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Hydrogenation of Glucose into Sorbitol using Ru-based Catalyst: A Short Review

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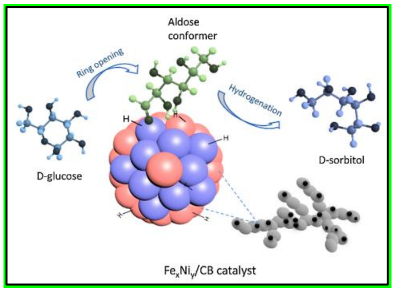
GRAPHICAL ABSTRACT



ABSTRACT

Glucose is one of the most abundant non-food biomasses on the earth, and it is one of the most promising fossil-fuel alternatives for the long-term production of commodity chemicals and fuels, with the potential for carbon-neutral technologies. Sorbitol produced by glucose hydrogenation, is the most potential carbohydrate-derived building block chemicals has been regarded as a promising alternative to petroleum and natural gas in future refinery. Catalytic hydrogenation of glucose into sorbitol has recently drawn attention. Heterogenous catalysts are preferred in this reaction due to their high efficiency and reusability. This paper discusses the catalytic performance and reusability of Ru-based catalysts, which has been demonstrated in numerous studies to have a high selectivity toward target products. The reaction mechanism of the glucose hydrogenation over a few heterogenous catalyst are also being highlighted. Additionally, critical challenges and potential future research approaches for heterogeneous catalytic hydrogenation of glucose to sorbitol are highlighted.

Keywords: Biomass; sorbitol; glucose hydrogenation; Ru-based catalyst

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1. INTRODUCTION

The Twelfth Malaysia Plan (12MP) for the period 2021-2025 is consistent with the shared prosperity initiative, which encompasses three dimensions; economic empowerment, environmental sustainability, and social re-engineering. It incorporates the blue economy, green technology, renewable energy, as well as climate change adaptation and mitigation [1]. The utilization of lignocellulosic biomass as a renewable raw material for both energy and valuable platform chemicals can be related to the 12MP dimension as biomass is listed in five types of renewable energy.

Due to the depletion of fossil energy resources and pressing environmental concerns, cellulosic biomass appears to be one of the most promising alternatives for producing chemicals, energy, and fuels [2]. Lignocellulose is the most abundant non-edible biomass source found in plant walls. It is composed of carbohydrate polymers cellulose and hemicellulose that are embedded in a lignin matrix. Unlike fossil fuels such as petroleum or coal, cellulose, as well as a primary source of monosaccharides, including glucose and fructose, has a high content of oxygen in its structure (c.a. 50 wt.%) in addition to hydrogen and carbon elements, which is a significant advantage in the synthesis of oxygen-containing chemicals such as sugar alcohols [3-4]. Cellulose is a promising raw material that is easier to distinguish than hemicellulose and lignin, and it can be employed in the conversion of various platform chemicals in the presence of various catalysts.

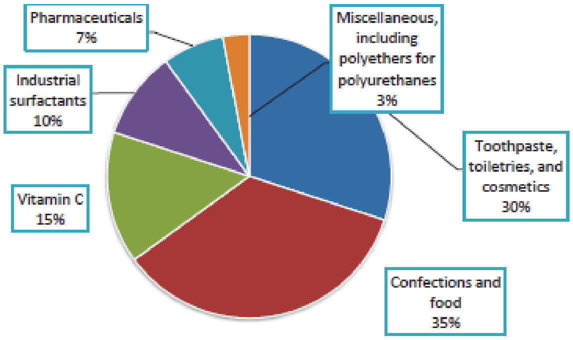


Figure 1: Major application of sorbitol [6].

According to US Department of Energy, sorbitol is one of the top 12 bioderived building blocks that can be easily converted into fuels and chemicals [5]. It is primarily employed in food and beverage, pharmacy, and cosmetic items, as well as an intermediate product in the manufacture of vitamin C, as seen in Figure 1 [6]. On a small scale, sorbitol can be extracted from various fruits such as apples, pears, peaches, apricots, and nectarines, and also dried fruits and some vegetables [7], but the most common reaction route for its industrial production is glucose hydrogenation.

Almost all sorbitol synthesis processes currently in use are based on the hydrogenation of glucose catalysed by metallic catalysts. High efficiency, ease of use, cheap cost, and relative environmental safety make the catalytic technique of sorbitol manufacturing employing heterogeneous systems increasingly viable [8]. Catalyst development in terms of controlled particle formation and modification of porosity, acidity, basicity, and metal support interactions resulted in an increase in catalytic performance [9]. Based on previous literature, Ru-based catalyst gave the highest activity and selectivity toward glucose reduction [10]. To our knowledge, however, the review on the influence of Ru-based catalysts in glucose hydrogenation, particularly in the manufacture of sorbitol, remains inadequate. Recent research and the performance of glucose hydrogenation over Ru-based catalysts, as well as the reaction mechanism over heterogenous catalysts that produces the required products, are discussed in this review.

