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CATALYTIC CONVERSION OF CELLULOSE TO LEVULINIC ACID USING SUPPORTED NOBLE METAL PALLADIUM CATALYST

(Penukaran Bermangkin dari Selulosa ke Asid Levulinik Menggunakan Mangkin Disokong Logam Adi Paladium)

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Abstract

In resolving the current energy crisis, it is vital to effectively use the abundant biomass to produce platform chemicals, for instance levulinic acid (LA). LA is very flexible for the formation of high value-added chemicals as it belongs to the family of carboxyl and ketone. This valuable platform chemical can be produced from cellulose (the most abundant biomass in nature). Palladium (Pd) as a noble metal was incorporated with catalyst supports (silica-alumina; SiO_2-Al_2O_3 and gamma-alumina; γ-Al_2O_3) by using wet impregnation method, aiming for 4 wt.% of noble metal on supports followed by catalyst calcination at 500 ˚C. The catalyst was characterized using Fourier-transform infrared spectroscopy (FTIR) and Brunauer–Emmett–Teller (BET). The effects of reaction parameters such as agitation speed, reaction temperature, and cellulose loading were investigated using this catalyst in a semi-batch reactor for 8 hours. The highest conversion of cellulose (73.9%) and yield of LA (43.3%) was achieved under these conditions: agitation speed of 1100 rpm, reaction temperature of 200 ˚C, and cellulose loading of 1.5 g with pre-reduction of Pd/SiO_2-Al_2O_3 catalyst (surface area and pore volume up to 485.6 m^2/g and 0.2459 cm^3/g, respectively) at 150 ˚C and agitation speed of 1300 rpm (in 5 bars of hydrogen, H_2 for 1 hour).

Keywords: Pd/SiO_2-Al_2O_3, cellulose, hydrolysis, levulinic acid

Abstrak

Dalam menyelesaikan krisis tenaga semasa, adalah sangat penting untuk menggunakan biojisim yang berkesan dalam menghasilkan bahan kimia platform seperti asid levulinik (LA). LA sangat fleksibel untuk pembentukan bahan kimia bernilai tinggi, kerana ia tergolong dalam keluarga karboksil dan keton. Bahan kimia platform yang berharga ini boleh dihasilkan dari selulosa (biojisim yang paling banyak terdapat di alam semula jadi). Paladium (Pd) sebagai logam adi boleh digabungkan dengan penampung mangkin (silica-alumina; SiO_2-Al_2O_3 and gamma-alumina; γ-Al_2O_3) yang dihasilkan menggunakan kaedah impregnasi basah yang bertujuan untuk 4% logam adi pada penampung mangkin diikuti oleh kalsinasi mangkin pada suhu 500 ˚C. Mangkin dicirikan menggunakan spektroskopi inframerah transformasi Fourier (FTIR) dan *Brunauer–Emmett–Teller* (BET). Kajian mengenai pengaruh parameter reaksi seperti kelajuan pengadukan, suhu tindak balas, dan pemuatan selulosa disiasat menggunakan mangkin ini dalam reaktor semi-kelompok selama 8 jam. Penukaran selulosa tertinggi (73.9%) dan hasil LA (43.3%) dicapai dalam keadaan ini; kelajuan pengadukan 1100 rpm, suhu tindak balas 200 ˚C, dan pemuatan selulosa 1.5 g dengan pra-pengurangan mangkin Pd/SiO$_2$-Al$_2$O$_3$ (luas permukaan dan isi pori 485.6 m^2/g dan 0.2459 cm^3/g, masing masing) pada suhu 150 ˚C dan kelajuan pengadukan 1300 rpm (dalam 5 bar hidrogen, H$_2$ selama 1 jam).

Kata kunci: Pd/SiO$_2$-Al$_2$O$_3$, selulosa, hidrolisis, asid levulinik

Introduction

Cellulose, a part of biomass, is a major component of lignocelluloses as it comprises 40-50% of lignocellulose composition. It is formed by dehydration and condensation of glucose produced from photosynthesis [1]. Starch, which is likewise created by photosynthesis but having a different characteristic than cellulose, can be classified as biomass. Starch, a polymer with α-1→4 glycosidic linkages, is soluble in hot water and is the main constituent of corn, potato, and rice. Even though considerable attention has been given to the production of fuels and chemicals, starch should be prioritized as a dietary source [2].

Furthermore, the amount of cellulose is so enormous that it is wasteful to simply let it decompose without exploring its potential benefits. The commercial feasibility of producing sugar alcohols such as sorbitol and mannitol, which are particularly valuable in the food sector as sweeteners and preservatives, by using hydrogenation method is one way to utilize this enormous resource [3]. When it comes to catalytic cellulose hydrolysis, LA is the main product produced after cellulose undergoes a few processes; 1) hydrolysis 2) dehydration and 3) rehydration [4]. Figure 1 shows the reaction pathway for the production of LA from cellulose.

