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HYDROLYSIS OF CELLULOSE TO GLUCOSE CATALYZED BY NOBLE METAL PALLADIUM (Pd) SUPPORTED ON SILICA-ALUMINA

(Hidrolisis Selulosa kepada Glukosa Bermangkin Logam Adi Paladium (Pd) Disokong pada Silika-Alumina)

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Abstract

Cellulose, a promising source of renewable energy, is currently receiving a lot of interest due to its potential application in the production of bioenergy. The catalytic conversion of cellulose into value-added compounds like glucose, which is subsequently fermented into bioethanol or dehydrated into platform chemicals, avoids the heavy reliance on fossil fuel economy tremendously. In this study, the catalytic conversion of cellulose to glucose was conducted using a supported noble metal catalyst. The wet impregnation method was used to synthesize 4 wt.% palladium (Pd) supported on silica-alumina (SiO_2-AlO_3), which was then calcined at 500 °C. Prior to reaction work, Fourier- transform infrared spectroscopy, thermogravimetric analysis, Brunauer-Emmett-Teller method, and particle size analysis were conducted to characterize the catalyst. To investigate the effect of the catalyst on the yield of glucose from cellulose, the catalyst loading was varied from 0.04 to 0.10 g. The results demonstrated that up to 23.6% yield of glucose was produced at 200 °C for 3 h with the catalyst and cellulose loading of 0.06 g and 0.3 g, respectively. Additionally, under these conditions, cellulose conversion was at its highest (78.7%). This study shows that the supported noble metal catalyst has the potential to enhance the hydrolysis step for the conversion of cellulose to glucose.

Keywords: glucose, heterogenous catalyst, hydrolysis of cellulose, palladium supported on silica-alumina, supported noble metal catalyst

Abstrak

Selulosa, sumber tenaga berpontesi yang boleh diperbaharui, kini menerima banyak perhatian kerana potensi aplikasinya dalam penghasilan biotenaga. Penukaran pemangkin selulosa kepada sebatian tambah nilai seperti glukosa, yang kemudiannya ditapai menjadi bioetanol atau dehidrasi menjadi bahan kimia platform, dapat membantu mengurangkan kebergantungan ekonomi kepada bahan api fosil. Di dalam kajian penyelidikan ini, penukaran pemangkin selulosa kepada glukosa telah dijalankan menggunakan mangkin logam adi yang disokong. Kaedah impregnasi basah digunakan untuk mensintesis 4 wt.% paladium (Pd) yang disokong pada silika-alumina (SiO_2-AlO_3), yang kemudiannya dikalsinasikan pada 500 °C. Sebelum memulakan kerja tindak balas, spektroskopi inframerah transformasi Fourier, analisis termogravimetri, kaedah Brunauer-Emmett-Teller, dan analisis saiz zarah

telah dijalankan untuk faktor pencirian mangkin. Untuk menyiasat kesan mangkin ke atas hasil glukosa daripada selulosa, pemuatan mangkin, berubah daripada 0.04-0.1g. Keputusan menunjukkan bahawa sehingga 23.6% glukosa dapat dihasilkan pada 200 °C selama 3 jam dengan mangkin dan pemuatan selulosa masing-masing, 0.06 g dan 0.3 g. Di samping itu, dalam keadaan ini ternyata penukaran selulosa berada pada tahap tertinggi, 78.7%. Kajian ini menunjukkan bahawa mangkin logam adi yang disokong berpotensi untuk meningkatkan langkah hidrolisis untuk penukaran selulosa kepada glukosa.

Kata kunci: glukosa, mangkin heterogen, selulosa hidrolisis, paladium disokong pada silika-alumina, mangkin logam adi disokong

Introduction

The increasing carbon footprint, greenhouse gas emissions, environmental pollution, and ecosystem imbalance are the main issues around the world today. These issues demonstrate the impending necessity for renewable energy. Biomass, or organic material derived from plants and animals, is a viable alternative for non-renewable resources as a feedstock for fuels. Biomass typically contains cellulose, lignin, and hemicellulose that can be converted into high-value chemicals and biofuels.