2. HYDROGENATION OF GLUCOSE

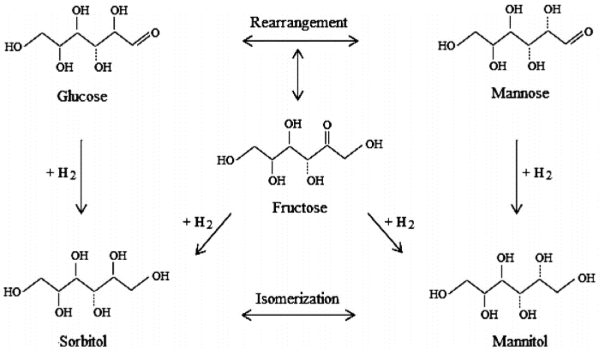
Glucose, also known as dextrose, is a type of carbohydrate known as a simple sugar (monosaccharides). C6H12O6 is the chemical formula for glucose and it can be found in fruits and honey, and it's the most common free sugar in higher animals' blood. Andreas Marggraf isolated glucose from raisins for the first time in 1747. Jean Dumas invented the name glucose in 1838, derived from the Greek word gleucos, which means "sweet" or "sugar," while Emil Fischer found the structure around the turn of the century [11]. Glucose is the most abundant form of simple sugars, and it can be acquired via acidic or enzymatic hydrolysis of large natural polysaccharides like cellulose and starch [12]. D-(+)-glucose is a 2,3,4,5,6-pentahydroxyhexaldehyde with a molecular weight of 180.16 kDa. D-Glucose is a polyalcohol as well as an aldehyde. It is classified as an aldose, which is a sugar with an aldehyde group. The suffix -ose denotes a sugar group, while -ald denotes an aldehyde group, which is responsible for the majority of chemical reactions of glucose [10]. Some of the physical properties of glucose are listed in Table 1.

All carbohydrate molecules contain hydroxyl groups which are available for reaction. Glucose and most other molecules of low molecular weight carbohydrates also have carbonyl groups available for the reaction. Hydrogenation is a chemical reaction in which hydrogen is added to a double bond formed between the oxygen atom and the carbon atom in the carbonyl group of an aldose or ketose contained in carbohydrates. D-glucose can be easily hydrogenated with hydrogen gas under pressure in the presence of catalyst. The product is d-glucitol, which is frequently referred to as sorbitol, with the suffix -itol denoting a sugar alcohol (an alditol) [11].

Table 1: Physical properties of glucose [8].

Physical Properties	**Characteristics**
Appearance	White, crystalline
Molecular weight	180.16 gmol-1
Melting point	150 C
Density	1.5620 g cm-3 (at 18 C)
Solubility in:	
Water	Very soluble
Ethanol	Slightly soluble
Ethyl Ether	Insoluble
Pyrimidine	Soluble

Sorbitol is produced by the hydrogenation of D-Glucose solutions obtained by hydrolysis of starch-containing crops (D-Glucose concentration up to 65 wt. %) in discontinuous batch slurry reactors at hydrogen pressures ranging from 5 – 15 MPa and temperatures between 100 and 180 ºC. Some by-products can be obtained during the hydrogenation process as a result of various side reactions as shown in Scheme 1: 1) D-Glucose can isomerize into fructose and mannose by Lobry de Bruyn–Alberda van Ekenstein rearrangements [13], which are further hydrogenated into mannitol and sorbitol [14], 2) The obtained sorbitol from the hydrogenation of D-Glucose, can be also isomerized into mannitol [15].



Scheme 1: Reaction network for glucose hydrogenation [10]

In order to obtain high reaction rate and products selectivity, a homogenous or heterogenous catalyst is often used [16]. Generally, homogeneous catalysts are present in the same phase as the reactants used in a chemical reaction, whereas heterogeneous catalysts are present in a different phase than the reactants, i.e., the catalysis is typically in a solid phase while the reactant is in a gaseous or liquid state [17]. Dissolvable homogeneous catalysts always record high catalytic activity because of the numerous catalytic sites available [18]. However, the difficult separation of product and catalyst has hampered their practical application. As a result, heterogeneous catalysts are preferred due to their environmental friendliness, high selectivity, ease of recovery and reutilization, and adaptability to a variety of media [19-20]. The perennial challenge for researchers working on hydrogenation of glucose is to design a stable catalyst with high activity and selectivity. As such, the objective of this short review is to highlight the catalytic hydrogenation of glucose to sorbitol using Ru-based catalysts, as well as the reaction mechanism involved, given that Ru-based catalysts have been shown to have a high catalytic activity.

