

TOTAL HYDROGENATION OF BIOMASS-DERIVED FURFURAL OVER RANEY NICKEL-CLAY NANOCOMPOSITE CATALYSTS

Rodiansono^{1,*}, Takayoshi Hara², and Shogo Shimazu²

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Lambung Mangkurat, Jl. A. Yani Km 35.8 Banjarbaru South Kalimantan 70713

²Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, University of Chiba, Jl. Yayoi-cho, Inage-ku, Chiba-shi, Chiba Japan 263-8522

Received December 5, 2012; Accepted February 17, 2013

ABSTRACT

Inexpensive Raney Ni-clay composite (R-Ni/clay) catalysts exhibited excellent activity and reusability in the total hydrogenation of biomass-derived furfural into tetrahydrofurfuryl alcohol under mild conditions. For the Raney Ni-bentonite (R-Ni/BNT) catalysts, the complete reaction was achieved at 393 K, 180 min giving almost 99% yield of tetrahydrofurfuryl alcohol. The R-Ni/BNT catalyst was found to be reusable without any significant loss of activity and selectivity for at least six consecutive runs.

Keywords: Raney Ni; clay-composite; total hydrogenation; furfural; furfuryl alcohol; tetrahydrofurfuryl alcohol

ABSTRAK

Katalis murah komposit Raney Ni-lempung (R-Ni/lempung) telah menunjukkan aktivitas dan dapat dipakai berulang-ulang untuk reaksi hidrogenasi total dari senyawa turunan biomasa furfural menjadi tetrahidrofurfural alkohol pada kondisi reaksi yang ringan. Untuk katalis Raney Ni-lempung bentonit (R-Ni/BNT), reaksi yang sempurna telah dicapai pada 393 K, 180 menit menghasilkan hampir 99% tetrahidrofurfural alkohol. Katalis R-Ni/BNT juga menunjukkan dapat dipakai berulang-ulang hingga enam kali reaksi berturut-turut tanpa kehilangan aktivitas dan selektivitasnya.

Kata Kunci: Raney Ni; lempung-komposit; hidrogenasi total; furfural; furfural alkohol; tetrahidrofurfural alkohol

INTRODUCTION

The hydrogenation of biomass-derived furfural (2-furaldehyde, FFald) into more valuable chemical products has been put a great interest to substitute for petroleum as source of chemical products. Furfural is currently too expensive for use as a fuel and its tendency to polymerize [1-2]. Furfural can be obtained from the triple acidic dehydration of xylose of the hemicellulose biomass fraction. Industrially, more than 300,000 metric tons/year of FFald are produced [3]. The hydrogenated product such as furfuryl alcohol (FFalc) and tetrahydrofurfuryl alcohol (THFalc) have been also studied to produce more valuable compounds such as levulinic acid, levulinate ester, and α,ω diols [4-6]. FFald also can be converted into methylfuran (MTF) and methyltetrahydrofuran (MTHF), important compound for gasoline-blended. In addition, its conversion into various valuable chemicals meets the current fashion for making chemicals from biomass resources [7-8].

Nickel-based catalyst is the most commonly used in hydrogenation of FFald both in liquid phase and vapor

phase reaction. Merat et al. evaluated the commercial supported nickel catalyst in liquid phase hydrogenation of FFald to FFalc with low in activity and selectivity. Only mixture of Ni- and Cu-supported catalyst led to the best results. However, the copper-based catalysts are toxic and unrecyclable [9]. Other modified Ni-based catalysts have been also reported in term of the enhancement of the activity and stability, for example, amorphous Ni-B doped by cobalt [10], ceria and iron [7], bimetallic Ni-Cu supported [8] and Raney-type nickel catalyst [12].

