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1. This work details the mechanism of glucose-to-sorbitol hydrogenation in isopropanol (IPA) as a liquid hydrogen donor, which offers a greener and more renewable option than pressurized H₂ gas used in conventional approach.
2. The findings suggest that the reaction proceeds through the metal-mediated transfer of two equivalent chemisorbed H atoms (H*) from IPA to glucose. However, sorbitol formation can suffer from the active combination between two H* adatoms to form H₂(g), which behaves as a parallel reaction that competes with glucose for H*. Such phenomenon resembles the challenge of low Faradaic efficiencies in the electroreduction of CO₂ and organic compounds, underscoring that H transfer selectivity is of broad interest to systems relying on *non-H₂* hydrogen source.
3. Future work should explore strategies that suppress H-H combination, e.g., by engineering metal crystallography, to increase the H addition selectivity to organic hydrogenation products.

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Production of polyols from sugars in biorenewable alcohol: Selectivity of hydrogen transfer on metal catalysts

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Abstract

Non-H₂ hydrogen donors, such as alcohols, should be explored for their potential to enhance flexibility in hydrogenation reactions, particularly in contexts where alcohols can be fermentatively produced from biowaste. This study investigates the aqueous-phase catalytic transfer hydrogenation (CTH) of glucose to sorbitol, revealing the mechanism of the activation of isopropanol (IPA) as a liquid H donor over carbon-supported Ru (Ru/C) catalyst. The surface characterization of catalysts and mass spectra of sorbitol obtained in deuterated solvents suggest that glucose is hydrogenated through the transfer of two equivalent chemisorbed H atoms (H*) on metallic Ru⁰, instead of the Meerwein–Ponndorf–Verley mechanism. The co-generation of H₂ gas hints that H* atoms are susceptible to combination among themselves instead of transferring to glucose. An expanded kinetic model including H-H combination as a parallel step to sorbitol formation can qualitatively predict CTH in varying reactant concentrations. The competition between H₂ formation and substrate reduction could vary with the Ru metal nanostructure and substrate energetics: Ru/Al₂O₃ can largely suppress H₂ in glucose CTH, whereas the H selectivity in maltose-to-maltitol CTH is double that in glucose-to-sorbitol. This study demonstrates a renewable H source that serves as a safer alternative to pressurized H₂ used in conventional hydrogenation. More importantly, it informs the rational design of catalysts by pinning down the significance of H-H combination, which should be moderated to improve H atom economy in chemical upgrading using non-H₂ reducing agents.

Keywords: Hydrogenation mechanism, Catalytic hydrogen transfer, Ru catalyst, Sustainable biorefinery.



1. Introduction

Utilizing biomass as a renewable carbon source to replace conventional petroleum-derived feedstocks has attracted increasing attention, driven by the global demand for renewable energy and carbon neutrality. Glucose, the most abundant unit in biomass, can be valorized into a variety of value-added chemicals such as acids and polyols [1-3]. The hydrogenation product sorbitol has broad applications including food, personal care, and pharmaceutical [4], while its production relies on H₂ gas in conventional practice. Catalytic transfer hydrogenation (CTH) is an emerging reduction strategy that replaces molecular H₂ with liquid-phase H donors, such as alcohols and organic acids [5]. By avoiding the use of pressurized H₂, CTH mitigates safety concerns and reduces costs associated with H₂ transportation, process equipment, and plant operation. Moreover, it potentially improves the sustainability of industrial processes because those organic H donors can be obtained from renewable resources, for instance, through the fermentation of waste rice straw and other biomass [6, 7].

The literature has focused on metal-catalyzed CTH for substrates with furan or aromatic rings (*e.g.*, furfural, guaiacol), which formed the basis of most mechanistic understanding to date. In general, CTH can proceed through metal hydride transfer, in which O–H and α -C–H of alcohols can be activated on metallic sites, donating two equivalent H adatoms that subsequently attack substrate [8, 9]; or through Meerwein–Ponndorf–Verley (MPV) reduction, where the H from O–H is captured by base or metallic site, followed by a concerted H transfer from the remaining α -C–H to substrate by forming a ring intermediate with a Lewis acid site [8]. The assignment of mechanisms can be complicated when catalysts carry both metallic and Lewis acid sites. MPV mechanism mediated by Ru oxides has been reported to prevail over Ru-based catalysts for the CTH of furan-



containing substrates, such as hydroxymethylfurfural [10] and furfural [11], while the metallic Ru catalyzed hydrogenolysis of the CTH products in both systems.

The polyols production from sugars CTH is yet to be thoroughly investigated. Due to the structural difference, it is questionable whether the CTH mechanisms of furanic/aromatic substrates apply to sugars. In the Ru-catalyzed CTH of cellulose and glucose, whether the active sites are the cationic Ru species ($\text{Ru}^{\delta+}$) [12] or the metallic Ru sites [13] remains controversial. To be specific, $\text{Ru}^{\delta+}$ were present on carbon-supported Ru (Ru/C) catalyst, which was suggested as the active sites in the CTH of cellulose to sorbitol and mannitol [12]. This disagrees with the study of glucose CTH, where metallic Ru in Ru/C was reported to enable the metal hydride mechanism based on the proton NMR spectra of sorbitol products obtained in deuterated solvents [13]. We believe that the advancement of heterogeneous catalysts should be built on a deeper understanding of such complex system, elucidating the activation of alcohol H donors along with meticulous assignment of active sites.

This study investigates the CTH mechanism of glucose to sorbitol over Ru/C catalyst in isopropanol (IPA) as the H donor. Our findings support that glucose CTH mainly follows the metal-mediated H transfer, where IPA releases two equivalent H^* adatoms that subsequently attack glucose. We developed a kinetic model informed by kinetic isotope effects (KIE) and calibrated against experimental data over a range of glucose and IPA concentrations. This model can explain the volcano-shaped dependence of sorbitol yield on glucose concentration and the stoichiometric excess of acetone, which was seldom highlighted in literature. Apart from reaffirming the event of H_2 formation, the kinetic model established in our study emphasizes its



competitive relationship with substrate hydrogenation. Accordingly, we propose possible strategies to improve H selectivity and/or sorbitol production in CTH, including catalyst support design and hydrogenation-first route from maltose. The findings suggest that H atom economy could be a potential focus area in future research advancing CTH catalysts.

2. Experimental Section

Chemicals and catalysts. Chemicals used in this study mainly included D-(+)-glucose (99.5%, Aladdin), D-fructose (99%, Aladdin), D-(+)-xylose (99%, Aladdin), D-(+)-maltose monohydrate (98.0%, Aladdin), D-glucose-1-¹³C (99 atom% ¹³C, Sigma-Aldrich), IPA ((CH₃)₂CHOH, 99.9%, Sigma-Aldrich), IPA-d1 ((CH₃)₂CHOD, 98 atom% D, Sigma-Aldrich), IPA-d8 ((CD₃)₂CDOD, 99 atom% D, Yuanye), tert-butanol (99.7%, Sigma-Aldrich), and D₂O (99.9 atom% D, Sigma-Aldrich). Water (18.2 MΩ·cm) was generated from a water purification system (Milli-Q). Ru supported on carbon (Ru/C, 5 wt% Ru, Macklin) and alumina (Ru/Al₂O₃, 5 wt% Ru, Riogen) were commercial catalysts.