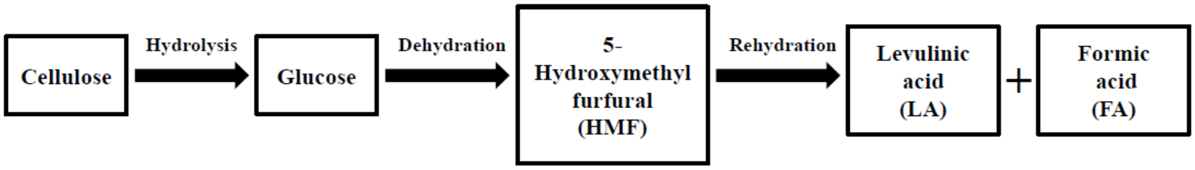

Figure 1. Reaction pathway for the production of LA from cellulose

LA is a water-soluble, organic compound that comes from the family of carboxylic acid and ketone, possessing a wide range of reactivity and functionality [5]. These two functional groups cause LA to be a very versatile building block for a vast chemical transformation of high-value organic chemicals, resin precursors, polymers precursors, and fuel additives with plenty of potential industrial applications [4]. Succinic acid and maleic anhydride are two high value-added chemicals that can be synthesized from LA and are useful in the food and textile industries, respectively. Aside from that, LA can be utilized as a starting material for the production of γ–valerolactone, as well as ethyl and methyl levulinate, making it a potential alternative to petroleum-based fuels or chemicals [6]. Aside from choosing LA as the final product, the reaction can be tuned up to produce various products with high yields, such as 5-hydroxymethylfurfural (HMF) and formic acid (FA).

Over the past decade, homogeneous catalysts have been used in many applications, including LA synthesis (using acids). Despite its efficiency, there are a few drawbacks to use this type of acid in the system, including the generation of additional wastes due to the difficulties of separation and recovery (environmental pollution). Besides that, this catalyst leads to equipment corrosion [7]. As a result, many researchers nowadays prefer to use heterogeneous catalysts in their systems, especially solid catalysts to overcome the issues that arise from the homogenous catalyst. Metal oxides, supported metals (nickel, Ni), H-form zeolites, carbonaceous acids, heteropoly acids, acid resins, magnetic acids, and functionalized silicas are the examples of solid catalysts that have garnered attention as promising and appealing catalysts for the hydrolysis of cellulose [8].

Recently, there has been a noticeable growth towards employing cheap, non-noble metal-based catalysts such as Ni, yet the study on this catalyst's stability and recyclability needs to be emphasized as leaching and sintering can be mainly responsible for the decreasing catalytic activity [9]. Hence, in this research study, Palladium (Pd), a noble metal that can be regenerated and recycled up to 20 times without observing any significant loss of activity [10] was utilized as a catalyst. Even though Pd is relatively expensive when used individually, Pd can be incorporated into high dispersion and narrow sizes distribution of catalyst support such as silica (SiO_2) and alumina (Al_2O_3). Despite the high cost of Pd, it is widely acknowledged for its high chemical stability and catalytic abilities [11].

Therefore, this research was conducted to study the effects of various reaction conditions such as agitation speed, temperature, and substrate loading on the production of LA from cellulose using noble metal, Pd supported on different catalyst supports such as silica-alumina (SiO_2 -Al_2O_3) and gamma-alumina (γ-Al_2O_3). As a result, the most suitable catalyst that was effective in the conversion of cellulose to LA (under the conditions studied) could be determined throughout the experiments.

Materials and Methods

Materials

For the synthesis of catalyst, palladium (II) nitrate ($Pd(NO_3)_2$) with 40% w/w of Pd, SiO_2-Al_2O_3 grade 135 (≤100%), and γ-Al_2O_3 (99.9%) were purchased from Sigma Aldrich and Alfa Aesar, respectively. As for the experimental work, microcrystalline cellulose (extra pure, 100%) from Acros Organics was used as substrates. In addition, glucose (>99.9%), HMF (>98%), LA (>98%), FA (>98%), and furfural (>99.9%) were used for standard reference calibration purposes. All the chemicals were analytical grade without further purification and distilled (DI) water was used for all the experiments.

Catalyst preparation

The solid noble catalyst was prepared using wet impregnation method. This method aimed to provide 5 g of 4 wt.% Pd on SiO_2-Al_2O_3 support. About 4.8 g of SiO_2-Al_2O_3 was weighed and spread on a petri dish. Then, 0.5 g of $Pd(NO_3)_4$ was dissolved in the minimum amount of DI water necessary to wet the SiO_2-Al_2O_3 support; this was found to be 3.3 ml of DI for 4.8 g of SiO_2-Al_2O_3. The diluted $Pd(NO_3)_4$ was dropped to the spread SiO_2-Al_2O_3 carefully using a syringe. The dropping was done in a circular motion where each $Pd(NO_3)_4$ droplet was at different point. After that, the $Pd(NO_3)_4$ was pressed using a spatula to achieve a homogenous mixture between $Pd(NO_3)_4$ and SiO_2-Al_2O_3. The prepared catalyst was dried using an oven at 110 ˚C for 12 hours to remove the excess moisture prior to calcination. The catalyst was then calcined at 500 ˚C for 5 hours. The catalyst was stored in a vial sealed with parafilm, and stored in desiccator prior to analysis and experimental work. The method was repeated to prepare 4 wt.% Pd on γ-Al_2O_3 support.

