(RESEARCH ARTICLE)

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Raney nickel synthesis for glucose hydrogenation without hydrogen gas

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Abstract

Hydrogenation of glucose into sorbitol has been a concern of researchers for a long time because it is an efficient and economical way of producing sorbitol. The researchers look for alternative metals that are higher in abundance and have good hydrogenation activity, such as nickel. In this study, porous nickel was prepared and used as a catalyst for the hydrogenation of glucose to sorbitol without adding hydrogen gas. The porous nickel needs two stages of making. First, prepare the Ni/Al metal alloys from the reduction of Ni(II) and Al(III). Second, the process of removing Al (0) metal from Ni/Al metal mixtures to produce porous Ni, generally called Raney Ni (RaNi). The prepared RaNi characterize using P-XRD and N2 physisorption. X-ray diffraction results show typical nickel (0) diffraction patterns at 2 theta 44.5° (111), 51.8° (200), and 76.4° (220). The results of N_2 physisorption on RaNi showed a surface area of 64 m^2/g and a pore diameter of 6.13 nm. The hydrogenation reaction of glucose without adding hydrogen gas was carried out for 6 hours at 80 °C using isopropyl alcohol as a hydrogen source. The reaction products were analyzed using 1H-NMR by observing the proton chemical shift of the methine and methylene groups of sorbitol at 3.53-3.78 ppm and using the DNS (3-5, dinitrosalysilic acid) test to determine the remaining glucose in the solution. The reaction product tested using DNS showed that the amount of glucose converted was 54% when RaNi was synthetic as a catalyst.

Keywords: Hydrogenation; Glucose; Sorbitol; Raney; Nickel

1. Introduction

Sorbitol, one of the largest sugar, has spread across many fields such as for food or table sugar, as sweetener, medicine, cosmetics, vitamin C, toothpaste, mouthwash, surfactants, pharmaceuticals, and polyether polyols [1],[2]. In 2016, sorbitol produced almost 1.8 billion tons each year and will get higher products every year. The presence of sorbitol is very important in many cases of diabetes because it is safe to use as a sugar substitute for glucose and does not reduce the sweet taste when consumed [3]. Hydrogenation of glucose is one interesting way to produce sorbitol because glucose is considered an abundant and easily available material [4]. The process of glucose hydrogenation requires a hydrogen source in the form of high-pressure hydrogen gas about 30 to 100 bar [5]. The use of hydrogen with high pressure is considered less efficient, relatively complicated, and has a low level of safety. However, the use of hydrogen gas is not the only way to do hydrogenation. It is also possible to use alcohol solvents such as ethanol, isopropyl alcohol, butanol, and formic acid as hydrogen donating agents in the hydrogenation process [6]. That process is known as a hydrogen transfer reaction.

Hydrogenation of glucose to sorbitol uses a transition metal catalyst because metals give high glucose conversion results and good selectivity to sorbitol. In its development, many researchers use inorganic compounds that have a high abundance to be used as catalysts in the hydrogenation process. The metal alloys, Ni/Cu/Al [7], AlNi [8], NiMoAl [9], Ni/SiO2 [10], and Raney Nickel [11] are catalysts that have been used in the hydrogenation of glucose into sorbitol using a fairly high hydrogen pressure.

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Raney nickel (RaNi) is a porous nickel catalyst that can be synthesized from Ni/Al metal alloys. Nickel chloride is an early precursor used in the preparation of nickel-aluminum alloys. To form the porous nickel structure, aluminum is removed from the metal alloy using a leaching process. Nickel can be an alternative to platinum group metals for hydrogenation reactions because it has good activity and selectivity. This can be seen from the use of RaNi in the reduction reactions of phenyl, naphthalene, acenaphthene, and chlorinated organic solvent dissolved in alkaline media [12]. RaNi also gives high conversion results in the reduction of benzophenone to diphenylmethane [12], hydrogenation of furfural to furfuryl alcohol [13], hydrogenation of benzophenone to benzydrol [14], and hydrogenation of glucose to sorbitol. Although that is claimed that the Ru catalyst is more promising to be used as a hydrogenation catalyst because it does not require a leaching process and has a high activity, RaNi still dominates the industry for the hydrogenation process [11]. The use of high-pressure hydrogenation gas is also undeniable from the hydrogenation reaction so that hydrogen gas can be dissolved in a glucose solution [15]. To prevent the use of high-pressure hydrogen gas, Gross (2001)[16] has transferred hydrogen from isopropyl alcohol (iPrOH) to alcohol compounds with satisfactory conversion results, so that the use of hydrogen gas can be avoided when carrying out hydrogenation reactions. Based on the description above, research on the hydrogenation of glucose into sorbitol using RaNi catalyst is an interesting research topic. The catalyst test for the hydrogenation of glucose into sorbitol was carried out under conditions without hydrogen gas and replacing the hydrogen donor source with water and alcohol solvents such as isopropyl alcohol (iPrOH) and ethanol.