Glucose CTH reaction. In a typical run of glucose CTH reaction, 16 mg of glucose, 16 mg of catalyst, and 4 mL of H₂O/IPA mixture (1:1 v/v) were added to a glass vial, unless otherwise stated. Herein, IPA was employed as both the H donor and solvent for glucose CTH, whereas water as the greenest solvent was introduced as a co-solvent to dissolve glucose. Pristine catalyst was used for all CTH experiments unless otherwise stated. Then, the vial was placed in a microwave reactor (Monowave 400, Anton Paar, pressure error ± 2 bar) for reaction. For reactions at a larger scale using another reactor (Flexiwave, Milestone), solution volume was increased to 10 mL,



alongside the proportional increase in substrate and catalyst loadings. The reactions followed a temperature program including a ramping stage with a ramping rate of 10 °C/min, followed by a holding stage at the designated temperature (the holding time in this stage is defined as reaction time). Note that the ramping time of the reactions for kinetic model establishment was minimized to ~0.5 min to obtain the initial reaction rates. The reacted solid-liquid mixture was separated using 0.45 µm mixed cellulose ester membrane filter. The solid (the spent catalyst) was vacuum dried at 50 °C for 6 h and reserved for characterizations.

Product identification and quantification. The concentrations of compounds in the liquid sample were typically quantified by high-performance liquid chromatography (HPLC, LC-2050C, Shimadzu) equipped with HPX-87H (Bio-Rad) column at 65 °C, using 5 mM H₂SO₄ as the mobile phase at a flow rate of 0.4 mL/min. During glucose CTH over Ru/C, the major by-products were fructose from isomerization (< 1.5 Cmol%) and degradation products including glycolic acid (< 1 Cmol%) and formic acid (< 1 Cmol%). Since this work focuses on hydrogenation and the yields of these by-products were negligible, their detailed product distribution is not shown. For reactions using fructose as the substrate, sorbitol was quantified using HiPlex-Ca column (Agilent) operated at 80 °C with water as the mobile phase at a flow rate of 0.6 mL/min. The molecular weights of isotope-labeled compounds were identified by mass spectrometry in electrospray ionization mode (ESI-MS, LCQ Fleet Ion Trap Mass Spectrometer, Thermo Scientific) using mobile phase consisting of methanol and water at a volume ratio of 80 to 20. Following CTH experiments under selected conditions, the gas in the headspace of glass vial (i.e., reactor vessel) was analyzed by gas chromatography (GC, Agilent 6890) equipped with an HP-PLOT Molesieve column (Agilent 19095P-MS0) and detected by thermal conductivity detector (TCD).



Characterization of catalysts. Particle size distribution and lattice spacing in catalysts were determined from transmission electron microscopy (TEM, JEM-F200, JEOL) images and selected area electron diffraction (SAED) ring patterns. The crystalline phases were determined by X-ray diffraction (XRD, Ultima IV, Rigaku). Lewis acid site was quantified based on Fourier transform infrared spectroscopy (FTIR, Tensor 27 FTIR Spectrometer, Bruker) after chemisorption and desorption of pyridine (pyridine-FTIR) at temperatures of 120, 150, and 180 °C; samples were pretreated at 350 °C under vacuum condition before pyridine sorption. The near-surface chemical states and coordination environment of Ru were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha X-ray photoelectron spectrometer, Thermo Scientific) and extended X-ray absorption fine structure (EXAFS, Shanghai Synchrotron Radiation Facility), respectively. *In situ* FTIR (Nicolet iS50 FTIR Spectrometer, Thermo Scientific) was used to probe surface species during IPA activation (gas flow rate was fixed at 50 mL/min during both pre-stabilization and holding stages). Nuclear magnetic resonance (NMR, VNMRS 600 MHz NMR spectrometer, Agilent) was used to determine H spectra in spent catalysts.

Chemical treatments of Ru/C catalyst. H₂ reduction of pristine catalyst was conducted at 400 °C for 2 h in a tube furnace using forming gas (5% H₂ in N₂); the reduced catalysts were collected for designated CTH experiments and characterization. Oxidized catalysts were prepared by oxidizing pristine catalysts (1 g catalyst dispersed in 15 mL water) using 0.5 mL 6 wt.% H₂O₂ aqueous solution. The mixture was agitated at room temperature for 10 min, followed by vacuum filtration and oven-drying at 105 °C for 2 h.



3. Results and Discussion

3.1. Glucose CTH to sorbitol with IPA as H donor over Ru/C

Preliminary screening test compares glucose CTH catalyzed by Ru/C in the presence of different alcohols as hydrogen donors. The results show that the system with IPA as the hydrogen source produced sorbitol yield significantly higher than other alcohols, including methanol, ethanol, 1-propanol, and 2-butanol, with various alkyl chains and hydroxyl group positions (**Figure S1**). Since the literature has discussed the dehydrogenation activities of various H donors [14, 15], the current study adopts a different perspective by investigating chemical events involving multiple reacting species on the catalyst surface. The following CTH experiments were all performed using IPA as the H donor (as schemed in **Figure 1a**).

Ru-catalyzed glucose CTH in IPA was conducted under broader conditions. At a reaction time of 20 min, sorbitol yield increased with temperature up to 140 °C but decreased at higher temperature probably due to over-reactions (**Figure 1b**). Time course at 140 °C shows that sorbitol yield increased with time and reached a plateau at 82.8 Cmol% within 20 min (**Figure 1c**). Note that the increasing trend in acetone production over time provides direct evidence of IPA dehydrogenation at O–H and α -C–H positions. A control experiment in a mixture of tert-butanol ((CH₃)₃COH) and water (140 °C, 10 min) did not produce sorbitol, suggesting that β -C–H was unlikely a H source. The lack of C=C-containing compounds in the product analysis further suggests a low probability of hydrogen transfer from the β -C–H and α -C–H positions of IPA. Instead, scission at O–H and α -C–H of IPA represents a more feasible route. The question comes down to how H atoms can be transferred from IPA to glucose. Two pathways are widely discussed: the metal hydride (or H adatoms) route that requires a H-bonded metal surface [16, 17] as well as MPV reduction that



involves the concerted intermolecular H atom transfer *via* a six-membered ring transition state facilitated by Lewis acid [11]. Considering that these pathways are characterized by the participation of distinct active sites (*i.e.*, metal or Lewis acid), Ru/C catalyst was subjected to detailed analyses.