Cellulose, the most abundant biomass on earth, has been studied widely since its discovery in the 19th century. It is a promising source of renewable energy, and currently, it is gaining a lot of attention due to its potential use in bioenergy production [1]. However, due to high crystallinity, cellulose faces several difficulties that prohibit its extensive utilization in the production of economically competitive biofuels. According to Li et al. [2], cellulose is less susceptible to enzymatic hydrolysis, less accessible, and less reactive at a higher degree of crystallinity. Hence, it is crucial to resolve the structure of cellulose for decomposition purposes to produce platform chemicals.

Glucose, which is a cellulose monomer unit, can be a promising starting compound to produce various value-added chemicals, such as levulinic acid (LA). The production of LA from glucose requires glucose to go through several processes, including rehydration and dehydration. Up to 56.8% of LA could be produced from glucose using a solid acid catalyst at 100 °C for 6 h [3]. Many high-value-added chemicals can be synthesized from LA, such as ethyl levulinate, succinic acid, and maleic anhydride. Ethyl levulinate acts as an oxygenated additive in fuels and is one of the examples of high-value organic chemicals produced from the esterification of LA with ethanol [4,5]. Meanwhile, succinic acid and maleic anhydride are well known to be useful in the food and textile industries, respectively.

Palladium (Pd), platinum (Pt), rhenium (Re), and gold (Au) are examples of noble metals with outstanding resistance to oxidation even at high temperatures. These metals have excellent catalytic properties and are widely employed, especially in the process of hydrogenation. Pt and Pd are well known for their efficiency in the hydrogenation of carbon-carbon multiple bonds (e.g., olefinic bonds, acetylenic triple bonds, and nitro compounds) compared to other metals, such as ruthenium [6]. Increasing the amount of Pt or Pd leads to an increase in the catalytic activity for the hydrogenation process.

Pt and Pd are known for their high cost and limited availability. Hence, the internal pores of silica (SiO_2) and alumina (Al_2O_3) support can be incorporated with tiny spheres of Pt or Pd rather than using the metals in their pure form as most of their atoms are wasted as only the surface of the atoms is involved in reactions [7]. Through the incorporation on the support, almost all expensive metal atoms are available on the particle surface where they can contribute to reactions, and none are wasted.

Heterogeneous catalysts, particularly metal catalysts (i.e., noble metal) incorporated on the support, are often employed in the conversion of cellulose to sugar alcohol via hydrogenation, in which high selectivity or yield of sugar alcohols can be achieved. Sorbitol with a selectivity of 69% was produced when the reaction was catalyzed by 1.5 wt.% Pt/SBA15 (fumed silica) [8]. Meanwhile, more than 40% of sugar alcohols (i.e., hexitols, ethylene glycol, 1,2-propanediol, and glycerol) were produced when 4 wt.% Pd/CNT (carbon nanotube)

was used as a catalyst [9]. Although supported noble metal catalysts are frequently used to produce sugar alcohols from cellulose via hydrogenation, the conversion of glucose from cellulose via hydrolysis must be considered as well. According to Kobayashi et al. [10], the hydrolysis of cellulose is the rate-determining step, and the noble metal catalysts enhance both the hydrolysis and hydrogenation steps. Once glucose is produced, the conversion of cellulose to sugar alcohols would be simpler. This concept is similar to that used to produce LA from cellulose. In this case, whether LA is produced in high yield depends on the production of glucose from cellulose. A recent study by Kamal et al. [11] discovered that by employing noble metal (i.e., Pd) supported on silica-alumina (SiO_2-Al_2O_3), up to 43.3% of LA was produced with cellulose conversion up to 73.9%. This shows that highly crystalline cellulose can be hydrolyzed to yield glucose, which can then be easier converted to other products, including 5-hydroxymethylfurfural (HMF), LA, and formic acid (FA) because the process only requires dehydration and rehydration. However, it is worth noting that studies on the use of noble metals incorporated into the support for the hydrolysis of cellulose are still lacking, although studies on the decomposition of cellulose to glucose using other heterogeneous catalysts have been widely established [12,13].