2. Material and methods

2.1. Equipment

The equipment we use in this research is a schlenk glass tube, electric heater, silicon oil bath, vacuum pump, apparatus, thermometer, magnetic stirrer, analytical balance, syringe, oven, spatula, filter paper, measuring pipette, and other standard laboratory glassware. The analytical instrument used in this research is XRD (Phillip Analytical) using a CuKα ray radiation source (λ=0.15406). XRD measurements were carried out in the range of 10°-80° 2θ with a scan rate of 5°/min. Physisorption analysis of N_2 gas using the BET method at 77 K using BELSORP-max Ver1.3.5 (Shimazu Lab, Department of Applied Chemistry and Biotechnology, Chiba University). The amount of nitrogen absorbed is used to calculate the surface area calculated using the BET equation.

The hydrogen transfer products of glucose to sorbitol were analyzed by using 1H-NMR (Nananalysis, 60 MHz) with D_2O solvent (Merck) to observe the typical chemical shift of the product compounds, and a Vis-NIR Spectrophotometer (Vernier SpectroVis Plus) for glucose analysis.

2.2. Materials

The materials in this research are $NiCl_2.6H_2O$ (*Merck*), $AlCl_3$ (*Merck*), hydrazine (*Merck* 80%), NaOH (*Merck*), ethanol (*Merck* 98%), formic acid (*Merck*), (+)anhydrate glucose (*Merck*), isopropyl alcohol (*Merck*), N_2 gas(PT. Trijaya), H_2 gas(PT. Sangkuriang), DNS (*Sigma Aldrich*), KNa tartrate ($KNaC_4H_4O_6.4H_2O$), and water (demineralized Amidis).

2.3. Method

2.3.1. Raney Nickel Catalyst Preparation

Raney Nickel (RaNi) catalyst contains a metal alloy of nickel and aluminum (NiAl) which is widely used as a catalyst in the hydrogenation process. The catalyst has two stages in the preparation process. First is, the formation of NiAl metal alloy by a hydrothermal process. Second, the leaching process of aluminum release from Ni-Al metal alloy. NiAl metal alloy was prepared using $NiCl_2.6H_2O$ (5.7 mmol; 1.365 mg) and $AlCl_3$ (6.8 mmol, 912 mg) salts and then dissolved in 5 mL H_2O. Then, those two solutions were mixed. The mixture was added 5 mL of 80% hydrazine solution (N_2H_4, 0.1 mol) and 5 mL of 4M NaOH. After stirring for 15 minutes, the mixture was put into a Teflon glass to be hydrothermally at 200°C for 24 hours. The reaction will produce a precipitate in the form of a blackish-gray solid. The solids formed were separated using the filtration method and washed using H_2O until the pH of the metal alloy washing solution was in the range of 8-9. After the desired pH was reached, the metal alloy was washed with ethanol twice. The solid metal alloy was dried in an oven at 60°C for 4 hours. NiAl dried alloys were characterized using XRD. The addition of NaOH aims to prevent of formation bayerite [Al(OH)₃] deposits which can cover the surface of a nickel catalyst. Leaching was carried out by mixing solid NiAl and NaOH solution (6M in 5 mL H_2O). The mixture was washed 6 times with demineralized water and 3 times with iPrOH for water removal. RaNi was stored in iPrOH solvent before being used to order to prevent the catalyst from being oxidized. Oxidizing will give decrease catalyst activity levels. RaNi catalyst was characterized by using XRD dan BET.

2.3.2. Catalytic Test of Raney Nickel for Glucose Hydrogen Transfer

RaNi catalysts were prepared for a catalytic test of glucose hydrogen transfer into sorbitol. RaNi was used at 5% w/w of glucose mass (1mmol). The temperature was prepared at 80°C. The solvent is iPrOH.