Catalyst characterization

The Fourier-transform infrared spectroscopy (FTIR) analysis was conducted with a Nicolet iS10 FTIR with a spectral resolution of 8 cm^{-1} at room temperature and accumulation of 5 scans in an open beam air background [12]. The spectrum ranged from 4000 cm^{-1} to 400 cm^{-1}. The Brunauer–Emmett–Teller (BET) method was used to determine the surface area and pore volume using Micromeritics 3Flex where the catalyst was degassed at 150 ˚C for 12 hours in N_2 prior to analysis.

Experimental procedure

The pre-reduction of catalyst and the experimental work for the catalytic conversion of cellulose to LA were carried out in a 100 ml stainless steel semi-batch reactor. The pre-reduction of catalyst was conducted with 5 bar of hydrogen gas (H_2). The desired temperature (130 ˚C and 150 ˚C) and agitation speed (600 rpm and 1300 rpm) were set according to the parameters studied for 1 hour. As for the reaction work, after the pre-reduction of catalyst, cellulose was loaded into the reactor containing catalyst and distilled water. The air inside the reactor was purged out using N_2

about three times. Once the desired temperature (170 ˚C and 200 ˚C) had been achieved, the stirring speed (1300 rpm) and timer were set accordingly. The reaction took place for 8 hrs. The samples were collected at the time interval of 0 min, 30 min, 60 min, 120 min, 180 min, and 480 min by opening the valve of the sample port. After releasing the gas inside the reactor, to stop the reaction, the reactor was quenched into a beaker with cold water.

The remaining solid product was collected and filtered using filter paper before drying in the oven at 100 ˚C overnight. The weight was recorded regularly until a constant weight of ±0.005 g was achieved. This data was essential for the calculation of cellulose conversion to products. The final weight of cellulose and cellulose conversion was calculated using Equations 1 and 2, respectively.

The weight of the cellulose could only be obtained at the end of the experiment because the reactor used was a semi-batch reactor. Thus, the remaining solid product could not be collected during the reaction process.

Product analysis

The liquid products were filtered to remove any impurities and analyzed using a High-Performance Liquid Chromatography (HPLC) system: Sugar SH1011 (SHODEX, Japan) with ion exclusion mode (column's physical size: 8.0 mm I.D X 300 mm) and UV as column and detector, respectively. An aqueous solution of sulphuric acid (0.05 M) at a flow rate of 1 ml/min was used as mobile phase and the column temperature was set at 40 ˚C [8].

$$\text{Weight}_{\text{final cellulose}}\ (a) = \text{Weight}_{\text{solid product after drying}} - \text{Weight}_{\text{filter paper}} - \text{Weight}_{\text{catalyst}} \tag{1}$$

$$\text{Cellulose conversion (\%)} = \frac{a - \text{Weight}_{\text{initial cellulose}}}{\text{Weight}_{\text{initial cellulose}}} \times 100\% \tag{2}$$

Results and Discussion

Catalyst characterization (FTIR)

The validation of the decomposition of precursor (nitrate) in the synthesized catalyst after calcination at 500˚C was verified by FTIR analysis. A FTIR spectrum comparison between catalysts before and after calcination was conducted, and the findings are presented in Figures 2 and 3. Table 1 shows the summary of the functional group present in this study.

Based on Figures 2 and 3, a similar trend of FTIR spectrum was obtained for each of the catalysts. The spectral range of 3600-3200 cm^{-1} and 1700-1600cm^{-1} were assigned to the stretching and bending modes of absorbed water molecules through hydrogen bonding, respectively [13,14]. The presence of C-O stretching band at the spectral range of 2400-2300 cm^{-1} represented atmospheric carbon dioxide (CO_2), an impurity and sign that contamination might have occurred [15,14].

The FTIR spectrum around 1450-1300 cm^{-1} proved the presence of nitrate precursor (NO_3^-) in the catalyst (before calcination) [16,17]. The diminishing intensity of the catalyst's peak after calcination implied that the decomposition of nitrate was successful at the calcination temperature of 500 ˚C [14]. As a result, it can be concluded that calcination temperature of 500 ˚C is effective in removing nitrate precursor. On the other hand, an extra peak was discovered from the FTIR spectra analysis for Pd/SiO_2-Al_2O_3 (Figure 2) at the range of 1200-1000 cm^{-1}, showing the presence of Si-O-Si [18,19].

Table 1. Summary of the functional group 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 (for Pd/SiO_2-Al_2O_3)	Si-O-Si

