



Research Article

Effective Production of Sorbitol and Mannitol from Sugars Catalyzed by Ni Nanoparticles Supported on Aluminium Hydroxide

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Abstract

Effective production of hexitols (sorbitol and mannitol) was achieved from sugars by means of nickel nanoparticles supported on aluminium hydroxide (NiNPs/AlOH) catalyst. NiNPs/AlOH catalyst was prepared by a simple and benign environmentally procedure using less amount of sodium hydroxide. ICP-AES and XRD analyses confirmed that the NiNPs/AlOH catalysts comprised a large amount of remained aluminium hydroxide (i.e. bayerite and gibbsite). The presence of aluminium hydroxide caused a high dispersion Ni metal species. The average Ni crystallite sizes that derived from the Scherrer's equation for former R-Ni and NiNPs/AlOH were 8.6 nm and 4.1 nm, respectively. The catalyst exhibited high activity and selectivity both hydrogenolysis of disaccharides (sucrose and cellobiose) and monosaccharides (glucose, fructose, and xylose) at 403 K for 24 h. The NiNPs/AlOH catalyst was found to be reusable for at least five consecutive runs without any significant loss of activity and selectivity. © 2013 BCREC UNDIP. All rights reserved

Keywords: supported-nickel nanoparticles; hydrogenation; sugar; sorbitol; mannitol

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1. Introduction

Sugar alcohols, polyols such as glycerol (G) and ethylene glycol (EG), are valuable oxygenated hydrocarbons which are tremendously useful as raw chemicals for the hydrogen resources, liquid fuels, pharmaceuticals, additives in ink, cosmetics and food. It has been urgently proposed that the source of commodity chemicals should be synthesized from renewable resources such as plant-

derived sugars and other biomass rather than fossil resources [1-2].

One of alternative synthetic routes for the above-mentioned alcohols is the hydrogenolysis of agro-based saccharides such as sucrose obtained from lignocellulose. Hydrogenolysis of sucrose required high temperatures and high pressures of hydrogen, although the selectivity for sorbitol and polyols was low [3-6]. The hydrogenolysis of sugars was first performed by Zartman and Adkiens in 1933 in the presence of a Cu-Cr₂O₃ catalyst at 30 MPa of hydrogen and 523 K to produce methanol (2.5 %wt), ethanol (8.4 %wt), H₂O (15.5 %wt) 1,2-

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propanediol (34.8 %wt), 2-(4-hydroxytetrahydrofuryl)-methylcarbinol (7.1 %wt), hexanetriol (10.3 %wt), hexanetetrol (7.1 %wt), and residue (14.2 %wt) [3]. Van Ling used a CuO-CeO₂/SiO₂ catalyst at 20 MPa atm of hydrogen and 498 K to obtain hexitols (H) (16 %wt), propane-1, 2-diol (PD) (18 %wt), glycerol (G) (31.3 %wt) and ethylene glycol (EG) (16 %wt) [4]. The multi-component (Ni, Mo and Cu)/kieselguhr catalyst was found to have a high activity for the hydrogenolysis of sucrose to produce glycerol (28 %wt), ethylene glycol (22 %wt), propylene glycol (PG) (13 %wt) and hexitols (H) (4 %wt) at 5 MPa of H₂ and 423 K [5]. Recently, the best yields of C₄₊ polyols were reported in a BASF patent [7], where in the presence of multi-metallics mixed oxide catalysts, sucrose could be converted to butane-1,2-diol (5-7 %wt) and hexane-1,2,5,6-tetrol (3-10 %wt) in aqueous solutions.

Nickel-based catalysts are one of the most common catalysts used for the aqueous phase hydrogenation of sugars to sugar alcohols, including Raney Ni [8-14]. However, the most critical drawbacks of Raney Ni are the pyrophoricity and stability. To reduce the pyrophoricity of Raney Ni, Petro and co-workers prepared non-pyrophoric Raney Ni composited with gibbsite and bayerite [15-17]. The pyrophoricity could be also eliminated by removal of adsorbed hydrogen or by addition of metal co-promoters (e.g., Fe, Mo and Cr) [8-10] to Raney Ni catalyst. It was found that the addition of metal co-promoters not only reduced the pyrophoricity but also enhanced the activity and stability astonishingly. In addition, the non-pyrophoric Raney Ni catalyst also showed higher activity and stability than as-prepared Raney Ni in an aqueous phase reforming (APR) of ethylene glycol for hydrogen production [19].