2.3.3. Analyze Product Glucose Hydrogen Transfer

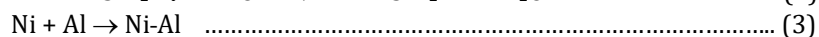The product of transfer hydrogen was analyzed by using ^{1}H-NMR (NMReady 60 MHz) D_2O solvent and spectrophotometer Vis–NIR.
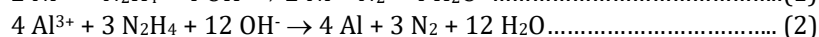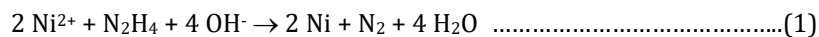
3. Results and discussion
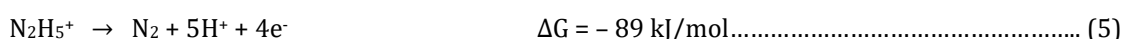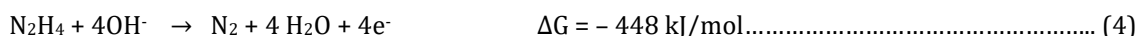
3.1. Raney Nickel Preparation

There are two processes of RaNi preparation, first NiAl preparation by hydrothermal process and second aluminum release process (leaching) from NiAl solid to get nickel pore (RaNi).

3.1.1. NiAl preparation by hydrothermal process

Metal alloys or nickel aluminum alloys are prepared from $NiCl_2$ and $AlCl_3$ salts using the hydrothermal method. That method is used to produce smaller particle sizes and to form a homogeneous system to obtain a high surface area product. Hydrazine solution has the function to reduce Ni (II) ions to become Ni(0) and Al(III) to become Al(0). The reduction of Ni(II) and Al(III) to NiAl metal alloy was signed by the formation of a grayish-black precipitate in alkaline conditions. The reaction of reduction Ni^{2+} and Al^{3+} by hydrazine and the formation of NiAl precipitate is explained as equation 1-3[17] below.

$$2\ Ni^{2+} + N_2H_4 + 4\ OH^- \rightarrow 2\ Ni + N_2 + 4\ H_2O \quad \text{..(1)}$$
$$4\ Al^{3+} + 3\ N_2H_4 + 12\ OH^- \rightarrow 4\ Al + 3\ N_2 + 12\ H_2O \text{...................................} (2)$$
$$Ni + Al \rightarrow Ni\text{-}Al \quad \text{...} (3)$$

Hydrazine works optimally as a reducing agent under alkaline conditions. This situation can be explained by the value of Gibbs free energy under alkaline conditions compared to under acidic conditions as shown in the equation below [18].

$$N_2H_4 + 4OH^- \quad \rightarrow \quad N_2 + 4\ H_2O + 4e^- \qquad \Delta G = -\ 448\ kJ/mol \text{...} (4)$$

$$N_2H_5^+ \quad \rightarrow \quad N_2 + 5H^+ + 4e^- \qquad \Delta G = -\ 89\ kJ/mol \text{...} (5)$$

The mol ratio of nickel salts and aluminum salts used in the preparation of metal alloys is 1:1.2. this comparison is used to prevent the reattachment of the released Al atoms with Ni atoms when the temperature is high (>100°C)[15]. Based on the procedure, hydrothermally NiAl rinse with water and ethanol to remove residues after the synthetic process. NiAl dry in an oven to remove ethanol and then stored in the dry state (Figure 1).

A B

Figure 1 Metal alloy (a) Hydrothermal preparation of NiAl (b) Commercial NiAl (Merck)

