Catalytic properties of bimetallic NiNP-M/AIOH (M = Sn, In, Ga, Ag, Nb, and Zr) on selective hydrogenation of furfural

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Abstract

A series of bimetallic NiNP-M/AIOH (M = Sn, In, Ga, Ag, Nb, and Zr) catalysts have been synthesised by a simple hydrothermal of the mixture of nickel nanoparticles supported aluminium hydroxide (NiNP/AIOH) and a salt solution containing those of the above metals at 423 K for 2 h. The synthesised catalysts were characterised by using ICP-AES, TG-DTA, XRD, N2-adsorption, and H2-chemisorption. The catalytic properties were evaluated on the selective hydrogenation of furfural (FFald) at 453 K for 90 minute. Reactant and products were characterised by GC, GC-MS, and 1H NMR. The presence of the second metal remarkably reduced the crystallite sizes of Ni metal as indicated by the broadened diffraction peak of Ni(111) species compared to the former of NiNP/AIOH. H2-uptake of Ni-M/AIOH also was lower than that of NiNP/AIOH. NiNP-Sn/AIOH and NiNP-In/AIOH catalysts showed extremely high selective hydrogenation towards furfuryl alcohol (FFalc) with almost 99% yield. We expect that the high activity and selectivity over Ni-Sn/AIOH and Ni-In/AIOH catalysts due to the formation of Ni-Sn or Ni-In alloys. On the other hand, NiNP-M/AIOH (M= Ga, Nb, Ag, Zr, and Ga) catalysts showed lower the catalytic activity than that of NiNP/AIOH catalyst. Therefore, further investigation of role of the second metal on the catalytic properties of NiNP-M/AIOH (M = Sn and In) catalysts is under progress.

Keywords: bimetallic catalysts, Ni-Sn alloy, Ni-In alloy, selective hydrogenation, furfural

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Introduction

Selective hydrogenation of furfural (FFald) to furfuryl alcohol (FFalc) is great industrial interest since it widely use in various applications[1]. Industrially, furfuryl alcohol was produced by liquid hydrogenation of furfural at the high temperature and H2-pressure by using copper-chronomite (Cu-Cr) catalysts which exhibits moderate in activity and selectivity. The main drawbacks of this catalyst system are toxicity and unrecyclable due to generated Cr2O3 and severe leaching of the metal into product[2-3]. Therefore, several attempts have been reported in order to replace Cu-Cr catalysts or to develop a new metallic catalyst system which have more efficient catalytic process and less severe of environmental problem.

Among developed metal catalysts, nickel-based catalyst with metal co-promotor or modified supports has been studied intensively due to its high activity for hydrogenation both of C=C and C=O. Several metal co-promoters were applied such as Cu [4, 8], Fe, Ce [5-7], and Sn [10] in order to improve its chemoselectivity towards C=O rather than to C=C. In this advantage, system based on Ni modified with Fe, Ce or heteropolyacids have been proved to be successful, reaching 98% selectivity to FFA at almost total conversion [5-8]. However, in some cases these modified nickel catalysts cannot reuse [4] and also showed moderate in activity or selectivity [10]. Recently, Merlo et al. reported that tin modified of Pt/SiO2 catalyst showed 96% selectivity to furfuryl alcohol and required 6 h to reach a complete reaction[9]. Moreover, the employing of noble metal catalyst is less favourable in economical advantageous. Therefore, the design less expensive the active and selective catalyst system for production furfuryl alcohol is an issue of interest, which still presents great challenges.

We recently have reported the chemoselective hydrogenation of FFald and various unsaturated carbonyl compounds over Ni-Sn catalysts both bulk and supported. The chemoselectivity of Ni-Sn alloy...
catalysts in C=O hydrogenation could be controlled by changing the additive amount of Sn [11-14]. In the present work, we try to describe the catalytic performances of our NINP-Sn and NINP-M (M = In, Ga, Ag, Nb, and Zr) catalysts that were obtained according to the previous reported [11] in the selective hydrogenation of FFald to FFalc. XRD investigations and its catalytic reactions on the catalytic conversion of biomass-derived furfural will be discussed.

