Supporting Information
for
Na-Melt Synthesis of Fine Ni_3Si Powders as a Hydrogenation Catalyst

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(1) Procedures for synthesis, characterization and evaluation of catalytic activities

(2) Measurement procedures of Ni dispersion, TOF (turn over frequency) and conversion rate of the prepared catalysts

(3) Powder XRD pattern of a commercial Ni_3Si ($Ni_3Si/Ni_{31}Si_{12}$) powder

(4) N_2 adsorption isotherm of Ni_3Si ($Ni_3Si/Ni_{31}Si_{12}$) powder (synthesized at 1123 K)

(5) FE-SEM image and EDX spot analysis of the synthetic Ni_3Si powder

(6) SEM image and SEM-EDX mapping of the synthetic Ni_3Si powder

(7) XPS spectra of the Si 2p core level of commercial and synthetic Ni_3Si powders

(8) Details of the catalytic activities of Ni and Ni_3Si

(1) Procedures for synthesis, characterization and evaluation of catalytic activities

Predetermined amount of Ni (99.9 %, 2 ~ 3 µm, Kojundo Chemical Lab.), Si (99.99 %, < 45 µm, Kojundo Chemical Lab.) and Na (99.95%, Sigma-Aldrich Co. LLC.) were padded into a BN pot, and then packed in a stainless cell (inner volume of ~ 10 cm^3) in Ar. The molar ratio of Ni : Si : Na was set as 3 : 1 : 2 (total amount of ~ 200 mg). The cell was set in a furnace and then the temperature was raised to 873, 998 or 1123 K (heating rate of 300 K/h). After 2 h duration, the cells were furnace cooled to room temperature. The products were washed by 2-propanol, ethanol and then water in air. The samples after wash were dried in vacuum at 353 K for 2 h. ***Caution! The order of washing solvent addition is important in order to prevent from combustion. Reaction of sodium and water is vigorous while that of sodium and alcohol with longer chain is more moderate.***

Crystalline phases were identified by powder X-ray diffraction (XRD; Rigaku RINT-TTR). The microstructure of the samples was observed by scanning electron microscopy (FE-SEM; Hitachi High-Technologies S-5500). N$_2$ adsorption isotherm was measured (Nova 3000e instrument, Quantachrome Instruments). X-ray Photoelectron Spectroscopy (XPS) and Hard X-ray Photoelectron Spectroscopy (HAXPES) analysis were conducted as described below.

<X-ray Photoelectron Spectroscopy (XPS)>
XPS (Quantera SXM,, ULVAC PHI) spectra were measured for the sample after heat treatment under a 5% H$_2$/Ar flow (500 mL min^{-1}) at 673 K for 0.5 h. XPS measurement was conducted with monochromatic Al Kα X-rays at 1486.6 eV, 14 kV and 1500 W. The base pressure was set below 1 x 10^{-7} Pa. The diameter of detection were 400 µmΦ, the take-off angle (TOA) was 45°. Here, the surface normal corresponds to a TOA of 90°. The pass energy and the energy step were set at 29.35 eV and 0.125 eV, respectively.

<Hard X-ray Photoelectron Spectroscopy (HAXPES)>
The Ni 2p$_{3/2}$ core level was determined by HAXPES measurements on the SPring-8 BL16XU beamline as described in the previous report [S1]. The photon energy was set at 7946.6 eV. The energies and angular distributions of the photoelectrons were assessed using a VG-Scienta R4000-HV hemispherical analyzer. The objective lens has an effective acceptance angle of approximately ±30º and an angular resolution of 1.32º. The stability of the system was confirmed using the Au 4f$_{7/2}$ photoelectron peak for an Au film on a Si substrate. The overall stability of the photoelectron energy was found to be within 50 meV. The angular distributions of the photoelectrons were determined at photoelectron take-off angles at 85º. Here, a take-off angle perpendicular to the surface is defined as 90º. The analysis depths of the HAXPES

measurements were calculated according to the previous report. [S2]

