of this system in view of energy consumption.

**Table 2. Effect of Ball-Milling Time on Conversion of Cellulose to n-Hexane over Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) Catalyst + HZSM-5$^a$**

| | | | | yield (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| entry | ball-milling time (h) | crystallinity (%) | conv. (%) | n-hexane | iso-hexanes | cyclic ethers | C5 | C4 | C3 | C2 | C1 | loss of carbon balance (%) |
| 1 | 0 | 80 | 51 | 34 | 0.8 | 0.3 | 2.9 | 0.3 | 0.2 | 0.1 | 0.1 | 13 |
| 2 | 0.5 | 20 | 90 | 67 | 2.1 | 1.1 | 5.1 | 0.6 | 0.5 | 0.1 | 0.2 | 13 |
| 3 | 1 | <5 | 95 | 70 | 2.5 | 1.2 | 5.3 | 0.6 | 0.5 | 0.1 | 0.2 | 14 |
| 4 | 1.5 | <5 | 99 | 78 | 2.6 | 1.2 | 6.3 | 0.8 | 0.7 | 0.2 | 0.4 | 9.8 |
| 5 | 2 | <5 | 97 | 83 | 3.0 | 1.3 | 6.3 | 0.7 | 0.6 | 0.2 | 0.3 | 2.2 |
| 6 | 3 | <5 | 97 | 81 | 3.0 | 1.2 | 6.2 | 0.7 | 0.6 | 0.2 | 0.3 | 4.9 |
| 7 | 4 | <5 | 98 | 81 | 3.3 | 1.1 | 6.7 | 1.1 | 0.9 | 0.3 | 0.4 | 4.0 |

$^a$iso-Hexanes: 2-methylpentane and 3-methylpentane. Cyclic ethers: 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran. C1, methane; C2, ethane; C3, propane; C4, butane; and C5, pentane. Reaction conditions: Cellulose (0.5 g), H$_2$O (9.5 g), n-dodecane (4 mL), Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) (0.15 g), HZSM-5 (Si/Al$_2$ = 90) (0.06 g), initial H$_2$ (6 MPa), 463 K, 12 h.

**Table 3. Effect of Reaction Temperature on Conversion of Ball-Milled Cellulose to *n*-Hexane over Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) Catalyst + HZSM-5[a]**

| | | | yield (%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| entry | temperature (K) | conv. (%) | *n*-hexane | HxOHs | *iso*-hexanes | cyclic ethers | C5 | C4 | C3 | C2 | C1 | loss of carbon balance (%) |
| 1 | 433 | 42 | 24 | 0.2 | 0.4 | 0.8 | 1.9 | 0.2 | 0.1 | 0.0 | 0.1 | 15 |
| 2 | 443 | 60 | 44 | 0.2 | 1.0 | 1.1 | 3.2 | 0.3 | 0.2 | 0.0 | 0.1 | 10 |
| 3 | 453 | 80 | 66 | 0.0 | 2.0 | 1.3 | 5.1 | 0.4 | 0.4 | 0.1 | 0.2 | 4.5 |
| 4 | 463 | 97 | 83 | 0.0 | 3.0 | 1.3 | 6.3 | 0.7 | 0.6 | 0.2 | 0.3 | 2.2 |
| 5 | 473 | 97 | 79 | 0.0 | 3.1 | 0.4 | 8.3 | 1.6 | 1.0 | 0.2 | 0.3 | 3.4 |
| 6[a] | 463 | 79 | 56 | 0.0 | 1.9 | 1.3 | 4.9 | 0.6 | 0.5 | 0.1 | 0.2 | 13 |

[a]HxOH: hexanol. *iso*-Hexanes: 2-methylpentane and 3-methylpentane. Cyclic ethers: 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran. C1, methane; C2, ethane; C3, propane; C4, butane; and C5, pentane. Reaction conditions: Cellulose (0.5 g; ball-milling time 2 h), H$_2$O (9.5 g), *n*-dodecane (4 mL), Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) (0.15 g), HZSM-5 (Si/Al$_2$ = 90) (0.06 g), initial H$_2$ (6 MPa), 12 h, and 6[a] is 6 h.