Methodology

Materials

Raney Ni-Al alloy ((50 wt% of Ni and 50 wt% of Al) Kanto Chemical Co. Inc.), NaOH (97%, WAKO), InCl₃·2H₂O (99.9%, WAKO), GaCl₃ (99.99%, Sigma-Aldrich), AgNO₃ (99.9%, Merck), NbCl₅·2H₂O (99.9%, WAKO), ZrCl₄·5H₂O (99.9%, WAKO), and SnCl₂·2H₂O (99.9%, WAKO) were purchased and used as received. All organic chemical compounds were purified using standard procedures prior to use.

Catalyst preparation

Synthesis of NINP/AIOH

Typical procedure of the synthesis of nickel nanoparticles supported on aluminium hydroxide catalyst (denoted as NINP/AIOH) is described as follows [11, 15, 16]: Raney Ni-Al alloy powder (1.0 g) was slowly added to a dilute aqueous solution of NaOH (0.31 M, 8 mL) at room temperature. The temperature was raised to 363 K and 1 mL of 3.1 M NaOH solution was subsequently added and stirred for 30 min. The mixture was placed into a sealed-Teflon autoclave reactor for hydrothermal treatment at 423 K for 2 h. The resulting precipitate was filtered, washed with distilled water until filtrate was neutralized, and then stored in water. The catalyst was dried under vacuum before the catalytic reaction.

Synthesis of NINP-Sn/AIOH

Typical procedure of the syntheses of the as prepared nickel-tin alloy supported on aluminium hydroxide catalyst (denoted as NINP-Sn/AIOH) is described as follows [11]. R-Ni/AIOH that was obtained from the above procedure was mixed with a solution that contained 3.96 mmol SnCl₂·2H₂O at room temperature and stirred for 2 h. The mixture was placed into a sealed-Teflon autoclave reactor for the hydrothermal treatment at 423 K for 2 h. The resulting precipitate was filtered, washed with distilled water, and dried under vacuum overnight. The as prepared nickel-tin nanoparticles alloy supported on aluminium hydroxide (NINP-Sn/AIOH) was intentionally treated by hydrogen at 673 K and produced the H₂-treated NINP-Sn/AIOH alloy catalyst.

Catalyst characterization

Powder X-ray diffraction (XRD) measurements were recorded on a Mac Science M18XHF instrument using monochromatic CuKa radiation (λ = 0.15418 nm). The XRD was operated at 40 kV and 200 mA with a step width of 0.02° and a scan speed of 4°min⁻¹ (α1 = 0.154057 nm, α2 = 0.154433 nm). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements were performed on an SPS 1800H plasma spectrometer by Seiko Instruments Inc. Japan (Ni: 221.7162 nm and Sn: 189.898 nm). The BET surface area (S_BET) and pore volume (V_p) were measured using N₂ 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 [17]. Scanning electron microscopy (SEM) images of the synthesised catalysts were taken on a JEOL JSM-610 SEM after the samples were coated using a JEOL JTEC-1600 autofine coater.

The H₂ uptake was determined through irreversible H₂ 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. The catalysts were subsequently cooled to room temperature under vacuum for 30 min. The H₂ measurement was conducted at 273 K, and H₂ uptake was calculated according to the method described in the literature [18, 19].

Catalytic reaction

Catalyst (0.05 g), FFald (1.1 mmol), and iso-PrOH (2 mL) as solvent were placed into a glass reaction tube, which fitted inside a stainless steel reactor. After H₂ was introduced into the reactor with an initial H₂ pressure of 3.0 MPa at room temperature, the temperature of the reactor was increased to 453 K. After 75 min, the conversion of FFald and the yield of FFalc were determined via GC analysis. The NINP-Sn/AIOH catalyst was easily separated using either simple centrifugation or filtration. The solvent was removed in vacuo, and the residue was purified via silica-gel column chromatography.