Dry NiAl and commercial NiAl (Merck) were characterized by XRD to get the XRD pattern. Possibility of getting metal oxide and hard phase to leach the NiAl, we may prevent all the possibility by saving NiAl in an alcohol solvent. Alcohol solvent may reduce Ni(II) to Ni(0).
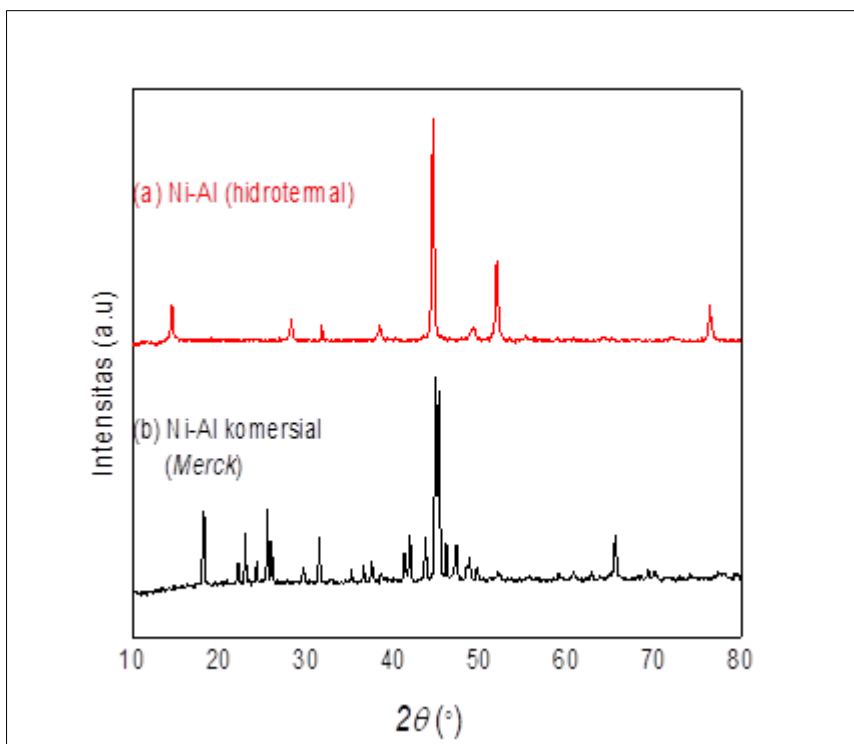

Figure 2 XRD pattern of (a) hydrothermal NiAl and (b) commercial NiAl (Merck)
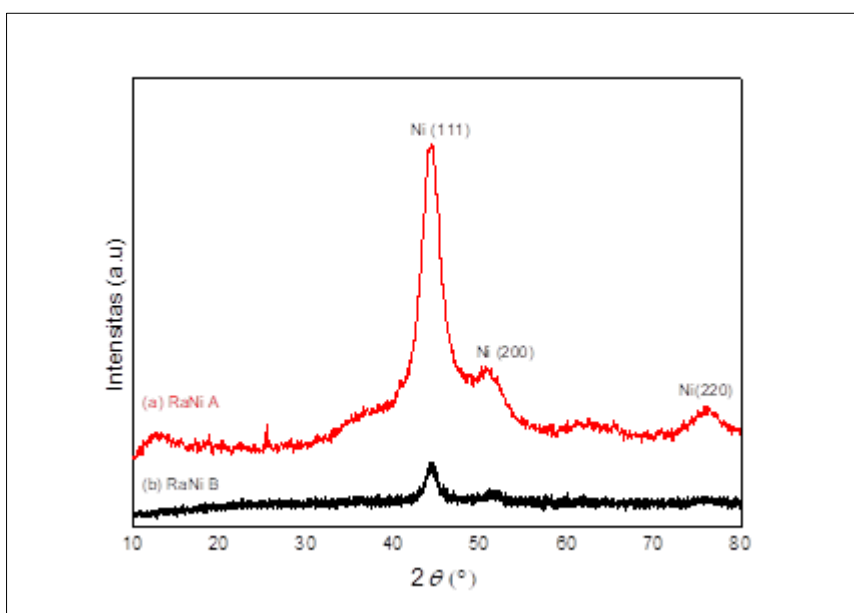
3.1.2. Raney Nickel preparation

Figure 3 XRD Pattern of (a) RaNi after leaching from hydrothermal NiAl and (b) RaNi after leaching from commercial NiAl (Merck)

Raney nickel (RaNi) catalyst has been successfully prepared by leaching aluminum metal from prepared NiAl. Below is the reaction that occurs in the leaching process (equation 6)[18]

2 Ni-Al + 2 NaOH + 6 H$_2$O → 2 Ni + 2 Na$^+$ + 2 Al(OH)$_4^-$ + 3 H$_2$...........................(6)
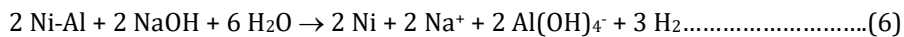
The amount of released Al during the leaching process is influenced by NaOH concentration and time of reaction. The higher of NaOH concentration and the longer time to use in the leaching process, the more aluminum will be released from the NiAl mixture. Based on Hoffer`s research [11], it was concluded that the longer time used for leaching will give a positive impact on dissolving aluminum oxide that may be present in metal alloys. The formed RaNi was characterized using X-ray diffraction. The diffractogram pattern of RaNi after leaching from hydrothermal NiAL shows an amorph phase (Figure 3).

