

Catalytic Production of Propanediol from Glucose Using $\text{Mg}(\text{OH})_2$ - Modified Ru/SiO_2 Catalysts

Dongsu Bi

Shanghai Institute of Technology

Xinming Mao

Shanghai Institute of Technology

cheng Hou

Tongji University

Yuanbo Song

Tongji University

Mengyu Jin

Tongji University

yang shi

Tongji University

Xiaoxia Wang

Tongji University

Chengtao Gao

Guizhou Institute of Technology School of Materials and Metallurgical Engineering; Guizhou Institute of Technology School of Materials and Energy Engineering

Shijie Wang

Tongji University

Zheng Shen

shenzheng@tongji.edu.cn

Tongji University <https://orcid.org/0000-0003-3668-7820>

Research Article

Keywords: 1,2-Propanediol, Retro-aldol condensation, Acid-base bifunctionality, Glucose isomerization

Posted Date: June 11th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-9852954/v1>

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Abstract

The efficient conversion process of 1,2-propanediol (1,2-PG) based on renewable biomass glucose can effectively get rid of the dependence on fossil fuels and open up a green and low-carbon sustainable alternative way for the production of this chemical. This study focuses on the reaction system for the selective hydrogenolysis of glucose to 1,2-propanediol (1,2-PG). To overcome the limitations of conventional catalysts—namely poor selectivity control and insufficient stability—we developed a novel core-shell structured Ru/SiO₂ catalyst modified with Mg(OH)₂. Through systematic optimization of the support pretreatment process, Ru active component loading method, Mg(OH)₂ modification amount, and core-shell interface regulation parameters, precise matching between the catalyst's microstructure (e.g., exposed degree of active sites, metal-support interaction strength, and surface acid-base properties) and its catalytic performance was successfully achieved. Among the screened metals (Cu, Ni, Ru, Sn, and Fe), Ruthenium (Ru) exhibited the highest catalytic activity; specifically, Mg(OH)₂ modification significantly enhanced the 1,2-PG yield to 24.97%, a substantial increase from the 2.45% observed for the unmodified Ru/SiO₂ catalyst. Through systematic optimization of reaction parameters, a maximum 1,2-PG yield of 33.9% was achieved under the following optimal conditions: 5 wt.% Mg(OH)₂ loading, 150 mg of catalyst, 180°C, 3 MPa H₂, and a reaction time of 3 h. Characterization via TEM, SEM, and TPD confirmed that the Mg(OH)₂ modification resulted in a core-shell structure endowed with both strong acidic and basic sites. Mechanistic studies revealed that this bifunctionality synergistically promotes the rate-limiting glucose-to-fructose isomerization step and the subsequent fructose retro-aldol condensation (RAC). Furthermore, the catalyst exhibited robust structural stability and maintained reusability after regeneration via calcination at 450°C. This work presents a promising bifunctional heterogeneous catalytic system for the sustainable production of 1,2-PG from renewable glucose.

1. Introduction

1,2-Propanediol (1,2-PG), also known as propylene glycol, is a high-value platform chemical with diverse industrial applications, including the production of unsaturated polyester resins¹, antifreeze², cosmetics, and pharmaceuticals³. Currently, 1,2-PG is produced almost exclusively via the hydration of propylene oxide, a feedstock derived from petroleum resources⁴. Increasing concerns over fossil fuel depletion and environmental pollution have stimulated significant research into sustainable and green routes for 1,2-PG production from renewable biomass resources^{5–7}. Among various biomass feedstocks, glucose—which is abundant, inexpensive, and readily available from the hydrolysis of cellulose—is considered an ideal starting material^{8–11}. However, the traditional chemical method requires a multi-step conversion reaction step, which is cumbersome and low in atomic economy. Therefore, we need an efficient one-step method to optimize the reaction process.

The direct catalytic hydrogenolysis of glucose into 1,2-PG is a highly attractive "one-pot" process¹², however, it remains scientifically challenging due to the involvement of a complex cascade of reactions. The generally accepted mechanism proceeds through three main steps: (1) the isomerization of glucose (an aldose) into fructose (a ketose), typically catalyzed by bases or acids^{13, 14}; (2) the retro-aldol condensation (RAC) of fructose into C3 intermediates, primarily dihydroxyacetone (DHA) and glyceraldehyde (GLY)^{15, 16}, which is also base-catalyzed; and (3) the subsequent hydrogenation of these C3 intermediates to 1,2-PG¹⁷, which occurs on metal catalyst sites.

The primary challenge in this process lies in controlling reaction selectivity, as this complex network is often hindered by competing side reactions. Most notably, the metal hydrogenation sites can prematurely hydrogenate the C6 glucose and fructose feedstocks to sugar alcohols, such as sorbitol and mannitol^{18, 19}, which are dead-end byproducts in this pathway. Furthermore, undesired C-C bond cleavage can lead to the formation of C2 and C1 byproducts, such as ethylene glycol (EG) and ethanol²⁰. Therefore, an efficient catalyst must be bifunctional²¹, incorporating both metal sites for hydrogenation and acid/base sites to promote the isomerization and RAC steps²². The key to high 1,2-PG yield is the precise balancing of these functions to ensure the C6 isomerization/RAC pathway is kinetically favored over the C6 hydrogenation pathway²². Various heterogeneous catalytic systems have been explored. Noble metals like Ru²³, Pt, and Pd, as well as non-noble metals like Ni and Cu, have been investigated for the hydrogenation function. Ruthenium (Ru) is often reported as a highly active metal for this conversion^{24, 25}. To introduce the necessary acid/base functionality, these metals have been combined with various supports, including solid acids (e.g., zeolites, niobic acid) and solid bases (e.g., MgO, CaO, hydrotalcites)^{26, 27}. Although basic supports are known to promote the crucial isomerization and RAC steps, many systems continue to suffer from low selectivity or catalyst instability. For instance, strong basic sites can catalyze the degradation of C3 intermediates, whereas metal nanoparticles often sinter or leach under harsh hydrothermal conditions^{28, 29}.

To address these challenges, new catalytic materials with precisely tuned bifunctionality and enhanced structural stability are required. The modification of a supported metal catalyst with a basic promoter, organized in a specific architecture, could be a viable strategy. Ideally, a core-shell structure can create a unique acid-base environment at the metal-support interface, potentially enhancing the desired cascade reaction while simultaneously protecting the metal nanoparticles³⁰. Herein, we report the development of a Mg(OH)₂-modified Ru/SiO₂ catalyst with a core-shell structure for the selective hydrogenolysis of glucose to 1,2-PG. We first compare the performance of Ru with other common metals (Cu, Ni, Sn, Fe) and demonstrate the superior promoting effect of the Mg(OH)₂ modification. The catalytic system is then systematically

optimized by investigating the effects of $\text{Mg}(\text{OH})_2$ loading, catalyst dosage, reaction temperature, and time. The structural and chemical properties of the catalyst are analyzed using TEM, SEM, XRD, and TPD to understand the origin of its performance. Finally, we probe the reaction mechanism using intermediate compounds and assess the catalyst's reusability to demonstrate its potential for practical application.

2. Material and methods

2.1 Experimental material

All chemical reagents used in this study were of analytical grade and used as received without further purification, unless otherwise specified. Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$, $\geq 99.5\%$), 1,2-propylene glycol ($\text{C}_3\text{H}_8\text{O}_2$, $\geq 99.5\%$), mannitol ($\text{C}_6\text{H}_{14}\text{O}_6$, $\geq 98\%$), sorbitol ($\text{C}_6\text{H}_{14}\text{O}_6$, $\geq 98\%$), and HPLC-grade methanol (CH_4O) were purchased from Sigma-Aldrich (St. Louis, MO, USA). 1,3-Dihydroxyacetone ($\text{C}_3\text{H}_6\text{O}_3$, $\geq 99\%$) was obtained from Mecox Lane. 1,2-Hexanediol ($\text{C}_6\text{H}_{14}\text{O}_2$, $\geq 98\%$), n-propanol ($\text{C}_3\text{H}_8\text{O}$, $\geq 99.5\%$), ethanol ($\text{C}_2\text{H}_6\text{O}$, $\geq 99.5\%$), and magnesium oxide (MgO , $\geq 98.5\%$) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ruthenium(III) chloride (RuCl_3 , with Ru content $\geq 37.5\%$) was purchased from Aladdin Reagent (Shanghai) Co., Ltd. (Shanghai, China). High-purity helium (N_2 , $\geq 99.5\%$) and hydrogen (H_2 , $\geq 99.5\%$) were obtained from Weichuangqiti. Deionized water was used throughout all experiments.