3. RECENT DEVELOPMENT OF RU-BASED CATALYST FOR HYDROGENATION OF GLUCOSE

3.1 Catalytic Activity of Ru-based Catalyst

Raney Ni catalysts are extensively used for sorbitol production; however, they present drawbacks such as Ni leaching and activity loss [21]. As an alternative to Ni-based catalysts, noble metals such as Ir, Rh, Pd, and Ru have been investigated as active phases in heterogeneous catalysts in the hydrogenation of glucose [22]. Ru demonstrated the highest catalytic activity and stability of all proposed active phases, resolving the issue of active phase leaching [23-24]. Ru metal is more expensive than Ni since it is a noble metal; consequently, Ru has been coated over several solid supports to minimise the final cost of the catalyst. Numerous studies have previously been conducted on Ru on activated carbon (AC) [25], silica [26], titanium dioxide (TiO_2) [27], NiO-modified TiO_2 [28], zeolites [29], and ordered mesoporous silica, MCM-41 [30], and MCM-48 [31].

Mishra et al. [28] investigated the effect of catalytic activity over HY zeolite supported Ru nanoparticles catalysts. Even after 10 hours of reaction time, no conversion of D-glucose was recorded as shown in Table 2, demonstrating Ru is the active metal centre in D-glucose hydrogenation. Ru/HYZ gave the highest D-glucose conversion compared to Ru/NiO-TiO_2 and Ru/TiO_2 with 19.4, 18.3 and 17.1%, respectively. When the response time was prolonged to 2 hours, the D-glucose conversion and sorbitol selectivity increased significantly. However, the reading started to decrease when 1.2 g of catalyst was used due to the increasing of by-product, D-mannitol formation. This demonstrated that 1.0 g of catalyst was adequate to achieve the maximum product selectivity (98.7%) and complete D-glucose conversion.

The catalytic activity of alumina silica-supported Ru materials depends on several factors including Ru oxidation state and synergistic effect between approximate Ru region and acid regions. Ru/TiO_2 with a metal loading around 1 wt.% was reported previously, showing high selectivity to sorbitol production around 93 %, at 120 ºC, 5.5 MPa H_2 and 120 min [32]. They observed a significant increase of the selectivity to sorbitol up to 97 %, after the modification of TiO_2 by impregnation nickel chloride and the following calcination (Ru/NiO-TiO_2, 1 wt % Ru). Zhu and his co-workers investigated on the ruthenium catalyst supported with a sulfonic acid functionalized silica (Ru/SiO_2–SO_3H) and Ru/SiO_2 for hydrogenolysis of cellulose into sorbitol and found that when using only sulfonic acid functionalized silica, a glucose yield of 56.6% was achieved, but sorbitol was not seen due to the lack of hydrogenation sites [26]. Meanwhile, the Ru/SiO_2 catalyst converted 36.2% of cellulose, but no sorbitol was produced. The bifunctional Ru/SiO_2–SO_3H catalyst revealed superior catalytic activity, converting 90.5% cellulose to sorbitol, and yielding 61.2% sorbitol. They specifically indicated a strong synergistic interaction between approximate Ru region and acid region in the conversion of cellulose to sorbitol.

An earlier study on hydrogenation of D-glucose using a Ru nanoparticles supported amine functionalized nanoporous polymer (AFPS) catalyst found that increasing Ru content in Ru/AFPS catalysts enhanced the formation of desired D-sorbitol, and 5Ru/AFPS catalyst (5 wt% of Ru) showed higher conversion and high D-sorbitol selectivity (98%) [33]. In comparison to non-functionalized polymer supported Ru catalyst (5Ru/PS), the catalyst 5Ru/AFPS exhibited higher catalyst performance. D-glucose isomerization is favoured by low Ru, resulting in more D-fructose while higher Ru catalysts promote D-glucose hydrogenation to produce D-sorbitol. Increased Ru content improved D-sorbitol selectivity, leading to a higher yield.

ZSM-5 zeolites with an adequate acidity and shape selectivity are frequently used as supports in hydrogenation processes [29]. They discovered that Ru/ZSM-5-TF (Ru species in ZSM-5 catalysts prepared via the latter approach) demonstrated significantly higher activity and selectivity than Ru/ZSM-5-MS (commercial microporous ZSM-5 zeolites with Si/Al = 38) and Ru/ZSM-5-AT (alkali-treated ZSM5 samples) (Si/Al = 38), with over 99% of D-glucose conversion and selectivity for D-sorbitol. The high performance of the catalyst can be described in term of bifunctional catalysis because of the presence of both acidic (support) and basic (metal) sites on the surface.