For example, in the study by Boonyakarn et al. [12], up to 11% of glucose was produced from cellulose, which eventually contributed to 8% yield of LA when 0.0025 M of chromium chloride ($CrCl_3$) catalyst was employed for 5 min at 220 °C. If the reaction period is prolonged, it is anticipated that the yield of LA will be higher than 8%. Joshi et al. [13] found that employing 2 wt.% of zirconium dioxide (ZrO_2) catalyst in the system produced up to more than 5% of glucose, contributing to the highest production of LA, which is above 80%. Hence, this research focused on the study of the effect of catalyst loading on the production of glucose from cellulose using noble metal (i.e., Pd) supported on SiO_2-Al_2O_3. As a result, the most suitable catalyst loading for the conversion of highly crystalline cellulose to glucose could be determined.

Materials and Methods

Materials

The catalyst was synthesized using palladium (II) nitrate ($Pd(NO_3)_2$) with 40% w/w of Pd and SiO_2-Al_2O_3 grade 135 (100%) purchased from Sigma Aldrich. Microcrystalline cellulose (extra pure, 100%) from Acros Organics served as the experimental work's substrate. As for standard reference calibration purposes, glucose (>99.9%), HMF (>98%), LA (>98%), FA (>98%), and furfural (>99.9%) were employed. All the chemicals were of analytical grade and used without further purification (unless otherwise stated), and distilled water was used for all the experiments.

Catalyst Preparation

First, 5 g of 4 wt.% Pd/SiO_2-Al_2O_3 catalyst was prepared using the wet impregnation method following the steps described in an earlier study [11]. The catalyst support, SiO_2-Al_2O_3, was weighed for approximately 4.8 g and spread on a petri dish before diluted palladium nitrate ($Pd(NO_3)_4$) was dropped onto the support using a syringe. A spatula was used to press $Pd(NO_3)_4$ until it was thoroughly mixed with SiO_2-Al_2O_3. Prior to calcination, the prepared catalyst was dried in an oven at 110 °C for 12 h to eliminate excess moisture. The catalyst was subsequently calcined for 5 h at 500 °C. The catalyst was kept in a parafilm-sealed vial and stored in a desiccator prior to analysis and experimental work.

Catalyst characterization

The prepared catalyst was characterized by Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) method, and particle size analysis. The TGA of the prepared catalyst was performed on a Mettler Toledo STARe software. The analysis was carried out from room temperature (30 °C) to 550 °C by employing a heating rate of 10 °C/min under the flow of 20 mL/min of high-purity air. The FTIR spectrum range was recorded from 4000 to 400 cm^{-1} on a Nicolet iS10 spectrometer with a spectral resolution of 8 cm^{-1} at room temperature and an accumulation of five scans in an open-beam air background. The surface area and pore volume of the prepared catalyst were determined by the BET method using a Micromeritics 3Flex surface characteristics analyzer, where the catalyst was

degassed at 150 °C for 12 h in nitrogen (N_2) prior to analysis. A Malvern Mastersizer 3000 particle size analyzer was used to conduct the particle size analysis.

Experimental procedure

The pre-reduction of the catalyst and the experimental work for the catalytic conversion of cellulose to glucose were carried out in a 20 mL stainless steel semi-batch reactor. For the pre-reduction of the catalyst, the catalyst and distilled water were loaded accordingly into the reactor. One bar of hydrogen (H_2) was inserted into the reactor. The timer and stirrer were set for 1 h and 1300 rpm, respectively, once the desired temperature of 150 °C was achieved. After 1 h, 0.3 g of cellulose was loaded into the reactor. The air inside the reactor was purged using N_2 three times. The stirrer (1100 rpm) and timer (30 min) were set accordingly once the reaction temperature reached 200 °C. The reaction was stopped by quenching the reactor into a water bath. The samples were collected, stored in a parafilm-sealed vial, and kept in a refrigerator prior to analysis. The experimental work was repeated for 60, 120, and 180 min.