Analytical GLC was performed by a Shimadzu GC-8A with a flame ionization detector equipped with Thermon-3000 packing. GC-MS was performed by a Shimadzu GC-17B with a thermal conductivity detector equipped with an RT-DEXs capillary column. Products were confirmed by the comparison of their GC retention time, mass, ¹H NMR and ¹³C NMR spectra with those of authentic samples.

Results and Discussion
The bulk composition of the catalysts was determined by using ICP-AES as summarized in Table 1. A series NiNP-M/AlOH with different metal co-promotors was successful prepared by simple impregnation of aqueous solution of metal chloride salt. The presence of aluminium hydroxide could cause the dispersion of Ni species in NiNP/AlOH or NiNP-M/AlOH, respectively.

Figure 1 shows the XRD patterns of Raney-Ni, NiNP/AlOH and NiNP-Sn/AlOH catalysts. Raney Ni showed diffraction peaks at 2θ = 44.3 and 51.6°, corresponding to Ni(111) and Ni(200), respectively. For NiNP/AlOH and NiNP-Sn/AlOH, 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°[15] were identified, confirming the presence of more Al(OH)₃ in NiNP/AlOH and NiNP-Sn/AlOH. XRD characterization reveals that in NiNP/AlOH and NiNP-Sn/AlOH, metallic Ni was dispersed in gibbsite and bayerite, which could be recognized as a Ni-Al(OH)₃ composite catalyst [20]. Furthermore, a broadened peak at 2θ= 44.8° with broad Ni(111) peak was observed for NiNP-Sn/AlOH catalyst in Figure 1(c).

Table 1. Chemical composition of R-Ni, NiNP/AlOH and NiNP-M/AlOH catalyst (M = Sn, In, Ag, Nb, and Zr)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Ni⁰/ mmolg⁻¹</th>
<th>M⁰/ mmolg⁻¹</th>
<th>Ni⁰/nm</th>
<th>Molar ratio Ni/Al</th>
<th>M/Ni</th>
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<tr>
<td>1</td>
<td>R-Ni</td>
<td>3.98</td>
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<td>7.9</td>
<td>6.37</td>
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<tr>
<td>2</td>
<td>NiNP/AlOH</td>
<td>3.46</td>
<td>-</td>
<td>6.3</td>
<td>0.91</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>NiNP-Sn/AlOH</td>
<td>3.09</td>
<td>1.04</td>
<td>4.2</td>
<td>0.64</td>
<td>0.34</td>
</tr>
<tr>
<td>4</td>
<td>NiNP-In/AlOH</td>
<td>3.01</td>
<td>1.14</td>
<td>4.8</td>
<td>0.86</td>
<td>0.37</td>
</tr>
<tr>
<td>5</td>
<td>NiNP-Ga/AlOH</td>
<td>3.23</td>
<td>1.08</td>
<td>5.0</td>
<td>0.78</td>
<td>0.33</td>
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<td>6</td>
<td>NiNP-Ag/AlOH</td>
<td>3.78</td>
<td>1.16</td>
<td>5.2</td>
<td>0.69</td>
<td>0.31</td>
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<td>7</td>
<td>NiNP-Nb/AlOH</td>
<td>3.21</td>
<td>1.21</td>
<td>5.2</td>
<td>0.72</td>
<td>0.38</td>
</tr>
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<td>8</td>
<td>NiNP-Zr/AlOH</td>
<td>3.28</td>
<td>1.13</td>
<td>5.4</td>
<td>0.59</td>
<td>0.34</td>
</tr>
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</table>

*Determined by ICP-AES. The value in the parenthesis indicates the Sn/Ni molar ratio. The average crystallite size of Ni was calculated from the full width at the half maximum (FWHM) of the Ni (111) diffraction peak according to the Scherer equation.

Figure 1. XRD patterns of (a) Raney Ni, (b) NiNP/AlOH, and (c) NiNP-Sn/AlOH catalysts.

