cek_IJC 2019 19(1)

by Maria Dewi

Selective Hydrogenation of Sucrose into Sugar Alcohols over Supported Raney Nickel-Based Catalysts

Rodiansono[*], Maria Dewi Astuti, Dwi Rasy Mujiyanti, and Uripto Trisno Santoso

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Lambung Mangkurat University, Jl. A. Yani Km 35.8, Banjarbaru 70713, South Kalimantan, Indonesia

* Corresponding author:

email: rodiansono@ulm.ac.id

Abstract: *Selective hydrogenation of sugars (e.g. sucrose, cellobiose, glucose, fructose, xylose, arabinose) into sugar alcohols (sorbitol, mannitol, xylitol, arabitol) can be achieved by means of supported Raney Ni-based catalysts. Various supporting materials such as the layered structure of clay (e.g. bentonite, taeniolite, smectite), metal oxides (e.g. Nb_2O_5, ZrO_2, Al_2O_3), and conventional supports (e.g. carbon, silica, zeolite (JRC-SZ1)) were employed to obtain high performance of supported Raney Ni-based catalysts. The conventional Raney Ni, Raney Ni/AlOH, and Ni-NP with relatively high dispersion exhibited superior catalytic activity compared with the various supported Raney Ni catalysts with the conversion of 100% and hexitols selectivity almost ~99%. The H_2 treatment of Raney Ni/SMT at a temperature of 473–773 K caused the increase in Ni(111) crystallite sizes as the conversion of sucrose with compromised decreased of hexitols product. The presence of acidic co-catalyst such as SnO, amberlyst-15, JRC-SZ1, JRC-Z5-90H1 on Raney Ni/AlOH catalyst significantly enhanced the formation of glycerol product even though the conversion of sucrose compromised decreased owing to the partial leaching of Ni metal into the reaction mixture.*

Keywords: *selective hydrogenation; sugars; sugar alcohols; supported Raney Ni; acidic co-catalysts*

■ INTRODUCTION

Cellulose, a linear polymer of D-glucose with β-1, 4-glycosidic bonds, can be readily hydrolyzed by mineral acids into glucose, which then can be hydrogenated to sorbitol and other polyols [1]. However, this process is not green and suffers from the common problems associated with the use of liquid acids, for example, corrosion and acid recovery or disposal. In attempts to solve these problems, the direct conversion of crystalline cellulose by using preciously noble metal-based catalysts such as Rh, Ru, Pd, and Pt have been employed [2]. Fukuoka and Dhepe [3-4], Luo et al. [5] recently showed that liquid acids can be replaced by solid acids for cellulose conversion into sorbitol and mannitol, but at relatively low yields, most likely owing to the robust structure of crystalline cellulose and its limited accessibility to the surface of acid sites. Alternatively, sugar alcohols (sorbitol or mannitol) can be synthesized from disaccharides (e.g.

sucrose or cellobiose) and monosaccharides such as glucose or fructose via hydrogenation using heterogeneous catalysts.

In published works, Raney nickel-based catalysts are one of the most common applied-catalysts for the aqueous phase hydrogenation of sugars to sugar alcohols [6-12]. One of its most important drawbacks is its pyrophoricity. In the presence of hydrogen and in many cases volatile organic solvents its application requires rigorous safety measures and is easily deactivated due to carbon residue on the surface or sintered under severe reaction conditions [12]. To reduce the pyrophoricity of Raney Ni, Petro and co-workers prepared non-pyrophoric Raney Ni (R-Ni NP) composited with gibbsite and bayerite. This catalyst was prepared in a similar way to the conventional Raney Ni, with the exception that much less NaOH (~1/10) was used for leaching of Al and consequently, much fewer waste

chemicals were generated for disposal. The R-Ni NP catalyst showed the same or higher catalytic activity than that of the conventional Raney Ni in liquid phase hydrogenation of nitrobenzene [13]. The pyrophoricity of Raney Ni catalyst could be also eliminated by removal of adsorbed hydrogen or by addition of metal co-promoters (e.g., Fe, Mo, Cr, Sn, P, and B) [12,14-15]. It was found that the addition of metal co-promoters not only reduced the pyrophoricity but also enhanced the activity and stability astonishingly. Gallezot et al. studied the promoted-nickel with molybdenum, chromium, iron, and tin for hydrogenation of glucose to sorbitol. Among the studied catalysts, tin promoted skeletal Raney Ni catalysts exhibited better stability than that of the unpromoted Raney Ni during the same period reaction time [12]. Li et al. reported the amorphous nickel-boron (Ni-B) alloy catalysts promoted with chromium, molybdenum, phosphor, and tungsten for hydrogenation of sucrose and it was found that tungsten-promoted Ni-B demonstrated the highest [14-15]. In our previous work, we have reported the effective production of sorbitol/mannitol from hydrogenation of sucrose and cellobiose over highly dispersed nickel nanoparticle supported on aluminum hydroxide (NiNPs/AlOH) catalysts with a high yield of sorbitol ca. > 96%. The catalysts were also stable and reusable for at least five consecutive reaction runs without any significant loss of its activity and selectivity [16]. Raney Ni supported on various clay type supports exhibited high activity for the total hydrogenation of biomass-derived furfural to tetrahydrofurfuryl alcohol [17].