2.2 Catalyst Preparation

(1) Ruthenium was introduced into the SiO_2 structure by equal-volume impregnation. $\text{RuCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in deionized water to form a homogeneous aqueous solution of $\text{H}_2\text{RuCl}_3 \cdot 6\text{H}_2\text{O}$, and SiO_2 powder was added to the above solution, which was stirred homogeneously and ultrasonicated for 15 min.

(2) The samples obtained above were static aged for more than 6 h at room temperature, then dried in an oven at 105°C for more than 6 h, and finally heated up to 450°C in a tube furnace at a rate of $2^\circ\text{C}/\text{min}$, and continuously roasted in static air for 4 h under the condition of 450°C to obtain Ru/SiO_2 .

(3) A certain amount of catalyst, deionized water and MgO precursor were added into the reaction kettle and mixed homogeneously, and then hydrothermally reacted under 5 MPa hydrogen pressure and 200°C for 4 h. Subsequently, the solid powder was transferred to a crucible and placed in a resistance furnace, and then heated up to 450°C with a heating rate of $2^\circ\text{C}/\text{min}$, and then continuously roasted under 450°C in static air for 4 h to burn off the impurities to obtain the $\text{Ru}/\text{SiO}_2@\text{Mg}(\text{OH})_2$ catalyst.

2.3 Selection of Catalyst Support Metal

In this study, Ru, Cu, Ni, Sn and Fe metals were selected to measure the yield of 1,2-propanediol by loading metal on silica alone and with $\text{Mg}(\text{OH})_2$ as the shell. Figure 1 illustrates that the $\text{Ru}/\text{SiO}_2@\text{Mg}(\text{OH})_2$ catalyst exhibited superior catalytic performance for the hydrogenolysis of glucose to 1,2-propanediol (1,2-PG) compared to other metal counterparts (Cu, Ni, Sn, Fe). In the absence of the $\text{Mg}(\text{OH})_2$ shell, the Fe-based catalyst showed the highest 1,2-PG yield (merely 2.62%), which is insufficient for practical application. Notably, the introduction of the $\text{Mg}(\text{OH})_2$ shell significantly enhanced the catalytic activity of all tested metals. The Ru-based catalyst demonstrated the most remarkable improvement, achieving a 1,2-PG yield of 24.97%. Consequently, the Ru-based catalyst was selected for further investigation and optimization in this study.

(Catalyst: 200 mg, Glucose: 200 mg, Deionized water: 10 mL, $\text{Mg}(\text{OH})_2$ loading: 7.5%, Reaction temperature: 200°C , Reaction time: 3 hours)

3. Results

3.1 optimization of reaction conditions

Effect of $\text{Mg}(\text{OH})_2$ Loading The effect of $\text{Mg}(\text{OH})_2$ loading on the yields of 1,2-propanediol (1,2-PG) and ethylene glycol (EG) is presented in Fig. 2(ab). The results indicate a strong correlation between base promoter loading and product distribution. At a loading of 2.5 wt.%, the yields of both 1,2-PG and EG increased rapidly; specifically, the 1,2-PG yield increased approximately 14-fold compared to the pristine Ru/SiO_2 system. This confirms that the $\text{Mg}(\text{OH})_2$ modification effectively promotes the formation of 1,2-PG. However, further increasing the loading beyond the optimum (5 wt.%) led to a decrease in yield, likely due to the excessive coverage of active sites or alterations in the acid-base balance.

Optimizing the catalyst dosage is pivotal for maximizing reaction efficiency while maintaining atom economy. To determine the balance between the abundance of active sites and mass transfer limitations, the influence of $\text{Ru}/\text{SiO}_2@\text{Mg}(\text{OH})_2$ loading on the catalytic performance was investigated. Figure 2(cd) illustrates the dependence of product yields on the dosage of the $\text{Ru}/\text{SiO}_2@\text{Mg}(\text{OH})_2$ catalyst. As the catalyst dosage was increased from 50 mg to 150 mg, the 1,2-PG yield rose significantly from 22.7% to 29.51%. This improvement is attributed to the increased availability of active acid-base sites, which provides the necessary driving force for the reaction cascade. However, increasing the dosage

beyond 150 mg led to a slight decline in 1,2-PG yield. Considering economic factors and catalytic efficiency, the optimal catalyst dosage was determined to be 150 mg.

Reaction temperature is a determinant parameter in biomass valorization, as it fundamentally dictates reaction kinetics and thermodynamic equilibrium. To investigate its impact on the hydrogenolysis efficiency and determine the optimal thermal condition, the reaction was conducted across a temperature range of 160–240°C. As depicted in Fig. 2(e,f), the yield of 1,2-PG exhibited a positive correlation with temperature initially. Elevating the temperature from 160°C to 180°C resulted in a yield increase from 20.33% to 24.89%. Since glucose hydrogenolysis involves endothermic steps (such as C–C or C–O bond cleavage), higher temperatures facilitate the reaction by overcoming the activation energy barrier, thereby enhancing the conversion efficiency. However, surpassing the optimal temperature of 180°C led to a marked decline in 1,2-PG yield. Although elevated temperatures accelerate the main reaction kinetics, they simultaneously promote undesired side reactions, such as polymerization or excessive cracking. This leads to the formation of byproducts and humins, consequently reducing the selectivity toward the target product.

Reaction time is a critical kinetic parameter that dictates the extent of substrate conversion and product stability. To identify the optimal temporal window where product formation outweighs degradation, the combined effects of reaction temperature and time were investigated. As illustrated in Fig. 2(g,h), the temporal evolution of product yields exhibited consistent trends across different temperatures. The yield of 1,2-PG increased initially, reaching a maximum of 33.9% at 180°C after 3 h. This indicates that a duration of 3 h is sufficient to achieve thermodynamic equilibrium or maximum conversion under these conditions. However, extending the reaction time beyond 3 h led to a discernible decline in yield. This reduction is likely attributed to the instability of 1,2-PG under prolonged exposure to hydrothermal conditions. The target product undergoes further hydrogenolysis or C–C bond cleavage, decomposing into smaller alcohols such as ethanol and n-propanol. Consequently, the optimal reaction conditions for the Ru/SiO₂@Mg(OH)₂ system were established as 180°C and 3 h.

3.2 Catalyst Characterization

3.2.1 Electron Microscopy (TEM & SEM)

The structural integrity and component distribution of the catalyst are critical for its catalytic performance. Therefore, electron microscopy was employed to visualize the formation of the core-shell architecture. Figure 3 illustrates the dispersion of Ru nanoparticles within the Ru/SiO₂@5Mg(OH)₂ composite. During the synthesis, the abundant hydroxyl groups under hydrothermal conditions (180°C) promoted the in-situ transformation of MgO into Mg(OH)₂. This is evidenced by the HRTEM analysis in Fig. 3d, where a lattice spacing of 0.304 nm was measured, assigned to the Mg(OH)₂ (001) plane. Additionally, the lattice spacing of 0.258 nm in Fig. 3b matches the characteristic plane of Ru, confirming that the active metal sites remain distinct and well-distributed. Complementary SEM observations (Figure S1) further reveal the macroscopic morphology: the Mg(OH)₂ phase evolved into sheet-like layers that tightly wrapped around the Ru/SiO₂ core, successfully establishing a distinct core-shell structure.

3.2.2 XRD Characterization

To verify the crystalline phases and assess the structural integrity of the composite catalyst, X-ray diffraction (XRD) patterns were analyzed (Fig. 4). Specifically, the impact of the alkaline modification on the support stability and metal dispersion was evaluated. The XRD profile of the Ru/SiO₂@5Mg(OH)₂ catalyst is presented in the figure. A characteristic diffraction peak at approximately $2\theta = 27.5^\circ$ was observed, suggesting that the SiO₂ support retained its structural integrity despite the harsh calcination and alkaline treatment. Furthermore, diffraction peaks located at $2\theta = 21.3^\circ$, 35.8° , and 37.4° were detected and indexed to the Ru crystal planes (JCPDS No. 88-2333), confirming the successful loading of ruthenium nanoparticles. Notably, upon the introduction of the Mg(OH)₂ shell, a discernible broadening of the Ru diffraction peaks was observed compared to the pristine samples. According to the Scherrer equation, this broadening indicates a reduction in crystallite size. This finding implies that the Mg(OH)₂ shell effectively physically confines the Ru nanoparticles, thereby preventing agglomeration and enhancing dispersion. Additionally, the absence of sharp crystalline Mg(OH)₂ peaks suggests that the magnesium shell exists primarily in an amorphous or highly dispersed state on the catalyst surface.