A set of data, including the weight of the filter paper before drying and the weight of the filter paper with solid residue after drying overnight, was recorded to determine the conversion of cellulose to glucose. The samples were filtered using filter paper before being dried at 60 °C overnight. The weight of the filter paper containing solid residue was recorded, and it was consistently maintained around ± 0.005 g. The final weight of cellulose and the cellulose conversion were calculated using Equations 1 and 2, respectively.

$$\text{Weight}_{\text{final cellulose (solid residue)}}\,(a) = \text{Weight}_{\text{filter paper with solid residue after drying}} - \text{Weight}_{\text{filter paper before drying}} - \text{Weight}_{\text{catalyst}} \quad (1)$$

$$\text{Cellulose conversion}\,(\%) = [(a - \text{Weight}_{\text{initial cellulose}}) / \text{Weight}_{\text{initial cellulose}}] \times 100\% \quad (2)$$

Product analysis

Glucose was quantified using a high-performance liquid chromatography system consisting of Sugar SH1011 column (SHODEX, Japan) with ion exclusion mode (column's physical size: 8.0 mm I.D. × 300 mm) and a refractive index detector as the column and detector, respectively. The mobile phase was an aqueous solution of sulfuric acid (0.05 M) flowing at a rate of 0.5 mL/min with a column temperature of 40 °C.

Results and Discussion

Catalyst characterization: TGA

Thermogravimetric analysis of the catalyst was carried out before and after calcination to validate the decomposition of nitrate precursors in the catalyst. Based on the differential thermal gravimetric analysis (TGA/DTG) pattern in Figure 1, two weight losses were observed between the temperature of 50 and 120 °C and also 200 and 300 °C for the catalyst before calcination. The first weight loss (I) can be linked to the removal of absorbed water [14,15], whereas the second weight loss (II) can be attributed to the decomposition of nitrates and the elimination of organic compounds [16]. Furthermore, at temperatures above 350 °C, no weight loss was observed, implying that no decomposition took place. Therefore, the calcination temperature was set at 500 °C to ensure the decomposition of nitrate precursors. After calcination, the catalyst only exhibited one weight loss, which occurred between 50 and 100 °C (I), according to the TGA/DTG pattern in Figure 1. However, no weight loss was recorded at temperatures higher than 100 °C, demonstrating that nitrate had completely decomposed. Hence, the optimal calcination temperature for ensuring a precursor-free catalyst is 500 °C. This finding agrees with the FTIR analysis, where no nitrate peak was found in the catalyst after calcination.