The analysis of the lattice spacing observed in TEM images and SAED ring patterns reveals both Ru and RuO₂ crystals in pristine Ru/C, although they cannot be observed in XRD due to the nanosize of 2.3±0.2 nm on average (**Figure 2a&b**). The EXAFS spectrum of Ru in Ru/C lies between those of Ru foil (metallic Ru⁰) and RuO₂ standards, indicating an average valence state between 0 and +4 (**Figure 2c**), which is complemented by the R-space results and wavelet transform analysis hinting at the co-existence of Ru–Ru and Ru–O/C bonding (**Figures 2d&e**). This agrees with the Ru 3p XPS spectra deconvolution, suggesting 76% cationic Ru^{δ+} and 24% Ru⁰ on catalyst surface (**Figure 2f**). The Ru oxides might account for the Lewis acid site amount of 15–48 μmol/g measured by pyridine-FTIR spectroscopy at 120–180°C (**Figure 2g**). As both metallic sites and Lewis acid sites were found on Ru/C, neither metal hydride (or H adatoms) transfer nor MPV step can be excluded from the glucose CTH mechanism at this point.

To identify the prevailing hydrogen transfer route, we first search for signals of hydride Ru–H. The possible Ru–H signals in the range of -8 ppm to -17 ppm [16–19] are absent from the ¹H NMR spectra of IPA-treated catalysts (**Figure 3a**), whereas the *in-situ* FTIR spectra of Ru/C under IPA flow shows no peak at ~1632 cm⁻¹ that is typically assigned to Ru–H [20] (**Figure 3b**), presenting no evidence of metal hydride formation. Nevertheless, the emerging peaks at 1720 and 1740 cm⁻¹ of the *in-situ* FTIR spectra could be assigned to the stretching vibrations of C=O of acetone [21,



22], suggesting that IPA can be rapidly activated on Ru/C and dehydrogenated to form acetone. When feeding an IPA-water mixture to Ru/C during *in situ* FTIR analysis (simulating the reaction solvent in CTH experiments), the formation of acetone remains noticeable. The results evidence feasible IPA activation on Ru/C catalysts. In addition, we observed that the reaction vessels remained pressurized (4-6 bar) even after cooling to *c.a.* 40°C, indicating the formation of non-condensable gas after glucose CTH (**Figure S2a**). Such gas product was confirmed to be H₂ by GC analysis (**Figure S3**). Molecular H₂ might emerge from the combination of two chemisorbed-H atoms (H*) that result from IPA activation on Ru surface. Such process is analogous to the Tafel step (2H* → H₂) in hydrogen evolution reaction. Therefore, while we may not expect strong Ru–H, the formation of chemisorbed H* on Ru and thus its participation in glucose CTH appear highly plausible.

3.2. Pathway of H transfer to glucose and the active site

It is possible that glucose CTH proceeds through hybrid, sequential H* transfer and MPV reduction. To examine the potential contribution of MPV reduction, glucose CTH was performed in a mixture of H₂O and fully deuterated IPA (IPA-d₈); the latter is assumed to exist as IPA-d₇ due to facile H/D exchange between H₂O solvent and –OD group in IPA. If CTH constitutes a MPV step, the α-C–D bond of IPA-d₇ is expected to donate the D atom directly to glucose through the formation of the MPV complex, resulting in sorbitol carrying at least one D atom (*i.e.*, C1-D; non-exchangeable with H from H₂O) (**Figure 4a**). However, the ESI-MS profile of sorbitol obtained in H₂O/IPA-d₇ (solvent **1**) shows a dominant signal at *m/z* 205, which corresponds to sorbitol without any D (adduct of [C₆H₁₄O₆+Na]⁺) (**Figure 4b**). Such profile highly resembles that of sorbitol from the control, *i.e.*, H₂O/IPA (without D; solvent **2**). These results rule out the possibility



of direct D transfer from the α -C–D of IPA to glucose. In essence, both H atoms (or both H and D atoms) were very likely to be chemisorbed on catalyst surface before attacking glucose. Note that any D* adatoms would be prone to H/D exchange with H₂O and become H*, accounting for the absence of D atoms in sorbitol derived in H₂O/IPA-d7.

To verify the absence of MPV step, glucose CTH was performed in D₂O/IPA-d1 (solvent **3**); in case that MPV took place, the resulting sorbitol would have received one H atom at C1 position (non-exchangeable) from the α -C–H of IPA-d1. Such possibility was not supported by the ESI-MS results, which show highly similar profiles of sorbitol obtained in solvent **3** and the fully deuterated medium, D₂O/IPA-d8 (solvent **4**; where two D addition is the only option). In both spectra, a signal of sorbitol-d2 [C₆H₁₂D₂O₆+Na]⁺ with the same relative intensity can be observed at m/z 207 (while sorbitol-d1 at m/z 206 may result from H/D exchange between sorbitol-d2 and mobile phase during ESI analysis) (**Figure 4b**). This suggests that two D atoms were transferred to glucose in solvent **3** as in solvent **4** regardless of the presence of α -C–H in the former, reaffirming our speculation that MPV is unlikely to occur in this study. This aligns with a previous study that reported the presence of C1–D in sorbitol obtained in a similar catalytic system (Ru/C, D₂O/IPA) based on proton NMR spectroscopy [13], advocating for the adatom addition path rather than MPV. Our study further shows that such adatom transfer mechanism prevails in low-water-content CTH of glucose, as evidenced by the similar ESI-MS profiles of products obtained in D₂O/IPA-d1 regardless of the solvent ratio (1:1 or 1:7 v/v; **Figure S4**).

The theory of H* adatom transfer should be underpinned by verifying metallic Ru sites as the active sites in glucose CTH. We altered the relative abundance of metallic phase by reducing the



pristine catalysts in H₂ gas, which was then validated through characterization as shown in **Figure S5**. It is observed that the particles were largely preserved in nanosize (2.6±0.9 nm) after reduction as depicted in the TEM images; thus the Ru dispersion (50%) was estimated to be comparable with pristine Ru/C (56%) based on the particle-size-dispersion relationship [23]. The XRD pattern of reduced Ru/C exhibits more prominent diffraction peaks assigned to metallic Ru compared to that of the pristine catalyst. The near-surface chemical states of Ru were analyzed through the curve fitting of the Ru 3p XPS spectra. The proportion of Ru⁰ (462.0 eV [24]) increased from 24.0% to 30.8% after reduction (**Figure 2f** & **Figure S5**). We remark that the samples can be partially oxidized when exposed to air during handling, which may account for the subtle differences in the XPS results. The Lewis acid sites amount on the reduced Ru/C decreased by 20-60% compared to the pristine Ru/C (**Figure S6**), indicating fewer surface Ru^{δ+}, *i.e.*, higher Ru⁰ content, after reduction, which corroborate the XPS results.

The reduced catalyst was then evaluated in glucose CTH experiment. It is evident that the reduced Ru/C achieved 2.3-2.8 times the sorbitol yield of the pristine catalyst at different temperatures. Because the particle size and dispersion remained comparable before and after reduction, the enhanced performance of glucose hydrogenation can be attributed to the increased fraction of Ru⁰ phase as the major active sites (**Figure 7a**). It is noteworthy that acetone production also triplicated (*e.g.*, 869.3 mmol/L for reduced Ru/C vs. 286.3 mmol/L for pristine Ru/C at 140 °C), suggesting Ru⁰ as the active sites for IPA dehydrogenation (to acetone) as well. Combining these observations, we believe that glucose CTH begins with the activation of IPA on metallic Ru to form two H* adatoms (and acetone), followed by two H* addition steps to glucose to form sorbitol.