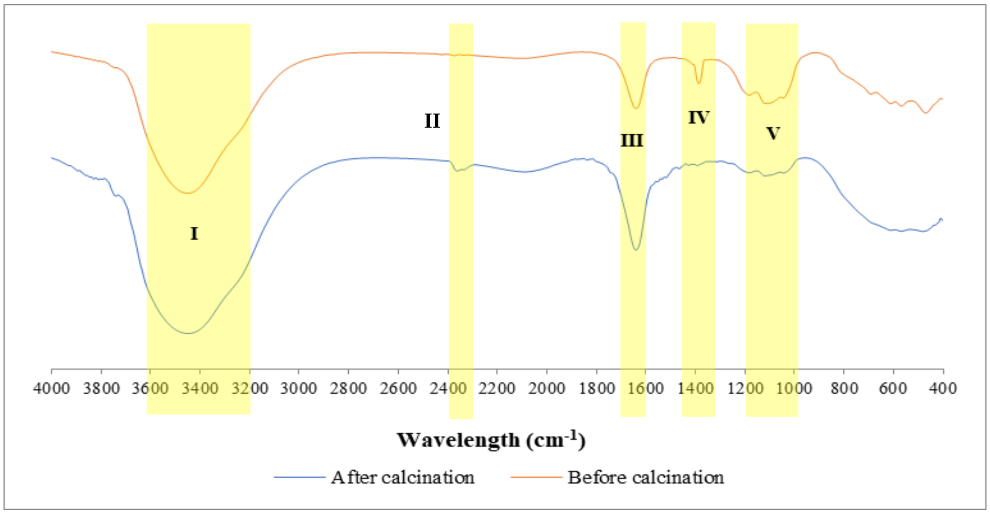

Figure 2. FTIR spectra before and after calcination for catalyst Pd/SiO_2-Al_2O_3

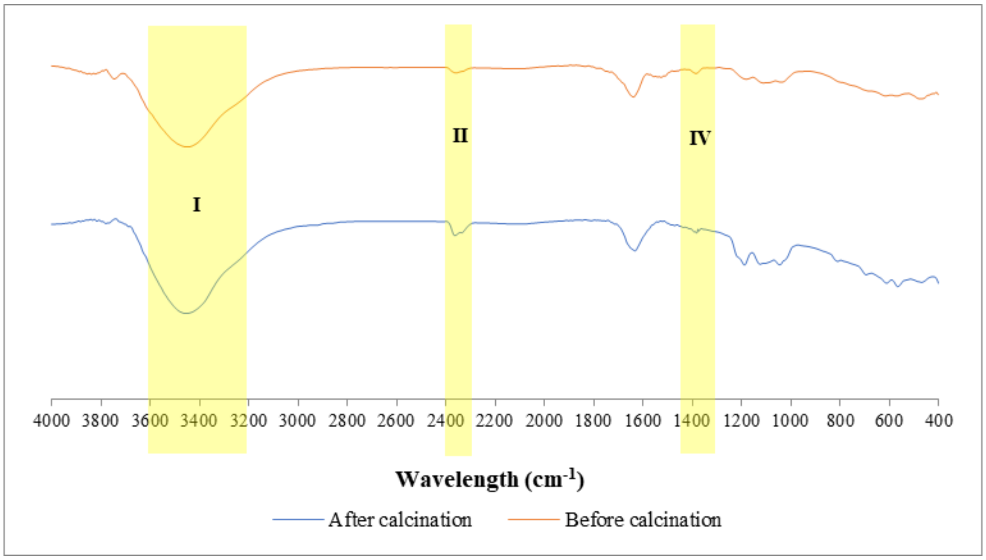

Figure 3. FTIR spectra before and after calcination for catalyst Pd/γ-Al_2O_3

Catalyst characterization (BET)

In heterogeneous catalysts, specific area and pore volume are significant factors to consider especially for the supported catalyst. The BET surface area and pore volume of raw supports and catalysts are listed in Table 2.

Based on Table 2, an increasing trend of surface area and pore volume was observed from raw SiO_2-Al_2O_3 to catalyst Pd/SiO_2-Al_2O_3 (after calcination). The surface area increased from 217.6 m^2/g to 485.6 m^2/g and the pore volume increased from 0.1068 cm^3/g to 0.2459 cm^3/g, which could be explained by the elimination of organic matters where many new pores were formed during the calcination [20]. However, for catalyst Pd/γ-Al_2O_3, the trend of the result was converse from that of the Pd/SiO_2-Al_2O_3 (after calcination) as the surface area and pore volume decreased from raw γ-Al_2O_3 to Pd/γ-Al_2O_3 possibly due to aggregation of catalyst, resulting in losing the surface area and decreasing the pore volume [21].

Catalyst Pd/SiO_2-Al_2O_3 possessed a high pore volume (0.2459 cm^3/g) and surface area (485.6 m^2/g) compared to catalyst Pd/γ-Al_2O_3 (pore volume and surface area of 0.0296 cm^3/g and 79.4 m^2/g, respectively) (Table 2). This could be due to the combination of materials such silica (SiO_2) and alumina (Al_2O_3) that significantly increased the porosity and surface area [22]. Moreover, this observation could be related to the findings according to Table 2 where the pore volume and surface area of the combined materials (SiO_2-Al_2O_3) were two times larger than raw γ-Al_2O_3.

Table 2. BET surface area, pore volume and particle size of raw supports and catalysts

Sample	**Surface Area**^{a} **(m^2/g)**	**Pore Volume**^{b} **(cm^3/g)**
SiO_2-Al_2O_3	217.6	0.1068
Pd/SiO_2-Al_2O_3 (After calcined)	485.6	0.2459
γ-Al_2O_3	101.3	0.0504
Pd/γ-Al_2O_3 (After calcined)	79.4	0.0296

[a]: Surface area is obtained from BET method,
[b]: Pore volume is obtained from BET method

