The selective hydrogenolysis of sucrose to sorbitol and polyols over nickel-tin nanoparticle catalyst supported on aluminium hydroxide

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Abstract. Low molecular alcohols were selectively produced from sugars such as sucrose; glucose and fructose by means of nickel-tin nanoparticle catalyst supported on aluminium hydroxide (NiNP-Sn/AlOH) in aqueous solution under hydrogen gas atmosphere from 383 to 453 K. NiNP-Sn/AlOH catalysts were easily obtained by a simple synthetic procedure according to our previous report. Nickel nanoparticles supported on aluminium hydroxide (NiNP/AlOH) was obtained from the alkali leaching of Raney Ni-Al alloy using a dilute sodium hydroxide solution at relatively low temperature. The mixture of NiNP/AlOH and a solution containing tin species was treated hydrothermally in the sealed-teflon autoclave reactor at 423 K for 24 h. The obtained catalysts were used without further treatment. In contrast, NiNP/AlOH catalyst gave only hydrogenated products such as mannitol and sorbitol. NiNP-Sn/AlOH catalyst is believed to facilitate the cleavage of C-C bonds of substrates to give low molecular alcohols such as glycerol, ethylene glycol and ethanol. It is intriguing that the addition of tin also facilitated the production of ethanol from sugar with 12% of selectivity at 453 K under 2.5 MPa of hydrogen gas. Selectivity of each alcohol mainly depended on the reaction temperature and the initial H2 pressure.

Keywords: hydrogenolysis, sucrose, sorbitol, nickel-tin nanoparticle, polyol

INTRODUCTION

Polyols such as sorbitol/mannitol, glycerol (G) and ethylene glycol (EG) are tremendously versatile oxygenated hydrocarbons as they are useful as raw materials for the production of hydrogen, perfumes, beer ingredients, pharmaceuticals, ink additives and liquid fuels. It has been proposed that commodity chemicals derived from fossil resources will inevitably be available from renewable resources such as plant-derived sugars and other compounds.

An alternative source of these polyols is the hydrogenolysis of agro-based saccharides such as sucrose. Hydrogenolysis of sucrose has been performed at high temperatures and high pressures of hydrogen, although the selectivity for sorbitol and polyols was low [1-4]. 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 (4 wt%), ethanol (13 wt%), 1,2-propanediol (54 wt%), 2-(4-hydroxytetrahydro-furyl)-methylcarbinol (11 wt%), hexanetriol (16 wt%) and hexanetetrol (11 wt%) [1]. Van Ling used a CuO-2SiO2 catalyst at 20 MPa of hydrogen and 498 K to obtain hexitols (16 wt%), propane-1,2-diol (PD) (18 wt%), glycerol (G) (31.3 wt%) and ethylene glycol (EG) (16 wt%) [2]. The multicompartment (Ni, Mo and Cu)/kieselguhr catalyst was found to have a high activity for the hydrogenolysis of sucrose to
produce industrially important 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 [3]. Recently, the best yields of C4+ products were reported in a BASF patent [4], where, in the presence multimetallics, mixed oxide catalysts and aqueous solutions of sucrose could be converted to 5-7 wt% butane-1,2-diol and 3-10 wt% hexane-1,2,5,6-tetrol.

Nickel-based catalysts are some of the most common catalysts used for the aqueous phase hydrogenation of sugars to sorbitol, including Raney-Ni. However, one of the most important drawbacks of Raney-Ni is its pyrophoricity and readily deactivated after several runs. To develop green and environmentally friendly processes, Petro and co-workers reported the preparation of a non-pyrophoric Raney nickel catalyst that consisted of metallic Ni, gibbsite and bayerite. Zhu et al. reported that the non-pyrophoric Raney nickel catalyst showed higher activity and stability than as-prepared Raney-Ni in an aqueous phase reaction (APR) of ethylene glycol for hydrogen production. Recently, we have reported the catalytic performance of nickel nanoparticle supported on aluminium hydroxide catalyst on the hydrogenation of sugars such as sucrose, glucose, fructose, and xylose to produce sorbitol/mannitol and xylitol. The addition of Sn to NiNP/AlOH to form NiNP-Sn alloy nanoparticles remarkably improved the chemoselectivity towards unsaturated alcohol in the hydrogenation of unsaturated carbonyl compounds [10, 11]. In this paper, we continue our study to evaluate the effect of the addition of tin (Sn) on nickel nanoparticle supported on aluminium hydroxide catalyst in sucrose hydrogenolysis.