3.3. Impact of H-H combination on sorbitol formation kinetics

Microkinetic study was performed for a deeper mechanistic understanding. Kinetic isotope effects (KIE) were studied to determine if IPA was involved in the kinetically relevant step in glucose CTH on Ru/C. The comparable yields of sorbitol obtained from glucose and glucose-1-¹³C (**Figure 5a**) suggest that C1 in glucose did not participate in the rate-determining step. Conversely, both sorbitol and acetone production decreased when using solvent IPA-d8 (or IPA-d7) that is characterized by α -C-D (*i.e.*, solvents **1&4**), compared to IPA (or IPA-d1) that carries α -C-H (*i.e.*, solvents **2&3**) (**Figure 5b**). Such result suggests that the activation of α -C-H (α -C-D) in IPA for H* formation is rate-limiting, which agrees with another CTH system (2,3-diphenylacrylonitrile CTH over a Zn-based catalyst) where the dissociation of α -C-H in methanol was proposed as the rate-determining step [25].

A kinetic model was then derived featuring the rate-determining IPA activation (equation derivation detailed in **Text S1**). We first considered the simplest reaction network involving only cascade steps – starting with IPA activation to give two H* atoms that are then added to glucose (**Scheme S1**). One may expect the rate law to be:

$$\text{Rate of sorbitol formation} = \frac{k_1 K_{IPA} C_{IPA}}{1 + K_G C_G + K_{IPA} C_{IPA}} \quad (\text{Eqn. 1})$$

where K_G and K_{IPA} are equilibrium constants of glucose and IPA adsorption, respectively; C_G and C_{IPA} are concentrations of glucose and IPA, respectively; k_1 is the rate constant of IPA dehydrogenation. It is noteworthy that the rate equation predicts a negative correlation between sorbitol yield and glucose concentration (C_G), which, however, is contradictory to the results of CTH experiments in varying C_G , at 0-11.1 mmol/L in particular (**Figure 6b**). Specifically, the CTH experimental results show a volcano-shaped pattern of sorbitol production as a function of C_G



(**Figure 6b**). Such discrepancy between theoretical prediction and actual observation suggests that a more complex model should apply.

We observe that acetone production over Ru/C consistently exceeded the stoichiometric amount by several tens of times (*i.e.*, acetone-to-sorbitol molar ratio $\gg 1:1$), hinting that a parallel reaction takes place and produces acetone. This aligns with our observation about H₂ formation (**Figures S2&3**). The pressure-based estimation of H₂ gas amount in moles (using ideal gas law) is close to the missing fraction of the H balance in CTH reaction (**Figure S2b**), suggesting molecular H₂ as the major gaseous product. Lining up these findings, we speculate that upon the dehydrogenation of IPA to acetone, the two released H* adatoms tend to combine with each other on Ru, producing molecular H₂; such path considerably competes with glucose reduction for the chemisorbed H* and thus sorbitol formation.

To verify, we expand the kinetic model by incorporating the competitive H₂ formation step (**Figure 6a**) and derive the following rate equation (details of derivation in **Text S2**):

$$\theta_G = \frac{K_G C_G}{1 + K_G C_G + K_{IPA} C_{IPA}} \quad (\text{Eqn. 2})$$

$$\text{Rate of sorbitol formation} = \frac{r_1 k_2 \theta_G}{k'_2 + k_2 \theta_G} \quad (\text{Eqn. 3})$$

where θ_G is the coverage of glucose, r_1 is the rate of IPA (α -C-H) activation, k_2 and k'_2 are the rate constants of sorbitol and H₂ formation, respectively. Experimental rate data and operating parameters (C_G , C_{IPA}) were fitted into the rate equation to approximate equilibrium constants (K_G and K_{IPA}) and rate constants (k_1 , k_2 , k'_2). The K_{IPA} was assumed to be 1 L mol⁻¹ [26] at the beginning and then optimized together with other constants using Excel Solver. These constants were then used in visualizing the reaction rate patterns – rates as a function of glucose and IPA



concentrations considering a certain range of K values. As shown in **Figures 6b&c**, the reaction rate patterns described by the model qualitatively capture the key features of the experimental results. Specifically, acetone decreases and sorbitol production exhibits a volcano-shaped pattern with increasing glucose concentration; changes in both products become less pronounced at high glucose concentrations (**Figure 6b**). When increasing IPA concentration, both acetone and sorbitol formation shows a logarithmic growth in simulation and experiments (**Figure 6c**). It is noted that the co-production of H_2 was documented in the cellulose CTH systems [12, 13] although this was not often discussed in broader CTH studies.

3.4. Potential strategy to enhance CTH

Inspired by the observation that most H^* atoms combine to form molecular H_2 rather than uptake by glucose, we propose a catalyst design strategy centering on the suppression of H-H combination to increase the formation of reduced organic product. We note that the sorbitol-to-acetone ratio (approximated as sorbitol-to- H_2 ratio) appears to be constant for Ru/C, regardless of CTH operating conditions and chemical pretreatments (*i.e.*, oxidation and reduction) of the catalysts (**Figure 7a**). To testify whether this is a generic phenomenon, supplementary glucose CTH experiments were performed using a different catalyst, *i.e.*, Ru/ Al_2O_3 . Likewise, it exhibits a constant sorbitol-to-acetone ratio and yet is distinct from that of Ru/C. The results imply that the degree of competition for H^* (between H_2 and sorbitol formation) can be controlled by more detailed descriptors of catalyst properties other than oxidation state; such properties could be altered by using different supports. A previous study also noted the distinct CTH performances of Ru catalysts on different supports [12].



Our results show that the sorbitol-to-acetone ratio over Ru/Al₂O₃ is approximately 8 times that of Ru/C, suggesting that glucose substrate becomes more competitive on Ru/Al₂O₃ in terms of H* uptake (**Figure 7a**). We speculate that the Ru sites on these two catalysts have different crystallography (*e.g.*, numbers and types of faces and edges), electron density, and/or ensemble size, as a result of metal-support interactions. Ru alloying may provide a feasible route to tune these characteristics as well. For example, phosphidation to form Ru₂P has been reported to dilute Ru-Ru ensemble and thus tune Ru characteristics [27]. Computational and experimental studies have shown that the Ru planes, adsorption positions (top, bridge), electron density, and Ru-Ru ensemble size can affect the adsorption of substrates (*e.g.*, toluene and CO probe molecule) [27] as well as H binding with a reported range of 0.08-0.48 eV [28-31].