It has been known that Raney nickel (R-Ni) catalyst has a high activity and selectivity in field of hydrogenation reaction. However, one of important drawback is pyrophoricity. Therefore several methods for reducing the pyrophoricity have been reported. The pyrophoricity could be eliminated by removing the adsorbed hydrogen or by addition of the non-precious metal co-promotor (e.g. Fe, Mo, Cr and Sn) to the NiAl alloy or during the preparation of Raney-Ni. The addition of the metal co-promotor not only reduced the pyrophoricity but also enhanced the activity and

* Corresponding author. Tel/Fax : +62- 511-478 3933
Email address : rodiansono@fmipa.unlam.ac.id

stability [13-18]. To reduce the pyrophoricity of Raney-Ni, Petro and co-workers prepared non-pyrophoric Raney-Ni catalyst that consisted of metallic Ni, gibbsite and bayerite [19-21]. Mahata and co-workers reported that the pyrophoricity of Raney-Ni could be eliminated by deposition of Ni species on the filamentous carbon or carbon that produced from methane under argon or helium atmosphere [22-24].

In the present study, we prepared Raney-Ni-clay composite by entrapping the nickel species into the space interlayer of clay structure via hydrothermal treatment under mild conditions in order to reduce the pyrophoricity and to improve the activity and stability in the total hydrogenation of biomass-derived FFald and other unsaturated carbonyl compounds.

EXPERIMENTAL SECTION

Materials

Raney NiAl alloy was purchased from Tokyo Chemical Industries Co. (TCI), sodium hydroxide (NaOH) was purchased and used as received from Wako Pure Chemical Industries, Ltd. Lithium-taeniolite (TN), Na-Bentonite (BNT), lithium hectorite (HT) and smectone SA (SMT) were donated by Kunimine Industries Co. Ltd. Furfural, furfuryl alcohol, tetrahydrofurfuryl alcohol, *iso*-propanol, ethanol were purchased from Tokyo Chemical Industries Co. (TCI). All organic chemical compounds were purified using standard procedures prior to use.

Instrumentation

The prepared catalyst was 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. 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 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 [25]. The H₂ uptake was determined

through irreversible H₂ chemisorption. After the catalyst was heated at 393 K under vacuum for 30 min, it was treated 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 [26].

Analytical GLC was performed on a Shimadzu GC-8A equipped with a flame ionisation detector and with Thermo 3000 and Silicone OV-101 packing. A Shimadzu 14A with a flame ionisation detector equipped with a RT- β DEXsa capillary column was used for product analyses of the hydrogenations of α,β -unsaturated aldehydes and ketones. GC-MS was performed on a Shimadzu GC-17B equipped with a thermal conductivity detector and with an RT- β DEXsm capillary column. ¹H and ¹³C NMR spectra were obtained on a JNM-AL400 spectrometer at 400 MHz; samples for NMR were dissolved in chloroform-*d*₁ with TMS as an internal standard. Products were confirmed by the comparison of their GC retention time, mass, ¹H and ¹³C NMR spectra with those of authentic samples.

Procedure

Preparation of Raney-Ni-clay composite

The Raney-Ni-clay composite catalysts were prepared by simple synthetic method. The clay materials that used in this research are lithium taeniolite (TN), lithium hectorite (HT), Na-bentonite (BNT, Kunipia F type), and anionic clay (hydrotalcite, HTLc). Raney-Ni was prepared by leaching NiAl alloy using concentrate aqueous solution of NaOH at room temperature for 2 h and then washed with deionized water and ethanol until the filtrate neutralized then the clay was added slowly and stirred for overnight at room temperature. The mixture was transferred into 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 Raney-Ni-clay composite was examined by heating up under air and it was found to be nonpyrophoric.

Total hydrogenation of furfural (FFald) and furfuryl alcohol (FFalc)

Catalyst (0.05 g), FFald (1.1 mmol), and *iso*-PrOH (3 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 2.0 MPa at room temperature, the temperature of the reactor was increased to 393 K. After 180 min, the product of the reaction was determined by GC analysis to calculate the conversion of FFald and the yield of FFalc. The R-Ni/BNT catalyst

Table 1. Physicochemical properties of the synthesized R-Ni clay composited catalysts

Entry	Catalyst	Ni ^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	104	151	11
2	R-Ni/BNT	3.67	111	30.8	6.9
3	R-Ni/TN	3.81	107	47.7	7.2
4	R-Ni/HTLc	3.89	101	60.3	7.6

^aDetermined 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). BNT = bentonite; TN = taeniolite; HTLc = hydrotalcite.

