# *In situ* Mg activator-based water donating hydrogenation of glucose to sorbitol

Lusha Qin School of Material Science and Engineering *Pusan National University* Busan, Republic of Korea qinlusha@pusan.ac.kr Sungho Lee School of Material Science and Engineering *Pusan National University* Busan, Republic of Korea mellowbass@pusan.ac.kr Oi Lun Li School of Material Science and Engineering *Pusan National University* Busan, Republic of Korea helenali@pusan.ac.kr

Abstract— This research firstly proposed a in situ hydrogen generation to convert glucose to sorbitol via Mg scarification. This process features the utilization of Mg powder as the hydrogen activator, water as the hydrogen source, commercial Ru/C as the catalyst, allowing the hydrogenation to occur under mild reaction conditions without the external supply of hydrogen. Efficient production of hydrogen inside the reaction solvent results in a glucose conversion rate of 96% as well as the sorbitol selectivity of 92% over Ru/C at 110 °C for 2 h. The hydrogenation behavior of this system is examined under the gradient Mg dosage, Ru/C loading, and reaction temperature. A wide application scope has been verified, which containing fructose, mannose, galactose, xylose, and cellobiose. Furthermore, the Ru/C applied in this process can be reutilized successfully without sacrificing its high catalytic activity and sorbitol selectivity. This hydrogenation system makes significant advances by removing the dependence on the external supply of high-pressure hydrogen. This is the first study of a self-propelling, highly active process to highly selective hydrogenation of sugars to polyol under mild conditions, thus providing an economical, safe, and sustainable alternative to conventional hydrogenation methods.

Keywords— Hydrogen generation, Mg-H<sub>2</sub>O reaction, glucose hydrogenation, sorbitol, sugar alcohol

#### Introduction

Cellulosic biomass is currently viewed as the potential "green chemical feedstock" in the industry [1]. The low price and natural abundance of biomass stimulate the research interest towards the conversion of biomass to value-added carbohydrate chemicals [2]. The reducing sugar constitutes a large fraction in the chemical composition of lignocellulose, which is also the primary precursor to be further converted to sugar alcohol [3]. Sugar alcohol, such as sorbitol, mannitol, and xylitol are popular additives in the industry of nutrition, cosmetics, and medical industry [4,5]. For example, the most productive sugar alcohol is sorbitol, the global sorbitol production is estimated to range from 500 to 800 M tons per year [6]. Although sugar alcohol can be produced naturally from the plants, which cannot meet the huge market demand. Thus, there is still a huge demand for sugar alcohol in the industry, which must be satisfied by the chemical conversion from cellulosic biomass [7]. The selective catalytic hydrogenation of natural sugar to sugar alcohol is regarded as an eco-friendly and most widely used process for the production of alternative sweeteners [8].

Hydrogenation is a versatile fundamental reaction in chemistry, has been extensively used in various processes in biomass transformation [1-2]. Besides the production of sugar alcohol from natural sugar, the hydrogenation process also has been applied to the transformation of lactic acid to 1,2propanediol, conversion of levulinic acid to y-valerolactone, and so on [9-11]. External hydrogen (H<sub>2</sub>) supply is one of the fundamental parts of the conventional hydrogenation process, which is satisfied by external hydrogen by compressed hydrogen gas cylinders. [15] As reported, the H<sub>2</sub> pressure primarily ranges from 2 to 10 Mpa under the temperature and reaction time within 180°C and 5h. Since the H<sub>2</sub> storage and transportation is still on the way of development, huge work has to be made to control the safety condition. The drawback of the H<sub>2</sub> external supply in the conventional hydrogenation process poses a threat to safety [16, 17]. Not only that, considering the relatively high price of H<sub>2</sub>, the massive consumption of H<sub>2</sub> in current hydrogenation methods leads to a large proportion of the overall input cost. Accordingly, the problems lying behind the conventional hydrogenation system were raised [18].

In recent years, the achievement of the hydrogenation process by in-situ hydrogen donors has received extensive concern. [19-21] For instance, the hydrogen-rich precursor, like ethanol, methanol, and some alkenes were investigated for hydrogenation of furfural and to 5-Hydroxymethylfurfural [22]. However, these organic hydrogen donors still suffer the problems of high cost and non-environmental and complex post-treatment. Additionally, the external supply of high-pressure gas is still required for these reported in-situ hydrogenation processes [20-23].