**METHOD**

Nickel nanoparticle supported on aluminium hydroxide (NiNP/AlOH) catalyst was prepared as described below [7]. Under gentle stirring, the Raney Ni alloy powder was slowly added to a dilute aqueous solution of NaOH at room temperature, and then 1 ml of 3.14 M NaOH solution was added at 363 K. The precipitate was washed with distilled water to neutralise the catalyst and was stored under water for further activity tests. The nickel-tin nanoparticle supported on aluminium hydroxide (NiNP-Sn/AlOH) catalyst was prepared in a similar fashion to NiNP/AlOH, except for the addition of tin solution during the alkali leaching of NiNP/AlOH followed by hydrothermal treatment at 423 K for 24 h [10]. The catalyst was then washed and filtered until the pH was neutral.

**CATALYST CHARACTERIZATION**

The prepared catalysts were characterized by 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 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 10²⁰ m² per atom Ni.
based on an equal distribution of the three lowest index planes of nickel (fcc) [12, 13].

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.

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, as shown below:

\[
\frac{X}{Y} = \frac{\text{sucrose concentration in product}}{\text{sucrose concentration in the loaded sample}} \times 100\% \\
\text{Product yield (mol%):} \quad Y = \frac{\text{mol of carbon product}}{\text{mol of carbon in sucrose introduced}} \times 100\%
\]

\[
\text{Product selectivity (mol%):} \quad S = \frac{\text{mol of each reaction product}}{\text{mol total of liquid product}} \times 100\%
\]

**RESULTS AND DISCUSSION**

**CATALYST CHARACTERIZATIONS**

The bulk composition of the catalysts was determined by using ICP-AES as summarized in Table 1. The dissolution of Al from NiAl alloy by using dilute NaOH solution was successful controlled, as indicated by remained Al 3.80 and 4.91 mmolg⁻¹ for NiNP/AlOH and NiNP-Sn/AlOH, respectively, which are much higher than that of the as-prepared Raney-Ni (0.63 mmolg⁻¹). The amount of introduced Sn to form NiNP-Sn/AlOH was 2.14 mmolg⁻¹ where the Ni/Sn mol ratio was 1.5. The presence of aluminium hydroxide could reduce the pyrophoricity of nickel metal and facilitate highly dispersed of Ni or Ni-Sn species in NiNP/AlOH or NiNP-Sn/AlOH, respectively.

The lists values of H₂ uptake and total specific surface area (S BET) and average crystallite sizes of Ni(111) are also summarized in Table 1. The H₂ uptakes of Raney-Ni, NiNP/AlOH, and NiNP-Sn/AlOH were 111.6 μmolg⁻¹, 104 μmolg⁻¹, and 103 μmolg⁻¹, respectively. The S BET of R-Ni, NiNP/AlOH and NiNP-Sn/AlOH were 66, 113 and 76.0 m²g⁻¹, respectively. The presence of remained aluminium hydroxide as bayerite and gibbsite and the addition of Sn slightly reduced the H₂ uptake. This result suggest that Sn species could be preferentially adsorbed and segregated on Ni surface rather than aluminium hydroxide and thus hinder hydrogen chemisorption on the nickel site. Our results are in good agreement with the previous reports that the addition of Sn [10] or Cr-Fe [5, 6] to R-Ni substantially reduced the H₂-chemisorption availability of nickel site.
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Table 1. Bulk composition, H₂ uptake, S_BET and crystallite size of Ni(111) for as-prepared Raney-Ni, NiNP/AIOH and NiNP-Sn/AIOH catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>NiP (mmolg⁻¹)</th>
<th>AP (mmolg⁻¹)</th>
<th>Sn⁺ (mmolg⁻¹)</th>
<th>H₂ uptake (nmolmg⁻¹)</th>
<th>S_BET (m²g⁻¹)</th>
<th>D(avg) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Raney-Ni</td>
<td>3.98</td>
<td>6.03</td>
<td>-</td>
<td>111.6</td>
<td>66</td>
<td>8.6</td>
</tr>
<tr>
<td>2</td>
<td>NiNP/AIOH</td>
<td>3.46</td>
<td>3.80</td>
<td>-</td>
<td>104</td>
<td>115</td>
<td>4.1</td>
</tr>
<tr>
<td>3</td>
<td>NiNP-Sn/AlOH</td>
<td>3.13</td>
<td>4.91</td>
<td>-</td>
<td>214</td>
<td>103</td>
<td>5.3</td>
</tr>
</tbody>
</table>

* Determined by ICP–AES. **H₂ uptake at 273 K (noted after correction for physical and chemical adsorption). **BET specific surface areas, determined by N₂ physisorption at 77 K. The average Ni crystallite sizes derived from the Scherrer’s equation of Ni(111). R-Ni = Raney nickel; NiNP/AIOH = supported nickel nanoparticles on aluminium hydroxide; NiNP-Sn/AlOH = supported nickel-tin nanoparticles on aluminium hydroxide.

