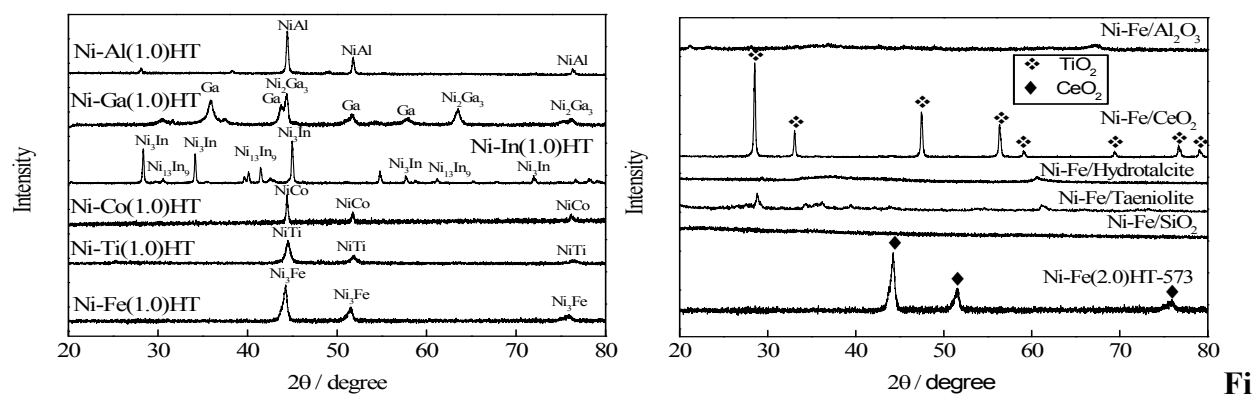


## Supporting Information

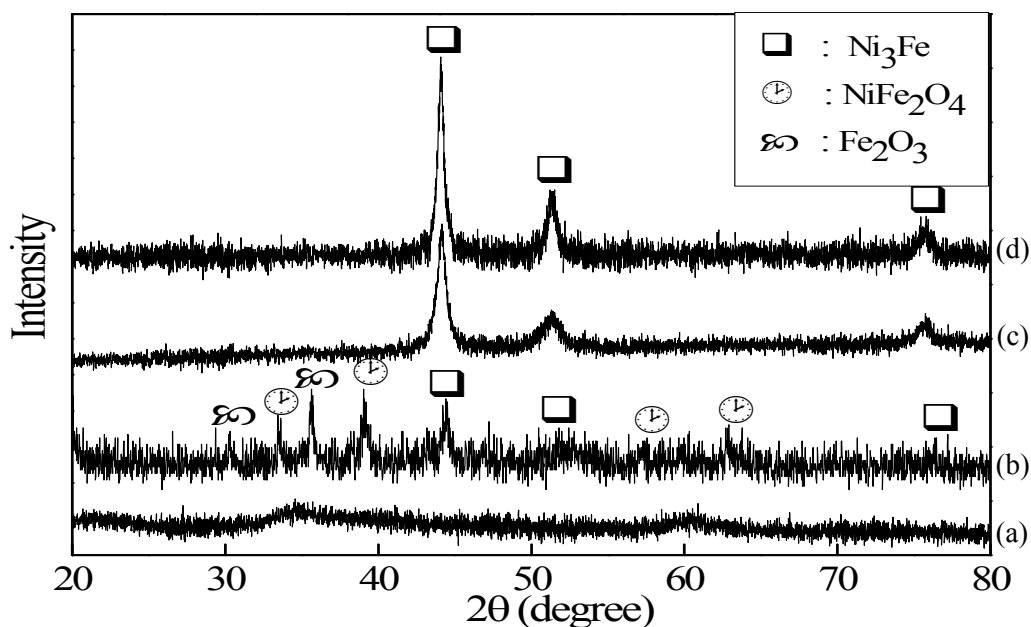
### Selective Hydrogenation of Unsaturated Carbonyls by Ni-Fe based Alloy Catalysts

Wahyu Satpriyo Putro,<sup>[a]</sup> Takashi Kojima,<sup>[a]</sup> Takayoshi Hara,<sup>[a]</sup> Nobuyuki Ichikuni,<sup>[a]</sup> and Shogo Shimazu\*<sup>[a]</sup>