Water as the most fundamental widespread solvent with high polarity can also serve as an ideal alternative to the organic hydrogen donors [24]. Inspired by the H<sub>2</sub> generation by the reaction of H<sub>2</sub>O and metal which of high energy density, a novel hydrogenation system driven by Mg-H<sub>2</sub>O reaction is developed [25]. Magnesium (Mg) and alloys are considered promising candidates due to their moderate triggering conditions and high theoretical hydrogen yield [26]. Especially, the low solubility of magnesium hydroxide (Mg (OH)<sub>2</sub>) precipitates in water promise the reaction solution can be maintained within a relatively stable pH range, which is one of the important factors to the high selectivity of sorbitol. It has the characteristics of low cost, accessibility, and ease to be operated. These facts promote the Mg as the promising H<sub>2</sub> gas activator to be applied in the water donating hydrogen system.

The noble metal-based catalysts have been determined with excellent catalytic performance on sugars hydrogenation in an aqueous environment. The investigation on the catalytic performance and excellent selectivity of Ru/C as the catalyst



Scheme 1. Proposed design of glucose hydrogenation to sorbitol over Ru/C catalyst in Mg driven water donating

is most attractive [27-30]. Therefore, it is highly desired that the efficiency of the novel hydrogenation system can be performed well by using Ru/C as the catalyst. this selfpropelling hydrogenation system.

Herein, the water donating hydrogenation system based on Mg as the activator is encouraged to be employed in the hydrogenation of biomass-derived reducing sugars to sugar alcohol over Ru/C catalyst. The parameters of Mg dosage, Ru/C loading, pH, and reaction temperature were optimized to achieve outstanding performance under relatively mild reaction conditions. Notably, the achieved conversion rate of glucose and selectivity of sorbitol is competitive to the reported conventional hydrogenation method. Also, the application scope is successfully broadened to various kinds of reducing sugars, containing fructose, mannose, xylose, arabinose, and cellobiose. Essentially, the recycle examination demonstrates the Ru/C catalyst used in this system can be easily recycled without the loss of catalytic activity. The advantages of this hydrogenation system include high technical-efficiency, economic-feasibility, and long-term sustainability compared to the conventional method. It is believed that this Mg activator-based watering hydrogenation system is of great potential for industrial application in the future.

# 1. Design of the Mg-H<sub>2</sub>O hydrogenation system

For the conventional method to reducing sugar hydrogenation, one of the most important prerequisites of the great catalytic performance is the external  $H_2$  gas supply of high pressure into the reactor. Herein, an innovative hydrogenation process is proposed, as shown in Scheme 1, the design of this work and the proposed reaction route are illustrated.

To examine the contribution and synergistic effect of Mg and Ru/C, comparative experiments have been conducted of blank control, Ru/C, Mg, Ru/C, and Mg. The experiments are performed in a stainless steel autoclave with 25ml, in which the detail experimental information is demonstrated in Supporting information. The conversion performance and distribution by different catalyst conditions are given in Table 1. The reaction temperature, reaction time is fixed at 110°C, 2h, respectively. In terms of the blank control and only Ru/C as the catalyst, there is no noticeable conversion of glucose occurs without the supply of H<sub>2</sub>. It is seen that the presence of

 $H_2$  is of great significance to develop the excellent performance of Ru/C for the hydrogenation reaction.

For Mg powders are added to the reaction solution without Ru/C catalyst, 19% of the glucose total conversion rate is obtained. The reaction between Mg powder and water can be confirmed by analysis of the solid product after the reaction. As shown in Fig. S1, the XRD pattern of the product demonstrates the production of Mg(OH)<sub>2</sub>, which also verifies the presence of H<sub>2</sub> gas during the hydrothermal hydrogenation reaction. The fructose and mannose as the main product is generated by the glucose isomerization since a small amount of Mg(OH)<sub>2</sub> is dissolved in the solution during the reaction process. Thus, the coordination between the H<sub>2</sub> activator and hydrogenation catalyst is particularly important to glucose hydrogenation to sorbitol, neither is indispensable in no external supply of the H<sub>2</sub> process.