3.2.3 Catalyst Acid-Base Property Analysis

The acid-base properties, which are crucial for the reaction mechanism, were investigated via TPD analysis. As shown in the CO₂-TPD profiles (Fig. 5a), the unmodified Ru/SiO₂ exhibited negligible basicity. In contrast, the Mg(OH)₂-modified catalyst showed a pronounced broad peak above 400°C, indicating the generation of strong basic sites due to the Mg(OH)₂ shell. Similarly, NH₃-TPD results (Fig. 5b) revealed that while pristine Ru/SiO₂ possessed few acidic sites, the modified catalyst displayed distinct strong acid peaks at 500°C. This emergence of acidity is likely due to the formation of Mg–O–Si linkages or magnesium silicate phases during hydrothermal synthesis, which introduces Lewis acidity alongside the inherent basicity.

3.2.4 Reusability Analysis

To assess the long-term stability and reusability of the prepared catalyst, recycling experiments were conducted over five consecutive cycles under two different conditions: direct reuse and thermal regeneration at 450°C (Fig. 6). As depicted in the results, the catalytic performance for the "Direct Reuse" samples exhibited a rapid and significant deterioration; the yield plummeted from an initial 33.9% in the first cycle to a mere 12.5% by the fifth cycle, suggesting a substantial loss of active sites or severe carbon deposition during the reaction. In stark contrast, the catalyst subjected to thermal regeneration displayed remarkable stability and recovery. Following treatment at 450°C, the yield was effectively restored to 31.0% in the second cycle and remained consistently high throughout subsequent runs. By the end of the fifth cycle, the regenerated catalyst still maintained a yield of 29.5%, representing a C5 retention of over 85% relative to the initial run. These findings underscore that the deactivation of the catalyst is reversible and its catalytic activity can be efficiently recovered via controlled thermal treatment, demonstrating the catalyst's robust potential for practical industrial applications.

4. Discussion

4.1 Structure-Activity Relationship of the Core-Shell Architecture

The superior catalytic performance of the Ru/SiO₂@Mg(OH)₂ composite, compared to the unmodified Ru/SiO₂ and other metal counterparts (Fig. 1), can be directly attributed to the successful construction of a bifunctional core-shell architecture. The characterization results provide strong evidence that the in-situ hydrothermal growth of Mg(OH)₂ creates a unique chemical environment around the Ru active sites.

Firstly, the formation of the Mg(OH)₂ shell serves as a crucial modulator of surface acidity and basicity. As evidenced by the CO₂-TPD and NH₃-TPD profiles (Figs. 5), the pristine Ru/SiO₂ support is chemically inert regarding acid-base functionality. However, the modified catalyst exhibits significant basic sites and emerging Lewis acidic sites. This induction of basicity is critical because glucose isomerization and retro-aldol condensation (RAC)—the initial steps in the reaction cascade—are base-catalyzed processes.

Secondly, the physical structure plays a protective role. The TEM and XRD data (Figs. 3 and 4) indicate that the Mg(OH)₂ shell encapsulates the Ru nanoparticles without completely blocking them, as evidenced by the high conversion rates. The shell likely imposes a confinement effect that restricts the aggregation of Ru nanoparticles during the hydrothermal reaction, addressing a common issue (sintering) found in supported metal catalysts. The optimal Mg(OH)₂ loading of 5 wt.% represents a balance point; loadings exceeding this value likely result in a shell that is too thick, physically blocking reactant access to the inner Ru sites, thereby diminishing the yield as observed in Fig. 2.

4.2 Mechanistic Insights into the Reaction Cascade

The conversion of glucose to 1,2-PG involves a complex network of series-parallel reactions. Control experiments using intermediate compounds (Table 1) profoundly elucidate the altered reaction pathways facilitated by this bifunctional catalyst. The unmodified Ru/SiO₂ catalyst exhibited a negligible 1,2-PG yield from glucose (2.4%) but a moderate yield from fructose (29.4%), confirming that glucose-to-fructose isomerization is the inherent kinetic bottleneck over monometallic surfaces. Upon Mg(OH)₂ modification, the 1,2-PG yield from glucose dramatically surged to 33.9%, demonstrating that the basic shell effectively accelerates this critical isomerization step.

Furthermore, the structural proximity of hydrogenation sites (Ru) and basic sites (Mg(OH)₂) enables a highly efficient tandem reaction. The base sites selectively cleave fructose via RAC into C3 intermediates (e.g., DHA and GLY), which immediately diffuse to the adjacent Ru sites for rapid hydrogenation into 1,2-PG. This synergistic proximity effectively suppresses the premature direct hydrogenation of C6 sugars into dead-end byproducts, such as sorbitol and mannitol.

4.3 Influence of Reaction Parameters on Selectivity

The sensitivity of the reaction to temperature highlights the competition between hydrogenation and C-C bond cleavage. At lower temperatures (160°C), the energy barrier for the RAC step may not be fully overcome, limiting 1,2-PG formation. As the temperature rises to 180°C, the endothermic C-C cleavage is favored, maximizing the yield.

However, the significant drop in yield above 180°C (Fig. 2e,f) and prolonged reaction times (Fig. 2g,h) indicates the occurrence of excessive hydrogenolysis. Under harsh hydrothermal conditions, 1,2-PG is susceptible to further C-C cleavage, degrading into smaller chain alcohols such as ethanol and ethylene glycol. This thermal instability emphasizes the necessity of precise kinetic control, which the Ru/SiO₂@Mg(OH)₂ system achieves effectively at the optimized conditions.

4.4 Comparison with State-of-the-Art Catalysts

The 1,2-PG yield of 33.9% achieved in this work is highly competitive with recent literature benchmarks for glucose hydrogenolysis. For instance, our result surpasses the ~25% yield reported for RuSn/AC catalysts, highlighting the superior efficacy of the core-shell confinement strategy

over traditional alloy-supported systems. Furthermore, the catalytic performance of our Ru/SiO₂@Mg(OH)₂ composite is comparable to the 34.1% yield obtained over the analogous Pt/deAl-beta@Mg(OH)₂ system. This demonstrates that Ruthenium can effectively serve as a viable alternative to Platinum in these core-shell architectures, offering similar high efficiency while potentially reducing catalyst costs. Unlike systems relying on acidic promoters such as Pd–WO_x, our base-promoted pathway effectively suppresses the formation of humins and coking precursors, contributing to the observed structural stability.

4.5 Catalyst Stability and Deactivation Mechanism

Industrial application requires catalysts with high stability. The reusability tests (Fig. 6) demonstrated that while the catalyst deactivates upon direct reuse, its activity is recoverable via calcination. The reversible nature of this deactivation suggests that it is not caused by the leaching of active metals or permanent structural collapse. Instead, it is likely due to the deposition of carbonaceous species (humins or oligomers) formed from sugar degradation, which cover the active sites. The fact that the initial yield is largely recovered after burning off these deposits confirms the robustness of the core-shell structure. The Mg(OH)₂ shell likely enhances hydrothermal stability by preventing the hydration and dissolution of the underlying silica support, a common failure mechanism for SiO₂-based catalysts in hot liquid water.