In the present report, an effective production of hexitols (sorbitol and mannitol) was achieved over supported-Ni nanoparticles on aluminium hydroxide (NiNPs/Al(OH)₃) catalyst under mild conditions from sugars (disaccharide: sucrose and cellobiose; monosaccharide: glucose and fructose) as model compound of biomass-derived sugars that can be obtained from lignocellulose/hemicellulose or cellulose.

2. Materials and Method

2.1. Materials and Instrumentations

Raney NiAl was purchased from Kanto Chemical Co. Inc. (50%wt Ni + 50%wt Al=50:50) and used as received. Sucrose (Wako Pure Chemical), D-(+) glucose (Wako Pure Chemical, 98%), D-(+) fructose (Kanto Chemical Co. Inc), D-(+) cellobiose (Kanto Chemical Co. Inc.), D(-) mannitol (Wako Pure Chemical, 99%), D(-) sorbitol (Wako Pure Chemi-

cal) and used as received.

2.2. Catalyst preparation

Ni nanoparticles supported on aluminium hydroxide (denoted as NiNPs/Al(OH)₃) catalysts were prepared as the following [14]. Under gentle stirring, Raney NiAl alloy powder was slowly added to a dilute aqueous solution of NaOH (0.31 M, 8 mL) at room temperature for 30 min, and then NaOH solution (3.14 M, 1 mL) was added to the mixture and stirred gently at 363 K for 20 min. The precipitate was washed with distilled water until the supernatant water became neutral and stored under water for further catalytic test.

Raney Ni (R-Ni) was conventionally prepared in the following procedure. One gram of the above Raney NiAl alloy was slowly added to an aqueous solution of NaOH (6 M, 10 mL) at 363 K under gentle stirring and was kept on stirring for 30 min for further alkali leaching. The precipitated was washed by distilled water until supernatant became neutral and then stored under water for the activity test.

2.3. Catalyst characterization

The prepared catalysts were characterized by powder X-ray Diffraction on a Mac Science MXP³ instrument using monochromatic CuK α radiation ($\lambda = 0.15418$ nm). It was operated at 40 kV and 20 mA with a step width of 0.02° and a scan speed of 2° min⁻¹. The mean crystallite size of Ni was calculated from the full width at half maximum (FWHM) of the Ni(111) diffraction peak according to the Scherrer equation and confirmed by H₂ and CO chemisorption. The bulk compositions of the catalysts were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), using a SPS1700 HVR of SII instrument.

Nickel surface area was determined by H₂ and CO chemisorption. After the catalyst was heated at 393 K under vacuum for 30 min, it was heated at 673 K under H₂ for 30 min and under vacuo for 30 min, followed by evacuation to room temperature for 30 min. The adsorption of H₂ or CO was conducted at 273 K. The active surface area was calculated from the volume of H₂ or CO desorbed by assuming an H/Ni or CO/Ni stoichiometry of 1 and a surface area of 6.77 x 10⁻²⁰ m² per atom Ni based on an equal distribution of the three lowest index planes of nickel (fcc) [20-21].

Nitrogen adsorption isotherms at 77 K were measured using 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 specific surface area by means of the BET equation. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of about 0.995. The Barrett–Joyner–Halenda (BJH) approach was used to calculate total pore volume and pore size distribution from desorption data [22].