Herein, we extend our investigation on the aqueous phase hydrogenation of sucrose into sorbitol or mannitol in the presence of supported Raney nickel catalysts under mild conditions. Supported Raney Ni catalysts were synthesized according to the procedure that has been reported elsewhere [17]. The effects of supports, H$_2$-treatment at elevated temperature, and the addition of various acidic co-catalysts on the activity and selectivity during the hydrogenation of sucrose to sorbitol/mannitol were studied systematically.

■ EXPERIMENTAL SECTION

Materials

Raney Ni-Al alloy (50 wt.% Al and 50 wt.% Ni) was purchased from Cica Reagent, Kantou Chemical, Ltd. Nb$_2$O$_5$, ZrO$_2$, TiO$_2$, active carbon (AC, S_{BET} = 815 m^{2}g^{-1}), sodium hydroxide (NaOH), sucrose, cellobiose, glucose, fructose, xylose, and arabinose were purchased and used as received from Wako Pure Chemical Industries, Ltd. Lithium-taenolite (TN), sodium-Bentonite (BNT), lithium- hectorite (HT) and smectite SA (SMT) were donated by Kunimine Industries Co. Ltd. SiO$_2$ (S_{BET} = 200 m^{2}g^{-1}) was purchased from Japan Aerosil Co. Microcrystalline of cellulose was purchased from Sigma Aldrich and used as received.

Instrumentation

The prepared catalyst was characterized by means of powder X-ray diffraction on a Mac Science MXP3 instrument using monochromatic CuKα radiation (λ = 0.15418 nm). It was operated at 40 kV and 20 mA. The experimental conditions corresponded to a step width of 0.02° and a scan speed of 2°/min. ICP-AES (inductive-coupled plasma-atomic emission spectroscopy) measurements were performed on an SPS 1800H plasma spectrometer of Seiko Instruments Inc. (Ni: 221.7162 nm).

The BET surface area (S_{BET}) and pore volume (V_P) were measured using N$_2$ physisorption at 77 K on a Belsorp Max (BEL Japan). The samples were degassed at 473 K for 2 h to remove physisorbed gases prior to the measurement. The amount of nitrogen adsorbed onto the samples was used to calculate the BET surface area via the BET equation. The pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of approximately 0.995 according to the Barrett–Joyner–Halenda (BJH) approach based on desorption data [18].

The reactant and products in the reactor (glucose, fructose, xylose, arabinose, and mannitol) were analyzed by using a JASCO RI-930 HPLC using an internal standard method. HPLC was performed with a Shodex KS-801 column (H$_2$O eluent), refractive index (RI)

intelligent detector, the pressure of 17 kg/m², a column temperature of 343 K and a flow rate of 0.6 mL/min. Analyses of sorbitol, glycerol, ethylene glycol and ethanol were performed by using an NH_2 column-Inertsil (Acetonitril-H_2O eluent) using an internal standard method, refractive index (RI) intelligent detector, the pressure of 45–50 kg/cm², a column temperature of 313 K and a flow rate of 1.0 mL/min.

The sugar conversion (mol %) and the product yield (mol %) were evaluated on a carbon basis [19], as shown below:

Sugars conversion (mol %):

$$X = \left(1 - \frac{sucrose\,conc.\ in\,product}{sucrose\,conc.\ in\,the\,loaded\,sample}\right) \times 100\%$$

Product yield (mol %):

$$Y = \frac{moles\,of\,carbon\,product}{moles\,of\,carbon\,in\,sucrose\,introduced} \times 100\%$$

Product selectivity (mol %):

$$S = \frac{mol\,of\,each\,reaction\,product}{mol\,total\,of\,liquid\,product} \times 100\%$$