The X-ray diffractograms of RaNi at typical peaks of 2θ 44.5° (111); 51.8°(200); and 76.4° (2200 correspond to the typical diffraction peaks of nickel metal. This situation can be explained by observing the XRD pattern of RaNi and the reference nickel metal (JCPDS: 04-0850)[19] in Figure 4 below. Both metals show the same pattern which proves that in RaNi there is only nickel metal.
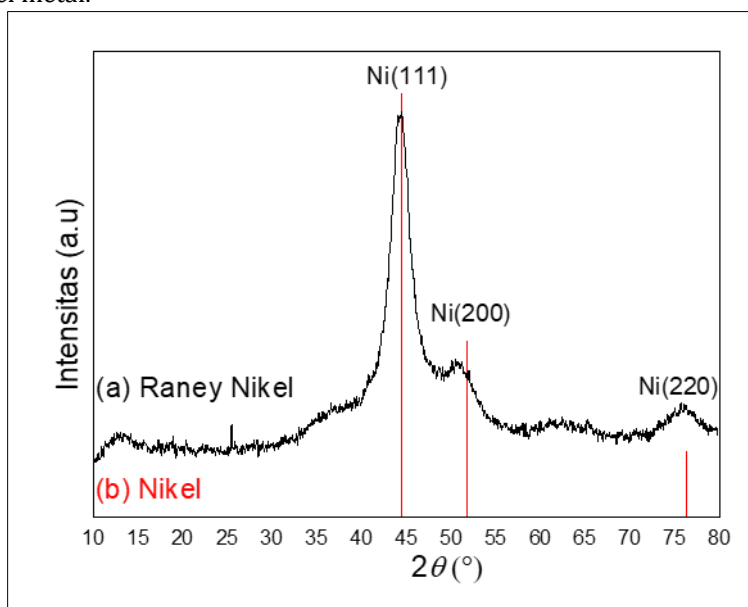

Figure 4 XRD pattern of (a) Raney nickel and (b) reference nickel

3.1.3. Measurement of Raney Nickel catalyst nitrogen physisorption isotherm

Measurement of nitrogen physisorption isotherm using BET method was carried out on RaNi catalyst as a result of leaching Al from hydrothermal NiAl to determine the surface area, pore volume, and pore size distribution. The result of the measurement of nitrogen physisorption using the BET method for synthetic RaNi catalyst is shown in Figure 5.