2.4. Hydrogenolysis of sucrose

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 H₂ was introduced into the reactor (initial pressure of H₂ 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 reactant and products in the reactor (glucose, fructose and mannitol) were analysed by using a JASCO RI-930 HPLC using an internal standard method. HPLC was performed with a Shodex KS-801 column (H₂O eluent), refractive index (RI) intelligent detector, pressure of 17 kg/m², 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 NH₂ column-Inertsil (Acetonitril-H₂O eluent) using an internal standard method, refractive index (RI) intelligent detector, pressure of 45-50 kg/cm², 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 [23], as shown below:

Sugars conversion (mol%):

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

Product yield (mol%):

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

Product selectivity (mol%):

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

3. Results and Discussion

3.1. Catalyst Characterization

The bulk composition of the catalysts was determined by using ICP-AES and the results are summarized in Table 1. The amount of bulk Ni species in R-Ni and NiNPs/AlOH was 3.98 mmol g⁻¹ and 3.46 mmol g⁻¹, respectively, while the bulk Al species was 0.63 mmol g⁻¹ and 3.80 mmol g⁻¹, respectively. The large amount of aluminium hydroxide as bayerite and gibbsite could reduce significantly the pyrophoricity of nickel metal and facilitate a highly dispersed of Ni species in NiNPs/AlOH. In order to ensure the pyrophoricity has been eliminated, the sample was put on the Whatman paper in the oven at 373 K for 1.5 h. No change of the color of the Whatman paper was observed, indicating the sample was totally non-pyrophoric.

The XRD patterns of R-Ni/AlOH showed the sharp diffraction peaks at 2θ = 44.3° and 51.6° which correspond to the Ni(111) and Ni(200) spe-

Table 1: Physicochemical properties the synthesized R-Ni and NiNPs/AlOH catalysts

Entry	Catalyst	Ni ^a (mmol g ⁻¹)	Al ^a (mmol g ⁻¹)	H ₂ ^b (mmol g ⁻¹)	S _{BET} ^c (m ² g ⁻¹)	D ^d (nm)
1	R-Ni	3.98	0.63	111.6	66	8.6
2	NiNPs/AlOH	3.46	3.80	51.5	113	4.1

^a Determined by ICP-AES. ^bH₂ uptake at 273 K (noted after corrected for physical and chemical adsorption). ^cBET specific surface areas, determined by N₂ physisorption at 77 K. ^dThe average Ni crystallite sizes derived from the Scherrer's equation of Ni(111). R-Ni = Raney nickel; NiNPs/AlOH = supported nickel nanoparticles on aluminium hydroxide.

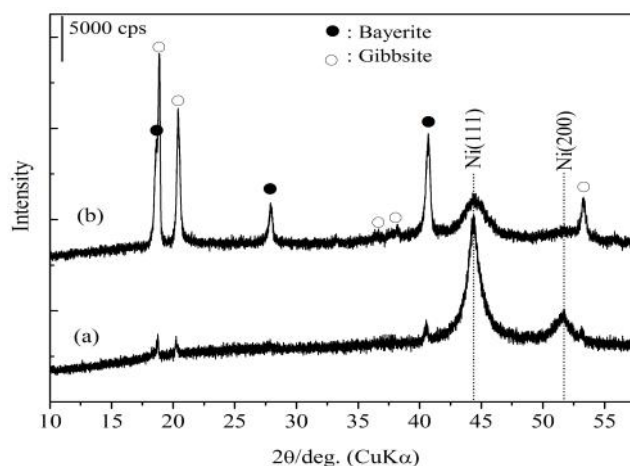


Figure 1: Powder X-ray diffraction (XRD) patterns of the synthesized R-Ni (a) and NiNPs/AlOH (b) catalysts.

cies, respectively (Figure 1a). The sharp diffraction peaks were also observed at $2\theta = 18.26^\circ$, 27.8° , and 40.54° that were recognised to bayerite and at $2\theta = 18.7^\circ$, 20.36° , 36.66° , 37.76° and 53.18° which were assigned to gibbsite (Figure 1b) [24].

The mean crystallite size of Ni for R-Ni and NiNPs/AlOH by means of XRD reflection of Ni(111) was 8.6 and 4.1 nm, respectively (Table 1). It is found that the crystallite size of Ni(111) for NiNPs/AlOH was much lower than that of the as prepared R-Ni. On the other, the dispersion of nickel metal in the NiNPs/AlOH system is higher than that of R-Ni due to the presence of residual aluminium hydroxide.