MCM-48 possessed an ordered cubic structure based on a narrow tridimensional pore and was used as one of the reaction's support materials [31]. Romero and his co-workers observed that the catalytic activity of Ru/MCM-48 remained constant and the yield of sorbitol was 90% after three cycles of hydrogenation reaction. The optimal temperature range for this reaction was 80-120 °C, as they noticed that when the reaction temperature exceeded 120 °C, the sorbitol yield decreased due to thermal degradation of D-glucose and isomerization of sorbitol into mannitol. Additionally, they conducted a comparative study with the Ru/MCM-41 catalyst [30] and proved that Ru/MCM-48 exhibited the highest stability, which they attributed to the pore structure difference between the two catalysts, as MCM-48 has a cubic pore structure, whereas MCM-41 has a hexagonal array of unidirectional pores, which can result in additional diffusional limitations or pore blockage.

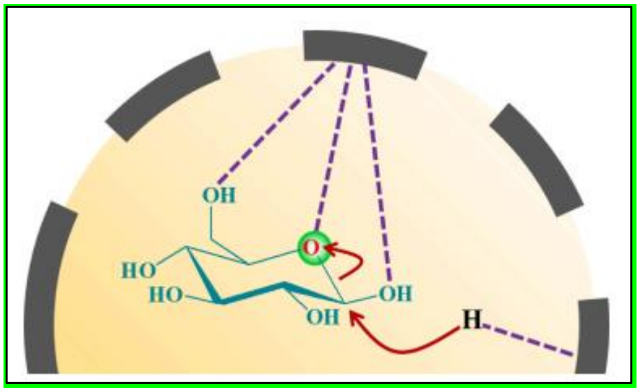
The effect of carbonized cassava dregs (CCD) supported on Ru catalysts on the conversion of D-glucose into D-sorbitol has been investigated and they discovered that as the carbonization temperature increased from 300 to 450 °C, the D-glucose conversion increased from 41.5 to 99.7% [25]. The same trend has been followed by the D-sorbitol yield where it showed an increment from 36.8% to 98.6%. Both glucose conversion and sorbitol yield decreased significantly when carbonization temperatures reached 500 °C, indicating a high carbon content in the carbonized cassava dregs, which may have resulted in a reduction in Ru metal binding sites. Other than that, Ru/AC catalyst also demonstrated excellent catalytic performance, with 100% glucose conversion and a sorbitol yield of 96.5%, suggested that the hydrogenation reaction occurred rapidly at a moderate temperature of 120 °C in the presence of Ru metal. In a comparison study with Pt/CCD, they noticed that lower sorbitol yield (93.3%) was recorded even though the glucose was completely converted, showing that Ru exhibited higher catalytic performance compared to Pt for this reaction.

Recently, a study done by Musci et al. [24] on the activity and selectivity of Ru catalysts supported on various materials, including gamma alumina (A), zirconia (Z), zirconia-alumina (Z-A), phosphate zirconia (ZP) and phosphate zirconia-alumina (ZP-A). The catalytic activity of these catalysts ranged in ascending order of glucose conversion: Ru/ZP < Ru/A < Ru/Z < Ru/Z-A < Ru/ZP-A. The size of the metallic particles and the properties of the support appear to play major roles in boosting the activity of the catalysts. Based on transmission electron microscopy (TEM) results, Ru/Z-A catalyst contained smaller Ru particles with 1.42 nm compared to Ru/ZP-A catalyst with 3.08 nm. According to Ruppert et al. [34], Ru particles smaller than 1 nm would be trapped in the support pores, decreasing their availability for the reaction. Thus, the literature reports corroborated their observations and proved that the most active catalyst was Ru/ZP-A which gave 97% of sorbitol selectivity with less amount of mannitol by-product.

3.2 Reaction Mechanisms

Nowadays, practically all sorbitol manufacturing procedures are based on the hydrogenation of glucose using metallic catalysts. Currently, this industrial process is dominated by the use of Raney Ni [4]. However, the technique is frequently ineffective and may contribute to environmental pollution as a result of Ni-Al alloy leaching. Amorphous alloys, which are thermodynamically non-equilibrium metastable materials having a long-range disordered but short-range ordered structure, have garnered increasing interest from academia and industry owing to its excellent catalytic properties when compared to their crystalline counterparts [35].