Procedure

Preparation of supported Raney Ni catalysts

The supported Raney-Ni catalysts were prepared by simple synthetic procedure according to our previous report [17]. Active carbon (AC), silica (SiO_2), Nb_2O_5, zeolite (JRC-SZ1), and ZrO_2, and various clay materials such as lithium taeniolite (TN), lithium hectorite (HT), and Na-bentonite (BNT, Kunipia F type) were employed as support materials. Raney Ni was prepared by leaching Ni-Al alloy using a concentrate aqueous solution of NaOH at room temperature for 2 h and then washed with deionized water and ethanol until the filtrate was neutralized then the clay was added slowly and stirred for overnight at room temperature. The mixture was transferred into a sealed-Teflon autoclave reactor for hydrothermal treatment at 423 K for 2 h. The solvent was removed by simple centrifugation then dried under vacuum for overnight. Prior to safety use (pyrophoricity), the supported Raney-Ni-clay was examined by heating up under air and it was found to be nonpyrophoric. In the case of Raney Ni, the catalyst was stored in H_2O and used as slurry to prevent the oxidation with air during handling. In addition, metal oxides or acidic co-catalysts were added by simple mixing at room temperature without further treatment.

Hydrogenation of sugars

A typical reaction of sugar was carried out in the following manner. Sucrose solution (mmol sucrose/Ni metal = ~85, 0.35 mmol of sucrose) was used as a reactant in an autoclave reactor system of Taiatsu Techno (a Pyrex tube was fitted inside of a sus316 jacket to protect the vessel from corrosion in acidic media). After H_2 was introduced into the reactor (initial pressure of H_2 was 1.0-3.0 MPa) at room temperature, then the temperature of the reactor was raised to the prescribed one in the range of 383–453 K for 24 h. The reaction products were analyzed by using JASCO RI-930 HPLC using internal standard method. HPLC was performed by Shodex KS-801 column (H_2O eluent), refractive index (RI) intelligent detector, pressure 16–17 kg/m², column temperature 70 °C and flow rate 0.6 mL/min.

■ RESULTS AND DISCUSSION

Catalyst Characterization

The XRD patterns of Raney Ni supported on various metal oxides such as Nb_2O_5, ZrO_2, SiO_2, zeolite (JRCZ) and active carbon (AC) are shown in Fig. 1. The specific diffraction peaks at 2θ of 44.6, 51.3, and 76.2° which can be recognized as the identical diffraction peaks of Ni(111), Ni(200), and Ni(220) phases are clearly observed [20]. In the case of clay supported Raney Ni catalysts that were also employed in this work, the physico-chemical properties and XRD patterns were already reported previously [17].

To evaluate the effect of nickel crystallite sizes on the activity and selectivity in the conversion of sucrose, the as-prepared R-Ni/SMT was treated under a hydrogen atmosphere at a temperature of 473–773 K for 1 h and the XRD patterns of H_2-treated R-Ni/SMT are shown in Fig. 2. The diffraction peak of Ni species at 2θ = 44.6; 51.2 and 76,3° that can be recognized as the diffraction peaks of Ni(111), Ni(200), and Ni(220) (111) intensified as the increase of temperature resulting the increase of crystallite sizes of Ni(111) owing segregation
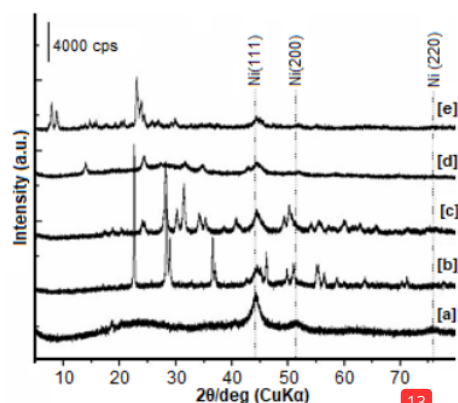
Fig 1. XRD patterns of Raney Ni catalysts on various supports of (a) active carbon (AC), (b) Nb₂O₅, (c) ZrO₂, (d) SiO₂, and (e) Zeolite (JRC-SZ1)
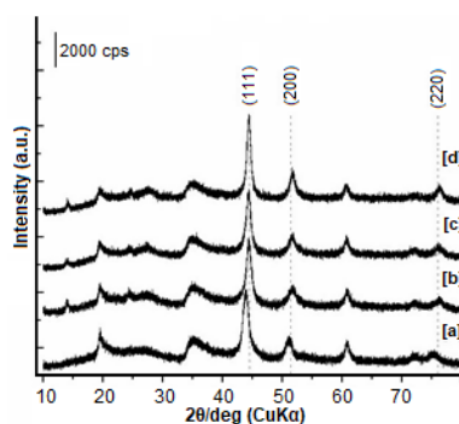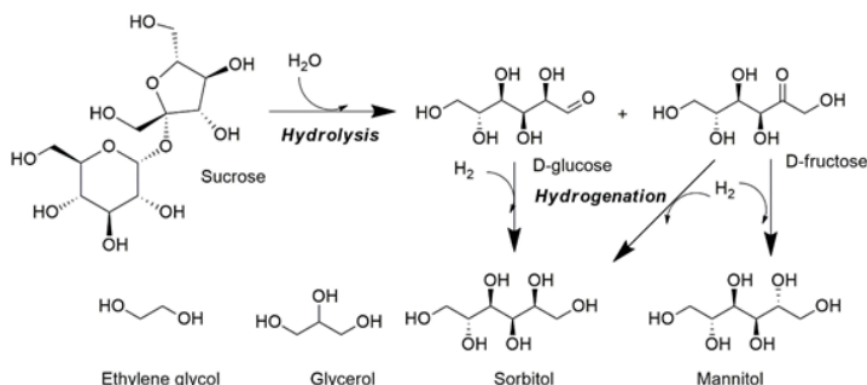
Fig 2. XRD patterns of R-Ni/SMT catalysts after H₂ treatment at (a) 473 K, (b) 573 K, (c) 673 K, and (d) 773 K