The specific surface area (S_{BET}) of the prepared catalysts that determined by N_2 adsorption at 77 K are also summarized in Table 1. The S_{BET} of R-Ni and NiNPs/AlOH were $66 \text{ m}^2\text{g}^{-1}$ and $113 \text{ m}^2\text{g}^{-1}$, respectively. The high specific surface area for NiNPs/AlOH sample may due to the presence of remained aluminium hydroxide [14-16]. The Ni surface area (S_{Ni}) of as prepared R-Ni was much higher than (almost 2 times) that of NiNPs/AlOH. Saliiently, S_{Ni} is at most 30% of the specific surface area (S_{BET}) for NiNPs/AlOH.

3.2. Hydrogenolysis of sucrose over various catalysts

First, we carried out the hydrolysis of sucrose in water under H_2 atmosphere in the absence of catalyst at 403 K for 24 h and the results are summarized in Table 2. The hydrogenolysis of sucrose in absence of catalyst gave the conversion and yield of 71 and 70.6%, respectively (Table 2, entry 1) and the products were glucose and fructose without the formation of hydrogenated products.

It can be observed that by using R-Ni catalyst, sucrose conversion was 94% with hexitols selectivity of 98% (mannitol/sorbitol ratio is 0.3) (Table 2, entry 2). In the case of NiNPs/AlOH catalyst, the

Table 2: Results of sucrose hydrogenolysis over various catalysts^a

Entry	Catalyst	Conv. (%)	Yield ^b (%)	Selectivity(%)		
				H(M/S) ^c	G	EG
1 ^d	No catalyst	71	70.6	0.0	0.0	0.0
2	R-Ni	94	86.1	98(0.3)	1.9	0.1
3	NiNPs/AlOH	99	96.3	>99(0.4)	0.0	0.3

^a Reaction conditions: substrate/Ni=85; sucrose, 0.35 mmol; H_2O , 5 mL; H_2 , 2.0 MPa; temp., 403 K; time, 24 h. ^b Total yield of liquid products included hexitols and Cn-alcohol (n = 3). H=hexitols (sorbitol + mannitol), EG=ethylene glycol and G=glycerol. ^c M/S (mannitol/sorbitol molar ratio). ^d The products were glucose and fructose without the formation of hydrogenated products.

conversion of sucrose was 99% (96.3% yield) and the selectivity of hexitols was >99% (mannitol/sorbitol ratio is 0.4). It is found that over NiNPs/AlOH catalyst, the selectivity towards mannitol moderately increased as reflected by mannitol/sorbitol ratio (Table 2, entry 3).

3.2.1. Time profiles

The reaction profile of sucrose hydrogenolysis at 403 K on the NiNPs/AlOH catalyst is shown in Figure 2. The conversion of sucrose and the yield of hexitols (mannitol and sorbitol) increased gradually with an increasing of reaction time and the completed reaction was achieved after 24 h.

3.2.2. Effect of reaction temperature

The influence of reaction temperature on the yield of hexitols over NiNPs/AlOH catalyst is shown in Figure 3. The conversion of sucrose was 98% at temperature of 383 K and completed reaction was achieved at 403 K for 24 h. The yield of hexitols (mannitol and sorbitol) gradually increased as temperature was increased and >99% yield was achieved at 423 K for 24 h.

3.2.3. Effect of H_2 initial pressure

To obtain the insight into the influence of the initial H_2 pressure on the hydrogenolysis of sucrose over NiNPs/AlOH catalyst, various initial H_2 pressures were applied and the results are shown in Figure 4. Although the conversion remained at nearly 100%, an increase of the initial hydrogen pressure resulted in increasing of hexitols. The highest yield of polyols was achieved at 2.0 MPa (99% yield of hexitols).

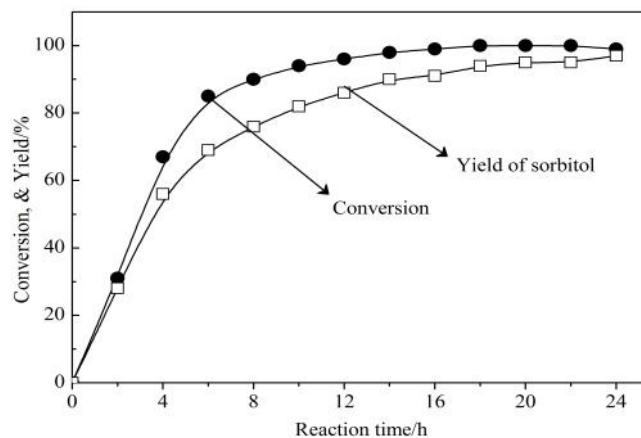


Figure 2: Time profiles of sucrose hydrogenolysis over NiNPs/AlOH catalyst. Reaction conditions: substrate/Ni = 85; sucrose, 0.35 mmol; H_2O , 5 mL; H_2 , 2.0 MPa; temp., 403 K.