**Table 4. Effect of Initial H$_2$ Pressure on Conversion of Ball-Milled Cellulose to *n*-Hexane over Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) Catalyst + HZSM-5[a]**

| | | | yield (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| entry | pressure (MPa) | conv. (%) | *n*-hexane | *iso*-hexanes | cyclic ethers | C5 | C4 | C3 | C2 | C1 | loss of carbon balance (%) |
| 1 | 2 | 90 | 57 | 2.5 | 2.5 | 8.3 | 1.2 | 1.0 | 0.4 | 0.5 | 17 |
| 2 | 4 | 96 | 73 | 2.8 | 1.3 | 7.9 | 0.7 | 0.6 | 0.2 | 0.3 | 9.5 |
| 3 | 6 | 97 | 83 | 3.0 | 1.3 | 6.3 | 0.7 | 0.6 | 0.2 | 0.3 | 2.2 |
| 4 | 8 | 95 | 80 | 2.7 | 1.0 | 5.7 | 0.5 | 0.4 | 0.1 | 0.2 | 3.6 |

[a]*iso*-Hexanes: 2-methylpentane and 3-methylpentane. Cyclic ethers: 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran. C1, methane; C2, ethane; C3, propane; C4, butane; and C5, pentane. Reaction conditions: Cellulose (0.5 g; ball-milling time 2 h), H$_2$O (9.5 g), *n*-dodecane (4 mL), Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) (0.15 g), HZSM-5 (Si/Al$_2$ = 90) (0.06 g), 463 K, 12 h.

**Table 5. Effect of Water Amount on Conversion of Ball-Milled Cellulose to *n*-Hexane over Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) Catalyst + HZSM-5[a]**

| | | | yield (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| entry | weight ratio of cellulose to water | conv. (%) | *n*-hexane | *iso*-hexanes | cyclic ethers | C5 | C4 | C3 | C2 | C1 | loss of carbon balance (%) |
| 1 | 1:19[a] | 97 | 83 | 3.0 | 1.3 | 6.3 | 0.7 | 0.6 | 0.2 | 0.3 | 2.2 |
| 2 | 1:9 | 96 | 78 | 3.3 | 0.3 | 6.9 | 0.7 | 0.7 | 0.2 | 0.3 | 5.2 |
| 3 | 1:4 | 96 | 74 | 4.2 | 0.9 | 6.6 | 1.0 | 1.3 | 0.3 | 0.3 | 7.5 |
| 4 | 1:1 | 98 | 69 | 6.2 | 0.2 | 6.0 | 1.4 | 1.7 | 0.5 | 0.3 | 13 |
| 5[b] | 1:1 | 99 | 71 | 6.2 | 0.2 | 6.6 | 1.1 | 1.4 | 0.4 | 0.3 | 12 |

[a]*iso*-Hexanes: 2-methylpentane and 3-methylpentane. Cyclic ethers: 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran. C1, methane; C2, ethane; C3, propane; C4, butane; and C5, pentane. Reaction conditions: Cellulose (1 g; ball-milling time 2 h), *n*-dodecane (4 mL), catalyst (0.3 g), HZSM-5 (Si/Al$_2$ = 90) (0.12 g). Cellulose (1:19[a]): (0.5 g; ball-milling time 2 h), *n*-dodecane (4 mL), Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) (0.15 g), HZSM-5 (Si/Al$_2$ = 90) (0.06 g), initial H$_2$ (6 MPa), 463 K, 12 h, and 5[b] is 24 h.

**Table 6. Conversion of Microcrystalline Cellulose to *n*-Hexane over Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) Catalyst + HZSM-5[a]**

| | | | yield (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| entry | temperature (K) | conv. (%) | *n*-hexane | *iso*-hexanes | cyclic ethers | C5 | C4 | C3 | C2 | C1 | loss of carbon balance (%) |
| 1 | 463 | 59 | 49 | 1.1 | 0.2 | 3.9 | 0.8 | 0.2 | 0.1 | 0.2 | 3.1 |
| 2 | 473 | 79 | 60 | 1.6 | 0.0 | 5.1 | 0.6 | 0.4 | 0.1 | 0.2 | 11 |
| 3 | 483 | 99 | 78 | 2.6 | 0.0 | 8.0 | 1.0 | 0.6 | 0.2 | 0.4 | 8.6 |
| 4 | 493 | 95 | 75 | 2.6 | 0.0 | 8.6 | 1.1 | 0.7 | 0.3 | 0.5 | 5.7 |