Scheme 1. Reaction of sucrose in presence of supported Raney Ni-based catalysts

of Ni species during H_2 treatment at elevated temperature [20]. By using the conventional method of Scherrer equation, the increase of Ni(111) crystallite sizes was from 7.0 nm (untreated) to 11.6 nm (after H_2-treatment at 773 K) (Table 2).

Hydrogenation of Sucrose over Various Supported Raney Ni

In the first experiment, we carried out the reaction of sucrose in water under an H_2 atmosphere in the absence of a catalyst at 403 K for 24 h. The conversion of sucrose was 71% and the yield was 70.6% which consisted of glucose and fructose without the formation of hydrogenated products (Table 1, entry 1). Then, we carried

out the catalytic conversion of sucrose over various supported Raney Ni at identical reaction conditions. The conversion and the yield of glucose, hexitols (sorbitol and mannitol), glycerol and other products over various supported Raney nickel catalysts were summarized in Table 1.

The conventional Raney Ni and Raney-Ni supported on aluminum hydroxide (Raney Ni/AlOH) catalysts demonstrated high conversion of sucrose (> 99%) and gave ~98% hexitols yields (entries 2 and 3) and high yield of hexitols remained even after the reaction time was extended to 24 (entry 4). This result indicates that Raney Ni/AlOH catalyst did not facilitate the further

Indones. J. Chem., 2019, 19 (1), 183 - 190

187

Table 1. Results of sucrose hydrogenation over various supported Raney Ni catalysts[a]

Entry	Catalyst	Conversion[a] (%)	Yield[a] (%)	Selectivity[b] (%)		
				Hexitols[c]	Glycerol	Others[d]
1[e]	No catalyst	71.0	70.6	0.0	0.0	0.0
2	Raney Ni	99.1	97.1	84.0	0.0	16.0
3	Raney Ni/AlOH	99.2	98.5	98.5	1.5	0.0
4[f]	Raney Ni/AlOH	>99	99.6	99.4	0.0	0.6
5	R-Ni/BNT	68.0	64.0	90.0	5.2	4.8
6[g]	R-Ni/HT	72.0	65.0	87.2	1.1	11.7
7[h]	R-Ni/TN	81.6	78.4	82.2	5.2	12.6
8[g]	R-Ni/SMT	78.0	76.0	90.0	9.0	1.0
9[g]	R-Ni/SiO₂	78.8	67.0	86.8	4.4	8.8
10	R-Ni/Nb₂O₅	87.8	73.2	72.8	6.2	21.0
11	R-Ni/ZrO₂	83.4	76.5	80.0	4.0	16.0
12	R-Ni/AC	92.0	90.0	95.0	3.7	1.3
13	R-Ni/JRC-SZ1	78.8	76.5	55.0	37.4	7.6
14[i]	Ni-NP	>99	98.0	94.0	0.0	6.0

[a]***Reaction conditions:*** substrate/Ni = 85; sucrose, 0.35 mmol); H₂O, 5 mL; H₂, 2.0 MPa; temp., 403 K; time, 24 h. [b]Total yield of liquid products included hexitols and Cn-alcohol (n=3). [c]Hexitols (sorbitol + mannitol). [d]Other products are included terminal diols C2-C4 according to GC-MS analysis. [e]The products were glucose and fructose without the formation of hydrogenated products. [f]The catalyst was hydrothermally treated at 423 K for 2 h. [g]Reaction time was 8 h. [h]Reaction time was 16 h. [i]The catalyst was synthesized using the colloidal method and after H₂ treatment at 673 K.