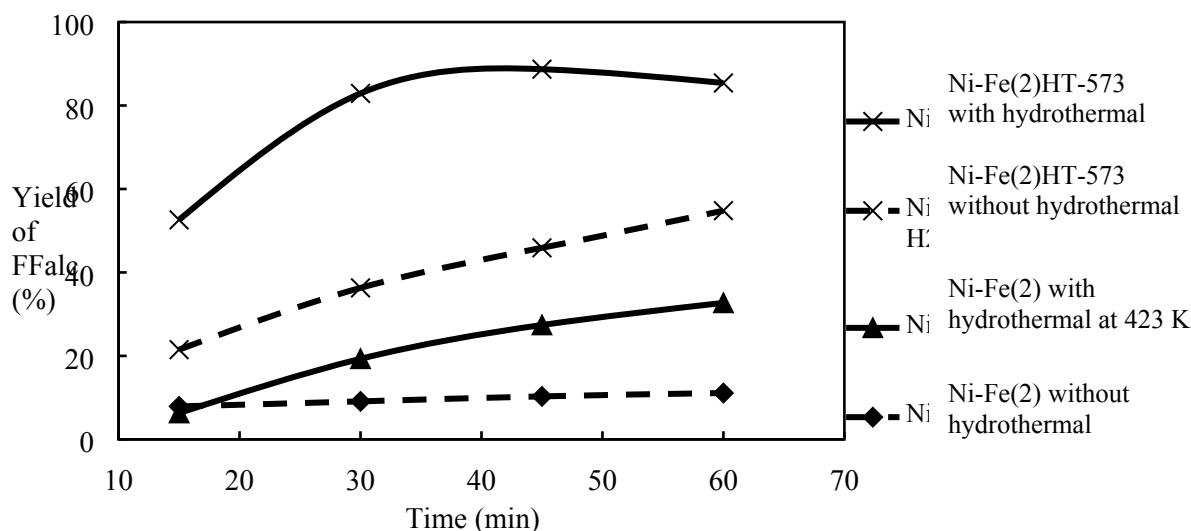
<sup>[a]</sup> Chiba University, Graduate School of Engineering, 1-33 Yayoi, Inage, Chiba 263-8522, Japan.



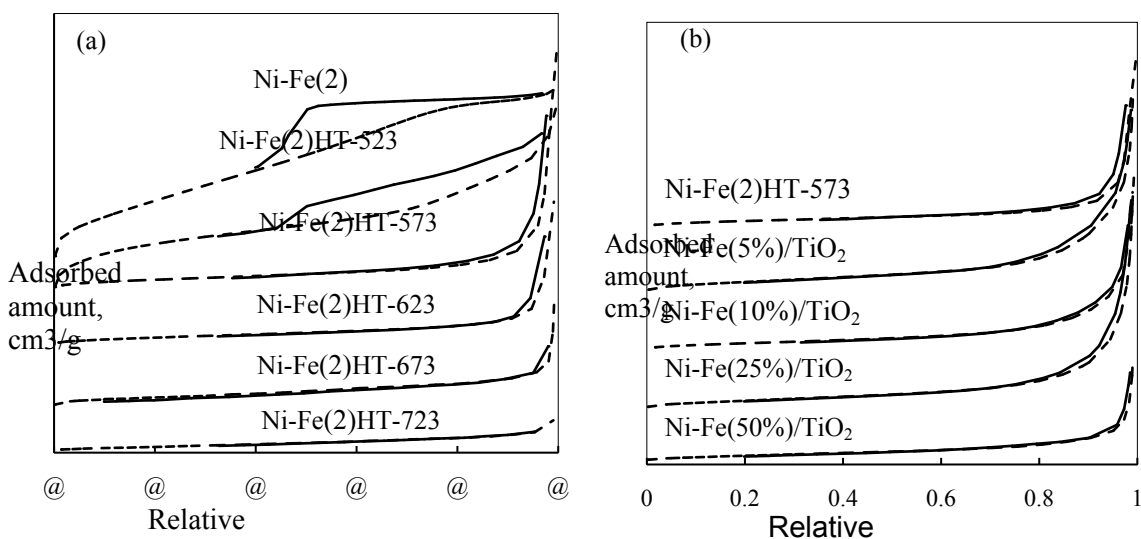
**Figure S1.** XRD patterns of (a) Ni-M (M = Fe, Ti, Co, In, Ga, Al) HT-673 catalysts, and (b) Ni-Fe(2)(wt. 25%) supported on M<sub>x</sub>O<sub>y</sub> (M<sub>x</sub>O<sub>y</sub> = SiO<sub>2</sub>, Taeniolite, Hydrotalcite, CeO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>) catalysts.