4.6 Reaction Mechanism Discussion

To elucidate the reaction pathway—specifically the glucose-to-fructose isomerization followed by retro-aldol condensation (RAC)—control experiments were conducted using various intermediates (Table 1). As shown in Table 1 (Entries 1 and 3), the unmodified Ru/SiO₂ catalyst yielded 29.4% 1,2-PG from fructose but only 2.4% from glucose. This stark difference highlights the significant kinetic barrier for glucose-to-fructose isomerization over the metal-only catalyst. However, upon Mg(OH)₂ modification, the yield from glucose increased dramatically from 2.4% to 33.9% (Entry 2), confirming that the base promoter significantly facilitates the isomerization step. Additionally, when comparing the conversion of fructose, the 1,2-PG yield increased from 29.4% to 37.4% with the modified catalyst. Furthermore, calculations based on dihydroxyacetone (DHA) and fructose conversion indicated that the RAC efficiency improved from 30.1% to 81.5% after Mg(OH)₂ loading. In conclusion, the bifunctional Ru/SiO₂@Mg(OH)₂ catalyst enhances 1,2-PG production by synergistically promoting both the glucose isomerization and the fructose RAC steps.

Table 1
Reaction effects of Ru/SiO₂ and Ru/SiO₂@Mg(OH)₂ catalysts for catalyzed intermediates

Entry	Catalyst	Reactant	Conversion (%)	Selectivity (%)				
				Propanedio	Ethylene glycol	Hydroxyacetone	1,2-Hexanediol	Hexito
1	Ru/SiO ₂	Glucose	100.0	2.4	2.0	22.2	4.1	5.7
2	Ru/SiO ₂ @5Mg(OH) ₂	Glucose	100.0	33.9	8.0	0.0	3.1	2.4
3	Ru/SiO ₂	Fructose	100.0	29.4	6.2	4.8	4.9	3.1
4	Ru/SiO ₂ @5Mg(OH) ₂	Fructose	100.0	37.4	3.9	0.0	2.9	4.3
5	Ru/SiO ₂	1,2-Hexanediol	6.8	0.0	0.0	0.0	-	-
6	Ru/SiO ₂ @5Mg(OH) ₂	1,2-Hexanediol	10.2	0.0	0.0	0.0	-	-
7	Ru/SiO ₂	Dihydroxyacetone	93.1	95.0	0.0	3.6	-	-
8	Ru/SiO ₂ @5Mg(OH) ₂	Dihydroxyacetone	87.1	45.9	0.0	10.2	-	-
9	Ru/SiO ₂	1,2-Propanediol	7.2	-	0.0	-	-	-
10	Ru/SiO ₂ @5Mg(OH) ₂	1,2-Propanediol	2.3	-	0.0	-	-	-
Note: Reaction conditions: Catalyst 150 mg, reactant solution 10 mL (11.25 mg/mL), initial H ₂ pressure 3 MPa, reaction temperature 180°C, reaction time 3 h								

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Figure 7. Mechanism of 1,2-propanediol preparation from glucose catalyzed by Ru/SiO₂@Mg(OH)₂

5. Conclusions

The efficient and selective valorization of glucose, the most abundant monosaccharide in nature, into 1,2-propanediol (1,2-PG) is of significant industrial importance. In this study, Ru was identified as the optimal active metal among various candidates for this transformation. We successfully developed and optimized a core-shell Ru/SiO₂@Mg(OH)₂ catalyst. Under optimized conditions (5 wt.% Mg(OH)₂, 180°C, 3 MPa H₂, 3 h), a maximum 1,2-PG yield of 33.9% was achieved. Detailed characterization revealed that the in-situ formed Mg(OH)₂ shell not only introduces essential acid-base bifunctionality—synergistically promoting glucose isomerization and retro-aldol condensation—but also effectively encapsulates Ru nanoparticles to prevent sintering. Furthermore, the catalyst exhibited excellent reusability after regeneration. In summary, this work provides a robust strategy for designing bifunctional catalysts that combine high activity, selectivity, and stability for sustainable biomass conversion applications.

Declarations

Declaration of competing interest

The authors declare that they have no competing interests.

Acknowledgments

This work was supported by the Key Projects of Intergovernmental International Scientific and Technological Innovation Cooperation (Grant No.2022YFE0120600).

References

1. Wang, S.; Jiang, J.; Gu, M.; Song, Y.; Zhao, J.; Shen, Z.; Zhou, X.; Zhang, Y., Glucose Hydrogenolysis into 1,2-Propanediol Using a Pt/deAl@Mg(OH)₂ Catalyst: Expanding the Application of a Core–Shell Structured Catalyst. *Nanomaterials* **2022**, *12* (21), 3771.
2. Głowka, M.; Krawczyk, T., New Trends and Perspectives in Production of 1,2-Propanediol. *ACS Sustainable Chemistry & Engineering* **2023**, *11* (19), 7274–7287.
3. Okolie, J. A., Insights on production mechanism and industrial applications of renewable propylene glycol. **2022**, (2589-0042 (Electronic)).
4. Garcia-Cano, J.; Gomis, V.; Font, A.; Calemme, V.; Gambarotta, E. F., Vapor-liquid equilibrium of 3-ethoxy-1,2-propanediol + water/ethanol/diethyl ether/glycerol/1,2-propanediol at different pressures. *Fluid Phase Equilibria* **2020**, *512*, 112519.
5. Ma, L.; Liu, H.; He, D., Recent Progress in Catalyst Development of the Hydrogenolysis of Biomass-Based Glycerol into Propanediols—A Review. *Bioengineering* **2023**, *10* (11), 1264.
6. Tian, J. Y.; Fan, Y. Y.; Wei, T.; Guo, Q. X.; Fang, W. G.; Guo, Y. L., Base-Free Conversion of 1, 2-Propanediol to Methyl Lactate in Methanol Over Cu-Modified Au/ Hydroxylapatite Catalysts. *CATALYSIS LETTERS* **2025**, *155* (1).
7. Anilan, A. E.; Sreekantan, S.; Racha, A.; Marimuthu, B., Towards efficient conversion of sucrose to 1,2-propanediol selectively over Cu-La on activated carbon support. *BIOMASS CONVERSION AND BIOREFINERY* **2025**, *15* (22), 29241–29257.
8. Zheng, M.; Pang, J.; Sun, R.; Wang, A.; Zhang, T., Selectivity Control for Cellulose to Diols: Dancing on Eggs. *ACS Catalysis* **2017**, *7* (3), 1939–1954.
9. Dong, B.; Wang, Y. J.; Han, L. L.; Cui, G. R.; Wang, Y. N.; Su, Z. W., Active ingredients in waste of distillers' grains and their resource utilization. *REVIEWS IN ENVIRONMENTAL SCIENCE AND BIO-TECHNOLOGY* **2025**, *24* (1), 191–215.
10. Kashyap, P.; Bhardwaj, S.; Chodimella, V. P.; Sinha, A. K., Carbon-based heterogeneous catalysts for conversion of cellulose and cellulosic feedstock. *BIOMASS CONVERSION AND BIOREFINERY* **2024**, *14* (3), 2937–2957.
11. Tang, X.; Yang, X. M.; Zhou, L. P., Conversion of cellulose to lactic acid via oxidation pretreatment combined with catalysis by MoO₃/Sn-Beta. *CELLULOSE* **2024**, *31* (3), 1509–1518.
12. Pang, J.; Zheng, M.; Li, X.; Jiang, Y.; Zhao, Y.; Wang, A.; Wang, J.; Wang, X.; Zhang, T., Selective conversion of concentrated glucose to 1,2-propylene glycol and ethylene glycol by using RuSn/AC catalysts. *Applied Catalysis B: Environmental* **2018**, *239*.
13. Meier, S., Kinetic variations in acid-catalyzed monosaccharide conversion. *CATALYSIS COMMUNICATIONS* **2020**, *135*.
14. Caratzoulas, S.; Davis, M. E.; Gorte, R. J.; Gounder, R.; Lobo, R. F.; Nikolakis, V.; Sandler, S. I.; Snyder, M. A.; Tsapatsis, M.; Vlachos, D. G., Challenges of and Insights into Acid-Catalyzed Transformations of Sugars. *JOURNAL OF PHYSICAL CHEMISTRY C* **2014**, *118* (40), 22815–22833.
15. Dongsri, S.; Rattanaphanee, P.; Wongkoblap, A., Production of lactic acid from cellulose using solid catalyst. *MATEC Web of Conferences* **2019**, *268*, 07006.
16. Bayu, A.; Karnjanakom, S.; Yoshida, A.; Kusakabe, K.; Abudula, A.; Guan, G. Q., Polyoxomolybdates catalysed cascade conversions of cellulose to glycolic acid with molecular oxygen via selective aldohexoses pathways (an epimerization and a [2+4] Retro-aldol reaction).