Fortunately, the integration of Ru/C and Mg has shown superior activity to the production of sorbitol from glucose without external H<sub>2</sub> supply. The total conversion percentage and the sorbitol selectivity up to 95% and 92% under comparably mild reaction conditions. Mg powders decompose H<sub>2</sub>O molecular to produce H<sub>2</sub> source, followed by the activation of  $H_2$  on Ru/C, then finally to be reduced the C=O to C-OH. Therefore, Mg and Ru/C perform their duties and cooperate for the reaction to proceed along the expected path. The presence of too much Lewis base should be avoided because they catalyze the formation of the undesirable byproduct and in parallel reaction path.-Therefore, little amount of Lewis acid is designed as an additive to balance the pH in the reaction solution, which is positive to the sorbitol-target reaction way. The trace amount of HCl is selected as the additive to regulate the reaction route. On one hand, HCl can react with the small amount of dissolved Mg(OH)<sub>2</sub> to balance acid-base conditions to targeted sorbitol production. On the other hand, the presence of magnesium chloride (Mg(Cl)<sub>2</sub>) provides the chloride ions (Cl<sup>-</sup>) to prevent the formation of magnesium oxide films [31]. It makes a positive effect on the production of H<sub>2</sub> by improving the interaction between Mg powder surface and water molecular. The conception of this hydrogenation system is established based on the principle of compress H<sub>2</sub> gas-free, technically-feasible, economicallyefficient. It is hoped to replace the traditional hydrogenation method with sugar alcohol production based on a highpressure supply of H<sub>2</sub> externally.

Table 1.	Catalyst	optimizatio	n of glucose	hydrogenati	on via Mg d	riven water de	onating hydro	ogenation system.
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Catalyst	Conversion (%)	Mannose (%)	Fructose (%)	Galactose (%)	Sorbitol (%)	Mannitol (%)	Other product (%)		
-	< 0.10	0.02	0.05		-	-	-		
Ru/C	< 0.10	0.03	0.03		-	-	-		
Mg	19	3.60	15	0.72	-	-	0.50		
Ru/C & Mg	96	0.52	2.95		87	4	-		
Reaction condition: Glucose (1.25 mmol, 100 mg), Ru/C (0.012 mmol, 50 mg), Mg powder (4.17 mmol, 100 mg), water									
solvent (12.5ml), 1N HCl (200ul), 110°C, 2h.									

## 2. Rationalization of the catalytic behavior

The parameters to the catalytic behavior of this Mg driven watering donating hydrogenation system was investigated for hydrogenation of glucose to sorbitol under various reaction condition. Fig. 1 shows us the time-dependent yield of sorbitol under various Mg, Mg dosage, water volume, Ru/C loading, and temperature. As shown in Fig. 1 (a), the influence of Mg dosage on the hydrogenation performance is clearly illustrated. For the condition of 25, 50, 75 mg dose of Mg added into the reactor, as the reaction progresses, the product yield gradually increases, and the rate of yield increase gradually slowed down. The higher amount of Mg powder added to the reactor favors the production of more hydrogen, which further contributes to the hydrogenation reaction of glucose to produce sorbitol. For the Mg dosage of 100 and 125 mg, the sorbitol production is reaching a peak within 2h reaction, followed by a slight decrease as the reaction continues. It is possible caused by the generation of by-products by the deviation of the reaction path. There is an optimized amount of the Mg powder towards the maximum sorbitol yield. The generally accepted reaction network is shown in the proposed reaction network shown in Fig. 2. First, fructose and mannose are generated by the isomerization of glucose under the action of hydroxide ion (OH-), which is in line with the reported opinion [32].  $H_2$  is produced via the Mg and H<sub>2</sub>O reaction, which is further activated by the Ru/C catalysts to be ready for hydrogenation. Glucose, fructose, and mannose are further reduced by the activated hydrogen to sorbitol and mannitol. The isomerization among glucose, fructose, and mannose provides a different route for the sorbitol generation. Concomitantly, sorbitol production rises. A very peculiar observation is that nearly no fructose accumulation has been observed during the reaction, suggesting the high reaction rate of sugars hydrogenation to