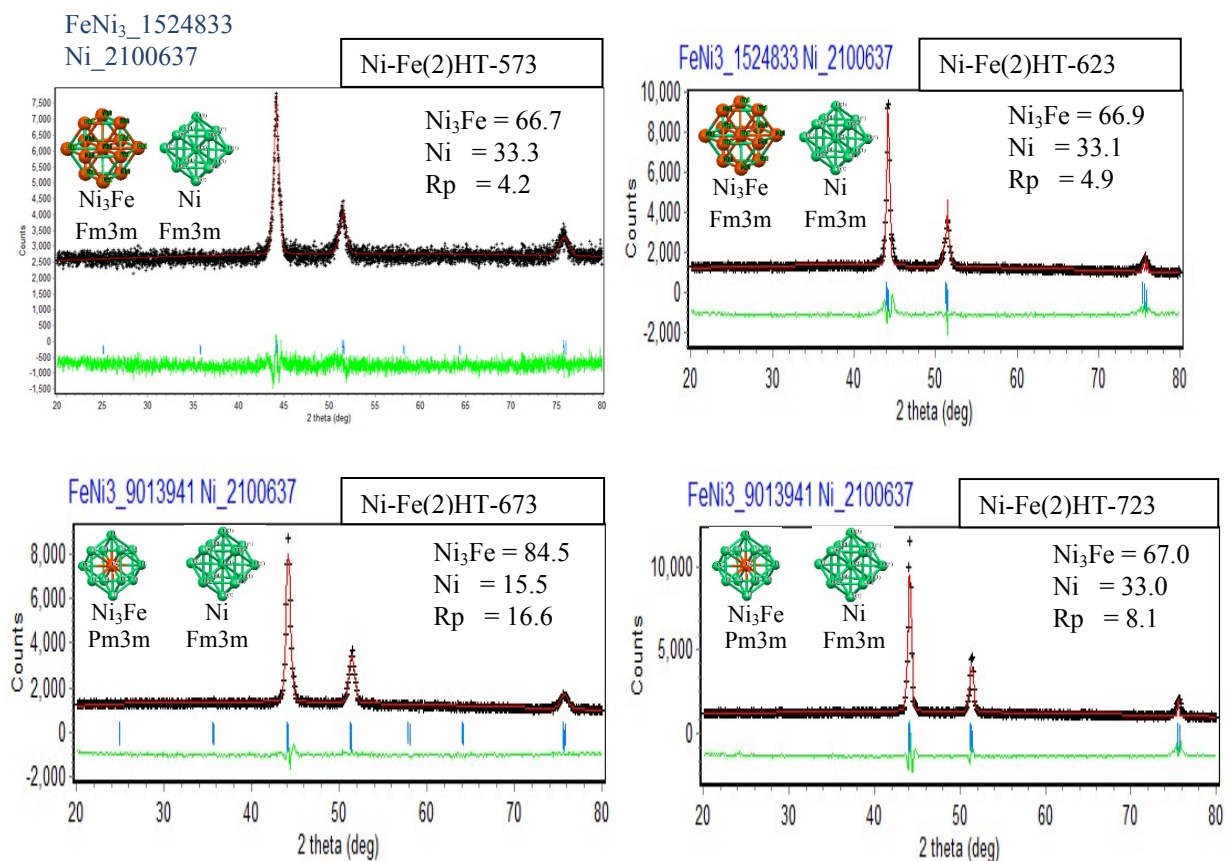
**Figure S2.** XRD patterns of (a) Ni-Fe(2) without hydrothermal and H<sub>2</sub> treatment, (b) Ni-Fe(2) hydrothermal at 423 K, without H<sub>2</sub> treatment, (c) Ni-Fe(2) without hydrothermal, H<sub>2</sub> treatment at 573 K, (d) Ni-Fe(2) hydrothermal at 423 K and H<sub>2</sub> treatment at 573 K.