Yang et al. [36] recently synthesised a hollow Ni-P nanospheres (NSs) catalyst and tested the performance of the catalyst on sugars hydrogenation reaction. They reported that hollow Ni-P amorphous alloy NSs demonstrated much higher catalytic performance to the commercial Raney Ni catalyst during liquid-phase hydrogenation of sugars to sugar alcohols, indicating a greater potential for practical applications. The high catalytic activity indicated that the hollow Ni materials with a nano porous chamber structure had several advantages, including ease of experimental handling and high accessibility for reactants in liquid-phase reactions, increased Ni active sites, and the presence of a more electron-rich inner surface, all of which are necessary for the development of highly efficient catalysts for certain processes. A model that illustrates the adsorption and hydrogenation of glucose on the inner surface of Ni-P-H can be depicted in Scheme 2. It is therefore expected that more electron-rich Ni active sites on the inner surface of Ni-P-H will be able to efficiently remove proton from glucose. However, the greater electron density on Ni active sites may stimulate the production of H species, which could enhance glucose hydrogenation performance.



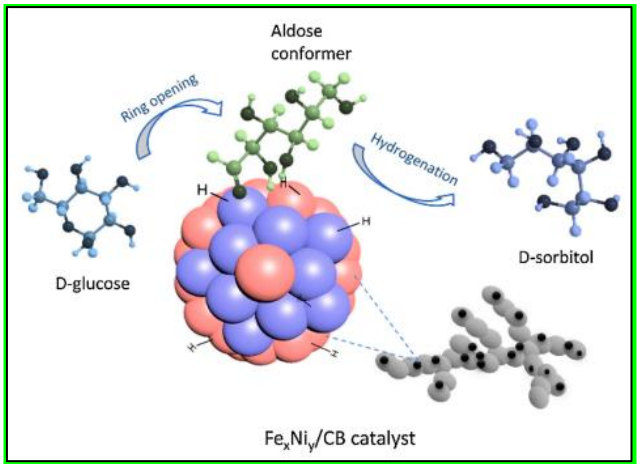
Scheme 2: Graphical illustration of the reaction mechanism between adsorbed glucose and hydrogen on Ni-P-H amorphous alloy catalyst [36].

A study on carbon black supported Ni (Ni/CB), Fe (Fe/CB) and Fe-Ni (FeNi/CB) alloy catalyst for glucose hydrogenation has been investigated by Fu et al. [37] and they found that Fe and Ni favour separate reaction routes while Fe-Ni alloy catalysts exhibited synergistic effects. The conversion of glucose and sorbitol yield were significantly increased when Fe and Ni formed an alloy. The catalytic conversion of glucose to sorbitol in the aqueous phase is schematically visualized in Scheme 3. The polarisation of

Table 2: Hydrogenation performance of glucose over different reaction conditions.