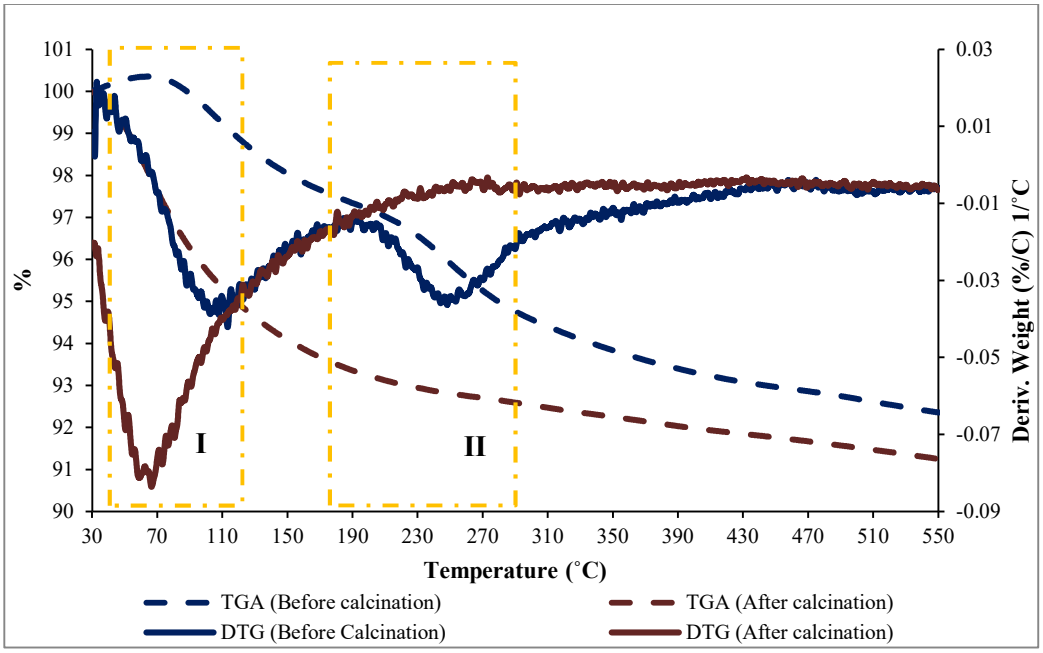

Figure 1. TGA and DTG of Pd/SiO_2-Al_2O_3 (before and after calcination)

Catalyst characterization: FTIR

The decomposition of the nitrate precursor in the synthesized catalyst was verified by FTIR. A comparison of the FTIR spectra of the catalyst before and after calcination is illustrated in Figure 2, and the functional groups present in this study are summarized in Table 1.

Table 1. Summary of the functional groups present in this study

Region	Wavelength (cm^{-1})	Peak Assignment
I	3600–3200	O-H stretching, strong, broad
II	2400–2300	C-O stretching
III	1700–1600	O-H bending
IV	1450–1300	NO_3^- (nitrate)
V	1200–1000	Si-O-Si

Based on Figure 2, the spectral range around 3600–3200 cm^{-1} (I) and 1700–1600 cm^{-1} (III) is attributed to the stretching and bending modes corresponding to water molecules by hydrogen bonding, respectively [17]. The C-O stretching band is due to the atmospheric carbon dioxide, an impurity where contamination occurred, which appeared in the spectral range of 2400-2300 cm^{-1} (II).

The spectral range around 1450–1300 cm^{-1} (IV) indicates the presence of nitrate precursor (NO_3^-) in the catalyst before calcination [18,19]. The NO_3^- bands disappeared from the catalyst after calcination, confirming the successful decomposition of nitrate under the calcination temperature of 500 °C. Hence, the optimum calcination temperature to remove nitrate precursor is 500 °C. In addition, the band assigned to Si-O-Si was observed in the spectral range of 1200–1000 cm^{-1} (V) [20]. This band proves the existence of the SiO_2 network in the catalyst.