Catalytic properties of hydrogenation of ethylene, acetylene, toluene and benzene were evaluated as follows. The mixture powder of Ni_3Si (synthesized at 1123 K, 10 mg) and quartz sand (Miyazaki Chemical Co., 250 ~ 420 μm, 2 g) were filled into a quartz glass tube (inner diameter: 10 mm) and set in a fixed bed continuous flow reactor. Prior to the catalytic activity measuements, the catalyst was treated under H_2 gas flow of 10 ml/mim at 673 K for 0.5 h. Then, the catalytic activities of hydorgenation reactions were evaluated using the model gases (see, detail in (2) below) of (a) ethylene to ethane (C_2H_4 : H_2 : He = 10 : 10 : 30 ml/min、 343 K), (b) acetylene to ethylene and ethane (acetylene: H_2 : He = 2 : 10 : 30 ml/min, 423 K), (c) benzene to cyclohexane (benzene : H_2 : He = 0.7 : 5 : 10 ml/min, 423 K) and (d) toluene to methyl-cyclohexane (toluene : H_2 : He = 0.2 : 5 : 10 ml/min, 423 K). All the reactions were carried out under an atmospheric pressure. Benzene and toluene were supplied as saturated vapor at room temperature using a bubbler equipped upstream. The reference samples of commercial powders of Ni_3Si (30 mg, the Ni_3Si ingot were pulverized in argon grove box, < 45 μm, Kojundo Chemical Lab.) and Ni (300 mg, < 150 μm, FUJIFILM Wako Pure Chemical) were evaluated in the same manner.

(2) Measurement procedures of Ni dispersion, TOF (turn over frequency) and reaction rate of the prepared catalysts

CO pulse chemisorption was performed using BELCAT II (Microtrac BEL) to estimate the Ni dispersion of the prepared catalysts. Prior to chemisorption, the catalyst was pretreated under a 5% H_2/Ar flow (40 mL min^{-1}) at 673 K for 0.5 h. After the reduction pretreatment, Helium (He) gas was introduced at the same temperature for 10 min to remove the chemisorbed hydrogen, followed by cooling to room temperature. A 10% CO/He pulse was introduced into the reactor, and the supplied CO flow was quantified downstream by a thermal conductivity detector.

Hydrogenation reactions of various hydrocarbons were conducted using a fixed bed flow reactor. The amount of the reactant and product in the outlet gas was measured using Gas Chromatography. Conversion was determined by the measured component ratios of (1) ethane (product) / ethylene (reactant), (2) ethylene + ethane / acetylene, (3) methyl cyclohexane / toluene and (4) cyclohexane / benzene.

TOF (turn over frequency) was determined using following equation:
$$TOF\ (s^{-1}) = \{P \times FR / (R \times T) \times Cv\} / \{Dp \times W \times X / Mw_{Ni}\}$$

  P: Gas pressure (atm)
  FR: Flow rate of the test gas (L s^{-1})
  R: Gas constant (L atm K^{-1} mol^{-1})
  T: Temperature (K)
  Cv: Conversion (-)
  Dp: Dispersion of Ni (%)
  W: Weight of catalyst (g)
  Mw_{Ni}: Molecular weight of Ni
  X = Relative amount of Ni (-)
      X for Ni = 1
      X for Ni_3Si = (Molecular weight of Ni × 3) /(Molecular weight of Ni_3Si)

Reaction rate (mmol g^{-1} s^{-1}) was determined by the measured conversion (typically below 30%) and the weight of the catalyst.

(3) Powder XRD pattern of a commercial Ni_3Si ($Ni_3Si/Ni_{31}Si_{12}$) powder [Kojundo Chemical Lab., Particle size < 45 μm]:

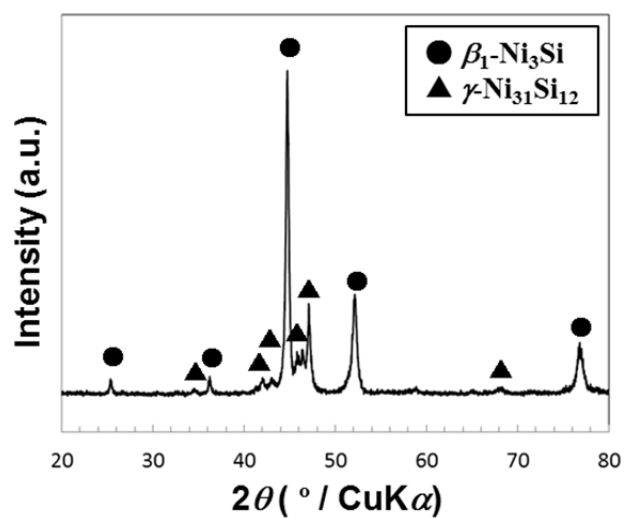The metallurgically prepared ingot was pulverized to powder in argon grove box.