conversion of sorbitol into glycerol or other small products and these results are consistent with the previous report [17]. Over various supported Raney Ni catalysts both the as-prepared and after H₂ treatment at 573 K, the conversion of sucrose and yields of hexitols were around 78–85% (entries 5-12). On the other hand, zeolite (JRC-SZ1) supported Raney Ni converted sucrose into hexitols, glycerol, and other products with the selectivity of 55, 37.4, and 7.6%, respectively (entry 13). It seems likely bifunctional catalyst whereas Raney Ni as the hydrogenation agent while JRC-SZ1 as a Brønsted acid site that required for the C-C cleavage [21]. In addition, unsupported nickel nanoparticle catalyst showed similar activity and selectivity to the Raney Ni/AlOH (entry 14). Therefore, it can be concluded that the conventional Raney Ni, Raney Ni/AlOH, and Ni-NP with relatively high dispersion exhibited superior catalytic activity compared with the various supported Raney Ni catalysts. Among clay-supported Raney Ni catalysts, R-Ni/SMT catalyst exhibited relatively higher activity and selectivity within the reaction time of 8 h (entry 8). Therefore, this catalyst was selected for further investigation of the effect

of H₂ treatment, reaction temperature, the addition of acidic co-catalysts, and the hydrogenation of various sugars.

Hydrogenation of Sucrose over H₂-Treated R-Ni/SMT Catalysts

To evaluate the effect of nickel crystallite sizes on the activity and selectivity in the hydrogenation of sucrose, the catalytic reactions over both the as-prepared and H₂-treated R-Ni/SMT were performed, and the results are summarized in Table 2.

The conversion of sucrose over the H₂-treated R-Ni/SMT increased gradually with the increase of temperature while hexitols selectivity decreased slightly compared with the as-prepared then almost constant at a temperature of 473 K. The increase in conversion might be as the result of the surface activity of reduced/hydride Ni° after H₂ treatment. Alternatively, the increase of Ni(111) crystallite sizes resulted in the more intimate interaction of the molecular reactant and Ni-hydride that facilitate the further reaction of sorbitol into other products.

Effect of Reaction Temperature on Sucrose Hydrogenation

The effect of reaction temperature on the conversion and yield of sugar alcohol in the hydrogenation of sucrose over R-Ni/SMT catalyst was performed and the results are summarized in Table 3.

It can be observed that the conversion of sucrose increased gradually as the increase of reaction temperature. The selectivity of the hexitols product was also decreased smoothly as the selectivity of other products increased, indicating further reaction occurred during the increase of reaction temperature (Table 4, entries 1-5).

Effect of Acidic Co-Catalysts on Sucrose Conversion

The effect of acidic co-catalysts addition to Raney Ni, Raney Ni/AlOH, and R-Ni/SMT catalysts was also evaluated in the hydrogenation of sucrose into hexitols, polyols (glycerol and ethylene glycol). Various acidic compounds such as Nb_2O_5, ZrO_2, SnO, zeolite (JRC-SZ1 and JRC-Z5-9OH1), allophane-SO_3, and amberlyst-15 were added to the reaction mixture and the results are summarized in Table 4.

The addition of Nb_2O_5, ZrO_2, and allophane-SO_3 to Raney Ni/AlOH catalyst did not affect to the product distribution of sucrose conversion (entries 1-3). Interestingly, SnO, amberlyst-15, JRC-SZ1, JRC-Z5-9OH1

Table 2. Results of hydrogenation of sucrose over supported R-Ni/SMT after H_2 treatment at different temperatures

Entry	Temp. (K)	D[a] (nm)	Conv.[b] (%)	Selectivity (%)		
				Hexitols[c]	Glycerol	Others[d]
1	RT	7.0	78.0	90.0	9.0	1.0
2	473	7.6	78.6	89.5	1.6	8.9
3	573	8.3	85.0	89.4	1.9	8.7
4	673	9.6	91.0	89.0	1.6	9.4
5	773	11.6	92.2	85.4	3.6	11.0

Reaction conditions: substrate/Ni = 85; sucrose, 0.35 mmol); H_2O, 5 mL; H_2, 2.0 MPa; temp., 403 K; time, 24 h. [a]Crystallite sizes of Ni(111), calculated by using the Scherrer equation. [b]Total yield of liquid products included hexitols and Cn-alcohol (n = 3). [c]Hexitols (sorbitol + mannitol). [d]Other products are included terminal diols C2-C4 according to GC-MS analysis.