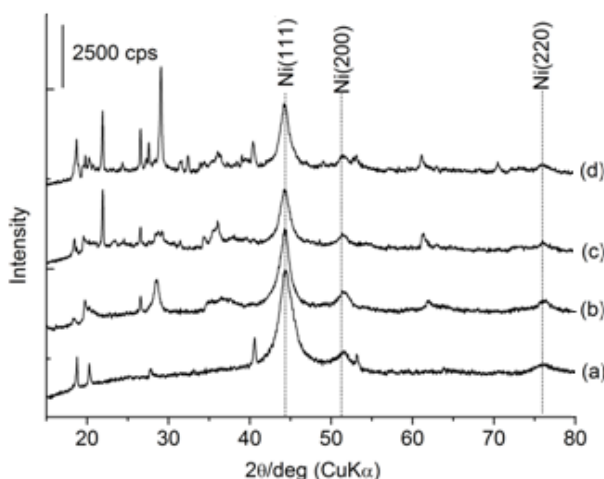


Fig 1. Powder X-ray diffraction (XRD) patterns of fresh Raney Ni-clay composited. (a) Raney Nickel (R-Ni), (b) R-Ni-bentonite (R-Ni/BNT), (c) R-Ni-taeniolite (R-Ni/TN), and (d) R-Ni-hydrotalcite (R-Ni/HTLc)

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.

Catalytic stability test

Catalytic stability test of R-Ni/BNT catalyst was performed on hydrogenation of FFald and FFalc until 6 runs. The used catalyst was separated by either simple centrifugation or filtration, washed with ethanol for 3 times (3 x 200 mL) then dried under vacua overnight for next reaction.

RESULT AND DISCUSSION

Catalyst Characterizations

Physicochemical properties

Three classes of the synthesized Raney Ni-clay composite were prepared by simple hydrothermal treatment of the mixture of Raney Ni that synthesized from Raney NiAl alloy using Petro's protocol [19-21] and clay (e.g. bentonite (BNT), taeniolite (TN), and hydrotalcite (HTLc)) under mild conditions. The

physicochemical properties of Raney Ni parents and Raney Ni-clay composite are summarized in Table 1.

Based on the ICP-AES analyses, the compositions of the parent Raney Ni and the synthesized Raney Ni-clay composite were approximately similar as shown in Table 1, entries 1-4.

The H₂ uptake, the BET surface area, and the average Ni crystallite sizes are also summarized in Table 1. The H₂ uptake of the synthesized Raney Ni-clay composite slightly increased for R-Ni/BNT (entry 2) and R-Ni/TN (entry 3), while the average Ni crystallite sizes of Raney Ni-clay composite (entries 2-4) decreased significantly. It can be concluded that the dispersion of Ni species on the BNT and TN higher than on the parent Raney Ni (entry 1).

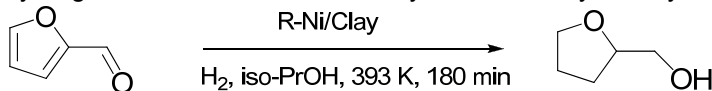
XRD analysis

The XRD patterns of the parent Raney-Ni and Raney Ni-clay composite are shown in Fig. 1. Three specific diffraction peaks of Ni species at 2θ of 44.2°, 51.6°, and 76.2° that corresponding to Ni(111), Ni(200), and Ni(220), respectively, clearly observed for each sample. The diffraction peak of Ni(111) of Raney Ni-clay composite slightly become broadened indicating the crystallite sizes of Ni(111) smaller than that of the parent Raney Ni one. The crystallite sizes of Ni(111) was calculate from the full width at half maximum (FWHM) of Ni(111) peak. For R-Ni was 11 nm, while for R-Ni/BNT, R-Ni/TN, and R-Ni/HTLc were 6.9 nm, 7.2 nm, and 7.6 nm, respectively (Table 1 entries 2-3). In addition, the crystal structure of the clay maintained even after the incorporation of Ni species via hydrothermal treatment. Therefore, Raney Ni-clay composites were successfully synthesized at relatively lower temperature using our simple method.