17. Gao, G.; Feng, S.; Jiang, Z.; hu, C.; Zhang, Q.; Tsang, D., Efficient Hydrogenation of Glucose to Polyols over Hydrotalcite-Derived PtNi Alloy Catalyst under Mild Conditions. *Industrial & Engineering Chemistry Research* **2023**.
18. Zhang, X.; Durndell, L. J.; Isaacs, M. A.; Parlett, C. M. A.; Lee, A. F.; Wilson, K., Platinum-Catalyzed Aqueous-Phase Hydrogenation of d-Glucose to d-Sorbitol. *ACS Catalysis* **2016**, 6 (11), 7409-7417.
19. Pandya, H.; Vinod, C. P.; Rathod, V.; Kantam, M. L., Kinetic Model of Hydrogenation of Glucose to Sorbitol on a Ni/Bentonite Catalyst. *Industrial & Engineering Chemistry Research* **2024**, 63 (11), 4771-4781.
20. Liu, C.; Shang, Y.; Qi, H.; Xianzhou, W.; Gui, J.; Zhang, C.; Zhu, Y.; Li, Y.-W., Effect of the ZrO₂ phase on Pd-based bifunctional catalysts for the hydrogenolysis of glucose. *Catalysis Communications* **2019**, 128.
21. Song, J.; Wang, D.; Wang, Q.; Cui, C.; Yang, Y. Selective Control of Catalysts for Glycerol and Cellulose Hydrogenolysis to Produce Ethylene Glycol and 1,2-Propylene Glycol: A Review *Catalysts* [Online], 2024.
22. Liu, C.; Zhang, C.; Sun, S.; Liu, K.; Hao, S.; Xu, J.; Zhu, Y.; Li, Y., Effect of W₂O₃ on Bifunctional Pd–W₂O₃/Al₂O₃ Catalysts for the Selective Hydrogenolysis of Glucose to 1,2-Propanediol. *ACS Catalysis* **2015**, 5 (8), 4612-4623.
23. Stadler, B. M.; Wulf, C.; Werner, T.; Tin, S.; de Vries, J. G., Catalytic Approaches to Monomers for Polymers Based on Renewables. *ACS Catalysis* **2019**, 9 (9), 8012-8067.
24. Cechanaviciute, I. A.; Antony, R. P.; Banko, L.; Quast, T.; Pokharel, S.; Ludwig, A.; Krysiak, O. A.; Schuhmann, W., Discovery of Highly Active Noble-Metal-Lean Mo-Ru Electrocatalysts for Hydrogen Evolution. *CHEMELECTROCHEM* **2025**, 12 (5).
25. Xie, S. H.; Ye, K. L.; Du, J. S.; Zhang, X.; Kim, D.; Loukusa, J.; Ma, L.; Ehrlich, S. N.; Marinkovic, N. S.; De Yoreo, J. J.; Liu, F. D., Ru/MgO catalyst with dual Ru structure sites for efficient CO production from CO₂ hydrogenation. *CHEMICAL ENGINEERING JOURNAL* **2024**, 487.
26. Buta, J. G.; Tefera, Z. T.; Alemea, M. T., Ru on N-doped ordered mesoporous carbon support for conversion of glucose to sorbitol via in-situ generated hydrogen species: A greener approach. *RENEWABLE ENERGY* **2025**, 240.
27. Jin, H. Q.; Chen, X.; Da, Y.; Fan, L.; Jiang, R.; Xiao, Y. K.; Yao, B. Q.; He, Q.; Yu, Y.; Chen, W., Identifying the Bifunctional Mechanism in Alkaline Water Electrolysis by Lewis Pairs at the Single-Atom Scale. *JOURNAL OF THE AMERICAN CHEMICAL SOCIETY* **2025**, 147 (4), 3874-3884.
28. Galiwango, E.; Butler, J.; Lotfi, S., A Review of Catalyst Integration in Hydrothermal Gasification. *Fuels* **2024**, 5, 375-393.
29. Xia, L. H.; Jian, Y. F.; Liu, Q. Y.; Liu, Y. J.; Wang, J. J.; Chai, S. N.; Jing, M. Z.; Albilali, R.; He, C., Boosted Light Alkane Deep Oxidation via Metal Bond Length Modulation-Induced C-C Bond Preferential Activation. *ENVIRONMENTAL SCIENCE & TECHNOLOGY* **2024**, 58 (7), 3472-3482.
30. Sreekantan, S.; Sreedharan, S.; Kirali, A. A. B.; Yadav, P.; Marimuthu, B., One-pot catalytic conversion of sucrose to 1,2-propanediol over titania supported Ni-Ce metal catalyst under milder reaction conditions. *Biomass Conversion and Biorefinery* **2024**, 14 (19), 24703-24714.
31. Abu Bakar, M.; Hamid, M. A. A.; Jalar, A.; Shamsudin, R., Synthesis of porous MgO into sheet-like structure via solution routes. In *FRONTIER OF NANOSCIENCE AND TECHNOLOGY*, 2011; Vol. 694, pp 625+.
32. Arena, F.; Di Chio, R.; Trunfio, G., An experimental assessment of the ammonia temperature programmed desorption method for probing the surface acidic properties of heterogeneous catalysts. *APPLIED CATALYSIS A-GENERAL* **2015**, 503, 227-236.
33. Morrow, C. P.; Olsen, A. A.; Kubicki, J. D., Quantum mechanical modeling of hydrolysis and H₂O-exchange in Mg-, Ca-, and Ni- silicate clusters: Implications for dissolution mechanisms of olivine minerals. *AMERICAN MINERALOGIST* **2014**, 99 (11-12), 2303-2312.

Tables

Table 1 Reaction effects of Ru/SiO₂ and Ru/SiO₂@Mg(OH)₂ catalysts for catalyzed intermediates

Entry	Catalyst	Reactant	Conversion (%)	Selectivity (%)				
				Propanedio	Ethylene glycol	Hydroxyacetone	1,2-Hexanediol	Hexito
1	Ru/SiO ₂	Glucose	100.0	2.4	2.0	22.2	4.1	5.7
2	Ru/SiO ₂ @5Mg(OH) ₂	Glucose	100.0	33.9	8.0	0.0	3.1	2.4
3	Ru/SiO ₂	Fructose	100.0	29.4	6.2	4.8	4.9	3.1
4	Ru/SiO ₂ @5Mg(OH) ₂	Fructose	100.0	37.4	3.9	0.0	2.9	4.3
5	Ru/SiO ₂	1,2-Hexanediol	6.8	0.0	0.0	0.0	-	-
6	Ru/SiO ₂ @5Mg(OH) ₂	1,2-Hexanediol	10.2	0.0	0.0	0.0	-	-
7	Ru/SiO ₂	Dihydroxyacetone	93.1	95.0	0.0	3.6	-	-
8	Ru/SiO ₂ @5Mg(OH) ₂	Dihydroxyacetone	87.1	45.9	0.0	10.2	-	-
9	Ru/SiO ₂	1,2-Propanediol	7.2	-	0.0	-	-	-
10	Ru/SiO ₂ @5Mg(OH) ₂	1,2-Propanediol	2.3	-	0.0	-	-	-

Note: Reaction conditions: Catalyst 150 mg, reactant solution 10 mL (11.25 mg/mL), initial H₂ pressure 3 MPa, reaction temperature 180°C, reaction time 3 h