[a]*iso*-Hexanes: 2-methylpentane and 3-methylpentane. Cyclic ethers: 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran. C1, methane; C2, ethane; C3, propane; C4, butane; and C5, pentane. Reaction conditions: Microcrystalline cellulose (0.5 g), H$_2$O (9.5 g), *n*-dodecane (4 mL), Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) (0.15 g), HZSM-5 (Si/Al$_2$ = 90) (0.06 g), initial H$_2$ (6 MPa), 24 h.

**Conversion of Microcrystalline Cellulose into *n*-Hexane.** Although cellulose after ball-milling can be easily converted to *n*-hexane with high yield (>80%), ball-milling is quite energy consuming. Direct conversion of as-received microcrystalline cellulose (MCC) to *n*-hexane is more attractive. Because of the difficulty in converting of microcrystalline cellulose, longer reaction time and higher reaction temperature were necessary. Table 6 lists the results of conversion of MCC to *n*-hexane. Even after 24 h, MCC was not converted completely at 463 K, and the yield of *n*-hexane was only 49%, which was much lower than that from ball-milled cellulose. As reaction temperature increased, the conversion of MCC and the yield of *n*-hexane increased quickly until 483 K. The yield of *n*-hexane from MCC reached 78% when the reaction temperature was 483 K. At 493 K, the conversion value was slightly decreased from the case at 483 K. Formation of

**Table 7. Reusability of Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) Catalyst + HZSM-5 in Conversion of Ball-Milled Cellulose to $n$-Hexane$^a$**

| entry | usage | conv. (%) | $n$-hexane | HxOH | $iso$-hexanes | cyclic ethers | C5 | C4 | C3 | C2 | C1 | loss of carbon balance (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | yield (%) | | | | |
| 1 | 1 | 97 | 83 | 0.0 | 3.0 | 1.3 | 6.3 | 0.7 | 0.6 | 0.2 | 0.3 | 2.2 |
| 2 | 2 | 93 | 71 | 1.6 | 2.7 | 1.4 | 6.4 | 0.7 | 0.6 | 0.2 | 0.3 | 8.2 |
| 3 | 3 | 91 | 71 | 1.6 | 2.9 | 1.7 | 6.0 | 0.6 | 0.5 | 0.2 | 0.2 | 6.4 |
| 4 | 4 | 91 | 66 | 1.6 | 3.2 | 1.8 | 5.7 | 0.6 | 0.7 | 0.2 | 0.2 | 11 |

$^a$HxOH: hexanol. $iso$-Hexanes: 2-methylpentane and 3-methylpentane. Cyclic ethers: 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran. C1, methane; C2, ethane; C3, propane; C4, butane; and C5, pentane. Reaction conditions: Cellulose (0.5 g; ball-milling time 2 h), H$_2$O (9.5 g), $n$-dodecane (4 mL), Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) (0.15 g), HZSM-5 (Si/Al$_2$ = 90) (0.06 g), initial H$_2$ (6 MPa), 463 K, 12 h.

insoluble polymers might increase the weight of solid residue, which could lower the nominal value of conversion. Therefore, the optimal temperature for conversion of microcrystalline cellulose was 483 K, and the highest yield of $n$-hexane was 78%.