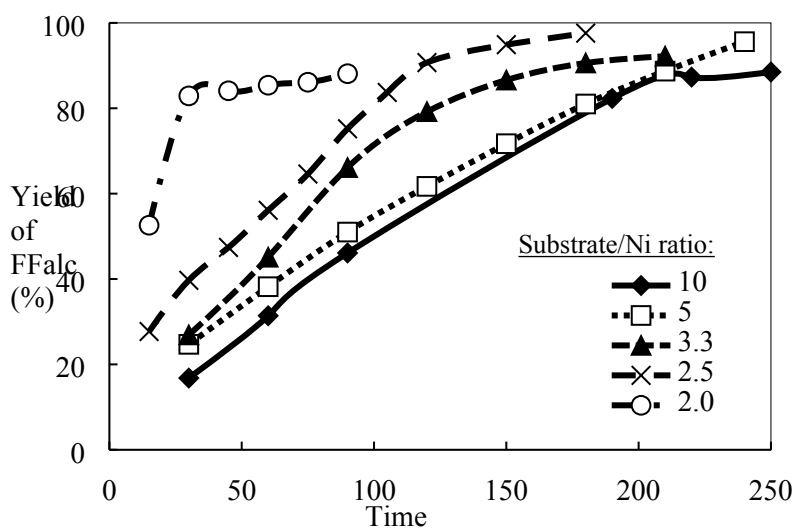
**Figure S3.** Effect of hydrothermal for catalytic performance of Ni-Fe alloy catalysts. *Reaction conditions:*  $C^{\circ}_{\text{SUBS}} = 0.367 \text{ M}$ ;  $W_{\text{CAT}} = 50 \text{ mg}$  (substrate/Ni = 2);  $V_{\text{iso-PrOH}} = 3 \text{ mL}$ ;  $P^{\circ}_{\text{H}_2} = 10 \text{ bar}$ ; and  $T = 423 \text{ K}$ . Yield determined by GC using an internal standard technique.



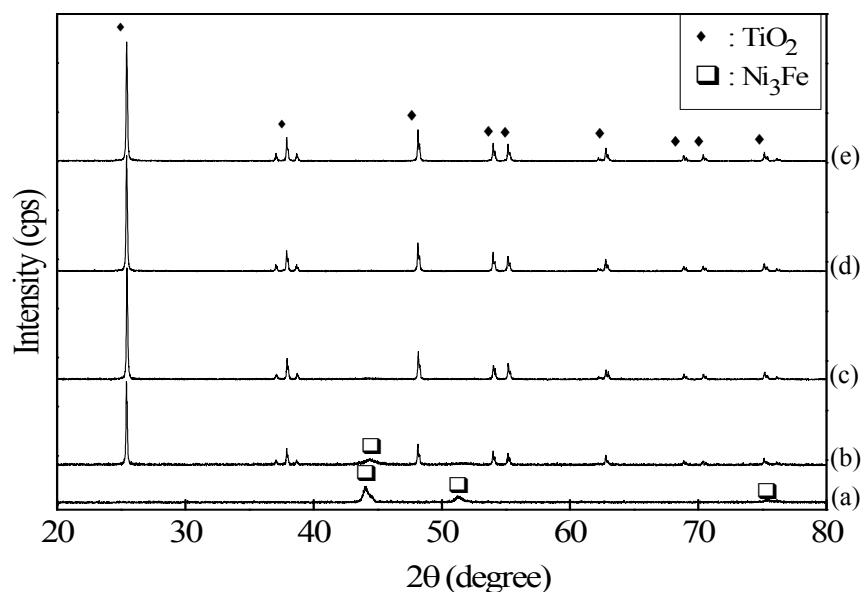
**Figure S4.** Typical  $\text{N}_2$  adsorption-desorption isotherm for Ni-Fe(2); (a) with various temperatures of  $\text{H}_2$  treatment, (b) loaded on  $\text{TiO}_2$  with various loading amounts of Ni-Fe alloy.