The average crystallite size of Ni for Raney-Ni, NiNP/AIOH and NiNP-Sn/AIOH by means of XRD reflection of Ni(111) was 8.6, 4.1 and 5.3 nm, respectively (Table 1). It is found that the crystallite size of Ni(111) for NiNP/AIOH and NiNP-Sn/AIOH lower than as prepared Raney-Ni, reflecting nickel metal more dispersed in the presence of residual aluminium hydroxide.

Figure 1 shows the XRD patterns of Raney-Ni, NiNP/AIOH and NiNP-Sn/AIOH catalysts. Raney Ni showed diffraction peaks at 2θ = 44.3 and 51.6°, corresponding to Ni(111) and Ni(200), respectively. For NiNP/AIOH and NiNP-Sn/AIOH, sharp peaks at 2θ=18.8, 20.2 and 50.7° assignable to gibbsite and bayerite at 2θ=18.2, 27.7, 40.6 and 53.1° [16] were identified, confirming the presence of more

Figure 1. XRD patterns of (a) Raney Ni, (b) NiNP/AIOH, and (c) NiNP-Sn/AIOH catalysts Al(OH)₃ in NiNP/AIOH and NiNP-Sn/AIOH. XRD characterization reveals that in NiNP/AIOH and NiNP-Sn/AIOH, metallic Ni was dispersed in gibbsite and bayerite, which could be recognized as a Ni-Al(OH)₃ composite catalyst [8]. Furthermore, a broadened peak at 2θ= 44.8° with broad Ni(111) peak was observed for NiNP-Sn/AIOH catalyst in Figure 1(c). According to the report of Xie et al., [17] and the crystallographical database, we conclude that the peak at 2θ= 44.8° can be assigned to Ni-Sn alloy.

CATALYTIC REACTIONS

First, we carried out the hydrolysis of sucrose in hot water under H₂ pressure in the absence of a catalyst at particular reaction conditions. The results showed that almost all of the sucrose was hydrolysed to glucose and fructose through the reaction shown in Scheme 1 part A.

CATALYTIC REACTION OVER VARIOUS CATALYST

Table 2 shows the performance of various Raney-Ni catalysts in the hydrogenolysis of sucrose. Raney-Ni catalysts showed a high conversion of ca. 94%, 87 mol% total yield and 96 mol% and 4% selectivities for hexitols (H) (sorbitol and mannitol) and glycerol (G), respectively (Table 2, entry 2). Surprisingly, nickel nanoparticles supported on aluminium hydroxide (NiNP/AIOH) catalyst also exhibited a high conversion of ca. 99 %, 97 mol% total yield and 99 mol% selectivity for ethenyl alcohol (EG) (entry 3). On the other hand, the hydrolysis of sucrose in absence of the catalyst gave 67% conversion and 67% yield of fructose and glucose (entry 1). It is intriguing that over NiNP-Sn/AIOH catalyst, at high conversion ca. >99% yielded the hydrogenolized products such as glycerol, ethylene glycol, and ethanol.

Table 2 Hydrogenolysis of sucrose using various catalysts
with selectivities of 30%, 21%, and 1%, respectively (entry 4).

**EFFECT OF REACTION TEMPERATURES**

Therefore, to further elucidate the performance of the NiNP-Sn catalyst, the hydrogenolysis of sucrose under various conditions was carried out and the results are summarized in Table 3. We found that the conversion of sucrose could be kept at ~100% with a further increase of the reaction temperature, although the total yield of polyols such as hexitols and polyols, H=hexitol (sorbitol + mannitol), EG=ethylene glycol, G=glycerol and EtOH=ethanol. No hydrogenated product was detected.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
<th>Selectivity (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>H</td>
<td>G</td>
</tr>
<tr>
<td>1</td>
<td>No catalyst</td>
<td>67</td>
<td>67</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Raney-Ni</td>
<td>94</td>
<td>87</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>NiNP/AIOH</td>
<td>99</td>
<td>97</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>NiNP-Sn/AIOH</td>
<td>&gt;99</td>
<td>96</td>
<td>48</td>
</tr>
</tbody>
</table>

* Reaction conditions: catalyst: 0.05 g, sucrose: 0.1 g (3.0 mmol), H2O:5 ml, H2: 2 MPa, at 24 h and 403 K; b) Total yield of liquid products included hexitol and polyols. H=hexitol (sorbitol + mannitol), EG=ethylene glycol, G=glycerol and EtOH=ethanol.