Catalytic Reactions

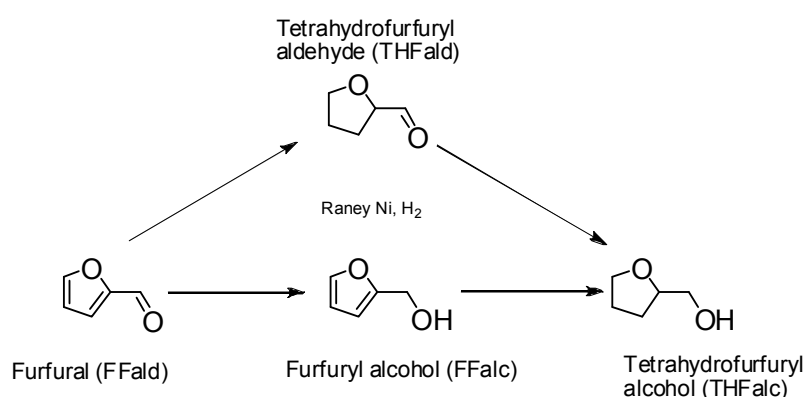
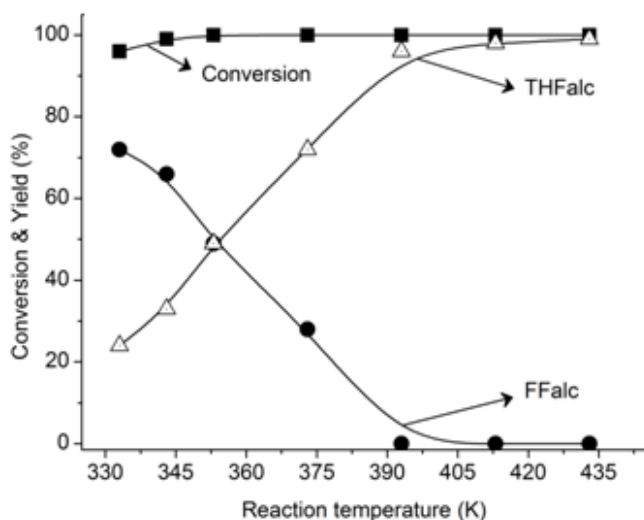
Catalytic reactions of various catalysts

Results for the total hydrogenation of furfural using Raney-Ni and Raney Ni-clay composite catalysts are summarized in Table 2, and the reaction scheme are shown in Scheme 1.

Table 2. Total hydrogenation of FFald over Raney Ni and Raney Ni-clay composite catalysts


Entry	Catalyst	Conversion (%)	Yield ^a (%)	Selectivity ^b (%)
1	R-Ni	99	99	49(51)
2	R-Ni/BNT	>99	>99	100(0)
3	R-Ni/TN	>99	>99	100(0)
4	R-Ni/HTLc	64	64	61(39)

Reaction conditions: FFald, 1.1 mmol (FFald/Ni ratio = 45); *iso*-PrOH (3 mL); H₂, 2.0 MPa, 393 K, 3 h. ^a Total Yield of FFalc and THFalc, determined by GC using an internal standard technique. ^b Selectivity to THFalc. The value in the parenthesis is the selectivity to FFalc. BNT = bentonite; TN = taeniolite; HTLc = hydrotalcite

**Scheme 1.** Proposed reaction pathway for total hydrogenation of furfural over Raney Nickel catalyst**Fig 2.** Effect of reaction temperature on the FFalc and THFalc yields over R-Ni/BNT catalyst. *Reaction conditions:* catalyst, 0.05 g (Ni/FFalc = 45); *iso*-PrOH, 3 mL, H₂, 2.0 MPa, 180 min