sorbitol and mannitol compared to the isomerization process. Mg dosage is highly reacted to the amount of  $H_2$  be generated during the reaction, thus affecting the reaction efficiency greatly. Additionally, since Mg powders dosage is regarding the amount of Mg(OH)<sub>2</sub> be produced, the pH of the solution varies with the Mg dosage. The by-product of mannitol would be promoted due to the enhanced mannose yield obtained from the first-step reaction. Also, it is known that the Mg-H<sub>2</sub>O reaction is exothermic. Locally high heat generation can lead to the formation of organic acids and other by-products. Therefore, the Mg powder dosage be Controlled within a reasonable range is the keystone to the highly selective production of sorbitol from glucose via this Mg-driven water donating hydrogenation system.

Water as the hydrogen source to produce hydrogen for the target reaction is of great significance to be investigated. The lower water content of 10 and 12.5 ml exhibits a higher yield of sorbitol compared to the water volume of 15ml. It is worth exploring that the two curves representing different water content cross overreaction time progress. The water content is closely related to the amount of hydrogen produced, pH of the solution, that key factors for the hydrogenation performance as discussed in the Mg dosage influence,

Next, the study on catalyst loading influence has been performed. The weight ratio of substrate to catalyst ranges from 8:1 (12.5 mg), 4:1 (25mg), 2:1(50 mg). The result shows that the high catalyst loading efficiently favors the high reaction rate. In the case of 50mg catalyst, the reaction rate within the first 2h is higher than the lower catalyst loading. For the lower catalyst loading, the H<sub>2</sub> molecular is still prepared for the hydrogenation After 2h reaction, which can not be activated by the Ru species on the carbon support. And the last 1 h, the sorbitol yield is still growing. It is due to some H<sub>2</sub> cannot be activated by Ru species, limiting the hydrogenation performance.

Substrata	Conversion (%)	Product (%)							
Substrate	Conversion (70)	Sorbitol	Mannitol	Galactitol	Xylitol	Arabitol			
Glucose	95	87	4	-	-	-			
Mannose	98	6	87	-	-	-			
Fructose	97	26	62	-	-	-			
Galactose	98	-	88	3	-	-			
Xylose	96	-	-	-	89	-			
Arabinose	95	-	-	-	-	91			
Cellobiose	76	71	_	_	_	_			

Table 2. Application scope of saccharides hydrogenation via Mg driven water donating hydrogenation system.

Reaction condition: Glucose (1.25 mmol, 100 mg), Ru/C (0.012 mmol, 50 mg), Mg powder (4.17 mmol, 100 mg), water solvent (12.5ml), 1N HCl (200µl), 110°C, 2h.



**Fig. 2.** Investigation of the catalytic behavior to glucose hydrogenation in Mg driven water donating hydrogenation system. (Reaction condition: (a) Glucose (1.25 mmol, 100 mg), Ru/C (0.012 mmol, 50 mg), water (12.5 mL), temperature (110°C). (b) Glucose (1.25 mmol, 100 mg), Ru/C (0.012 mmol, 50 mg), Mg powder (4.17 mmol, 100 mg), temperature (110°C). (c) Glucose (1.25 mmol, 100 mg), Mg powder (4.17 mmol, 100 mg), water (12.5 mL), temperature (110°C). (d) Glucose (1.25 mmol, 100 mg), Ru/C (0.012 mmol, 50 mg), Mg powder (4.17 mmol, 100 mg), water (12.5 mL).