3.2.4. Hydrogenolysis of various sugars

We also intentionally carried out the catalytic reaction of various sugars by means of NiNPs/AlOH catalyst under the same reaction conditions and the results are summarized in Table 3. Sucrose was hydrogenolyzed hexitols and small amount of ethylene glycol (99% conversion, 96% yield of hexitols) (entry 1). In the case of cellobiose hydrogenolysis, the conversion was 90% (89% yield of hexitols) and the selectivity to glucose was 14% (entry 2). On the other hand, glucose, fructose, and

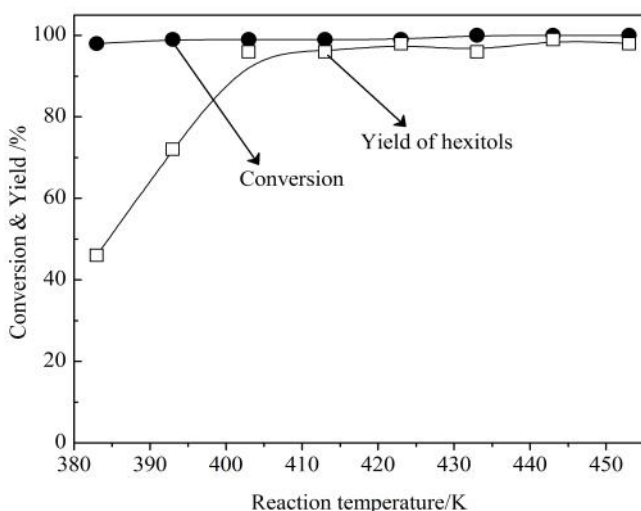


Figure 3: Effect of temperature reaction on the product distribution in sucrose hydrogenolysis over NiNPs/AlOH catalyst. *Reaction conditions:* substrate/Ni =85; sucrose, 0.35 mmol; H₂O, 5 mL; H₂, 2.0 MPa; 24 h.

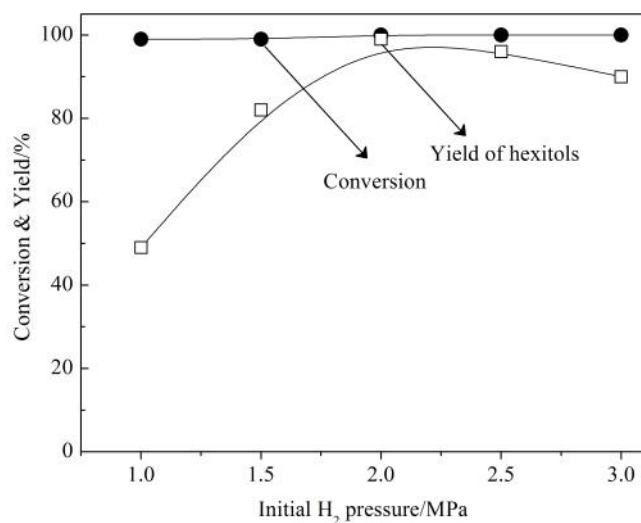


Figure 4: Effect of initial H₂ pressure on the product selectivity in sucrose hydrogenolysis. *Reaction conditions:* substrate/Ni=85; sucrose, 0.35 mmol; H₂O, 5 mL; 403 K; 24 h.

xylose gave hexitols and xylitol as main products (>90% yield). The hydrogenolyzed product of C₂₋₃ polyols such as glycerol and ethylene glycol were also observed over the catalyst (entries 3-4).