On the R-Ni catalyst, FFald conversion was 99% with a furfuryl alcohol (FFalc) yield of 48.5% (Table 2, entry 1), whereas, on the R-Ni/BNT and R-Ni/TN catalysts, >99 yields of THFalc were obtained without FFalc formation (Table 2, entries 2 and 3). In contrast,

the R-Ni/HTLc gave only 64% FFald conversion with selectivity of furfuryl alcohol and tetrahydrofurfuryl alcohol of 61% and 39%, respectively (Table 2, entry 4). Therefore, further investigation in total hydrogenation of furfural will be made for R-Ni/BNT and R-Ni/TN catalysts such as effect of reaction temperature, initial H₂ pressure, time profiles, and reusability.

Effect of reaction temperature

The influence of reaction temperature on the conversion of FFald and yield of THFalc over R-Ni/BNT catalyst is shown in Fig. 2. The yield of THFalc gradually increased while the yield of FFalc gradually decreased as temperature was increased, and complete formation of THFalc (~99%) was achieved at 393 K. It is clearly observed that at 333-343 K, the yield of FFalc (72%) higher than that of THFalc (24%) indicating hydrogenation of C=O bond is favorable rather than C=C bond. These results are consistent to our previous results on the chemoselective hydrogenation of furfural over Ni-Sn alloy catalysts [27-28].

Effect of initial H₂ pressure

The effect of the initial H₂ pressure on the FFald conversion and yield of FFalc and THFalc is shown in

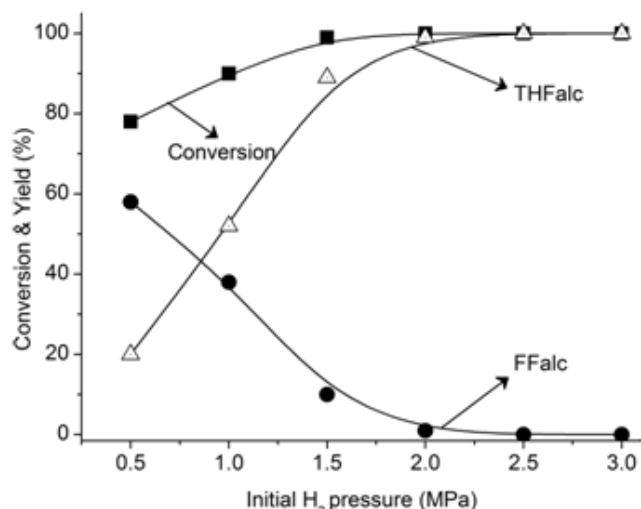


Fig 3. Effect of initial H₂ pressure on the FFalc and THFalc yields over R-Ni/BNT catalyst. *Reaction conditions:* catalyst, 0.05 g (Ni/FFalc = 45); iso-PrOH, 3 mL, reaction temp., 393 K, 180 min

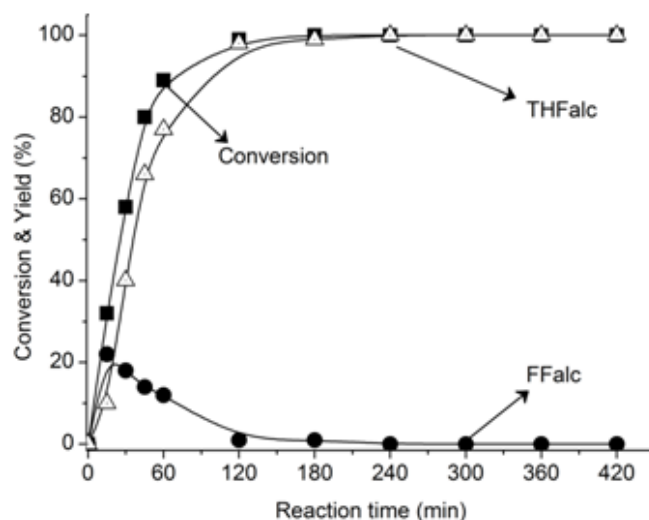


Fig 4. Time profile of the total hydrogenation of FFalc and THFalc yields over R-Ni/BNT catalyst. *Reaction conditions:* catalyst, 0.05 g (Ni/FFalc = 45); iso-PrOH, 3 mL, H₂, 2.0 MPa, 180 min