Last but not least, the temperature impact is confirmed by the hydrogenation reaction carried out under a series of gradient temperatures. Reaction temperature function as the key factor to the degree of Mg-H<sub>2</sub>O reaction. which is reasonably associated to the H<sub>2</sub> gas to be produced for the hydrogenation process. The illustration of the time course sorbitol yield on the temperature is displayed in Fig. 3 (d). For the reaction temperature at 90°C. In the initial stages from 30 to 90min, the sorbitol production increased rapidly, especially from 60 to 90 min. The sorbitol yield keeps growing from 90 to 120 min with a comparatively lower increasing rate. It can be explained that Mg powder reacts slowly with water at a relatively low temperature. The formation of surface oxide film prevents the Mg powder from fully reacting with water to generate H<sub>2</sub>. The accumulation of H<sub>2</sub> in the first 30 min leads to the high reaction efficiency of the period from 30 to 90 min. For the high temperature of 110 and 130 °C, accelerating the H<sub>2</sub> generation rate is conducive to the uniform deposition of Mg(OH)<sub>2</sub>, which is positive to the successive reaction of the Mg surface and water molecular to generate H<sub>2</sub>. After 90 min of reaction, the increasing rate dropped down gradually, which caused by the formation of by-products, mainly containing mannitol, organic acid. The maximum yield of sorbitol is obtained at 110°C for 2h, the corresponding sorbitol selectivity up to 92 % under the total conversion rate of 96 %.

#### 3. Recycle test of Ru/C catalyst

The reusability of Ru/C catalysts used in this Mg-driven water donating hydrogenation system was investigated. Fig. S3 - S6. show us the morphology, XRD pattern, the nitrogen  $(N_2)$  adsorption-desorption isotherm, XPS characterization of the Ru/C before and after reaction. It suggests that the chemical-structure and chemicals-stated of Ru/C is well-preserved during the hydrogenation process, making the stable catalytic ability can be developed in the reuse process.



**Fig. 3.** The recyclability of Ru/C to glucose hydrogenation used in Mg driven water donating hydrogenation system.

Table 3. Comparison and limitations of conventional hydrogenation of sugars to sugar alcohol

Substrate	Catalysts	H <sub>2</sub> pressure (Mpa)	Temperature (°C)	Time (h)	Conversion rate (%)	Yield <sup>a</sup> (%)	Selectivity <sup>b</sup> (%)	Ref	
Glucose	Ru/AC	1.6	180	3	100	89	89	24	
Glucose	Ru/C	2	120	4	81.3	61.7	76	25	
Glucose	Ru/polymer	5.5	100	1	69	67.5	98	26	
Fructose	Ru/C	10	100	20	100	40	40	27	
Xylose	Ru/zeolite	5.5	120	2	62	61	98	28	
Glucose	Ru/C/Mg	/	100	2	95	87	92	This work	
<sup>a</sup> Vield is for the main product sorbital mannital or vulital <sup>b</sup> the selectivity of main product									

<sup>a</sup> Yield is for the main product, sorbitol, mannitol, or xylitol. <sup>b</sup> the selectivity of main product.

Additionally, the reusability of Ru/C used in the Mgdriven water donating hydrogenation system was verified. As shown in Fig. 4, the glucose conversion rate, sorbitol yield, and sorbitol selectivity are 95%, 87%, and 92%, respectively. After a three-time cycle test, the catalytic ability can be maintained well compared to the fresh use. The glucose conversion rate, sorbitol yield, and sorbitol selectivity reached 92%, 83%, and 90%. Therefore, the Ru/C catalysts could be reused in this Mg-driven water donating hydrogenation system without seriously sacrificing its high activity and selectivity to sorbitol.

# 4. Determination of application scope

The hydrogenation of different monomeric sugars by using this water donating hydrogenation system was characterized in Table 2, including glucose, mannose, fructose, galactose, xylose, arabinose, and cellobiose. The total conversion rates and the selectivity ranges from 94-97% and 95-99 % under 110 °C for 2h respectively. For the hydrogenation of glucose and mannose, sorbitol/mannitol constitutes a large fraction of the products. The isomerization of glucose, fructose, and mannose occurs during the hydrogenation process, which contributes to the formation of the second product of mannitol or sorbitol. Fructose in these sugar substitutes has shown a distinct result, which lies in the lower ratio between the sorbitol and mannitol compared to glucose and mannose. The different tautomeric produced during the reaction forms of fructose have different adsorption strengths on the surfaces of hydrogenation catalysts and individual hydrogenation rates. [34]

Cellobiose is a kind of disaccharide that has been used as the substrate. As shown in Table 2, the corresponding conversion rate, sorbitol yield is slightly less than the monosaccharides hydrogenation process. But it is still comparable to the catalytic performance of cellobiose hydrogenation to the glucose reported in the literature [35,36]. This Mg-driven water donating hydrogenation system is applicable in various reducing sugars hydrogenation to produce sugar alcohol.