3.3 Reusability test

A reusability test was performed on the NiNPs/AlOH catalyst, and the results are summarized in Table 4. The used NiNPs/AlOH catalyst was easily separated by either simple centrifugation or filtration after the reaction. The activity and selectivity of NiNPs/AlOH catalyst was maintained (>99%) even after five consecutive runs. The amount of Ni and Al that leached into the reaction solution was 0.1% and 3.0%, respectively.

The XRD patterns of the recovered R-Ni and

Table 3: Results of hydrogenolysis of various sugars over NiNPs/AlOH catalyst^a

Entry	Substrate	Conv. (%)	Yield ^b (%)	Selectivity(%)		
				H(M/S) ^c	G	EG
1	Sucrose	99	96	>99(0.4)	0.0	0.3
2 ^d	Cellobiose	90	89	86(0.0)	0.0	0.0
3	Glucose	>99	>99	93.0(0.0)	4.0	3.0
4	Fructose	>99	>99	92.0(0.1)	2.0	6.0
5	Xylose	>99	>99	96.2(0.0)	1.0	2.8

^a *Reaction conditions:* substrate/Ni=85; sugar, 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 C_n-alcohol (n 3). H=hexitols (sorbitol + mannitol), EG=ethylene glycol and G=glycerol. ^c M/S (mannitol/sorbitol molar ratio). ^d Selectivity to glucose was 14%.

Table 4: Results of reusability test for NiNPs/AlOH catalyst in sucrose hydrogenolysis^a

Entry	Run	Conv. (%)	Yield ^b (%)	Selectivity(%)		
				H(M/S) ^c	G	EG
1	1 st	99	96	>99(0.4)	0.0	0.3
2	2 nd	>99	98	99(0.3)	1.0	0.0
3	3 rd	>99	98	99(0.3)	1.0	0.0
4	4 th	>99	95	99(0.4)	1.0	0.0
5	5 th	98	95	98(0.4)	2.0	0.0

^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 C₍₂₋₃₎ alcohol. H=hexitols (sorbitol + mannitol), EG=ethylene glycol and G=glycerol. ^c M/S (mannitol/sorbitol molar ratio).

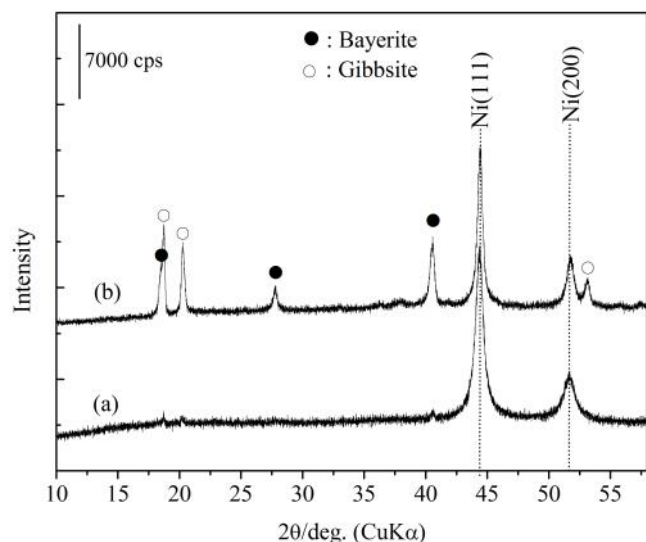


Figure 5: XRD patterns of the recovered NiNPs/AlOH catalyst after the fifth reaction run.

NiNPs/AlOH catalysts after the fifth run are shown in Figure 5. It can be observed that the diffraction peak of Ni metal species slightly intensified, indicating aggregation of Ni particle occurred during the reaction. The average crystallite sizes of Ni(111) were 14.7 nm and 17.5 nm for used R-Ni and used NiNPs/AlOH catalysts, respectively.

4. Conclusion

Effective production of hexitols (sorbitol and mannitol) was achieved from sugars by means of supported nickel nanoparticles on aluminium hydroxide (NiNPs/AlOH) catalyst. The catalyst exhibited high activity and selectivity both hydrogenolysis of disaccharide and monosaccharide. The NiNPs/AlOH catalyst was found to be reusable for at least five consecutive run without any significant loss of activity and selectivity.

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