Table 3. Total hydrogenation of FFalc over Raney Ni and Raney Ni-clay composite catalysts

Entry	Catalyst	Conversion (%)	Yield ^a (%)
1	R-Ni	68	68
2	R-Ni/BNT	>99	>99
3	R-Ni/TN	>99	>99
4	R-Ni/HTLc	27	27

Reaction conditions: FFalc, 1.1 mmol (FFalc/Ni ratio = 45); iso-PrOH (3 mL); H₂, 2.0 MPa, 393 K, 3 h. ^a Yield of THFalc, determined by GC using an internal standard technique. The value in the parenthesis is the selectivity to FFalc. BNT = bentonite; TN = taeniolite; HTLc = hydrotalcite

Fig. 3. FFald conversion and THFalc yield gradually increased as the initial H₂ pressure increased, whereas the yield of FFalc decreased smoothly to almost 0% between 2.0 and 2.5 MPa.

Time profiles

The reaction profiles of FFald hydrogenation at 393 K on R-Ni/BNT catalysts are shown in Fig. 4. The conversion of FFald increased gradually to form FFalc and THFalc. The formation of FFalc was observed at the initial reaction then gradually decreased to almost 0% at 180 min, whereas the complete formation of THFalc (>99%) was achieved at the same time. In order to confirm the reaction route of the total hydrogenation of FFald over R-Ni/BNT catalyst under the same reaction conditions, hydrogenation of FFalc also carried out and the results are summarized in Table 3. R-Ni/BNT and R-Ni/TN catalysts gave >99% yield of THFalc after 180 min at 393 K (Table 3, entries 2 and 3). The parent R-Ni and

R-Ni/HTLc catalysts gave only 68% and 27% yield of THFalc under the same conditions (Table 3, entries 1 and 4). It is concluded that R-Ni/BNT and R-Ni/TN were superior in activity compared with the parent R-Ni catalyst.

The scope of the present R-Ni/BNT catalyst in the hydrogenation of various aldehydes and ketones was examined, as summarized in Table 4. Hydrogenation of the α,β -unsaturated aldehyde, cinnamaldehyde, over R-Ni/BNT yielded 92% phenyl propanol at 393 K for 360 min (entry 1). Cinnamyl alcohol yielded 95% phenyl propanol at 393 K for 360 min h (entry 2), cyclohexane carboxaldehyde yielded 95% cyclohexane methanol (entry 3), while crotonaldehyde yielded 91% butanol under the same conditions (entry 4). In the case of the hydrogenation of the α,β -unsaturated ketone, 2-cyclohexene-1-one, a 90% yield of cyclohexanol was obtained at 393 K for 360 min (entry 5). In addition, the hydrogenation of 3-cyclohexencarboxaldehyde yielded 99% 3-cyclohexenethanol at 393 K after 360 min (entry 6).

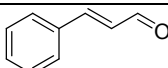
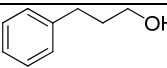
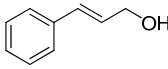
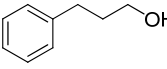
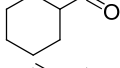
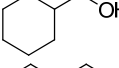
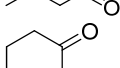
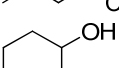
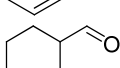
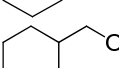
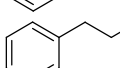
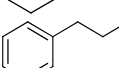
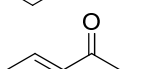
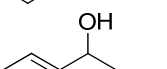
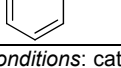
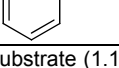
Hydrogenation of the aromatic aldehyde, 3-phenylpropanal, showed a high yield of aromatic alcohol (entry 7, 98%). Furthermore, hydrogenation of aromatic ketone, acetophenone, gave high yields of 1-phenylethanol (96%) at 393 K after 360 min (entry 8).