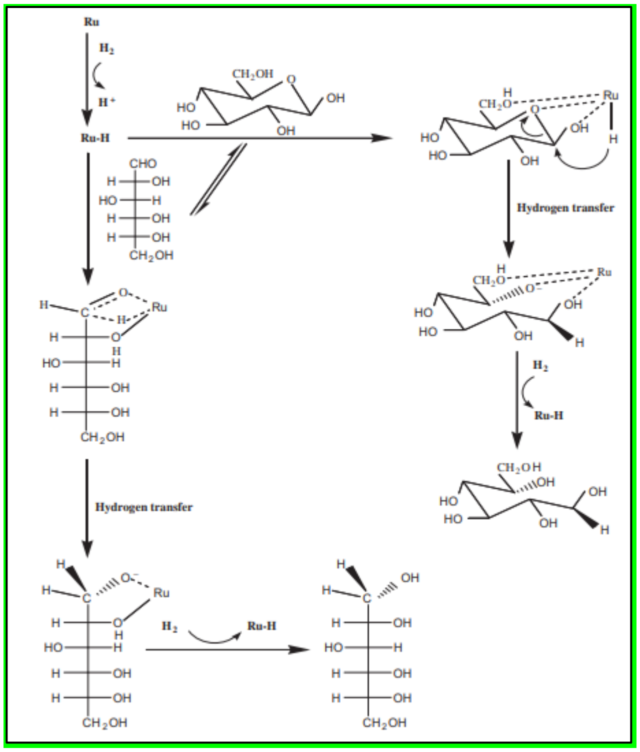
Catalyst	**Temperature (°C)**	**Time (h)**	**Catalyst amount (g)**	**Percentage of solution and catalyst (%)**	**Pressure (MPa)**	**Glucose Conversion (%)**	**Product selectivity (%)**				**Ref.**
							D-Sorbitol (SB)	**D-Mannitol (MN)**	**D-Fructose (FR)**	**Others**	
HYZ	120	0.3	-	D-glucose = 40 g	5	-	-	-	-	-	[28]
Ru/HYZ	120	0.3	1.0	D-glucose = 40 g Ru = 1	5	19.4	97.6	-	-	-	[28]
Ru/HYZ	120	2	1.0	D-glucose = 40 g Ru = 1	5	100	98.7	0.7	-	Non identified products = 0.6	[28]
Ru/HYZ	120	2	1.2	D-glucose = 40 g Ru = 1	5	100	98.5	1.0	-	Non identified products = 0.5	[28]
Ru/NiO-TiO_2	120	0.3	1.0	D-glucose = 40 g Ru = 1	5	18.3	96	-	-	-	[28]
Ru/AFPS	100	1	0.1	D-glucose = 11.10 mmol Ru = 1	5.5	15	94	3	2	Non identified products = 1	[33]
Ru/AFPS	100	1	0.1	D-glucose = 11.10 mmol Ru = 2	5.5	31	96	2	1	Non identified products = 1	[33]
Ru/AFPS	100	1	0.1	D-glucose = 11.10 mmol Ru = 3	5.5	50	98	1.0	0.5	Non identified products = 0.5	[33]
Ru/AFPS	100	1	0.1	D-glucose = 11.10 mmol Ru = 5	5.5	69	98	1.5	-	Non identified products = 0.5	[33]
Ru/ZSM-5-TF	120	2	0.5	D-glucose = 50 g Ru = 1	4	99.6	99.2	-	-	-	[29]
Ru-MCM-41	120	2	-	D-glucose = 10 Ru = 3.98	3	100	83.13	-	-	-	[30]
Ru-MCM-48	120	0.4	-	D-glucose = 7.35 g/dm^3 Ru = 4.04	2.5	89.56	89.56	-	-	-	[31]
Ru/TiO_2	120	0.3	-	D-glucose = 7.35 g/dm^3 Ru = 3.98	2.5	91.39	91.39	-	-	-	[31]
Ru/C	120	0.2	-	D-glucose = 7.35 g/dm^3 Ru = 5	2.5	94.75	94.75	-	-	-	[31]
Ru/AC	120	1.5	1.0	D-glucose = 10 Ru = 5	3	100	96.5	-	-	-	[25]
Ru/CCD	120	1.5	1.0	D-glucose = 10 Ru = 5	3	99.7	98.6	-	-	-	[25]
Pt/CCD	120	1.5	1.0	D-glucose = 10 Ru = 5	3	100	93.3	-	-	-	[25]
Ru/A	90	7	25	D-glucose = 0.9 g Ru= 3	1.25	33	100	-	-	-	[24]
Ru/Z	90	7	25	D-glucose = 0.9 g Ru= 3	1.25	42	99	-	-	-	[24]

the C=O bond then facilitates the nucleophilic addition of hydrides (H adatoms) on the metal surface, resulting in the formation of sorbitol. They concluded the Ni-based catalyst was deactivated due to particle development, surface oxidation, and leaching, whereas the Fe-Ni alloy catalyst demonstrated obvious stability advantages over the monometallic Ni catalyst.



Scheme 3: Fe_xNi_y alloy catalysts supported on carbon black for aqueous-phase hydrogenation of glucose to sorbitol [37].

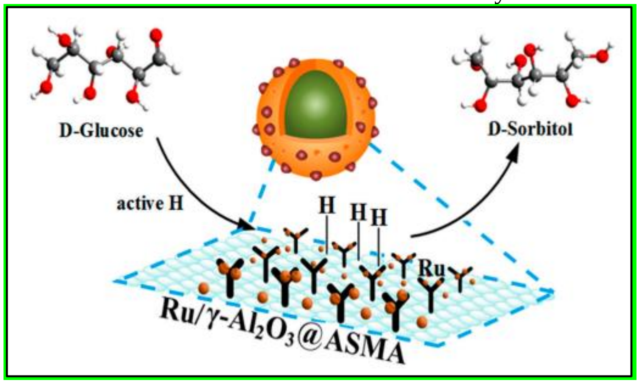
These Ni-based catalysts demonstrated strong catalytic activity despite their high H_2 pressure need and lower selectivity for D-sorbitol. Additionally, the need for special care while handling Raney Ni, the leaching of Ni, and the ease with which catalysts can be deactivated are significant difficulties with Ni-based catalysts. Among the metal catalysts investigated, it was discovered that supported Ru catalysts were more active and selective than Raney Ni catalyst. Ru-based catalysts functioned at a lower H_2 pressure, exhibited no leaching, less sensitive to deactivation, and are recyclable [38]. Zhang et al. [30] described the molecular process for the conversion of glucose to sorbitol utilising Ru/MCM-41 as a catalyst. On the basis of Scheme 4, it has been presumed that H_2 absorbs and activates on the active sites of the catalysts before reacting with the glucose carbonyl group. As a consequence of the irreversible reaction between glucose and activated hydrogen (H^+) on the catalyst surface, sorbitol is produced as the final liquid phase product. The hydrogenation of glucose on a Ru/MCM-41 catalyst is a multistep process that begins with hydrogen dissolution and diffusion in the reaction media, followed by its absorption on the catalyst surface, activation, and lastly interaction with the carbonyl group on glucose to form sorbitol [39].