**Catalyst Stability.** Table 7 shows the results of the activity tests of the reused Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) catalyst. The method of catalyst reuse was as follows: The catalyst was washed with water and dried at 383 K for 12 h and calcined in air at 773 K for 3 h. This step was for removing the deposited carbon on the catalyst. Before the activity test, the reduction pretreatment was carried out in the same way as for the fresh catalyst. The yield of $n$-hexane was decreased from 83% to 71% for the second run (first recycling). Further changes were small in subsequent runs. It is feasible to recycle the Ir-ReO$_x$/SiO$_2$ catalyst + HZSM-5 under the present reaction conditions. To identify the cause of the catalyst deactivation, inductively coupled plasma (ICP) and XRD characterizations were conducted. ICP analysis of the reaction solution after filtering off the catalyst showed no leaching of Ir (below detection limit) and very slight leaching of Re (0.62 wt %). The XRD patterns that were assigned to HZSM-5 were almost the same even after the fourth run (Figure 3a,b), indicating high hydrothermal
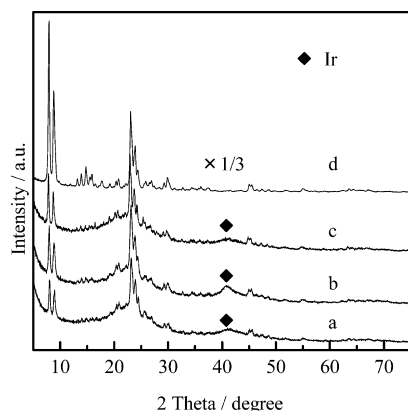


**Figure 3.** XRD patterns of Ir-ReO$_x$/SiO$_2$ catalyst combined with HZSM-5: (a) after first reaction, (b) after fourth reaction, (c) after first reaction (483 K, 24 h), and (d) HZSM-5.

stability of HZSM-5. This was also supported by the XRD analysis (Figure 3c) of the catalysts after higher temperature reaction (483 K, 24 h). However, the peaks (Figure 3b) that were assigned to the Ir metal after the fourth run became sharper than those of the catalysts after the first reaction (Figure 3a), indicating the aggregation of Ir metal during regeneration. This could be the reason that the catalyst showed slight deactivation during recycling process.

**Reaction Mechanism.** For the conversion of cellulose to sugar alcohols, it is generally believed that the first step is hydrolysis of cellulose to water-soluble cello-oligosaccharides or glucose, which are readily hydrogenated into sugar alcohols.[62] In the case of converting cellulose to $n$-hexane, the steps of hydrogenolysis of sugar alcohols are necessary in addition to hydrolysis and hydrogenation. In the time course of cellulose conversion over Ir-ReO$_x$/SiO$_2$ + HZSM-5 (Figure 1), the conversion of cellulose almost corresponded with the net yield of alkanes, indicating that hydrolysis of $\beta$-1,4-glycosidic bonds of cellulose into soluble sugars is the rate-determining step.

In the conversion of cellulose, sugars,[57] and sorbitol,[57] small amounts of C1−C5 alkanes and $iso$-hexanes were formed. When reaction tests were performed with $n$-hexane as the reactant, no $n$-hexane was converted with or without HZSM-5 after 2 h. These facts showed that C1−C5 alkanes and $iso$-hexanes are produced in the hydrogenolysis step of sugar alcohols. C1−C5 alkanes can be formed by retro-aldol condensation, decarbonylation, or C−C hydrogenolysis of intermediates. Huber et al. investigated in detail that the C−C bond cleaves in hydrodeoxygenation of sorbitol over Pt/SiO$_2$−Al$_2$O$_3$ and found that decarbonylation is the main pathway.[63] In our previous work,[57] $iso$-pentanes were obtained as byproducts via hydrogenolysis of pentanediols and pentanols (1-pentanol, 2-pentanol, and 3-pentanol) when using Ir-ReO$_x$/SiO$_2$ with HZSM-5 as catalysts. When the reactions were performed only using HZSM-5 as the catalyst, the main product was 2-pentene, and branched molecules were hardly produced. Therefore, $iso$-hexanes could be produced by isomerization of the alkenes that were formed by dehydration of alcohols with the aid of acid (Figure 4).
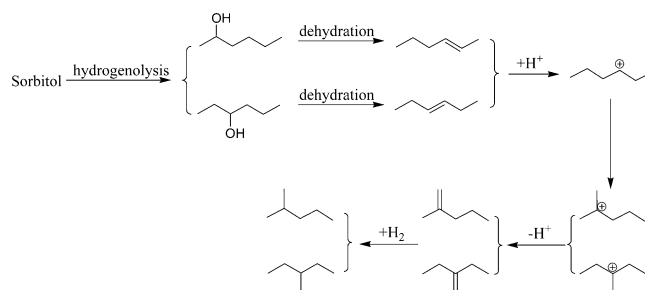