Reusability

A reusability test was performed on the R-Ni/BNT catalyst, and the results are summarized in Table 5.

The used R-Ni/BNT catalyst was easily separated by either simple centrifugation or filtration after the reaction. The activity of the catalyst maintained for at

Table 4. Hydrogenation of various ketones and aldehydes catalyzed by R-Ni/BNT catalyst^a

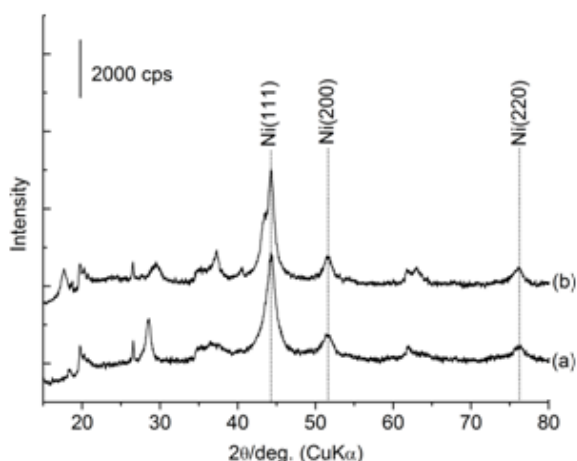
Entry	Substrate	Product	Convsn/% ^b	Yield/% ^c
1			94	92
2			99	95
3			>99	98
4			96	91
5			97	90
6			>99	99
7			>99	98
8			98	96

^a Reaction conditions: catalyst (0.05 g), substrate (1.1 mmol), *iso*-PrOH (3 mL), H₂ (2 MPa), 393 K, 360 min. ^b Conversion. ^c Yield, determined by GC using an internal standard technique

Table 5. Results of the reusability test for R-Ni/BNT catalyst in the total hydrogenation of FFald

Run ^a	1	2	3	4	5	6
Conversion (%)	>99	>99	99	99	99	99
Yield ^b (%)	>99	>99	99	99	99	99

Reaction conditions: FFald, 1.1 mmol (FFald/Ni ratio = 45); *iso*-PrOH (3 mL); H₂, 2.0 MPa, 393 K, 3 h. ^a The used catalyst was washed by ethanol and dried under vacua at room temperature without further treatment for next reaction. ^b Yield of THFald, determined by GC using an internal standard technique

**Fig 5.** Powder X-ray diffraction (XRD) patterns of fresh (a) and used (b) R-Ni-bentonite (R-Ni/BNT)

least six consecutive runs. The amount of Ni species that leached into the reaction solution was lower than the detection limit of the ICP-AES analysis and the XRD patterns of the recovered R-Ni/BNT are shown in Fig. 5.

The used catalyst can be used for the next reaction without any treatment.

The comparison of the XRD patterns of the fresh and recovered R-Ni/BNT is shown in Fig. 5. The diffraction profiles show that Ni species in R-Ni/BNT maintained after the sixth run and the intensity of Ni(111) was also similar to the fresh one.

CONCLUSION

Raney Ni-clay composite catalysts were successfully synthesized by simple procedure. The catalysts exhibited excellent activity and reusability in the total hydrogenation of biomass-derived furfural into tetrahydrofurfuryl alcohol. For the R-Ni/BNT catalysts, the complete reaction was achieved at 393 K, 180 min and gave almost ~99% yield of tetrahydrofurfuryl alcohol. The activity of the R-Ni/BNT catalyst maintained even after six consecutive runs. The recovered R-Ni/BNT catalyst can be used for the next reaction without any significant loss of activity and selectivity.

ACKNOWLEDGEMENT

First author would like to acknowledge to Dr. Eng. Indri Adilina Badria for fruitful discussions of ^1H and ^{13}C NMR data analyses.