Scheme 4: Mechanism of glucose hydrogenation over Ru/MCM41 [30].

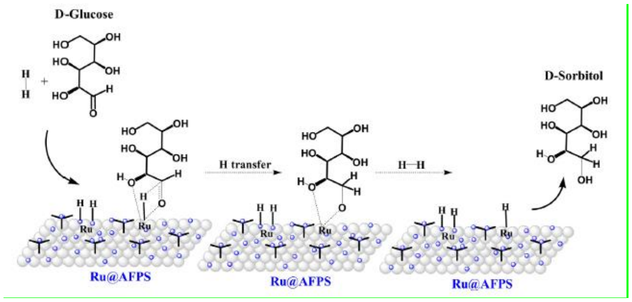
Zhao et al. [2] reported that a core-shell-like sphere ruthenium catalyst, identified as 5%Ru/γ-Al_2O_3@ASMA, has been successfully synthesized through impregnating the ruthenium nanoparticles (NPs) on the surface of the amino poly (styrene-co-maleic) polymer (ASMA) encapsulating γ-Al_2O_3 pellet support. The 5%Ru/γ-Al_2O_3@ASMA is effective for glucose hydrogenation and exhibited a consistent sorbitol yield of over 90% in both batch and trickle bed reactors, showing the potential practicality of the core-shell-like catalyst for efficient sorbitol production. H_2 was first adsorbed on the uniformly scattered Ru catalytic sites to create the active hydrogen species during the hydrogenation process. As soon as the active hydrogen combines with glucose molecules, it attacks the carbonyl groups of the reactant, and the target sorbitol can be produced and desorbed into the mixed solution as shown in Scheme 5. Since the exterior -OH and -NH_2 on the ASMA shell form strong hydrogen bonds, as opposed to the pure van de Waals force between Ru NPs and the γ-Al_2O_3 pellet, it is possible to bind the Ru NPs to the support much more strongly. The strong interaction between Ru NPs and ASMA encapsulating γ-Al_2O_3 would further enhance the catalyst's recyclability.

As discussed in earlier section, the hydrogenation of D-glucose to D-sorbitol was shown to be highly efficient using Ru/AFPS catalysts [33]. The catalyst containing 5%wt Ru (5Ru/AFPS) demonstrated high D-glucose conversion and selectivity (98%). The hydrogenation of D-glucose to D-sorbitol using a Ru catalyst supported by AFPS is a three-phase catalytic reaction (gas–liquid–solid). It has been demonstrated that Ru placed on mesoporous polymeric supports can adsorb more H_2 than the metal itself via hydrogen spillover. According to this approach, the



Scheme 5: The hydrogenation route from glucose to sorbitol using 5%Ru/γ-Al_2O_3@ASMA pellet as catalyst [2].

progression of D-glucose hydrogenation can be explained by H_2 diffusion, the production of activated hydrogen (H-Ru), and the reaction of D-glucose with active hydrogen on the catalyst surface. The proposed process for D-glucose hydrogenation employing a Ru/AFPS catalyst is detailed in Scheme 5. Hydrogen is transmitted from air to liquid and then dissolved at the gas–liquid interface during the hydrogenation of D-glucose to D-sorbitol. The dissolved hydrogen in the liquid phase then spills over onto the catalyst surface, where it is activated by the catalyst's active metal (Ru) centres. D-carbonyl glucose's group combines with activated H and Ru to form a cyclic transition structure. The hydrogen transfer then occurs, and the addition of H_2 results in the formation of active H and the product D-sorbitol. D-sorbitol diffuses into the liquid phase after desorbing from the catalyst. The freshly formed active hydrogen can then be used to convert another molecule of D-glucose, and the hydrogenation cycle can continue. The results indicated that a catalyst nano porous structure with a diverse range of pores, a high specific surface area, and the presence of functional groups on the surface played a critical role in improving the catalyst's performance.



Scheme 6: The reaction mechanism proposed for D-glucose hydrogenation to D-sorbitol using a 5Ru/AFPS catalyst [33].

3.3 Catalyst Deactivation

Although the hydrogenation of D-glucose to D-sorbitol appears straightforward, in practise, D-glucose is converted not only to a single product, d-sorbitol, but also to a variety of different by-products, as illustrated in Scheme 1. Some of the by-products are generated via non-catalytic pathways. The commercial manufacture of sorbitol is facilitated by the stability of the catalyst used in the glucose hydrogenation process. Sintering and catalyst poisoning are two drawbacks that should be prevented. Apart from that, metal leaching must be minimised, as it clogs active sites and limits the use of sorbitol in food and medicine. Table 3 summarised the previous studies on the reusability of different heterogenous catalysts for hydrogenation of glucose.