Effects of agitation speed during pre-reduction of catalyst and reaction work

Based on Figure 4, at higher agitation speed, an increasing trend in the yield of LA was observed for both of the catalysts. This increasing trend of yield was also seen for HMF and FA, except for glucose possibly because glucose was converted to other products (HMF, LA, and FA). LA produced from cellulose was at the highest (33.5%) when the reaction agitation speed was at 1100 rpm with pre-reduction of Pd/SiO_2-Al_2O_3 catalyst at 1300 rpm. Up to 20.6% of cellulose was successfully converted to products. This high conversion of cellulose and production of LA might be due to the high agitation speed during the reaction; increasing the agitation speed increases the contact area and relative velocity between the two phases, and hence diminishes any external diffusion limitations [23]. Furthermore, the higher surface area and pore volume of Pd/SiO_2-Al_2O_3 catalyst (485.6 m^2/g and 0.2459 cm^3/g, respectively) caused the high conversion of cellulose and yield of LA as these properties led to the high availability of catalytic activity sites [24]. Thus, high catalytic activity could occur during the reaction compared to the usage of Pd/γ-Al_2O_3 catalyst, which possessed a smaller surface area and pore volume of 79.4 m^2/g and 0.0296 cm^3/g, respectively. Owing to these properties, an increment of only 6.4% of LA yield was observed for catalyst Pd/γ-Al_2O_3 when an increase of reaction speed from 200 rpm to 1100 rpm was employed, with 12.2% of cellulose being converted to products.

Even though the usage of high agitation speed during the pre-reduction catalyst (activation) is not as crucial as high temperature [25], increasing agitation speed during the pre-reduction of catalyst might improve the performance of the catalyst by increasing the surface contact of the catalyst with H_2 which can activate the catalyst prior to the reaction [26]. The pre-reduction for both of the catalysts was aimed to reduce palladium oxide to metallic Pd. As a result, it can be concluded that the reaction agitation speed of 1100 rpm with the catalyst pre-reduction agitation speed at 1300 rpm was the most ideal condition in this study for further experimentation.

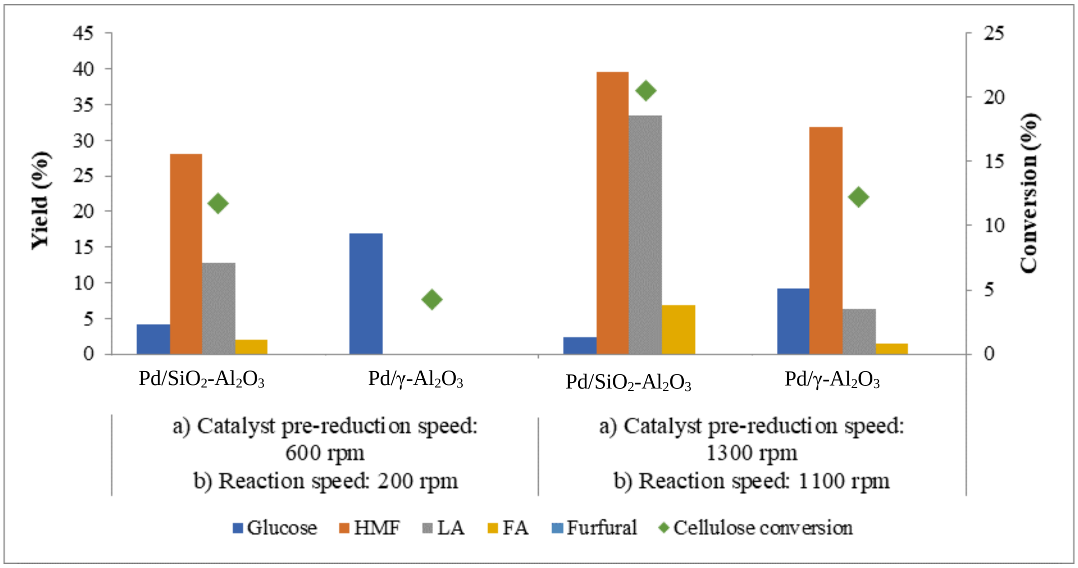

Figure 4. Effects of agitation speed on the conversion of cellulose to LA at 8 hours. Note: a) Catalyst pre-reduction condition: 0.5 g of catalyst, and 5 bar of H_2 at 130 ˚C for 1 hour; b) Reaction condition: 4 g of cellulose, 0.5 g of catalyst, reaction temperature of 170 ˚C, and reaction time of 8 hours.

Effects of temperature during pre-reduction of catalyst and reaction work

Temperature plays a significant role in the production of LA from cellulose, particularly at higher temperatures as demonstrated in a previous study [27]. The effects of temperature on the production of LA from cellulose at different cellulose loading is shown in Figure 5.

Based on Figure 5, a significant increment in the conversion of cellulose and production of LA was observed when the reaction temperature increased from 170 ˚C to 200 ˚C with catalyst pre-reduction at 150 ˚C. Except for glucose, the production of intermediate products and by-products such as HMF and FA, respectively also increased as the reaction temperature rose. According to this study, as the temperature increased (from 170 ˚C to 200 ˚C), the cellulose conversion increased gradually from 20.6% to 73.9% when Pd/SiO_2-Al_2O_3 catalyst (pre-reduction of catalyst at the temperature of 150 ˚C) was employed in the system where the highest LA was produced (up to 43.3%) possibly since the higher reaction temperature accelerated the rate of chemical reaction and provided a faster route for the cellulose to convert to products [8]. Furthermore, a higher reaction temperature promotes greater contact between cellulose and water molecules, resulting in a complete process of cellulose bond breaking to form LA [28]. A similar trend of results was observed with Pd/SiO_2-Al_2O_3 catalyst when

$Pd/\gamma\text{-}Al_2O_3$ catalyst was employed in the system; the conversion of cellulose and yield of LA increased as the reaction temperature increased. However, the conversion of cellulose and yield of LA were lower using $Pd/\gamma\text{-}Al_2O_3$ catalyst in the system compared to $Pd/SiO_2\text{-}Al_2O_3$ catalyst. The conversion of cellulose and yield of LA were only up to 37.1% and 9.5%, respectively.