The surface area of synthesized RaNi is known to be 64 m^2/g, lower than RaNi in the previous studies (80 m^2/g) [11]. The pore volume of RaNi was 0.0977 cc/g and the pore diameter was 6.13 nm. This measurement data shows RaNi has almost the same surface area as RaNi reference. The RaNi pattern of N$_2$ physisorption isotherm has released Al from NiAL metal alloy. The type of this pattern shows type IV hysteresis. Type IV hysteresis gives us information that the pattern will be observed on solid samples, small pores, and uniform pores. At the same pressure, the volume of gas at the time of adsorption is smaller than the volume of desorption. This indicates that there is a possibility of gas condensing in very small capillary pores to the adsorbent at a pressure below the gas saturation pressure in the mesoporous [20]. In this study, the catalytic test of RaNi of glucose was carried out in iPrOH solvent at 80 °C and a hydrogen transfer reaction time of 6 hours. The temperature was chosen because the solvent used (iPrOH) has a boiling point of 82.6 °C. Figure 5 shows the conversion of glucose to sorbitol for the reaction using the catalyst hydrothermal NiAl, commercial NiAl, RaNi resulting from hydrothermal NiAl, and RaNi from commercial NiAl.
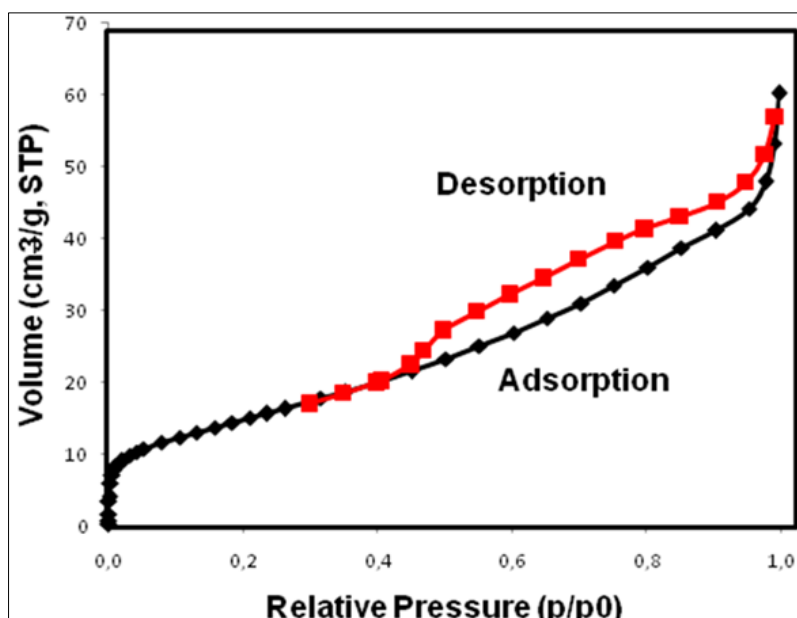
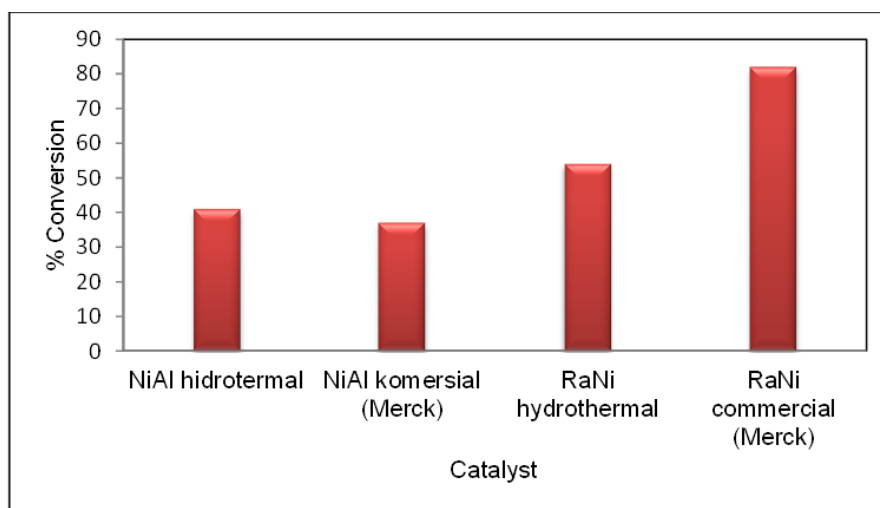**Figure 5** Nitrogen physisorption isotherm of hydrothermal Raney nickel

Figure 6 Catalyst effect for glucose hydrogen transfer

The hydrothermal method to produce RaNi has a lower conversion than commercial RaNi. That happens because of the difference in the surface area of the nickel formed and the possibility of the bayerite ($Al(OH)_3$) formation during the leaching process so that it closes the pores of the nickel surface [11]. The activity of RaNi on the conversion of glucose to sorbitol is strongly influenced by the surface area. A wider surface area of the catalyst will increase the ability of the catalyst to bind more hydrogen from the hydrogen source. According to previous studies, the presence of pores is an important factor for catalysts because pores can control the catalytic process [20]. Hydrogen transfer reactions can use several solvents as hydrogen sources, such as alcohol, water, and formic acid [6]. Isopropyl alcohol is used as a hydrogen source because iPrOH shows good activity when used in the hydrogen transfer of glucose to sorbitol. After donating hydrogen, iPrOH is converted to acetone.

4. Conclusion

Porous nickel (0) can be used as a catalyst in the hydrogenation reaction of glucose to sorbitol without the use of hydrogen gas. As a hydrogen source, isopropyl alcohol is used as a solvent. 53% of glucose conversion was observed when the hydrogen transfer reaction on glucose was carried out for 6 hours at 80°C using porous Ni(0) resulting from

the release of Al from NiAl metal alloy.

Compliance with ethical standards

Acknowledgments

Authors have contributed to the paper`s development.

Disclosure of conflict of interest

The authors have no conflict of interest to declare. All co-authors have seen and agree with the manuscript.

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