Figures

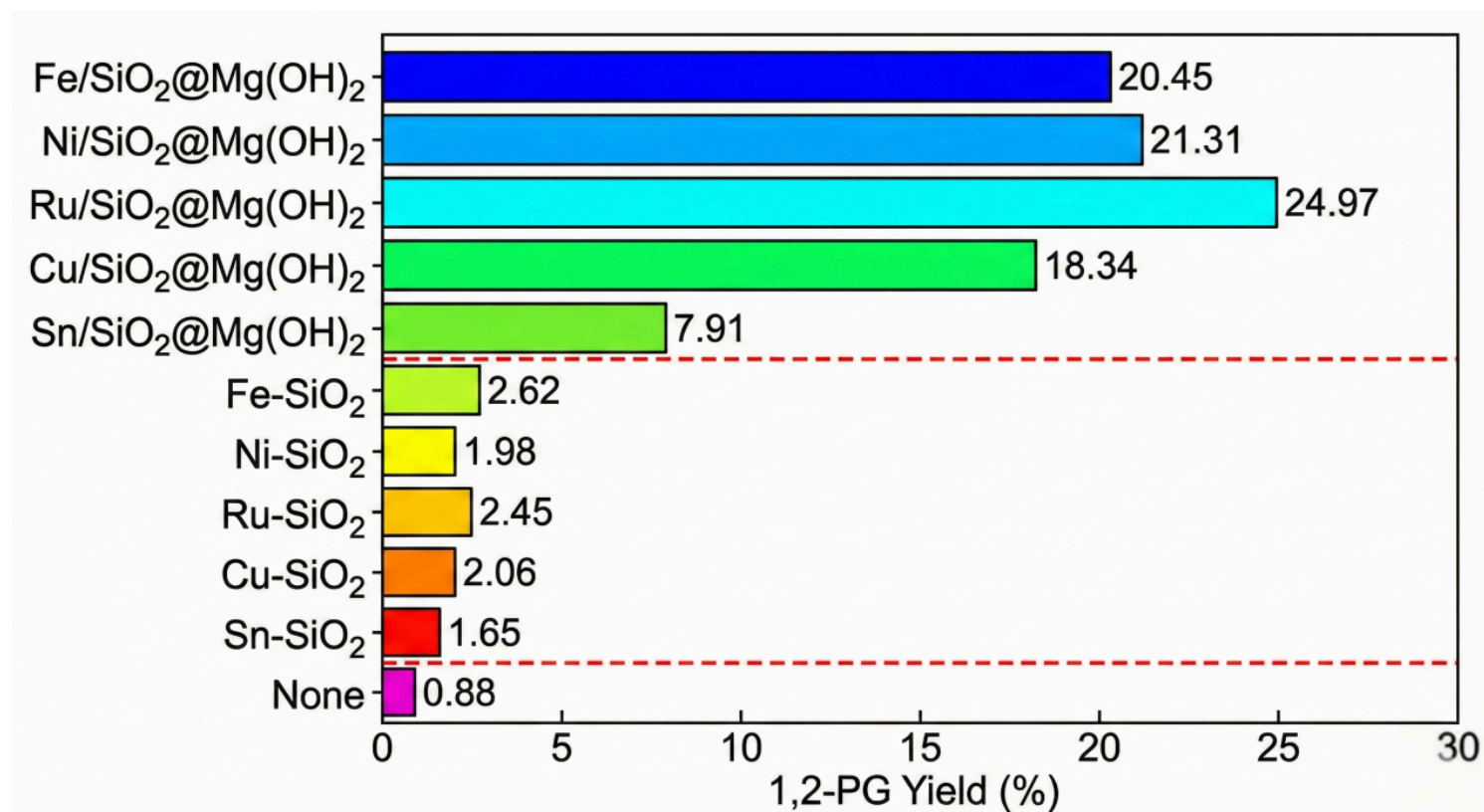


Figure 1

Effect of different metal catalysts on 1,2-propanediol yield

(Catalyst: 200 mg, Glucose: 200 mg, Deionized water: 10 mL, Mg(OH)₂ loading: 7.5%, Reaction temperature: 200°C, Reaction time: 3 hours)

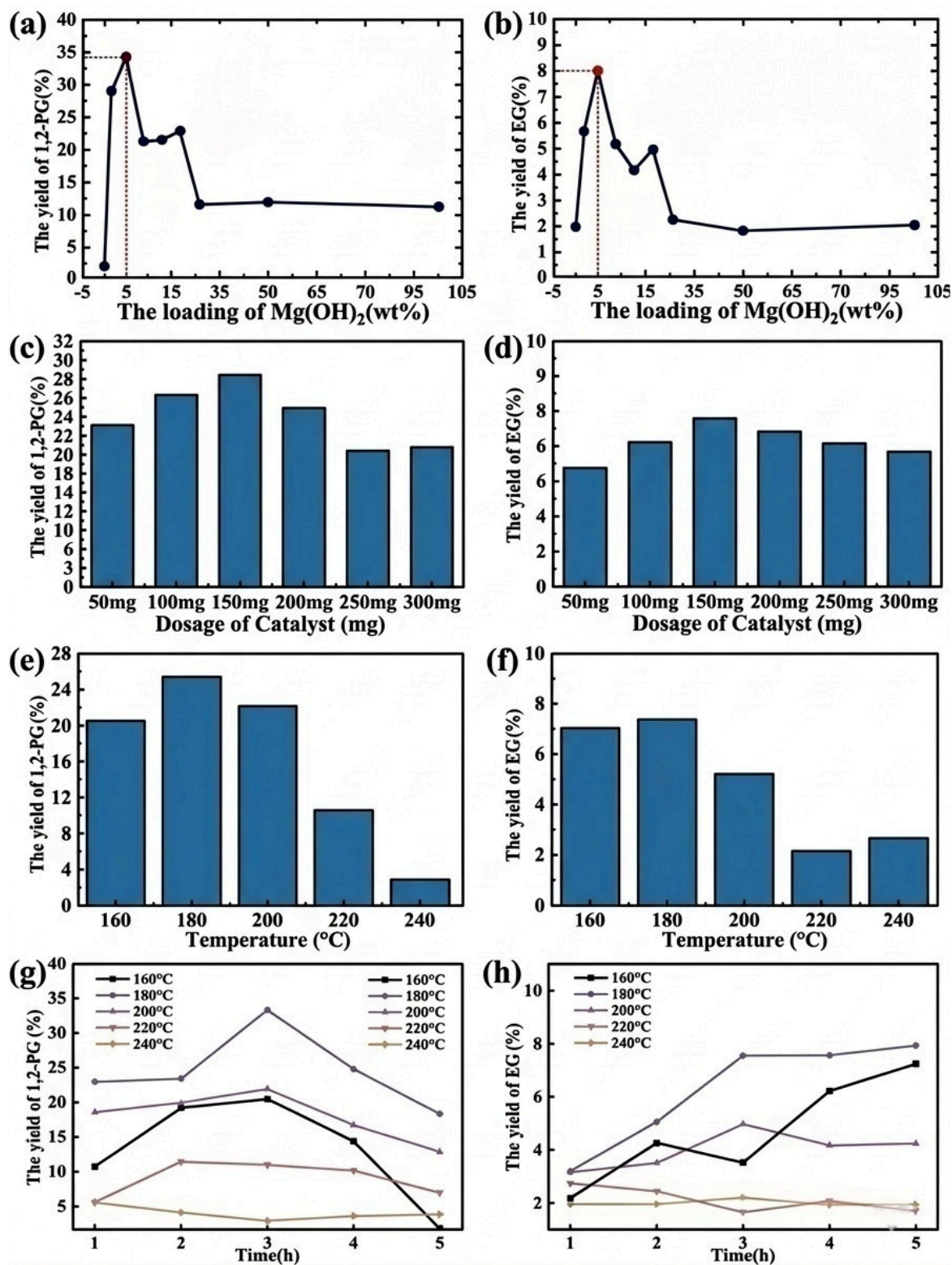


Figure 2

Effect of (a, b) $Mg(OH)_2$ loading (wt%), (c, d) catalyst dosage (mg), (e, f) reaction temperature ($^{\circ}C$), and (g, h) reaction time (h) on the yields of 1,2-propylene glycol 1,2 - PG and ethylene glycol (EG).