REFERENCES

- Huber, G.W., Iborra, S., and Corma A., 2006, *Chem. Rev.*, 106, 9, 4044–4098.
- Corma, A., Iborra, S., and Velty, A., 2007, *Chem. Rev.*, 107, 6, 2411–2502.
- Montane, D., Salvado, J., Torras, C., and Farriol, X., 2002, *Biomass Bioenergy*, 22, 4, 295–304.
- Xu, W., Wang, H., Liu, X., Ren, J., Wang, Y., and Lu, G., 2011, *Chem. Commun.*, 47, 3924–3926.
- Lange, J.P., van de Graaf, W.D., and Haan, R.J., 2009, *ChemSusChem*, 2, 5, 437–441.
- Koso, S., Furikado, I., Shimao, A., Miyazawa, T., Kunimoria, K., and Tomishige, K., 2009, *Chem. Commun.*, 15, 2035–2037.
- Li, H., Luo, H., Zhuang, L., Dai, W., and Qiao, M., 2003, *J. Mol. Catal. A: Chem.*, 203, 267–275.
- Reddy, B.M., Reddy, G.K., Rao, K.N., Khan, A., and Ganesh, I., 2007, *J. Mol. Catal. A: Chem.*, 265, 1-2, 276–282.
- Merat, N., Godawa, C., and Gaset, A., 1990, *J. Chem. Technol. Biotechnol.*, 48, 2, 145–159.
- Luo, H., Li, H., and Zhuang, L., 2001, *Chem. Lett.* 404–405.
- Li, H., Zhang, S., and Luo, H., 2004, *Mater. Lett.*, 58, 2741–2746.
- Baijun, L., Lianhai, L., Bingchun, W., Tianxi, C., and Iwatani, K., 1998, *Appl. Catal. A*, 171, 1, 117–122.
- 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, *Appl. Catal. A*, 253, 2, 437–452.
- Hoffer, B.W., Crezee, E., Mooijman, P.R.M., van Langeveld, A.D., Kapteijn, F., and Moulijn, J.A., 2003, *Catal. Today*, 79-80, 35–41.
- Shabaker, J.W., Huber, G.W., and Dumesic, J.A., 2004, *J. Catal.*, 222, 1, 180–191.
- Shabaker, J.W., and Dumesic, J.A., 2004, *Ind. Eng. Chem. Res.*, 43, 12, 3105–3112.
- Shabaker, J.W., Simonetti, D.A., Cortright, R.D., and Dumesic, J.A., 2005, *J. Catal.*, 231, 1, 67–76.
- Huber, G.W., Shabaker, J.W., and Dumesic, J.A., 2003, *Science*, 300, 5628, 2075–2077.
- Petró, J., Bóta, A., László, K., Beyer, H., Kálmán, E., and Dódony, I., 2000, *Appl. Catal. A*, 190, 1-2, 73–86.
- Petró, J., Hegedüs L., and Sajó, I.E., 2006, *Appl. Catal. A*, 308, 50–55.
- Petró, J., US Patent 2000, 6, 153–554.
- Mahata, N., Cunha, A.F., Órfão, J.J.M., and Figueiredo, J.L., 2008, *Appl. Catal. A*, 351, 2, 204–209.
- Mahata, N., Cunha, A.F., Órfão, J.J.M., and Figueiredo, J.L., 2009, *Catal. Commun.*, 10, 1203–1206.
- Mahata, N., Cunha, A.F., Órfão, J.J.M., and Figueiredo, J.L., 2010, *ChemCatChem*, 2, 3, 330–335.
- Lowell, S., Shields, J.E., Thomas, M.A., and Thommes, M., *Characterization of porous solids and powders: surface area, pore size and density*, Kluwer Academic Publishers, Netherlands, 2004, Chapter 8.
- (a) Bartholomew, C.H., Pannel, R.B., and Butler J.L., 1980, *J. Catal.*, 65, 2, 335–347. (b) Bartholomew, C.H., and Pannel, R.B., 1980, *J. Catal.*, 65, 2, 390–401.
- Rodiansono, Hara, T., Ichikuni, N., and Shimazu, S., 2012, *Chem. Lett.*, 41, 769–771.
- Rodiansono, Hara, T., Ichikuni, N., and Shimazu, S., 2012, *Catal. Sci. Technol.*, 2, 2139–2145.