Considering the experimental conditions were optimized in each work, the common reaction condition on hydrogenation of sugars over ruthenium-based catalysts from various reports was roughly compared in Table 3. First, glucose is the most extensively studied for the production of sugar alcohol. Ruthenium catalysts based on different supports have been reported. For instance, Lazaridis et al.

reported that hydrogenation of glucose over 5 % Ru-AC under 1.6 MPa H<sub>2</sub>. The total conversion rate was 100%, yet the sorbitol yield was about 63 % at the elevated reaction temperature of 180 °C for 3 h. As reported in Guo's research, the 5 wt.% Ru/C as catalysts to hydrogenation of glucose to sorbitol gave the sorbitol yield 50.2% with the selectivity of 61.7 under 4.0 Mpa  $H_2$  at 120 °C for 2h. The 5 wt % of Ru nanoparticles supported on nanoporous polymer has been investigated by Dabbawala et.al, which results in a conversion rate of 69.0 % and sorbitol yield of 67.6 % under the hydrogenation pressure of 5.5 Mpa at  $100^{\circ}$ C for 1 h. Besides, the hydrogenation of fructose over Ru/C under 10 Mpa H<sub>2</sub> at 100 °C for 20 h has been conducted by Heinen, the total conversion percentage and the selectivity of mannitol were 100% and 40%, respectively. Hydrogenation of xylose to xylitol via Ru/Zeolite catalyst was investigated by Mishra, the conversion of xylose and the selectivity of xylitol were 62 % and 98 %, respectively, which is performed under the H<sub>2</sub> pressure of 5.5Mpa, the temperature at 120  $^{\circ}$ C for 1h. In this work, the hydrogenation of glucose was conducted under the Mg dosage of 0.2 g, the temperature of 110  $\,^\circ\! \mathbb{C}\,,$  the reaction time of 2 h. The generated H<sub>2</sub> pressure can be estimated as 0.05 Mpa, which is much lower than the H<sub>2</sub> pressure reported in the literatures. However, it is noted that the conversion rate of glucose, the yield of sorbitol, and the selectivity of sorbitol up to 95%, 87%, and 92%, individually. The in-situ generation of H<sub>2</sub> improves the interaction among hydrogen, catalyst surface, and substrate, which benefits the high efficiency of sugar hydrogenation.

## I. CONCLUSION

In sharp contrast to the conventional hydrogenation method with an external supply of high-pressure H<sub>2</sub> gas, a proposal to a self-propelling hydrogenation system is firstly established in this research. An innovative hydrogenation process supported by the in-situ generated H<sub>2</sub> is realized via Mg-H<sub>2</sub>O reaction, contributing to the glucose hydrogenation to sorbitol with the total conversion rate of 95% and sorbitol selectivity of 92% under relatively mild reaction condition at 110°C for 2h. The relatively high solubility of in-situ generated H<sub>2</sub> in the reaction solution, allows the improved mass transfer, promoting the interaction among H<sub>2</sub>, Ru/C catalyst, and glucose molecular, further favoring the excellent catalytic performance. Furthermore, this wide application of this new approach is approved in the hydrogenation of various reducing sugars to the corresponding sugar alcohol with promising selectivity. Upon undergoing recycle test, the Ru/C catalyst maintained its catalytic activity and selectivity, clearly representing this new system will not negatively affect the sustainability of the catalyst. We believe that this simultaneous hydrogen generation and glucose hydrogenation process could serve as the potential alternative to conventional hydrogenation systems, which is highly expected to make a significant contribution to the sustainable biomass upgrading process.

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#### **Experimental:**

# **Supporting information**

# Reagents

D(+)-Glucose of GR grade was obtained from Junsei Chemical Co.,Ltd. Fructose, Mannose, Galactose, Xylose, and Arabinose were purchased from Sigma Aldrich. Magnesium powder was obtained from Samchun Chemicals Co.Ltd. 5 wt% Ru/C was purchased from Sigma Aldrich.