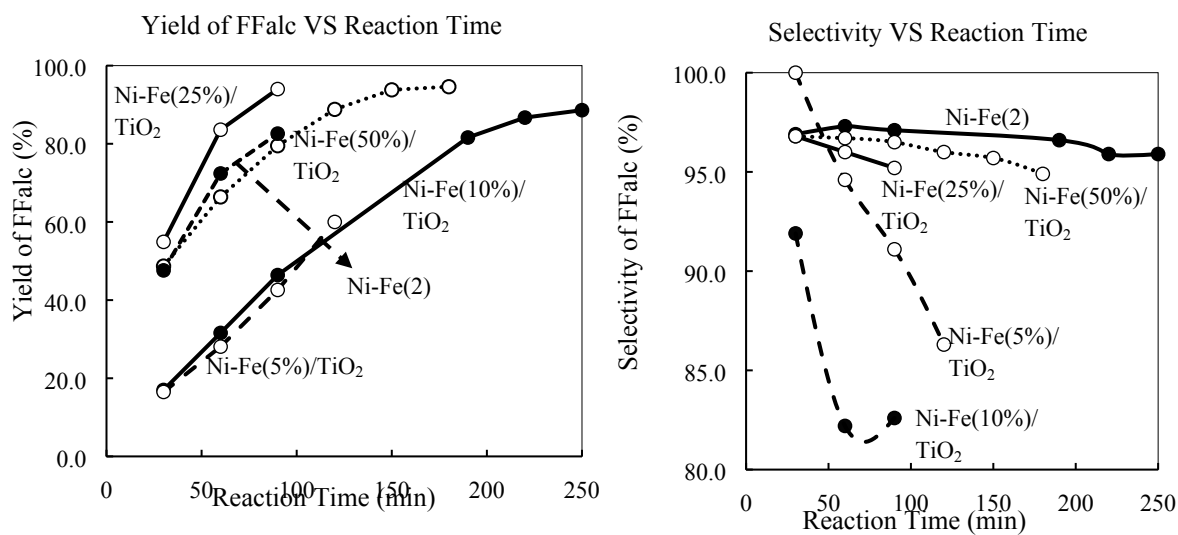
**Figure S5.** Multi-Rietveld analysis program LH-Riet profiles of powder XRD data of Ni-Fe(2) alloy catalysts with various temperatures of H<sub>2</sub> treatment. Data points (black line); calculated line, (red line); difference line, (green line); marker points (blue vertical line).



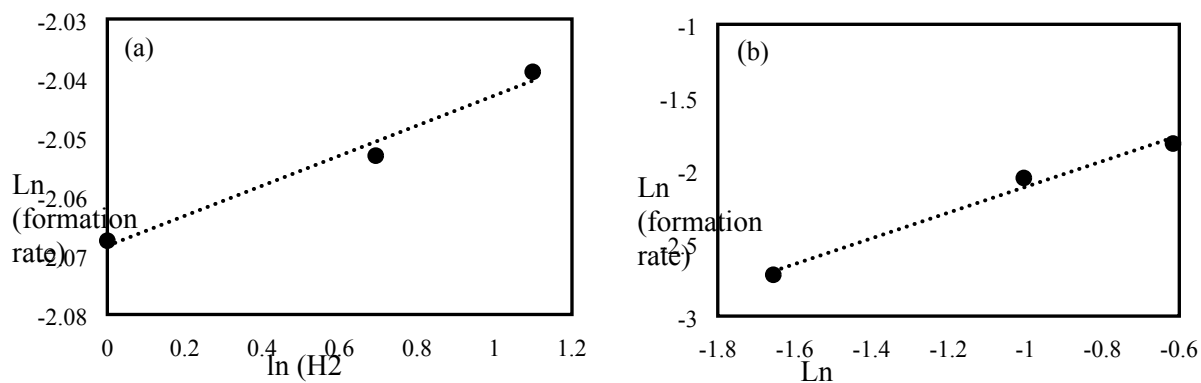
**Figure S6.** Effect of Substrate/Ni ratios on the yield of furfuryl alcohol (FFalc) by using Ni-Fe(2)HT-573 catalysts. Reaction conditions:  $C_{\text{SUBS}}^{\circ} = 0.367 \text{ M}$ ;  $V_{\text{iso-PrOH}} = 3 \text{ mL}$ ;  $P_{\text{H}_2}^{\circ} = 10 \text{ bar}$ ; and  $T = 423 \text{ K}$ . Yield determined by GC using an internal standard technique.