**Figure 4.** Probable formation routes of $iso$-hexanes.

Some of the cyclic ethers such as 2,5-dimethyltetrahydrofuran (2,5-DMTHF) and 2-methyltetrahydropyran (2-MTHP) were also formed in the process. 2,5-DMTHF could be produced by dehydration of glucose to 5-hydroxymethylfurfural (HMF) over acid (HZSM-5) and successive hydrogenation and hydrogenolysis of formed HMF.[9] 2-MTHP could be produced
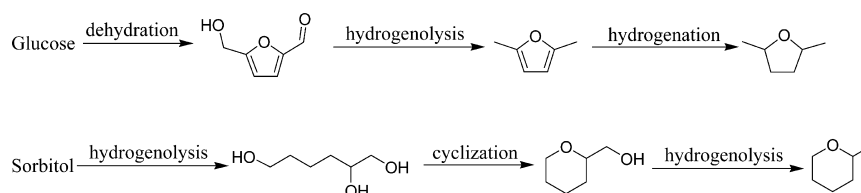
**Figure 5.** Formation routes of cyclic ethers.

**Table 8. Conversion of Cellulose over Different Catalysts**[a]

| entry | catalyst | conv. (%) | yield (%) | | | | | | | | | | | loss of carbon balance (%) |
| | | | *n*-hexane | HxOH | *iso*-hexanes | cyclic ethers | C5 | C4 | C3 | C2 | C1 | sorbitol | glucose | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | − | 36 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 9.6 | 27 |
| 2 | HZSM-5 | 51 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 11 | 39 |
| 3 | Ir-ReO$_x$/SiO$_2$ + HZSM-5 | 53 | 35 | 0.1 | 1.1 | 1.1 | 3.2 | 0.3 | 0.3 | 0.1 | 0.1 | 0.1 | 0.0 | 11 |
| 4[a] | − | 35 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 7.4 | 27 |
| 5[a] | HZSM-5 | 44 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 9.5 | 34 |
| 6[a] | Ir-ReO$_x$/SiO$_2$ + HZSM-5 | 42 | 28 | 3.3 | 1.1 | 0.5 | 4.2 | 0.3 | 0.2 | 0.1 | 0.1 | 0.0 | 0.0 | 4.4 |

[a]HxOH: hexanol. *iso*-Hexanes: 2-methylpentane and 3-methylpentane. Cyclic ethers: 2,5-dimethyltetrahydrofuran and 2-methyltetrahydropyran. C1, methane; C2, ethane; C3, propane; C4, butane; and C5, pentane. Reaction conditions: Cellulose (0.5 g; ball-milling time 2 h), H$_2$O (9.5 g), *n*-dodecane (4 mL), Ir-ReO$_x$/SiO$_2$ (Re/Ir = 2) (0.15 g), HZSM-5 (Si/Al$_2$ = 90) (0.06 g), initial H$_2$ (6 MPa), 463 K, 2 h. Microcrystalline cellulose (4[a], 5[a], 6[a]): (0.5 g), initial H$_2$ (6 MPa), 483 K, 2 h.

**Scheme 1. Reaction Pathway for Conversion of Cellulose over Ir-ReO$_x$/SiO$_2$ Catalyst Combined with HZSM-5**
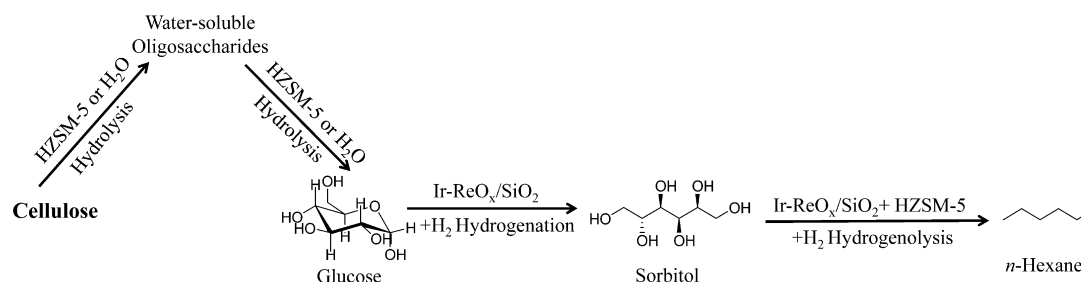


by the cyclization of 1,2,6-hexanetriol to tetrahydropyran-2-methanol (THPM) and successive hydrogenolysis of THPM (Figure 5).