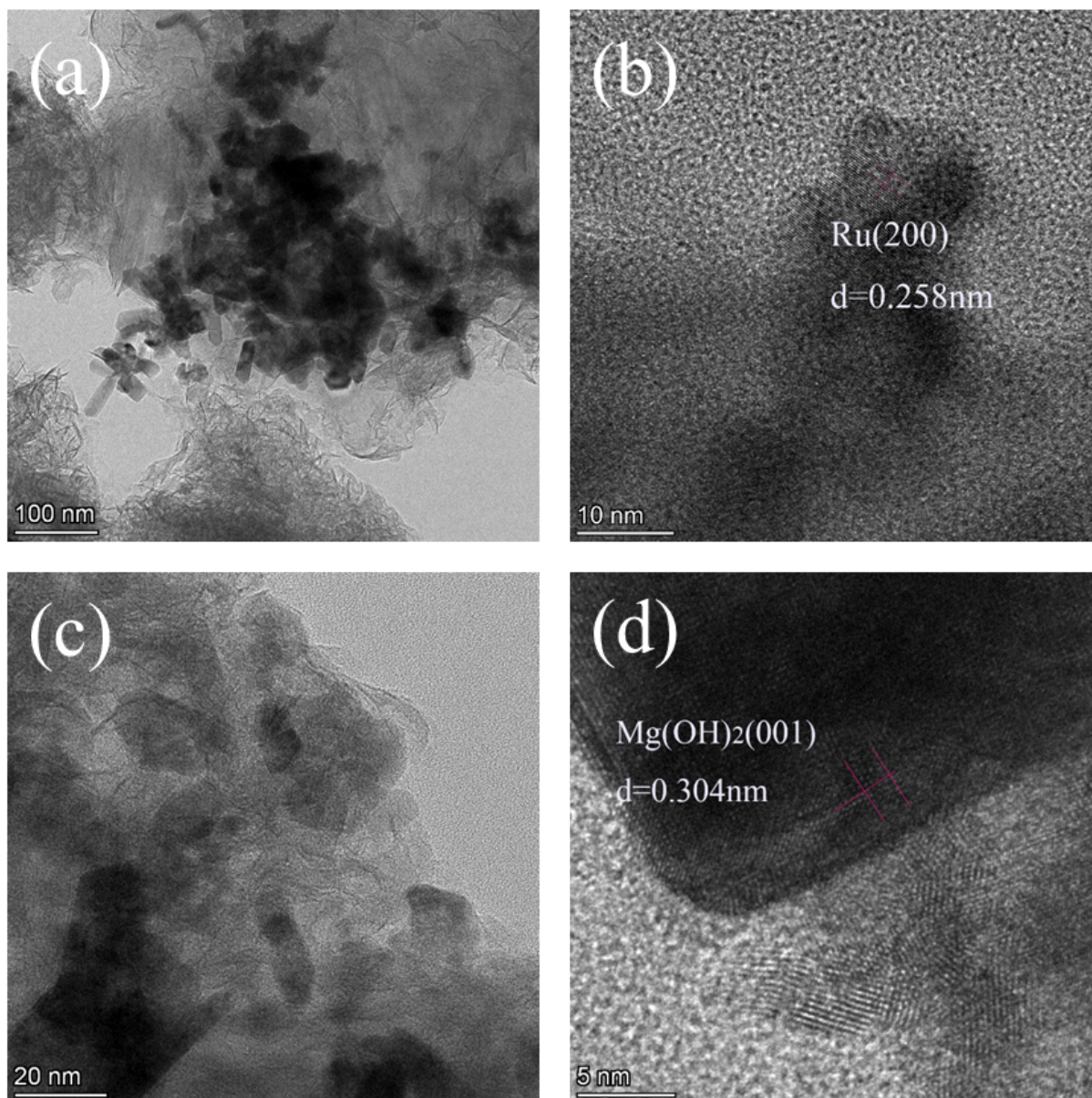


Figure 3

TEM characterization pattern of Ru/SiO₂@Mg(OH)₂ catalysts

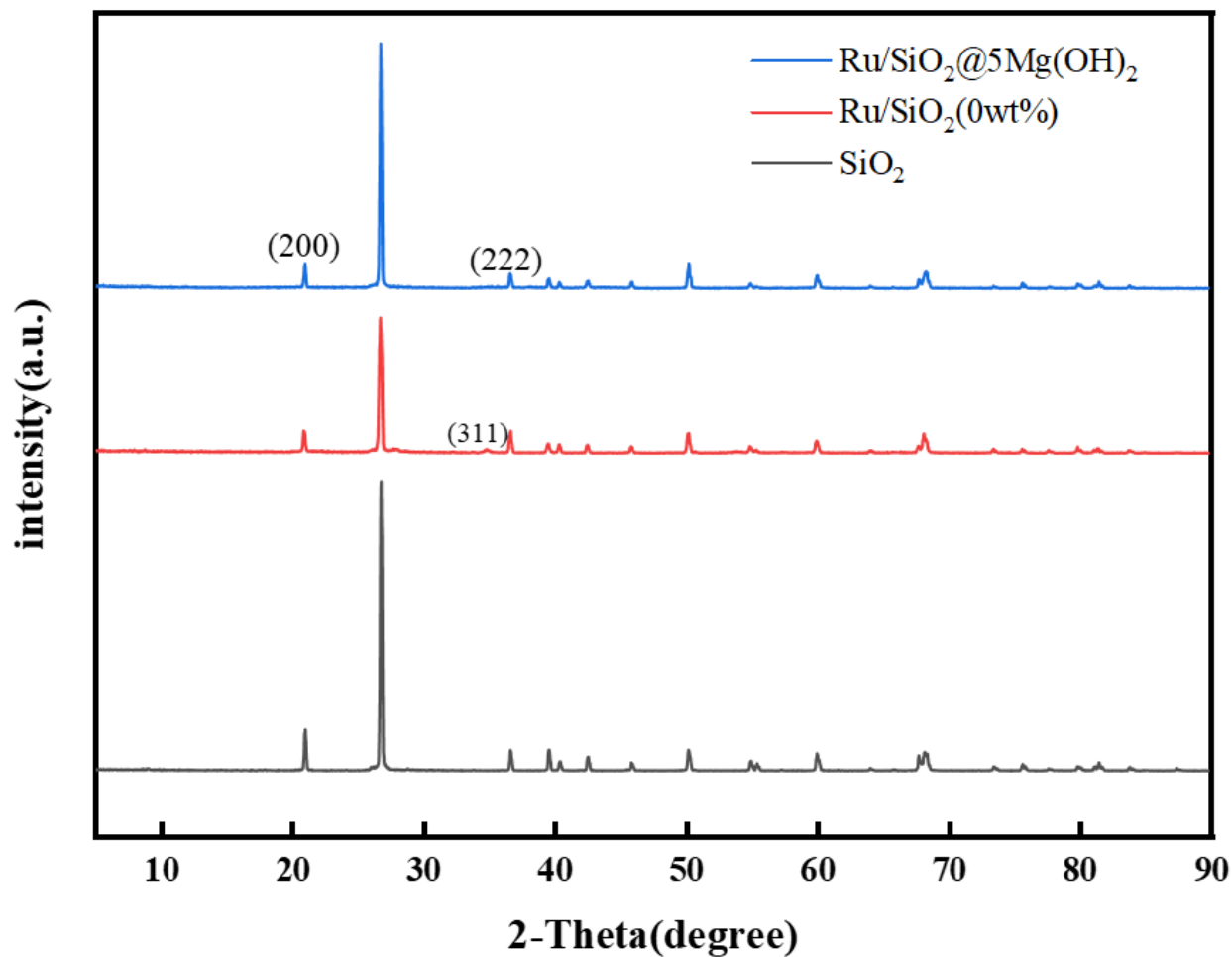


Figure 4

The XRD patterns of SiO₂ and catalysts with different Mg(OH)₂ loading

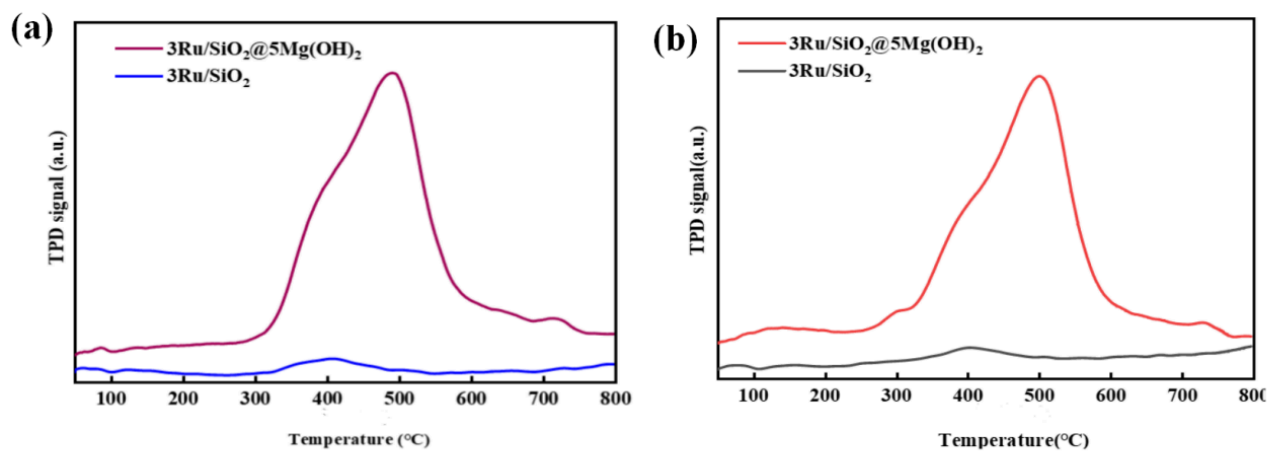


Figure 5