Moreover, one of the parameters that improved the catalyst efficiency was increasing the temperature from 130 ˚C to 150 ˚C during the pre-reduction of the catalyst. It is advised to heat the catalyst at a high temperature during the catalyst pre-reduction for the metal to finely disperse on the support. Under these high temperatures during heating the catalyst, the mobility of the catalyst can be enhanced, increasing the active site of the catalyst, and thus greatly influencing the catalytic activity [25].

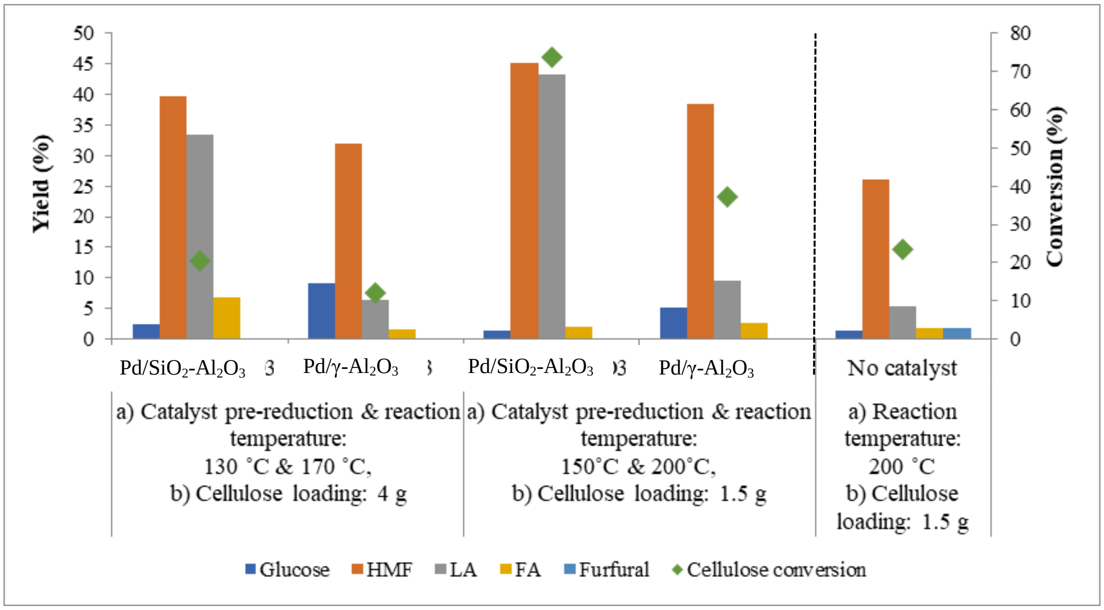

Figure 5. Effects of temperature on the conversion of cellulose towards LA at 8 hours. Note: a) Catalyst pre-reduction condition: 0.5 g of catalyst, agitation speed of 1300 rpm, and 5 bar of H_2 for 1 hour; b) Reaction condition: 0.5 g of catalyst, agitation speed of 1100 rpm, and reaction time of 8 hours

Effects of substrate loading

Based on Figure 5, the yield of LA increased gradually for all the catalysts ($Pd/SiO_2\text{-}Al_2O_3$ and $Pd/\gamma\text{-}Al_2O_3$) when 1.5 g of cellulose was used in the reaction (under high-temperature conditions). Increasing the substrates loading might lead to the increasing cellulose availability for the conversion, with a high concentration of LA being produced; however, the yield of LA was shown to eventually decrease as the cellulose loading increased. This might be due to the reactivity diminution or insufficient catalyst dosage for the additional cellulose [4].

Moreover, a blank experiment (without catalyst) was conducted for reference purposes. It was conducted under the ideal condition highlighted in this study. LA produced was at its lowest (5.3%) compared to the other reactions that used catalyst. This might be due to the side reaction that occurred during the reaction where it resulted in the production of furfural [29]. According to Figure 5, it can be highlighted that the production of HMF was more favorable if no catalyst was employed in the system.

Figure 6 shows the reaction profile of reaction using Pd/SiO_2-Al_2O_3 under the high condition in cellulose depolymerization, leading to the formation of LA. According to Figure 6, the yield of all products (HMF, LA, and FA) increased overtime except for glucose. An increasing yield of glucose was reported until 2 hours of reaction, then the yield subsequently decreased. This might be due to the glucose already being used up in converting to other products. Since the hydrolysis of cellulose to glucose was the rate-determining step, once glucose was formed, it was much easier to break down the glucose bond to other products. Hence, it resulted in the formation of HMF (5.73%), LA (17.4%), and FA (0.77%) at the 30 min of reaction time. As a result, 73.9% of cellulose was converted to products, and 43.4% of LA yield was produced at the end of the reaction.