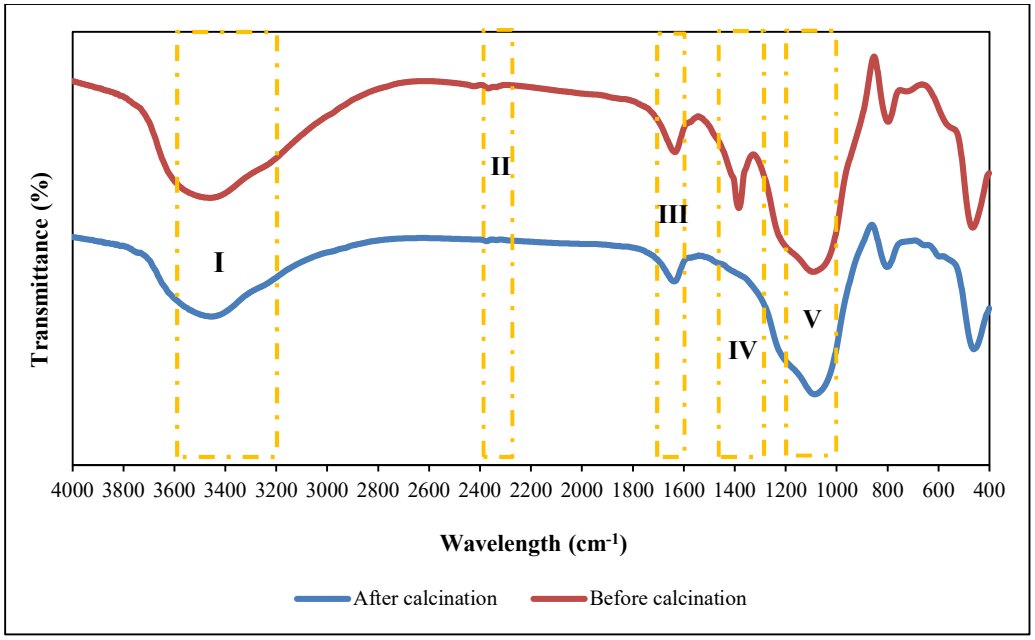

Figure 2. FTIR spectra of Pd/SiO_2-Al_2O_3 (before and after calcination)

Catalyst characterization: Surface area, pore volume, and particle size

Information on the surface area, pore size distribution, and particle size of the catalyst is essential, especially for catalytic reaction work. The BET surface area, pore volume, and particle size of the catalysts are presented in Table 2.

Table 2. BET surface area, pore volume, and particle size of the catalyst

Sample	Surface Area[a] (m^2/g)	Pore Volume[b] (cm^3/g)	Particle Size[c] (µm)
Pd/SiO_2-Al_2O_3 (before calcination)	501.9	0.2552	93.7
Pd/SiO_2-Al_2O_3 (after calcination)	485.6	0.2459	98.0

[a]: Surface area was obtained from the BET method
[b]: Pore volume was obtained from the BET method
[c]: Particle size was determined using a Malvern Mastersizer 3000 particle size analyzer

Based on Table 2, the surface area and pore volume of the catalyst decreased after the catalyst was calcined. The surface area and pore volume decreased after calcination by up to 16.2 m^2/g and 0.0093 cm^3/g, respectively. The decrease in surface area and pore volume is possibly due to the aggregation of the catalyst [21]. Even though calcination reduces the BET surface area and pore volume, it has the potential to secure the existence of a stable structure of the catalyst [22]. In addition, the catalyst has a higher surface area and pore volume than Wang et al. (329 m^2/g) [23], which are 485.6 m^2/g and 0.2459 cm^3/g, respectively.

The influence of surface area can be explained by the concept of collision theory, where the bigger the surface area, the greater the chances of the particle being exposed to each other [24]. Meanwhile, the information on pore size distribution is crucial for the catalyst's active sites [25]. According to Klinghoffer et al. [26], both properties greatly influence the catalytic activity and the reaction rate, whether they promote the reaction to be faster or otherwise.

Based on Table 2, the particle size of the catalyst increased as the surface area and the pore volume of the catalyst decreased after calcination. When the particle size of a catalyst is reduced, the surface area increases, and the shape changes, resulting in a larger number of reactive edge sites. This might be due to calcination, which results in increased crystallinity of the catalyst [27,17].

Effect of catalyst loading on the yield of glucose and conversion of cellulose

Figure 3 illustrates the effect of catalyst loading on the yield of glucose and cellulose conversion. Based on Figure 3, the highest conversion of cellulose and yield of glucose was 78.7% and 23.6%, respectively, when 0.06 g of catalyst was employed in the reaction. As catalyst loading increased from 0.04 to 0.06 g, the yield of glucose increased continuously increase. However, a further increase in catalyst loading from 0.08 to 0.10 g resulted in a decrease in the glucose yield and cellulose conversion. This finding was also observed in the study by Yan et al. [28]. This might be due to an unwanted side reaction from higher catalyst loading. Additionally, higher catalyst loading could make the reaction mixture more viscous, resulting in a slower reaction [29]. Therefore, the effect of mixing decreases and the mass transfer resistance in the mixture increases. Consequently, less cellulose is available for the reaction. Thus, no additional catalyst should be added when the amount of the catalyst has met the requirement of the reaction.