Table 3. Results of hydrogenation of sucrose at different reaction temperatures over R-Ni/SMT catalyst

Entry	Temp. (K)	Conv. (%)	Yield[a] (%)	Selectivity (%)	
				Hexitols[b]	Others[c]
1	403	94	90	95	5
2	423	95	89	95	5
3	433	98	97	83	17
4	443	>99	87	81	19
5	453	>99	96	77	23

Reaction conditions: substrate/Ni = 85; sugar, 0.35 mmol); H_2O, 5 mL; H_2, 2.0 MPa; temp., 403-453 K; time, 24 h. [a]Total yield of liquid products included hexitols and Cn-alcohol (n = 3). [b]Hexitols (sorbitol + mannitol). [c]Other products are included terminal diols C2-C4 according to GC-MS analysis.

Table 4. Influence of acidic co-catalysts on catalytic conversion of sucrose over Raney Ni/AlOH catalyst[a]

Entry	Co-catalyst	Conversion (%)	Yield[a] (%)	Selectivity (%)		
				Hexitols[b]	Glycerol	Others[c]
1	Nb_2O_5	53.1	49.0	81.9	10.4	7.7
2	ZrO_2	57.8	43.2	80.4	7.0	12.6
3	Allophane-SO_3	84.3	78.6	89.7	6.3	4.0
4	SnO	60.8	56.2	22.6	74.6	2.9
5	Amberlyst-15	39.3	26.9	30.0	65.5	4.5
6	JRC-SZ1	54.1	45.2	27.3	69.0	3.7
7	JRC-Z5-9OH1	50.4	47.0	23.4	74.5	2.1
8	R-Ni/SMT 673K/H_2 + Amberlyst-15	64.7	45.0	46.2	50.7	3.1
9	R-Ni/SMT 673K/H_2 + JRC-Z5-9OH1	84.0	77.8	36.6	61.5	1.9
10	Raney Ni + Amberlyst-15	98.0	87.2	42.5	57.5	0.0

Reaction conditions: substrate/Ni = 85; sucrose, 0.35 mmol); H_2O, 5 mL; H_2, 2.0 MPa; temp., 403 K; time, 24 h. [a]Total yield of liquid products included hexitols and Cn-alcohol (n = 3). [b]H = hexitols (sorbitol + mannitol). [c]Other products are included terminal diols C=2-4 according to GC-MS analysis.

Table 5. Results of catalytic conversion of various sugars over R-Ni/SMT catalyst

Entry	Substrate	Conv. (%)	Yield[a] (%)	Selectivity (%) Sugar alc.	Others[c]
1	Sucrose	78	76	90	10
2	Cellobiose	64	60	94	6
3	Glucose	>99	93	95	5
4	Fructose	>99	99	98	2
5	Xylose	>99	98	98	2
6	Arabinose	>99	97	90	10
7	Sorbitol	11	7	0	97

Reaction conditions: substrate/Ni = 85; sugar, 0.35 mmol); H_2O, 5 mL; H_2, 2.0 MPa; temp., 403 K; time, 24 h. [a]Total yield of liquid products included hexitols (sorbitol + mannitol), xylitol, arabitol, and Cn-alcohol (n = 3). [c]Other products are included terminal diols C2-C4 according to GC-MS analysis.

acidic co-catalysts enhanced drastically the formation of glycerol product even though the conversion of sucrose compromised decreased due to the partial leaching of Ni metal into the reaction mixture (entries 4-7). In the case of R-Ni/SMT 673 K/H_2 and Raney Ni catalysts, similar results were also obtained. A significant improvement of glycerol selectivity was achieved after the addition of amberlyst-15 or JRC-Z5-9OH1 (entries 8-10) and these results are consistent with the Raney Ni/JRC-SZ1 as mentioned before (Table 1, entry 13). Therefore, it can be concluded that the presence of acidic co-catalyst could enhance the catalytic performance of Raney Ni for hydrogenolysis of sucrose.

Catalytic Conversion of Various Sugars

We also intentionally evaluated the catalytic performance of the as-prepared R-Ni/SMT catalyst on hydrogenation of various sugars under the identical reaction conditions and the results are summarized in Table 5.

Sucrose was converted into hexitols (sorbitol and mannitol) with 90% selectivity and a small amount of other products (entry 1). In the case of cellobiose substrate, the conversion was only 64% (94% selectivity of hexitols) and the selectivity to glucose was 6% as other products (entry 2). On the other hand, glucose, fructose, and xylose gave hexitols and xylitol as main products (> 90% yield), respectively (entries 3-6). In addition, R-Ni/SMT catalyst did not active for the conversion of

sorbitol as indicated only 11% conversion and total yield of 7% (entry 7).