Tuning adsorption via surface engineering might make a feasible avenue to mitigate H-H combination and alter H transfer selectivity in CTH. Conceptual energy profiles are proposed to illustrate this theory (**Figure 7b&c**). On surfaces that allow stronger binding (*i.e.*, lower energy level), the activation energy of H₂ formation would increase, considering that H-H combination is typically *endothermic* and thus has a *late* transition state (as opposite to dissociative H₂ adsorption). In cases where glucose hydrogenation is *exothermic*, which has been supported by theoretical calculations for certain precious metal faces [32, 33], an *early* transition state is presumed. Its energy level might lower along with the reactants to a similar extent, possibly maintaining a constant activation energy of sorbitol formation. We infer that due to such thermodynamic difference (endothermic vs. exothermic), strengthening glucose and H binding on the metal surface might slow H₂ formation while sustaining sorbitol formation, leading to a higher apparent rate of the latter.



We proceed to examine CTH of more biomass-derived sugars over Ru/C, including fructose-to-sorbitol, xylose-to-xylitol, and maltose-to-maltitol conversion (**Figure 8**). In general, this CTH system can be applied to diverse monosaccharides sourcing from various natural polysaccharides (e.g., starch, cellulose, and hemicellulose) and disaccharide such as maltose. It is noteworthy that the turnover frequency (TOF) of maltose-to-maltitol CTH was 4.8 times that of the glucose-to-sorbitol system, while the TOF of acetone formation was only 2.4 times, corresponding to doubled selectivity of H transfer to polyol product. These results hint at the significant role of substrates in governing H transfer selectivity, of which the adsorption energies and their impact on reaction kinetics should be further studied. Our result also suggests that a sequential hydrogenation-hydrolysis route on readily available maltose syrup may offer higher efficiency and H atom economy of sorbitol production than glucose CTH, which should be verified in future research. Previously reported Ru-based CTH reactions on various biomass-derived substrates (e.g., furfural, guaiacol) were summarized in **Table S1**. Overall, the reported systems typically required hour-scale reaction time to achieve high conversion and/or yield; in this study, minute-scale reaction time was adopted for sorbitol yields $\geq 80\%$.

We remark that the low H atom economy in our CTH system resembles the longstanding challenge in electrochemical reduction reactions, where H_2 evolution is considered a side reaction that lowers Faradaic efficiency in the electroreduction of CO_2 [34] and larger organic molecules [35]. It appears that H transfer selectivity presents a challenge to broader systems – both thermocatalysis and electrocatalysis – that rely on *non- H_2* hydrogen source, which is worthy of further investigations.



4. Conclusion

In summary, we validate a chemisorbed-H (H^*) atom transfer mechanism of glucose CTH to form sorbitol over Ru/C catalyst using IPA as the hydrogen source. On metallic Ru active sites, the reaction proceeds with the rate-determining activation of IPA, specifically at the O–H and α -C–H positions, releasing two equivalent H^* adatoms for supply to glucose. However, combination among surface H^* to form molecular H_2 emerges as a highly competitive H-consuming step in parallel with glucose-to-sorbitol formation; the former should be suppressed to increase H selectivity to sugar alcohols as the target products. This mechanistic study deepens our understanding of the transfer and fate of hydrogen in a CTH system, guiding the development of catalysts with higher H atom economy.

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6. Author contributions

Q.Z., Z.L., and X.L. performed experiments and analyzed data. Q.Z. wrote the manuscript and prepared data visualization. I.K.M.Y. reviewed and/or edited the manuscript before submission. All authors contributed substantially to discussion of the content and the writing of the article.

7. Competing interests

N.A.



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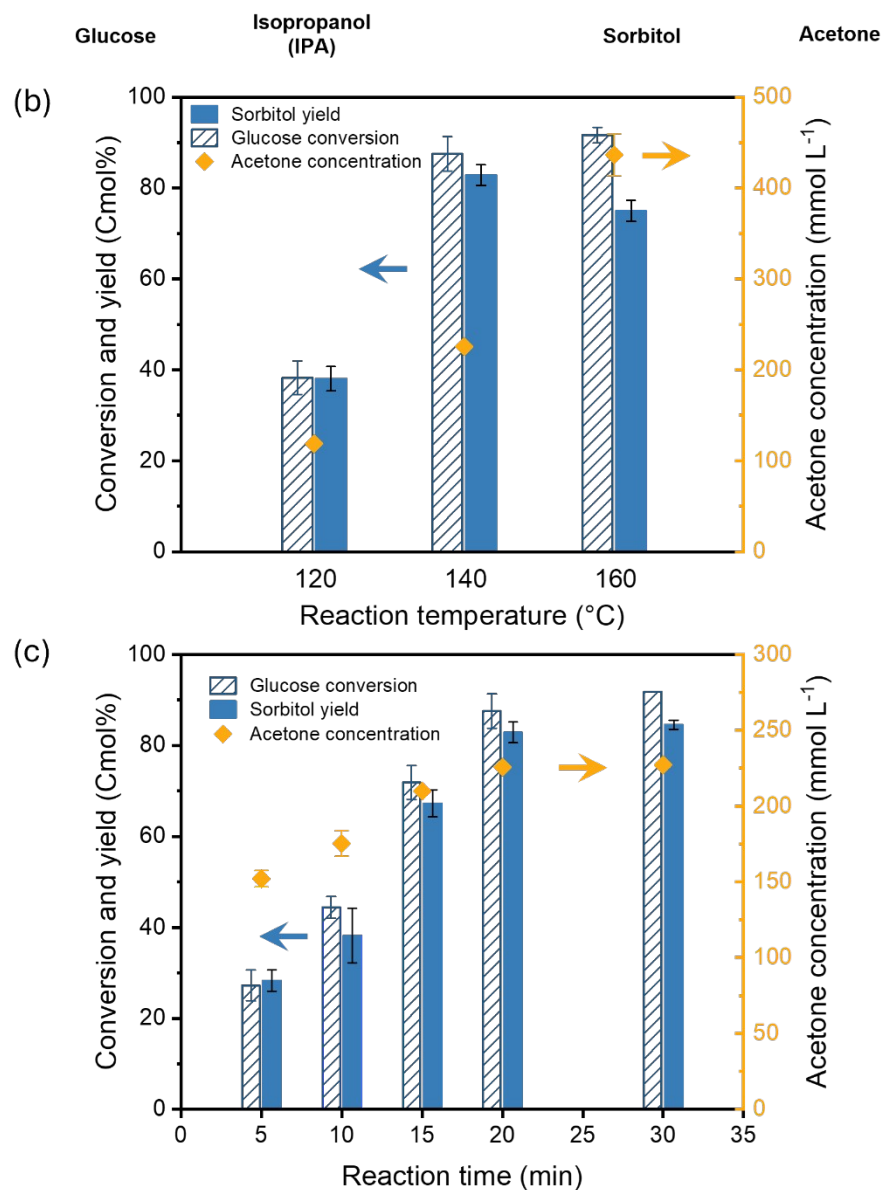
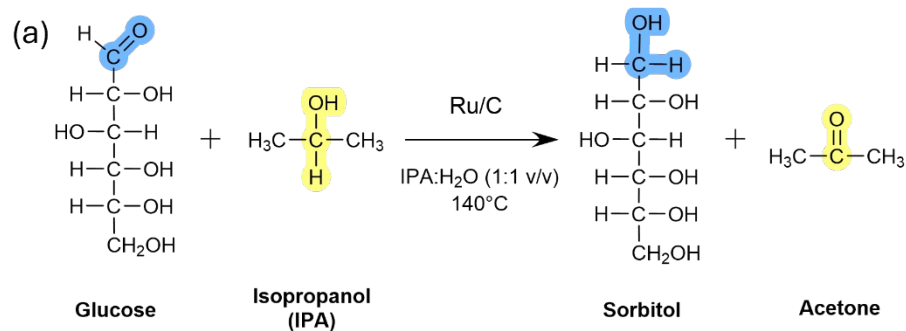


Figure 1. (a) Scheme of glucose CTH to sorbitol with IPA as the H donor; glucose CTH over Ru/C catalyst: (b) various temperatures within 20 min and (c) time course at 140 °C (Reaction conditions: 16 mg glucose, 16 mg Ru/C, 2 mL IPA and 2 mL water; Monowave 400).