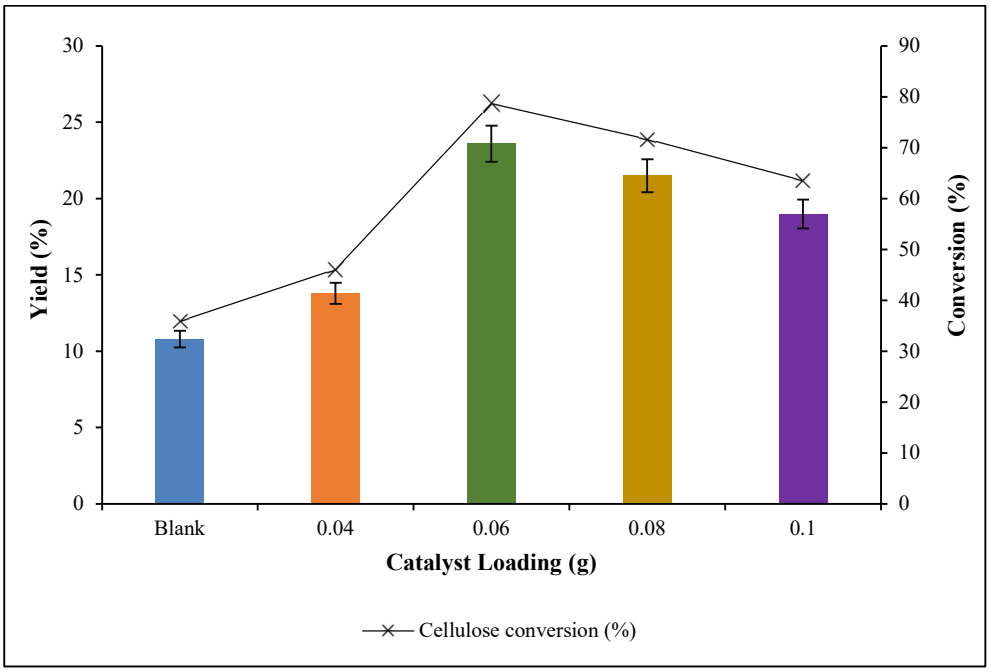

Figure 3. Effect of catalyst loading on the yield of glucose and cellulose conversion at 3 h. Note: a) Pre-reduction of catalyst conditions: 10 mL of distilled water, agitation speed of 1300 rpm, and 1 bar of H_2 for 1 h at 150 °C, b) reaction conditions: 0.3 g of cellulose, reaction temperature of 200 °C, agitation speed of 1100 rpm, and reaction time of 3 h

Besides, a reaction without the catalyst (blank) was conducted as a reference. Without the catalyst, the yield of glucose and conversion of cellulose were at their lowest levels of 10.8%, and 35.9%, respectively, as shown in Figure 3. This proves that in the presence of a catalyst, cellulose can be converted efficiently, and more glucose can be produced. The catalyst creates a distinct reaction pathway, reducing the activation energies of individual reaction stages and accelerating the process of reaching equilibrium by lowering the activation

energies of various reaction steps [30].

Conclusion

Several findings can be summarized from this study which are the TGA pattern demonstrates that the nitrate precursor in the catalyst can be decomposed at temperatures above 350 °C, the FTIR's diminishing peak at 1450–1300 cm^{-1} for the catalyst after calcination indicates that the nitrate precursor has been successfully removed at a calcination temperature of 500 °C, and the catalyst with higher surface area (485.6 m^2/g) and larger pore volume (0.2459 cm^3/g) contributed to the high yield of glucose and conversion of cellulose up to 23.6% and 78.7%, respectively. This proves that a supported noble metal catalyst with high surface area and large pore volume can provide a faster route in producing glucose from cellulose with high crystallinity.

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