■ **CONCLUSION**

Selective hydrogenation of sugars (e.g. sucrose, cellobiose, glucose, fructose, xylose, arabinose) into sugar alcohols (sorbitol, mannitol, xylitol or arabitol) can be achieved by means of supported Raney Ni-based catalysts. The conventional Raney Ni, Raney Ni/AlOH, and Ni-NP with relatively high dispersion exhibited superior catalytic activity compared with the various supported Raney Ni catalysts with conversion > 90% and hexitols selectivity almost 95%. The H_2 treatment of Raney Ni/SMT at a temperature of 473-773 K caused the increase in Ni(111) crystallite sizes as the conversion of sucrose with compromised decreased of hexitols product. The presence of acidic co-catalyst such as SnO, amberlyst-15, JRC-SZ1, JRC-Z5-9OH1 on Raney Ni/AlOH catalyst significantly enhanced the formation of glycerol product even though the conversion of sucrose compromised decreased owing to the partial leaching of Ni metal into the reaction mixture.

■ **ACKNOWLEDGMENTS**

■ **REFERENCES**

[1] Dhepe, P.L., and Fukuoka, A., 2008, Cellulose conversion under heterogeneous catalysis, *ChemSusChem*, 1 (12), 969–975.

[2] Zhou, C.H., Xia, X., Lin, C.X., Tonga, D.S., and Beltramini, J., 2011, Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels, *Chem. Soc. Rev.*, 40 (11), 5588–5617.

[3] Fukuoka, A., and Dhepe, P.L., 2006, Catalytic conversion of cellulose into sugar alcohols, *Angew. Chem.*, 118 (31), 5285–5287.

[4] Fukuoka, A., and Dhepe, P.L., 2006, Catalytic conversion of cellulose into sugar alcohols, *Angew. Chem. Int. Ed.*, 45, 5161–5163.

[5] Luo, C., Wang, S., and Liu, H., 2007, Cellulose conversion into polyols catalyzed by reversibly formed acids and supported ruthenium clusters in hot water, *Angew. Chem. Int. Ed.*, 46 (40), 7636–7639.

[6] Hoffer, B.W., Crezee, E., Mooijman, P.R.M., van Langeveld, A.D., Kapteijn, F., and Moulijn, J.A., 2003, Carbon supported Ru catalysts as promising alternative for Raney-type Ni in the selective hydrogenation of D-glucose, *Catal. Today*, 79-80, 35–41.

[7] Kusserow, B., Schimpf, S., and Claus, P., 2003, Hydrogenation of glucose to sorbitol over nickel and ruthenium catalysts, *Adv. Synth. Catal.*, 345 (1-2), 289-299.

[8] Castoldi, M.C.M., Câmara, L.D.T., and Aranda, D.A.G., 2009, Kinetic modeling of sucrose hydrogenation in the production of sorbitol and mannitol with ruthenium and nickel-Raney catalysts, *React. Kinet. Catal. Lett.*, 98 (1), 83–89.

[9] Makke, M., Kieboom, A.P.G., and van Bekkum, A., 1985, Hydrogenation of D-fructose and D-fructose/D-glucose mixtures, *Carbohydr. Res.*, 138 (2), 225–236.

[10] van Gorp, K., Boerman, E., Cavenaghi, C.V., and Berben, P.H., 1999, Catalytic hydrogenation of fine chemicals: Sorbitol production, *Catal. Today*, 52 (2-3), 349–361.

[11] Hoffer, B.W., Crezee, E., Devred, F., Mooijman, P.R.M., Sloof, W.G., Kooyman, P.J., van Langeveld, A.D., Kapteijn, F., and Moulijn, J.A., 2003, The role of the active phase of Raney-type Ni catalysts in the selective hydrogenation of D-glucose to D-sorbitol, *Appl. Catal., A*, 253 (2), 437–452.

[12] Gallezot, P., Cerino, P.J., Blanc, B., Flèche, G., and Fuertes, P., 1994, Glucose hydrogenation on promoted Raney-nickel catalysts, *J. Catal.*, 146 (1), 93–102.

[13] Petró, J., Bóta, A., László, K., Beyer, H., Kálmán, E., and Dódony, I., 2000, A new alumina-supported, not pyrophoric Raney-type Ni-catalyst, *Appl. Catal., A*, 190 (1-2), 73–86.

[14] Li, H., Wang, W., and Deng, J.F., 2000, Glucose hydrogenation to sorbitol over a skeletal Ni-P amorphous alloy catalyst (Raney Ni-P), *J. Catal.*, 191 (1), 257–260.

[15] Li, H., Li, H., and Deng, J.F., 2002, Glucose hydrogenation over Ni–B/SiO$_2$ amorphous alloy catalyst and the promoting effect of metal dopants, *Catal. Today*, 74 (1-2), 53–63.