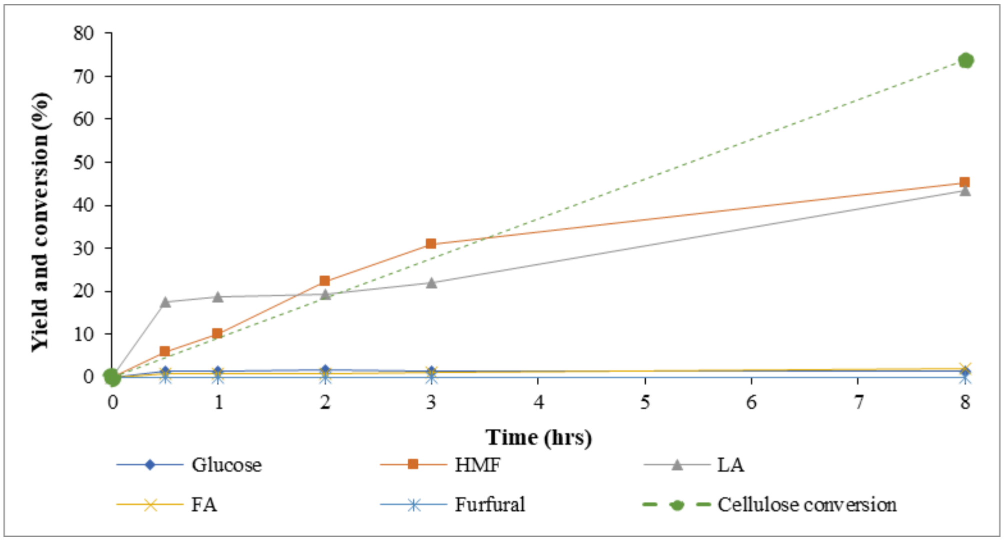

Figure 6. Reaction profile for catalyst Pd/SiO_2-Al_2O_3. Note: Reaction condition: 1.5 g of cellulose, 0.5 g of catalyst (pre-reduction at an agitation speed of 1300 rpm in H_2 at 150˚C for 1 hour), reaction temperature of 200 ˚C, agitation speed of 1100 rpm, and reaction time of 8 hours.

Conclusion

From this research, it can be concluded that the conversion of cellulose to LA is highly influenced by the reaction parameters: agitation speed (1100 rpm), temperature (200 ˚C), and substrate loading (1.5 g) with catalyst pre-reduction at the temperature of 150 ˚C and stirred at 1300 rpm for 1 hour. It was observed that under these conditions, the LA produced was at the highest which was 43.3% and the conversion of cellulose was up to 73.9%. Moreover, the higher surface area (485.6 m^2/g) and pore volume (0.2459 cm^3/g) of Pd/SiO_2-Al_2O_3 catalyst showed better performance to produce LA from cellulose compared to Pd/γ-Al_2O_3.

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References

1. Caretto, A. and Perosa, A. (2013). Upgrading of levulinic acid with dimethylcarbonate as solvent/ reagent. *Sustainable Chemistry & Engineering*, 1(8): 6-11.
2. Dhepe, P. L. and Fukuoka, A. (2007). Cracking of cellulose over supported metal catalysts. *Catalysis Surveys from Asia*, 11(4): 186-191.
3. Shrotri, A., Kobayashi, H. and Fukuoka, A. (2018). Cellulose depolymerization over heterogeneous catalysts. *Accounts of Chemical Research*, 51(3): 761-768.
4. Peng, L., Lin, L., Zhang, J., Zhuang, J., Zhang, B. and Gong, Y. (2010). Catalytic conversion of cellulose to levulinic acid by metal chlorides. *Molecules*, 15: 5258-5272.
5. Signoretto, M., Taghavi, S., Ghedini, E. and Menegazzo, F. (2019). Catalytic production of levulinic acid (LA) from actual biomass. *Molecules (Basel, Switzerland)*, 24(15): 1-20.
6. Jeong, H., Jang, S., Hong, C. and Kim, S. (2016). Levulinic acid production by two-step acid-catalyzed treatment of *Quercus mongolica* using dilute sulfuric acid. *Bioresource Technology*, 225: 1-28.
7. Thunyaratchatanon, C., Sinsakullert, W., Luengnaruemitchai, A. and Faungnawakij, K. (2019). 5-hydroxymethylfurfural production from hexose sugars using adjustable acid- and base-functionalized mesoporous SBA-15 catalysts in aqueous media. *Biomass Conversion and Biorefinery*, 2019: 1-15.
8. Li, G., Liu, W., Ye, C., Li, X. and Si, C. L. (2018). Chemocatalytic conversion of cellulose into key platform chemicals. *International Journal of Polymer Science*, 2018: 1-20.
9. Li, X., Zhang, L., Wang, S. and Wu, Y. (2020). Recent advances in aqueous-phase catalytic conversions of biomass platform chemicals over heterogeneous catalysts. *Frontiers in Chemistry*, 7(948): 1-21.
10. Xu, S., Yan, X., Bu, Q. and Xia, H. (2017). Catalytic conversion of cellulose into polyols using carbon-nanotube-supported monometallic Pd and bimetallic Pd–Fe catalysts. *Cellulose*, 24(6): 2403-2413.
11. Yoshimura, A., Tochigi, S. and Matsuno, Y. (2021). Fundamental study of palladium recycling using “dry aqua regia” considering the recovery from spent auto-catalyst. *Journal of Sustainable Metallurgy*, 7(1): 266-276.
12. Kamal, P. N. S. M. M., Mohamad, N. I., Serit, M. E. A., Rahim, N. S. A., Jimat, N. I. and Alikasturi, A. S. (2020). Study on the effect of reaction and calcination temperature towards glucose hydrolysis using solid acid catalyst. *Materials Today: Proceedings*, 31(8)**:** 282-286.
13. Benkhaled, M., Morin, S., Pichon, C., Thomazeau, C., Verdon, C. and Uzio, D. (2006). Synthesis of highly dispersed palladium alumina supported particles: Influence of the particle surface density on physico-chemical properties. *Applied Catalysis A: General*, 312(1–2): 1-11.
14. Yabushita, M., Kobayashi, H., Hara, K. and Fukuoka, A. (2014). Quantitative evaluation of ball-milling effects on the hydrolysis of cellulose catalysed by activated carbon. *Catalysis Science and Technology*, 4(8): 2312-2317.
15. Anderson, I. E., Shircliff, R. A., MacAuley, C., Smith, D. K., Lee, B. G., Agarwal, S., Stradins, P. and Collins, R. T. (2012). Silanization of low-temperature-plasma synthesized silicon quantum dots for production of a tunable, stable, colloidal solution. *Journal of Physical Chemistry C*, 116(6): 3979-3987.
16. Zhang, H., Huang, H., Ji, Y., Qiao, Z., Zhao, C. and He, J. (2010). Preparation, characterization, and application of magnetic Fe-SBA-15 mesoporous silica molecular sieves. *Journal of Automated Methods and Management in Chemistry*, 2010(1463–9246): 323509.