The distribution of the products at the different reaction temperatures, a higher temperature is helpful in the cleavage of C–C bonds, whereas it inhibits the cleavage of the C–O bonds. Additionally, further degradation of hexitols and diols is known to happen at higher reaction temperatures.

As shown in Scheme 1, there are two possible reaction pathways in the aqueous phase hydrogenolysis of sucrose over the NiNP-Sn/AIOH catalyst. First, sucrose is hydrolysed to glucose and fructose (path A) and then hydrogenated to hexitols (sorbitol and mannitol) in situ (path B). Some of the hexitols may be further decomposed to smaller compounds such glycerol, ethylene glycol and ethanol through C-C bond cleavage (path C). To confirm this proposed reaction path, we examined the hydrogenolysis of sorbitol and mannitol under the same reaction conditions (Table 4). The results showed that ethylene glycol was exclusively formed from sorbitol, whereas mannitol gave only glycerol. The hydrogenolysis of glycerol under the same reaction conditions showed little production of ethylene glycol and ethanol. Second, the hexitols products could be hydrogenolyzed directly to glycerol, ethylene glycol and ethanol. In the hydrogenation of glucose and fructose, the products were hexitols, glycerol, ethylene glycol and ethanol (path D). We also carried out the hydrogenolysis...
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Table 4 Performance of NiNP-Sn/AlOH catalyst with various substrates

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Conv. (%)</th>
<th>Yield (mol%)</th>
<th>Selectivity (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fructose</td>
<td>94</td>
<td>92</td>
<td>46</td>
</tr>
<tr>
<td>2</td>
<td>Glucose</td>
<td>&gt;99</td>
<td>97</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>Sorbitol</td>
<td>13</td>
<td>11</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Mannitol</td>
<td>10</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Glycerol</td>
<td>2</td>
<td>1</td>
<td>-</td>
</tr>
</tbody>
</table>

a) Reaction conditions: catalyst: 0.05 g, H2O: 5 ml, H2: 2 MPa, for 24 h at 403 K. b) Total yield of liquid products was hexitol and polyols. H=hexitol (sorbitol + mannitol), EG=ethylene glycol, G=glycerol and EtOH=ethanol. c) Reaction time of 9 h.

Table 5. Effect of initial H2 pressure on the hydrogenolysis of sucrose over the NiNP-Sn/AlOH catalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>H2/MPa</th>
<th>Conv. (%)</th>
<th>Yield (mol%)</th>
<th>Selectivity (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>79</td>
<td>72</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>&gt;99</td>
<td>70</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>&gt;99</td>
<td>96</td>
<td>48</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>&gt;99</td>
<td>85</td>
<td>31</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>&gt;99</td>
<td>78</td>
<td>31</td>
</tr>
</tbody>
</table>

a) Reaction conditions: catalyst: 0.05 g, sucrose: 0.1 g (3.0 mmol), H2O: 5 ml, 403 K, 24 h. b) Total yield of liquid products included hexitol and polyols. H=hexitol (sorbitol + mannitol), EG=ethylene glycol, G=glycerol and EtOH=ethanol. (30%), and ethylene glycol (22%) (Table 5, entry 3).

**CONCLUSION**

In conclusion, a new and efficient catalytic route for the production of hexitols (sorbitol + mannitol), glycerol and ethylene glycol by catalytic hydrogenolysis of sucrose using nickel-tin nanoparticles supported on aluminium hydroxide (NiNP-Sn/AlOH) catalyst has been developed. A simple and environmentally friendly preparation of NiNP/AlOH with and without the addition of tin species as a promoter led to high activity and selectivity in the aqueous phase hydrogenolysis under mild conditions. It was interesting to find that the NiNP/AlOH and NiNP-Sn/AlOH catalysts could be easily recovered from the reaction mixture by filtration, and the catalyst could be conveniently reused without any further treatment.

**ACKNOWLEDGMENT**

Rodiansono would like to express thank to Dr. Eng. Y. Oogaki for the kind help in measurement of the catalytic reaction results.

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