[16] Rodiansono, R., and Shimazu, S., 2013, Effective production of sorbitol and mannitol from sugars catalyzed by Ni nanoparticles supported on aluminium hydroxide, *Bull. Chem. React. Eng. Catal.*, 8 (1), 40–46.

[17] Rodiansono, R., Hara, T., and Shimazu, S., 2013, Total hydrogenation of biomass-derived furfural over Raney nickel-clay nanocomposite catalysts, *Indones. J. Chem.*, 13 (2), 101–107.

[18] Lowell, S., Shields, J.E., Thomas, M.A., and Thommes, M., 2004, *Characterization of Porous Solids and Powders: Surface Area, Pore Size And Density*, Kluwer Academic Publishers, Netherlands, 101–128.

[19] Qi, X., Watanabe, M., Aida, T.M., and Smith, Jr., R.L., 2008, Catalytic conversion of fructose and glucose into 5-hydroxymethylfurfural in hot compressed water by microwave heating, *Catal. Commun.*, 9 (13), 2244–2249.

[20] JCPDS-ICDD, 1991, *Powder diffraction files*, JCPDS-International Center for Diffraction Data (JCPDS-ICDD).

[21] Saxena, U., Dwivedi, N., and Vidyarthi, S.R., 2005, Effect of catalyst constituents on (Ni, Mo, and Cu)/Kieselguhr-catalyzed sucrose hydrogenolysis, *Ind. Eng. Chem. Res.*, 44 (5), 1466–1473.

cek_IJC 2019 19(1)

1	Submitted to Lambung Mangkurat University Student Paper	**3**%
2	Rodiansono Rodiansono, Maria Dewi Astuti, Kamilia Mustikasari, Sadang Husain, Sutomo Sutomo. "Recent progress in the direct synthesis of γ-valerolactone from biomass-derived sugars catalysed by Raney nickel-tin alloy supported on aluminium hydroxide", Catalysis Science & Technology, 2020 Publication	**3**%
3	Chen Luo, Shuai Wang, Haichao Liu. "Cellulose Conversion into Polyols Catalyzed by Reversibly Formed Acids and Supported Ruthenium Clusters in Hot Water", Angewandte Chemie, 2007 Publication	**3**%
4	docplayer.net Internet Source	**2**%
5	Zhu, Ling-Jun, Ping-Jun Guo, Xian-Wen Chu, Shi-Run Yan, Ming-Hua Qiao, Kang-Nian Fan, Xiao-Xin Zhang, and Bao-Ning Zong. "An	**1**%

environmentally benign and catalytically efficient non-pyrophoric Ni catalyst for aqueous-phase reforming of ethylene glycol", Green Chemistry, 2008.
Publication

6   Di Li, Xinyu Li, Jinlong Gong. "Catalytic Reforming of Oxygenates: State of the Art and Future Prospects", Chemical Reviews, 2016
Publication   1 %

7   Rodiansono Rodiansono, Maria Dewi Astuti, Takayoshi Hara, Nobuyuki Ichikuni, Shogo Shimazu. "Efficient hydrogenation of levulinic acid in water using a supported Ni–Sn alloy on aluminium hydroxide catalysts", Catalysis Science & Technology, 2016
Publication   1 %

8   A P Damayanti, H P Dewi, Ibrahim, Rodiansono. "Selective hydrogenation of levulinic acid to γ-valerolactone using bimetallic Pd-Fe catalyst supported on titanium oxide", IOP Conference Series: Materials Science and Engineering, 2021
Publication   1 %

9   Li, L.. "BO"3^3^-/ZrO"2/Mo-MCM-41 mesoporous molecular sieve as catalyst for dimerization of rosin in supercritical CO"2", Catalysis Communications, 200704
Publication   1 %

| 10 | Submitted to Universitas Jenderal Soedirman
Student Paper | 1% |

| 11 | Hui Li, Hong Lin, Songhai Xie, Weilin Dai, Minghua Qiao, Yufeng Lu, Hexing Li. "Ordered Mesoporous Ni Nanowires with Enhanced Hydrogenation Activity Prepared by Electroless Plating on Functionalized SBA-15", Chemistry of Materials, 2008
Publication | 1% |

| 12 | Qi, Xinhua, Haixin Guo, and Luyang Li. "Efficient Conversion of Fructose to 5-Hydroxymethylfurfural Catalyzed by Sulfated Zirconia in Ionic Liquids", Industrial & Engineering Chemistry Research, 2011.
Publication | 1% |

| 13 | mafiadoc.com
Internet Source | 1% |

| 14 | J. Petró, A. Bóta, K. László, H. Beyer, E. Kálmán, I. Dódony. "A new alumina-supported, not pyrophoric Raney-type Ni-catalyst", Applied Catalysis A: General, 2000
Publication | 1% |