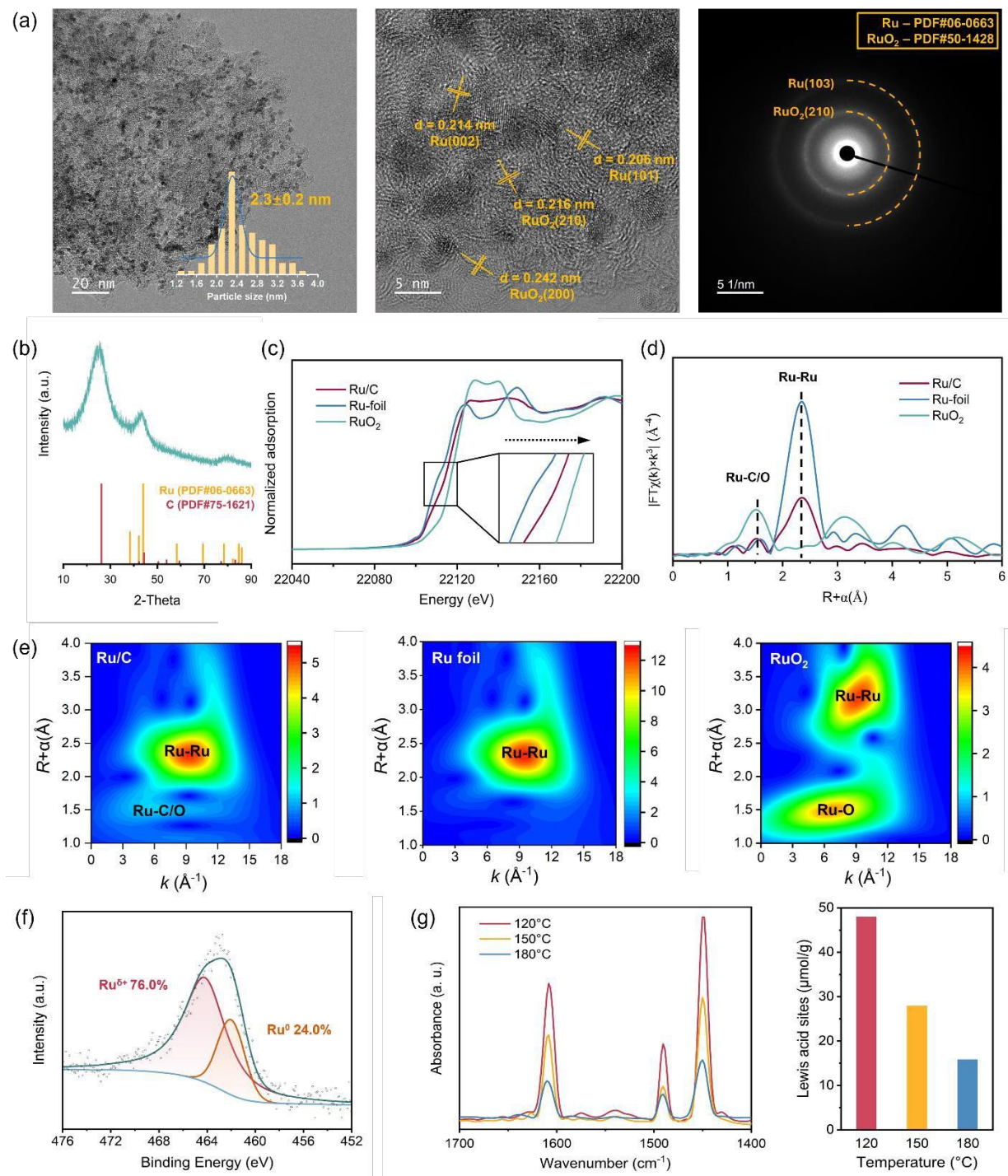


Figure 2. Characterization of Ru/C: (a) TEM images and SAED ring patterns with typical lattice spacing and particle size distribution; (b) XRD pattern with peak references; EXAFS spectra of (c) E-space, (d) Rspace, and (e) wavelet transform analysis with comparison to Ru foil and RuO₂; (f) Ru 3p XPS spectra deconvolution results; and (g) pyridine-FTIR spectra and corresponding Lewis acid site quantification at various pyridine desorption temperatures.



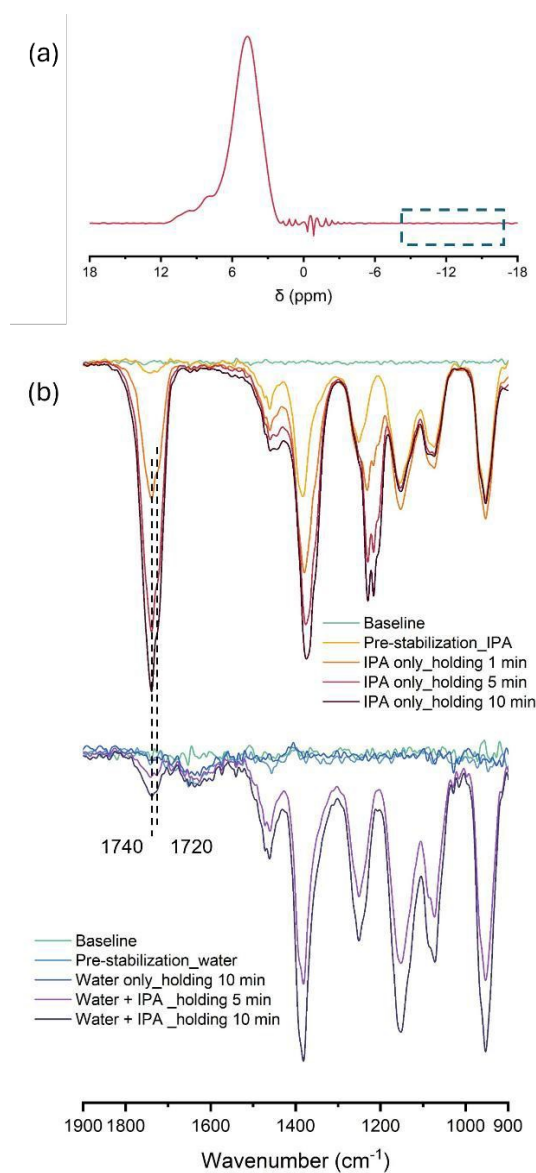


Figure 3. (a) ^1H NMR spectra of IPA-treated Ru/C (Treatment conditions: 40 mg pristine Ru/C, 5 mL IPA and 5 mL water; 140 °C, 30 min; Flexiwave); (b) *in situ* FTIR spectra of Ru/C under the flow of IPA and water only and IPA-water (1:1 v/v) mixtures (Pre-stabilization temperature: 50 °C, holding temperature: 80 °C; flow rate of each solvent vapor: 50 mL/min).