Figure 2. XRD patterns of the synthesised NiNP-M/AlOH (M = In, Ag, Ga, Nb, and Zr) catalysts as-prepared. (a) NiNP-In/AlOH, (b) NiNP-Ag/AlOH, and (c) NiNP-Ga/AlOH, (d) NiNP-Nb/AlOH, (e) NiNP-Zr/AlOH.
The XRD patterns of the as prepared NiNP-M/AlOH and H2-treated Ni-M(1.0) catalysts are shown in Figure 2 and Figure 3, respectively. As shown in Figure 2, the as prepared Ni-M/AlOH also showed the sharp diffraction peaks at same position to the Ni-Sn/AlOH system as has been already showed in Figure 1. After H2 treatment at 673 K, the evolution of Ni-Sn alloy phase formation was observed at 2θ of 30.3°, 38.6°, 43.5°, 44.6° and 44.8° that recognised as Ni5Sn3(101), Ni6Sn3(102), Ni6Sn3(110), and Ni6Sn3(203), respectively [20] (Figure 3a). On the other hand, the diffraction peaks of bayerite and gibbsite completely disappeared after H2 treatment at 673 K indicating the transformation of crystalline bayerite or gibbsite into amorphous alumina which have no detectable peaks in XRD analysis [21, 22]. In the case of NiNP-In/AlOH and NiNP-Nb/AlOH, the formation of Ni-In or Ni-Nb alloy phases were not observed by using XRD measurement. In addition, the diffraction peaks of Ni metal at 2θ of 51.6° and 76.2° corresponding to Ni(200) and Ni(220) were also observed (Figure 3a-c).

Hydrogenation of furfural

Results of the selective hydrogenation of FFald using Ni-M/AlOH catalysts are summarized in Table 2 and the reaction pathways are shown in Scheme 1.

It can be observed that by using Raney Ni catalyst, 99.6% of FFald was converted and gave selectivity of FFalc and THFalc 49% and 51%, respectively (entry 1). On the other hand, R-Ni/AlOH converted FFald to give >98.4% THFalc (entry 2), indicating that R-Ni/AlOH hydrogenated both C=C and C=O of FFald. Moreover, Sn/AlOH was not active as catalysts and did not produce the hydrogenated products under the same conditions (entry 3). By using Ni-Sn/AlOH catalysts, FFalc yield was 91% while tetrahydrofurfuryl alcohol (THFalc) yield was 3.26%, respectively (entry 4). The hydrogenation of furfuryl alcohol only gave 8.7% conversion at the same reaction conditions (entry 5). In the case of NiNP-In/AlOH catalyst, the selectivity towards FFalc and THFalc were 94% and 6%, respectively (entry 6), while over NiNP-Ga/AlOH, NiNP-Ag/AlOH, and NiNP-Nb/AlOH catalysts gave low conversion of FFald and low selectivity towards FFalc (entries 7-9). Moreover, NiNP-Zr/AlOH showed high conversion of FFald (>99%) with almost the product was THFalc (entry 10). Therefore, we conclude that the formation of a Ni-Sn alloy may facilitate in the adsorption mode of the FFald molecule through the C=O group, giving rise to much higher yields and selectivity of FFalc rather than THFalc. These results are consistent with the fact that no tetrahydrofurfuryl aldehyde (THFald) was observed in all the catalytic results. Therefore, we speculate that FFald hydrogenation by NiNP-Sn/AlOH and NiNP-In/AlOH catalysts do not proceed via THFald due to the formation of the Ni-Sn alloy (Scheme 1).

The H2-treatment of the as prepared NiNP-M/AlOH at 673 K and evaluation of its catalytic performances in furfural hydrogenation were carried out. The conversion, yield, and selectivity, are summarised in Table 3.