17. Amadine, O., Essamlali, Y., Fihri, A., Larzek, M. and Zahouily, M. (2017b). Effect of calcination temperature on the structure and catalytic performance of copper-ceria mixed oxide catalysts in phenol hydroxylation. *RSC Advances*, 7(21): 12586-12597.
18. Yadav, M. K., Kothari, A. V. and Naik, D. G. (2009). Morphological silica-supported acid catalyst for esterification of aliphatic fatty acid. *Green Chemistry Letters and Reviews*, 2(3):181-197.
19. Shah, K. A., Parikh, J. K., Dholakiya, B. Z. and Maheria, K. C. (2014). Fatty acid methyl ester production from acid oil using silica sulfuric acid: Process optimization and reaction kinetics. *Chemical Papers*, 68(4): 472-483.
20. Amadine, O., Essamlali, Y., Fihri, A., Larzek, M. and Zahouily, M. (2017a). Effect of calcination temperature on the structure and catalytic performance of copper-ceria mixed oxide catalyst in phenol hydroxylation. *RSC Advances*, 7:12586-12597.
21. Inmanee, T., Pinthong, P. and Jongsomjit, B. (2017). Effect of calcination temperatures and mo modification on nanocrystalline (γ-χ)-Al_2O_3 catalysts for catalytic ethanol dehydration. *Journal of Nanomaterials*, 2017(2011): 1-9.
22. Rahmati, M., Huang, B., Mortensen, M. K., Keyvanloo, K., Fletcher, T. H., Woodfield, B. F., Hecker, W. C. and Argyle, M. D. (2018). Effect of different alumina supports on performance of cobalt Fischer-Tropsch catalysts. *Journal of Catalysis*, 359: 92-100.
23. Ahlkvist, J. (2013). Formic and levulinic acid from cellulose via heterogeneous catalysis. Doctoral dissertation, Umeå Universitet.
24. Klinghoffer, N. B., Castaldi, M. J., Nzihou, A. (2012). Catalyst properties and catalytic performance of char from biomass gasification. *Industrial and Engineering Chemistry Research*, 51(40): 13113-13122.
25. Fadoni, M. and Lucarelli, L. (1999). Temperature programmed desorption, reduction, oxidation and flow chemisorption for the characterisation of heterogeneous catalysts. Theoretical aspects, instrumentation and applications. *Studies in Surface Science and Catalysis*, 120: 177-225.
26. Shim, W. G., Lee, J. W. and Kim, S. C. (2008). Analysis of catalytic oxidation of aromatic hydrocarbons over supported palladium catalyst with different pretreatments based on heterogeneous adsorption properties. *Applied Catalysis B: Environmental*, 84(1-2): 133-141.
27. Yuan, Z., Long, J., Xia, Y., Zhang, X. and Wang, T. (2016). Production of levulinic acid from *Pennisetum alopecuroides* in the presence of an acid catalyst. *Bioresources*, 11(2): 3511-3523.
28. Watanabe, M., Aizawa, Y., Iida, T., Aida, T. M., Levy, C., Sue, K. and Inomata, H. (2005). Glucose reactions with acid and base catalysts in hot compressed water at 473 K. *Carbohydrate Research*, 340: 1925-1930.
29. Liu, L., Li, Z., Hou, W. and Shen, H. (2018). Direct conversion of lignocellulose to levulinic acid catalyzed by ionic liquid. *Carbohydrate Polymers*, 181(7): 778-78.