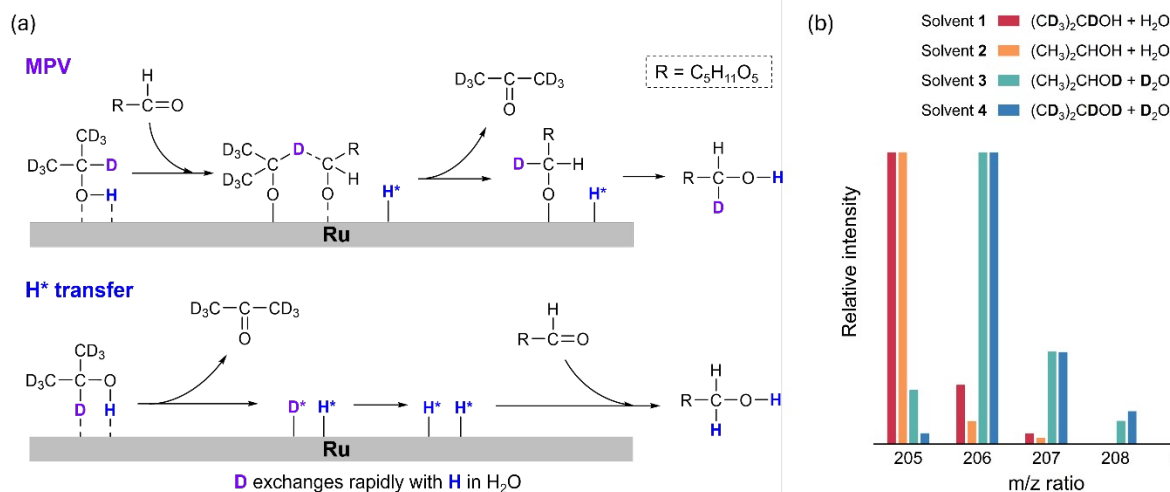


Figure 4. (a) Two possible mechanisms of glucose CTH to sorbitol in solvent 1 (H donor IPA-d8 assumed as IPA-d7 in H₂O solvent); (b) ESI-MS profile of products from glucose CTH in various D-labelled solvents (Reaction conditions: 16 mg glucose, 16 mg Ru/C, 2 mL IPA and 2 mL water; 140 °C, 10 min; Monowave 400. Assignment of main adducts: m/z 205 for [C₆H₁₄O₆+Na]⁺, m/z 206 for [C₆H₁₃DO₆+Na]⁺, and m/z 207 for [C₆H₁₂D₂O₆+Na]⁺).

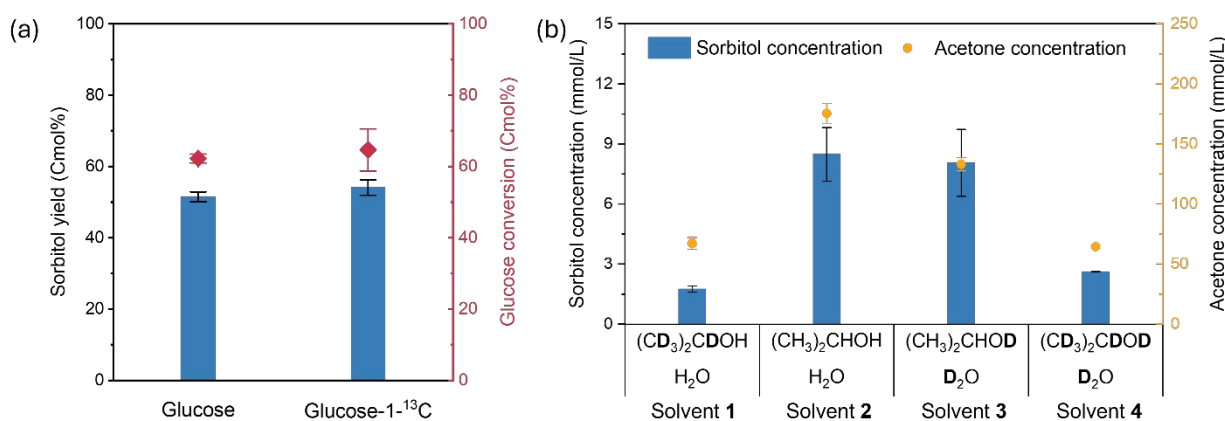


Figure 5. Effects of (a) ¹³C at glucose C1 and (b) D-labelled solvents on glucose CTH kinetics (Reaction conditions: 16 mg glucose, 16 mg Ru/C, 2 mL IPA and 2 mL water; Monowave 400; (a) 120 °C, 30 min; (b) 140 °C, 10 min).