Guo et al. [29] efficiently reused Ru/ZSM-5-TF for glucose hydrogenation for five trials under the same reaction conditions (4% catalyst ratio, 4 MPa H_2, 2 h, 220 °C). They observed that the catalyst recorded high glucose conversion and sorbitol selectivity in all cycles. The reaction liquid remained colourless after filtration and almost no Ru leaching was detected by ICP. No aggregation of Ru nanoparticles was observed using TEM images. They claimed that the reduction of glucose conversion from 99.7 to 88.2% after the fifth run could be a result of the regeneration method used, but the spent catalyst showed no obvious loss of the catalytic activity after being washed with water, ethanol, or acetone for three times each. Thus, deactivation could be induced by an accumulation of organic and inorganic species adsorbed on the surface of the catalyst.

The sufficient stability of supported Ru catalysts was also demonstrated by Mishra et al. [28] for hydrogenation of glucose over Ru/HYZ catalyst. They reported that within four cycles, the glucose conversion rate dropped from 100 to 94%, and the sorbitol selectivity dropped from 98 to 94%. As a result, the catalyst is capable of being reused up to four times without losing its activity. According to the TEM images shown in Figure 3, both fresh and spent catalysts exhibited no perceptible morphological changes following four runs. The high catalyst stability revealed the strong interaction between the active Ru species and the HY zeolite support.

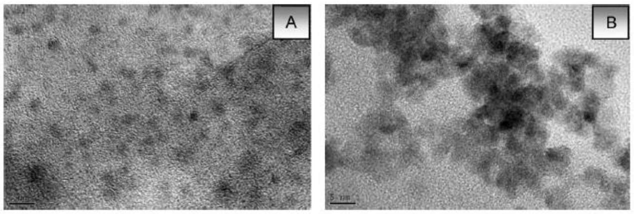


Figure 2: TEM images of (A) fresh catalyst and (B) spent catalyst after four runs [28].

Dabbawala et al. [33] conducted another reusability study on glucose hydrogenation using Ru/AFPS under optimised conditions and found that only 2% glucose conversion was reduced (from 68 to 66%) after fifth cycles. Due to the absence of Ru leaching into the reaction mixture, the catalyst is reusable for up to five cycles under the reaction conditions used. Some additional peaks were detected in the FTIR spectra of used catalysts which could be attributed to the adsorption of substrate or/and product molecules. The TEM images revealed no changes in the morphology of the catalyst. A small amount of Ru nanoparticle aggregation was identified, which may account for the slight decrease in catalyst performance observed with spent catalysts. The observation established that the catalyst is sufficiently stable during the reaction due to the strong interaction between Ru metal and AFPS support, which is encouraging for sugar-to-sugar alcohol conversion.

Table 3: Reusability studies using various catalysts for glucose hydrogenation.

Catalyst	Number of Cycles	Conversion of glucose (%)	Ref.
Ru/HYZ	4	100-94	[28]
Ru/ZSM-5-TF	5	99.7-89.2	[29]
Ru/AFPS	5	68-66	[33]

4. CONCLUSION AND FUTURE PERSPECTIVE

The hydrogenation of glucose into sorbitol over Ru-based catalysts was reviewed. Briefly, different catalytic performances were obtained depending on the catalysts used, and the data proved that more than 80% sorbitol yield was achieved when Ru-based catalysts were used in this reaction. It was shown that the catalyst-to-glucose ratio or metal loading factor had a substantial effect on hydrogenation performance in relation to reaction time and temperature. Increases in reaction time and temperature significantly improved glucose conversion. The sorbitol yield or selectivity may be reduced because of glucose or sorbitol degradation. Also, the supported Ru catalyst demonstrated a little reduction in sugar conversion across many reuse cycles. Thus, supported Ru catalysts were proved to be the most efficient reusability for glucose hydrogenation to sorbitol.

Numerous studies have been conducted into the use of heterogeneous catalytic hydrogenation to produce sorbitol from monosaccharides such as glucose, and highlighted its advantages, including its flexibility, high efficiency, and environmental friendliness. However, significant goals have yet to be met. For instance, synthesising a catalyst with environmentally friendly, non-toxic, high stability, and selectivity towards a target product. Additionally, more cost-effective sorbitol synthesis under low to moderate operating parameters (time, temperature, pressure, and amount of catalyst) is a challenge that must be overcome. Other than that, in order to obtain a high-purity product, the separation of sorbitol from residual glucose or other by-products formed should be resolved.

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