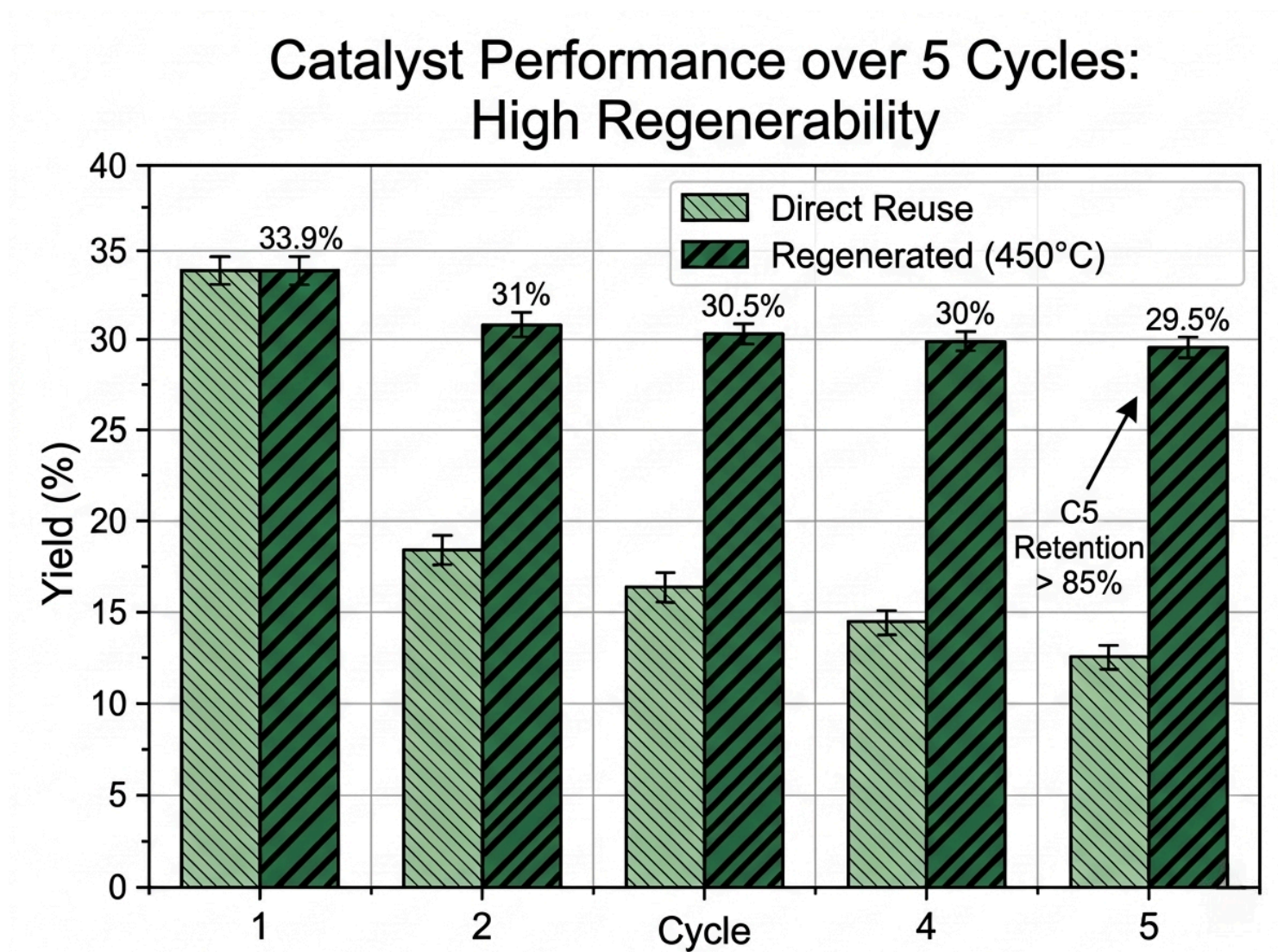


Figure 6

Analysis on the Reusability of Ru/SiO₂@Mg(OH)₂ Catalyst

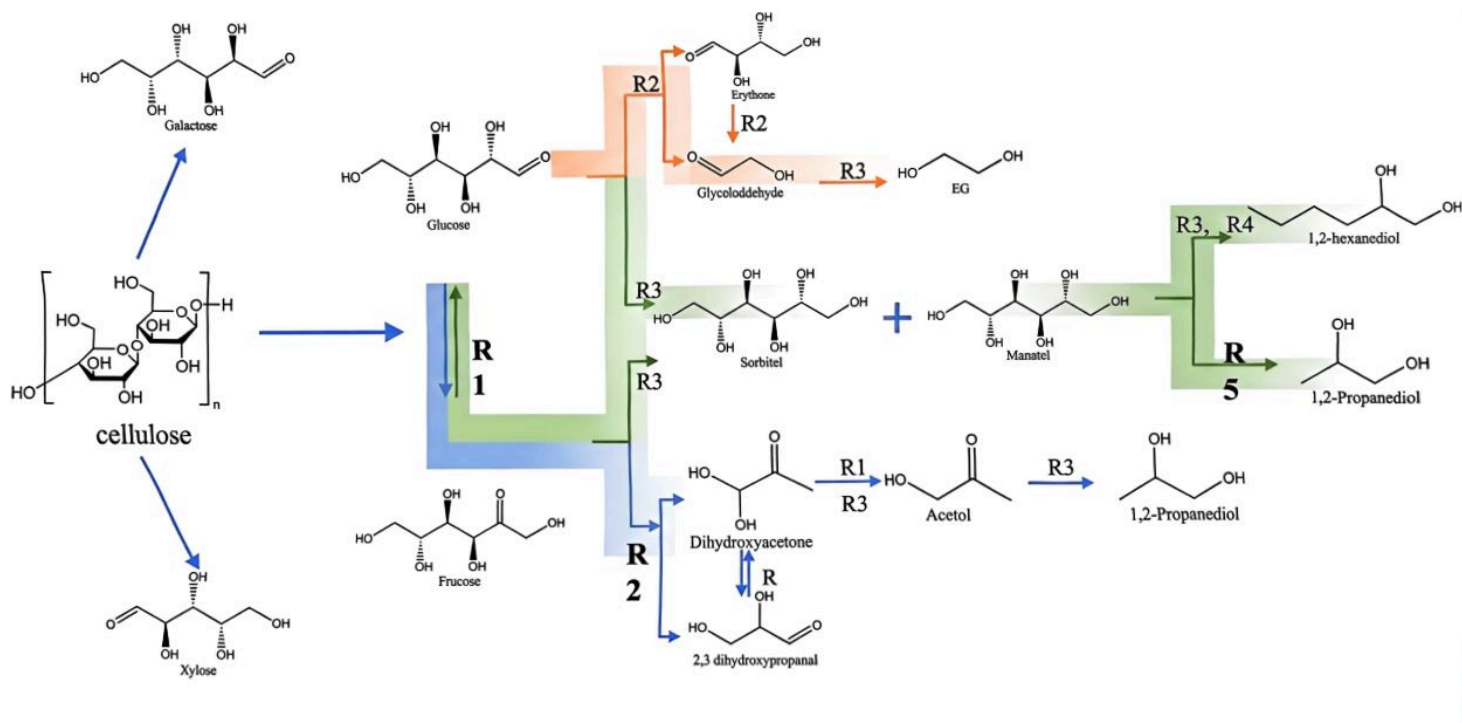


Figure 7

Mechanism of 1,2-propanediol preparation from glucose catalyzed by $\text{Ru/SiO}_2\text{@Mg(OH)}_2$

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