It can be seen that over H2-treated NiNP-Sn/AlOH and NiNP-In/AlOH catalysts, FFald was completely converted into FFalc (>99% yield) whereas THFalc was retained (~1.0% yield) (entries 1 and 2). On the other hand, hydrogenation of FFald over H2-treated NiNP-Ga/AlOH, NiNP-Ag/AlOH, NiNP-Nb/AlOH, and NiNP-Zr/AlOH resulted almost >99% selectivity towards THFalc (entries 3-6). In addition, hydrogenolysed products of 1,2-pentanediol and 1,5-pentanediol were observed over H2-treated NiNP-Nb/AlOH and NiNP-Zr/AlOH catalysts as indicated in other products (entries 5 and 6). These results are consistent with the previous works that the formation of Ni-Sn or Ni-In alloy phases are believed to be responsible for the high chemoselectivity towards C=O bond [11, 12].
Table 2. Catalytic hydrogenation of furfural by means of various catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv.</th>
<th>Y_{FFalc}</th>
<th>Y_{THFalc}</th>
<th>S_{FFalc}</th>
<th>S_{THFalc}</th>
<th>Other*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Raney-Ni</td>
<td>99.6</td>
<td>98.9</td>
<td>49.0</td>
<td>51.0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>NiNP/AlOH</td>
<td>87.9</td>
<td>84.0</td>
<td>1.6</td>
<td>98.4</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Sn/AlOH</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>NiNP-Sn/AlOH</td>
<td>95.0</td>
<td>94.2</td>
<td>96.6</td>
<td>3.4</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>5c</td>
<td>NiNP-Sn/AlOH</td>
<td>8.7</td>
<td>5.2</td>
<td>-</td>
<td>100</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>NiNP-In/AlOH</td>
<td>60.8</td>
<td>60.8</td>
<td>94.0</td>
<td>6.0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>NiNP-Ga/AlOH</td>
<td>12.8</td>
<td>12.0</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td></td>
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<tr>
<td>8</td>
<td>NiNP-Ag/AlOH</td>
<td>44.9</td>
<td>43.8</td>
<td>31</td>
<td>69</td>
<td>0</td>
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<td>9</td>
<td>NiNP-Nb/AlOH</td>
<td>47.3</td>
<td>45.3</td>
<td>26</td>
<td>74</td>
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<td></td>
</tr>
<tr>
<td>10</td>
<td>NiNP-Zr/AlOH</td>
<td>&gt;99</td>
<td>96.0</td>
<td>0</td>
<td>100</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

*Reaction conditions: catalyst (50 mg), furfural (1 mmol), isopropyl alcohol (3 mL), H₂ 2 MPa, 1 h, 453 K. The hydrogenolysed product based on GC and GC-MS analyses.

Table 3. Catalytic hydrogenation of FFald over H₂-treated NiNP-M/AlOH catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv.</th>
<th>Y_{FFalc}</th>
<th>Y_{THFalc}</th>
<th>S_{FFalc}</th>
<th>S_{THFalc}</th>
<th>Others*</th>
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<tbody>
<tr>
<td>1</td>
<td>NiNP-Sn/AlOH</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>99</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>NiNP-In/AlOH</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>NiNP-Ga/AlOH</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>NiNP-Ag/AlOH</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>0</td>
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<tr>
<td>5</td>
<td>NiNP-Nb/AlOH</td>
<td>&gt;99</td>
<td>94</td>
<td>5</td>
<td>95</td>
<td>6</td>
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</tr>
<tr>
<td>6</td>
<td>NiNP-Zr/AlOH</td>
<td>&gt;99</td>
<td>83</td>
<td>2</td>
<td>98</td>
<td>16</td>
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</table>

*Reaction conditions: catalyst (50 mg), furfural (1 mmol), isopropyl alcohol (3 mL), H₂ 2 MPa, 1 h, 453 K. The hydrogenolysed product based on GC and GC-MS analyses.

Conclusion

Ni-Sn/AlOH and Ni-In/AlOH catalysts both as prepared and H₂-treated showed extremely high selective hydrogenation towards furfuryl alcohol (FFalc) with almost 99% yield. We expect that the high activity and selectivity over Ni-Sn/AlOH and Ni-In/AlOH catalysts due to the formation of Ni-Sn or Ni-In alloys. On the other hand, Ni-M/AlOH (M= Nb, Ag, Zr, and Ga) catalysts showed lower the catalytic activity than that of NiNP/AlOH catalyst.

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