**Figure S7.** XRD patterns of bulk and  $\text{TiO}_2$  supported Ni-Fe alloy with various loading amounts of Ni-Fe. (a) bulk Ni-Fe(2)HT-673, (b) Ni-Fe(wt. 50%)/ $\text{TiO}_2$ , (c) Ni-Fe(wt. 25%)/ $\text{TiO}_2$ , (d) Ni-Fe(wt. 10%)/ $\text{TiO}_2$ , (e) Ni-Fe(wt. 5%)/ $\text{TiO}_2$ .

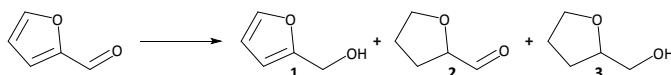


**Figure S8.** Time profile investigation of various loading amount of Ni-Fe alloy supported on  $\text{TiO}_2$ . Reaction conditions:  $C^{\circ}_{\text{SUBS}} = 73.4 \text{ mM}$ ;  $W_{\text{CAT}} = 10 \text{ mg}$  (Substrate/Ni = 2);  $V_{\text{iso-PrOH}} = 3 \text{ mL}$ ;  $P^{\circ}_{\text{H}_2} = 10 \text{ bar}$ ; and  $T = 423 \text{ K}$ .



**Figure S9.** Effect of (a) initial H<sub>2</sub> pressure and (b) furfural concentration over bulk Ni-Fe(2)HT alloy catalysts.

**Table S1.** Comparison data for liquid-phase chemoselective hydrogenation of unsaturated carbonyls



Catalyst	P <sub>H<sub>2</sub></sub> (MPa)	T (K)	t (min)	Conv. (%)	Sel. of <b>1</b> (%)	Ref.
Pt-Cu hollow-core	2	423	720	100	100	[1]
7.5%Pt@g-C <sub>3</sub> N <sub>4</sub>	1	373	300	95	>99	[2]
Pd-Cu/MgO	0.6	383	30	98	98	[3]
Cu(3):Zn(2):Cr(1):Zr(4)	2	443	210	96	96	[4]
Co/SBA-15	2	423	90	91	96	[5]
Ni-Cu/Al <sub>2</sub> O <sub>3</sub>	5	403	100	90	100	[6]
Fe(NiFe)O <sub>4</sub> -SiO <sub>2</sub>	2	363	240	94	100	[7]
Ni-Sn(3-2)HT-673	3	383	75	67	100	[8]
Ni-Fe(2-1)HT-573	1	423	30	90	92	This Work

## References

- [1] S. Huang, N. Yang, S. Wang, Y. Sun, Y. Zhu, *Nanoscale* **2016**, *8*, 14104–14108.
- [2] X. Chen, L. Zhang, B. Zhang, X. Guo, X. Mu, *Sci. Rep.* **2016**, *6*, 28558.
- [3] K. Fulajtárova, T. Soták, M. Hronec, I. Vávra, E. Dobročka, M. Omastová, *Appl. Catal. A Gen.* **2015**, *502*, 78–85.
- [4] R. V. Sharma, U. Das, R. Sammynaiken, A. K. Dalai, *Appl. Catal. A Gen.* **2013**, *454*, 127–136.
- [5] M. Audemar, C. Ciotonea, K. De Oliveira Vigier, S. Royer, A. Ungureanu, B. Dragoi, E. Dumitriu, F. Jérôme, *ChemSusChem* **2015**, *8*, 1885–1891.
- [6] S. A. Khromova, M. V. Bykova, O. A. Bulavchenko, D. Y. Ermakov, A. A. Saraev, V. V. Kaichev, R. H. Venderbosch, V. A. Yakovlev, *Top. Catal.* **2016**, *59*, 1413.
- [7] A. Halilu, T. H. Ali, A. Y. Atta, P. Sudarsanam, S. K. Bhargava, S. B. Abd Hamid, *Energy & Fuels* **2016**, *30*, 2216–2226.
- [8] Rodiansono, S. Khairi, T. Hara, N. Ichikuni, S. Shimazu, *Catal. Sci. Technol.* **2012**, *2*, 2139.