# **Reaction procedure**

The experiment was carried out in the stainless-steel autoclave with PTFE liner of 25ml. The glucose concentration is 0.2 mol/L. The loading of 5 wt. % Ru/C catalyst varies from 12.5, 25, to 50 mg. The mixture of substrate and Ru/C catalyst was treated with magnetic stirring for 2h. Then, Mg powder (25, 50, 75, 100, 125 mg) and 200ul of 1N HCl were added to the substrate-catalyst mixture, followed by heating in the oven. The reaction temperature was evaluated at 90, 110, 130°C and reaction time was varied from 30, 60, 90, 120, 150, 180 min.

#### Characterization

Scanning electron microscopy (SEM) images were taken using JEOL JSM-7610F scanning electron microscope at an accelerating voltage of 15kV. The phase structure was identified by X-ray diffraction (XRD) patterns, which is recorded by using a Rigaku Ultima IV X-ray diffractometer with monochromatic Cu Ka radiation operating at 40kV and 40mA. Nitrogen adsorption/desorption experiments were performed for the determination of specific surface area, total pore volume (at P/Po = 0.99), and pore size distribution based on the BET method (Brunauer-Emmett-Teller (BET) analyzer; Shimadzu, TriStar-II 3020, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed at normal emission by using Al Ka monochromatic radiation (hv = 1486.7 eV) of an X-ray gun, operating with 300 W (12 kV/25 mA) power using an (XPS, JEOL, JPS-9010MC, Japan). The spectra were collected in the region of the C 1s, O 1s, Ru 3p, Ru 3d. The binding energies were then corrected for the surface-charging effects during the measurements by using the C1s core level (284.6 eV) of the adventitious carbon as an internal reference.

#### **Products analysis**

The aqueous products were detected by high performance liquid chromatography (HPLC) SHIMADZU JP/LC-20A), RPM-Monosaccharide Pb+2 (8%) and Rezex ROA-organic acid h<sup>+</sup> column, Refractive index detector, RID). The conversion rate was determined by the ratio of the Carbon content in reactants and products, which is calculated by the equation as given by:

Conversion rate (%) = 
$$\frac{m_{glucose(0)} - m_{glucose(t)})}{m_{glucose(0)}} \times 100\%$$

Where m  $_{glucose (0)}$  is the initial weight of glucose charged in the reactor, m  $_{glucose(t)}$  is the weight residual glucose after hydrogenation reaction., and the is calculated by using the following equation:

 $m_{glucose(t)} = c_{glucose} \times v$ 

where C <sub>glucose(t)</sub> can be obtained by the HPLC result, V is the total volume of the reaction solution. The yield of products was determined by the carbon moles ratio in the product and glucose. The yield was calculated as given by

$$C(\%)$$
 in glucose =  $\frac{m_{glucose(0) \times 0.40}}{12}$ 

*Yield* of sorbitol (%) =  $\frac{c_{sorbitol \times V \times 6}}{180 \times C(\%) \text{ in glucose}} \times 100\%$ 

*Yield* of mannitol (%) = 
$$\frac{C_{mannitol \times V \times 6}}{180 \times C(\%) \text{ in glucose}} \times 100\%$$

 $Selectivity (\%) = \frac{\text{Yield of sorbitol/mannitol (\%)}}{\text{Conversion rate (\%)}} \times 100\%$ 



Fig. S1. XRD pattern of fresh Mg and solid powder collected after reaction.



Fig. S2. The reaction pathway to glucose hydrogenation via Mg driven water donating system over Ru/C catalyst.



Fig. S3. SEM images of Ru/C before and after use. (a) Fresh Ru/C, (b) Ru/C after use.



Fig. S4. Nitrogen adsorption and desorption and particle size of fresh Ru/C (a, b) and recycled Ru/C (c, d)



Fig. S5. XRD pattern of fresh Ru/C and recycled Ru/C.



Fig. S6. XPS spectra of Fresh Ru/C (a, b) and recycled Ru/C (c, d).