To understand the functions of the HZSM-5 and Ir-ReO$_x$/SiO$_2$ catalysts, we carried out the reaction of cellulose without catalysts or with only HZSM-5 (Table 8). We have already reported that hydrogenolysis activity of Ir-ReO$_x$/SiO$_2$ is enhanced by addition of HZSM-5.[56] Even without catalysts, some of the cellulose was converted in the reaction conditions (entries 1 and 4). It was reported that high-temperature water can produce some concentration of H$^+$ because the ion product ($K_w$) of water at high temperature is higher than that of ambient liquid water.[64] These H$^+$ from water accelerate the dissolution and hydrolysis of cellulose. The conversion of cellulose and the yield of glucose increased with the aid of HZSM-5, suggesting that HZSM-5 enhanced the hydrolysis of cellulose for its intrinsic acid sites (entries 2 and 5). Promotion of hydrolysis of hemicellulose by H-zeolites has been reported in the literature.[65] All of the reaction mixtures without Ir-ReO$_x$/SiO$_2$ catalyst (entries 1, 2, 4, and 5) turned brownish during the reaction, which is in contrast to the colorless solution in the reactions using Ir-ReO$_x$/SiO$_2$ catalyst. The products are mainly glucose and oligosaccharides and were different from those using Ir-ReO$_x$/SiO$_2$ catalyst. A small amount of 5-hydroxymethylfurfural (HMF) was also detected in the mixture

without Ir-ReO$_x$/SiO$_2$ catalyst that contribute to the high chemical reactivity of glucose. No hydrogenation or hydrogenolysis products were formed, indicating that the Ir-ReO$_x$/SiO$_2$ catalyst is essential for the reduction reactions. When the Ir-ReO$_x$/SiO$_2$ catalyst was combined with HZSM-5 (entries 3 and 6), the conversion of cellulose was almost the same as that without Ir-ReO$_x$/SiO$_2$ catalyst, and only the selectivity pattern was changed, indicating that the Ir-ReO$_x$/SiO$_2$ catalyst does not work for hydrolysis of cellulose but only for hydrogenation and hydrogenolysis.

On the basis of the above results, a reaction scheme could be obtained (Scheme 1). First, protons produced from HZSM-5 or hot water catalyzes the hydrolysis of cellulose to water-soluble oligosaccharides. This step is the rate-determining one. Oligosaccharides are further hydrolyzed to glucose. Then, glucose is hydrogenated to sorbitol over the Ir-ReO$_x$/SiO$_2$ catalyst. Finally, hydrogenolysis of sorbitol over Ir-ReO$_x$/SiO$_2$ and HZSM-5 produces the end product *n*-hexane.

## ■ CONCLUSIONS

The Ir-ReO$_x$/SiO$_2$ + HZSM-5 binary catalyst system was effective in the one-pot conversion of cellulose to *n*-hexane. The highest yield of *n*-hexane is 83% from ball-milled cellulose and 78% from microcrystalline cellulose. The preferable reaction temperature is 463 and 483 K for ball-milled and

microcrystalline cellulose, respectively. The yield of *n*-hexane kept above 70% even using a high weight ratio of ball-milled cellulose to water (1:1). Recycling the Ir-ReO$_x$/SiO$_2$ catalyst + HZSM-5 is feasible under the reaction conditions. The reaction pathway was presented: First, high-temperature water and/or HZSM-5 promote the hydrolysis of cellulose to glucose via water-soluble oligosaccharides. Then, glucose is hydrogenated to sorbitol over the Ir-ReO$_x$/SiO$_2$ catalyst. Finally, hydrogenolysis of sorbitol by the over Ir-ReO$_x$/SiO$_2$ and HZSM-5 process produces the end product *n*-hexane.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Picture of the glass vessel after feeding, TG-DTA analysis of Ir-ReO$_x$/SiO$_2$ + HZSM-5 after reaction, and results of repeated tests. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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