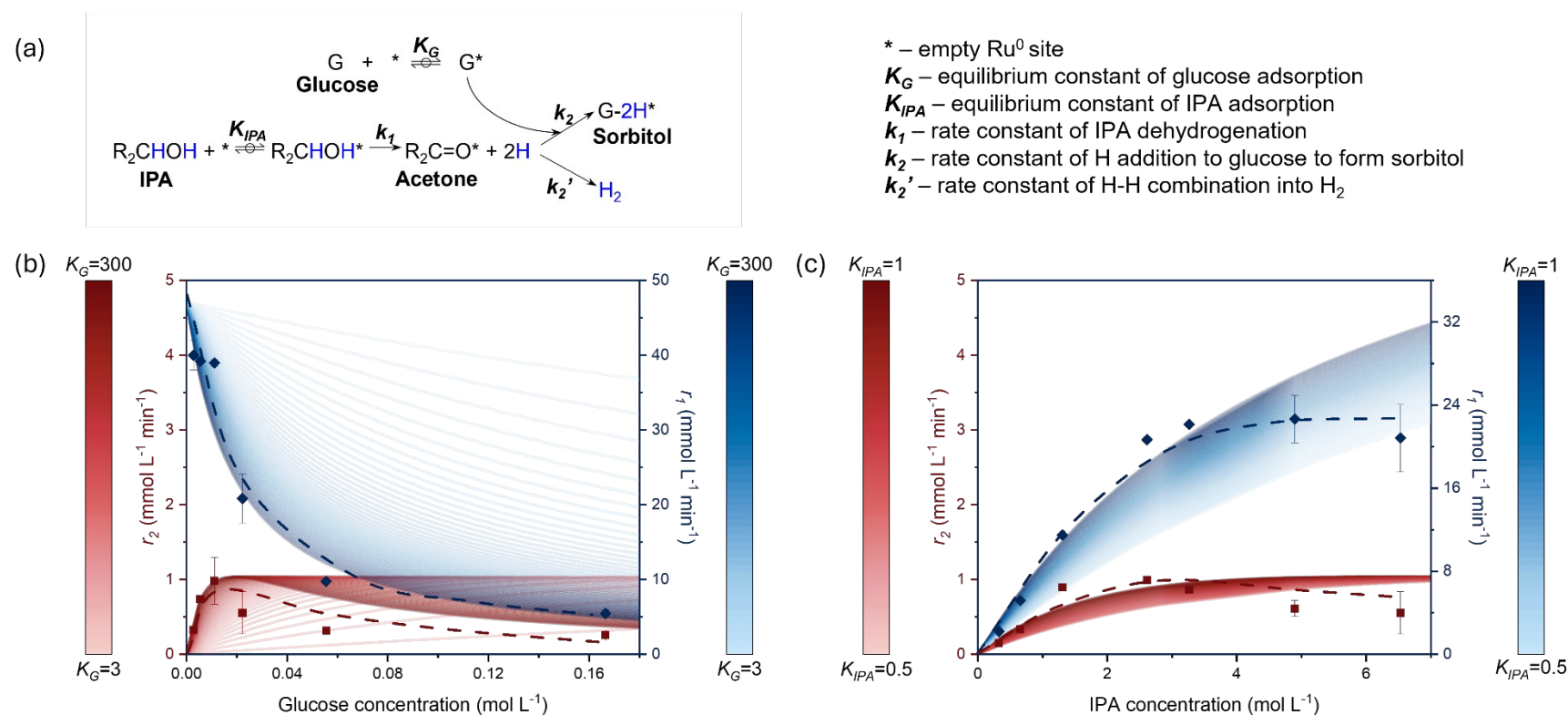


Figure 6. (a) Proposed scheme to establish kinetic equations; Experimental results (scatters and dashed trend lines) and predicted trends (solid lines) of rate of IPA dehydrogenation (r_1) and rate of H addition to glucose (r_2) as a function of (b) glucose loading in solvent comprising 2 mL IPA and 2 mL water and (c) as a function of IPA concentration at a glucose loading of 16 mg and total solvent volume of 4 ml (Reaction conditions: 140 °C, 5 min; Monowave 400). Predicted trends were obtained using Eqn. 2 and Eqn. 3, where $K_{\text{IPA}} = 0.726 \text{ L mol}^{-1}$ in (b), $K_G = 204 \text{ L mol}^{-1}$ in (c), $k_1 = 5.70 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$, $k_2 = 7.58 \times 10^{-5} \text{ mol L}^{-1} \text{ min}^{-1}$ and $k_2' = 8.26 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$ were optimized by using Excel Solver based on experimental data.

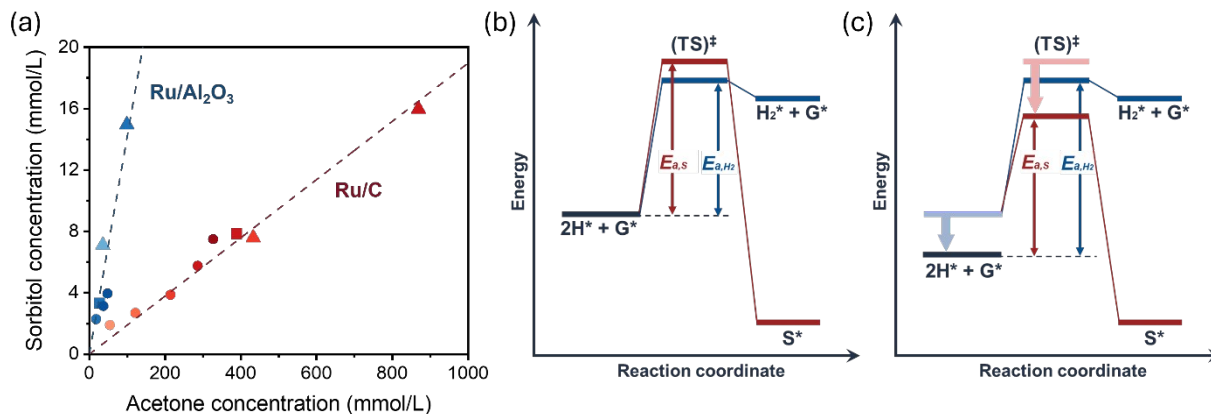


Figure 7. (a) Correlations between sorbitol and acetone concentration over different Ru/C and Ru/Al₂O₃ catalysts: pristine – circle, oxidized – square, reduced – triangle (Reaction conditions: 0.04 g glucose, 0.04 g catalyst, 5 mL IPA and 5 mL water; reaction temperature range of 80-160 °C – color from light to dark; 30 min; Flexiwave); Energy profiles of hydrogenation of glucose (G) to sorbitol (S) and H-H combination into H₂ under the hypothetical scenarios of (b) weak binding and (c) strong binding of H and glucose on a catalyst surface. E_a – activation energy; TS – transition state.



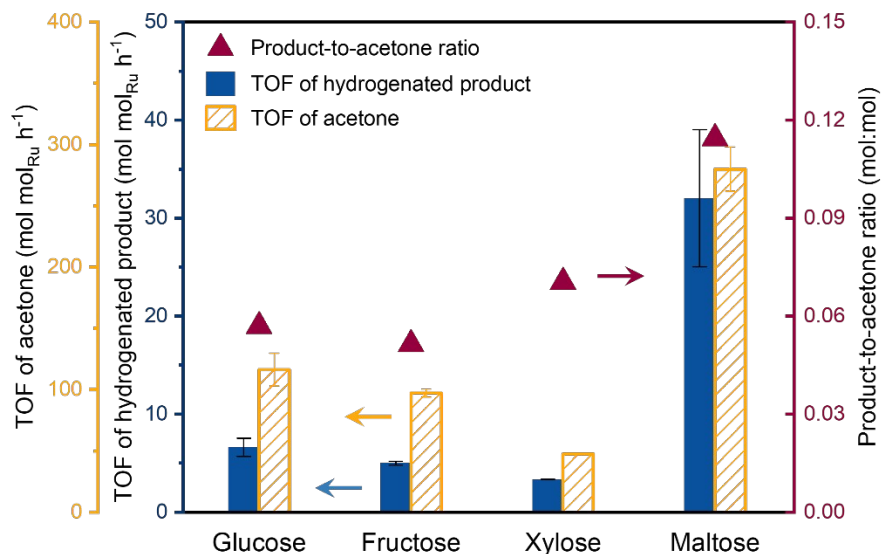


Figure 8. CTH of glucose, fructose, xylose, and maltose over Ru/C with IPA as H donor: TOF of formation of hydrogenation products (i.e., sorbitol, sorbitol, xylitol, and maltitol, respectively) and acetone as well as their ratio (Reaction conditions: 111 mmol/L substrate, 16 mg Ru/C, 2 mL IPA and 2 mL water; 140 °C, 20 min; Monowave 400).



Data Availability Statements

View Article Online
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The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available.