Figure S1. Powder XRD pattern of commercial Ni_3Si

(4) N_2 adsorption isotherm of Ni_3Si ($Ni_3Si/Ni_{31}Si_{12}$) powder (synthesized at 1123 K)

BET specific surface area of 3.11 m^2/g was derived from N_2 adsorption isotherm of the synthetic Ni_3Si powder. We hypothesized that all particles were spherical with density of 8.04 g/cm^3 (β_1-Ni_3Si) and then the average particle size of ~ 250 nm was deduced from the specific surface area (3.11 m^2/g).
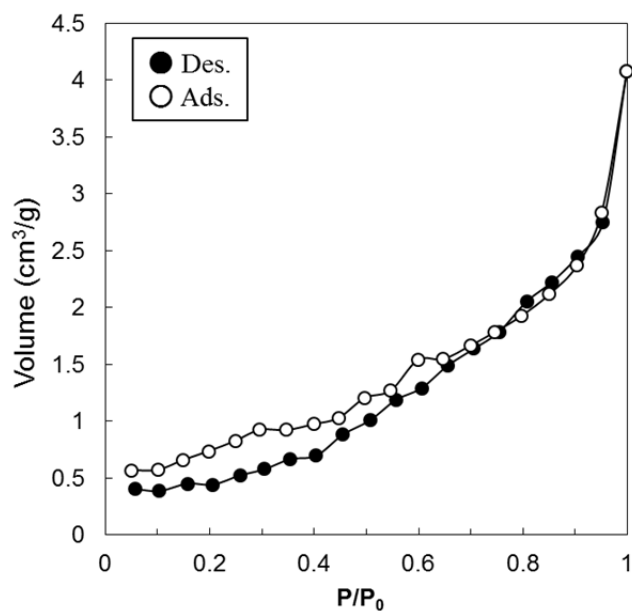

Figure S2. N_2 adsorption isotherm of Ni_3Si powder

(5) FE-SEM image and EDX spot analysis of the synthetic Ni_3Si powder

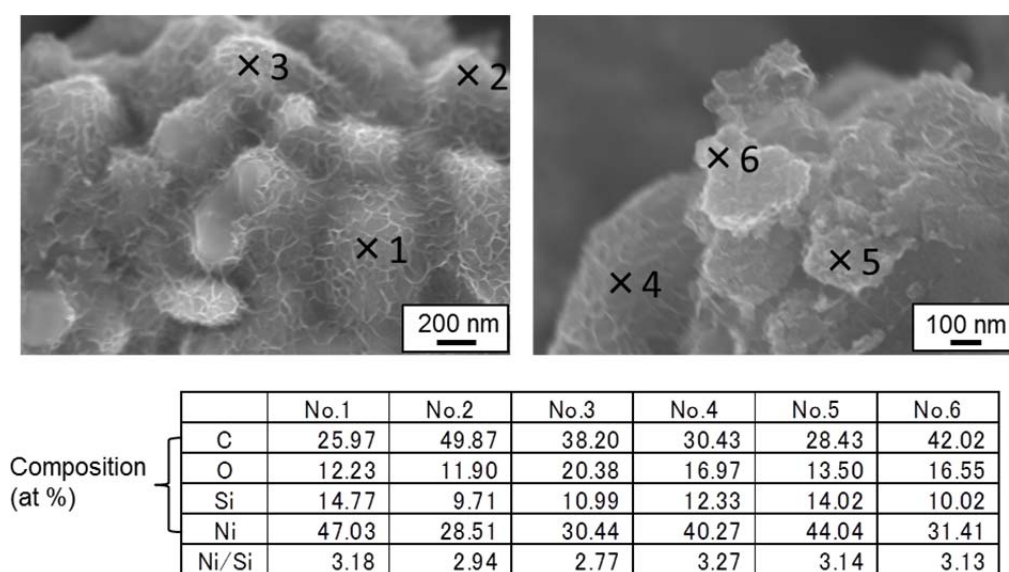EDX spot analysis data suggest that the primary particles have composition of Ni/Si of ~ 3/1.

		No.1	No.2	No.3	No.4	No.5	No.6
Composition (at %)	C	25.97	49.87	38.20	30.43	28.43	42.02
	O	12.23	11.90	20.38	16.97	13.50	16.55
	Si	14.77	9.71	10.99	12.33	14.02	10.02
	Ni	47.03	28.51	30.44	40.27	44.04	31.41
	Ni/Si	3.18	2.94	2.77	3.27	3.14	3.13

Figure S3. FE-SEM images and EDX spot analysis for the synthesized Ni_3Si powder

(6) SEM image and SEM-EDX mapping of the synthetic Ni_3Si powder

Ni and Si are rather homogeneously distributed over all of the powders. Some particles are Ni-rich, suggesting that a trace amount of unreacted Ni would exist while these unreacted phases were not detected by XRD (Fig.1 in the main text).
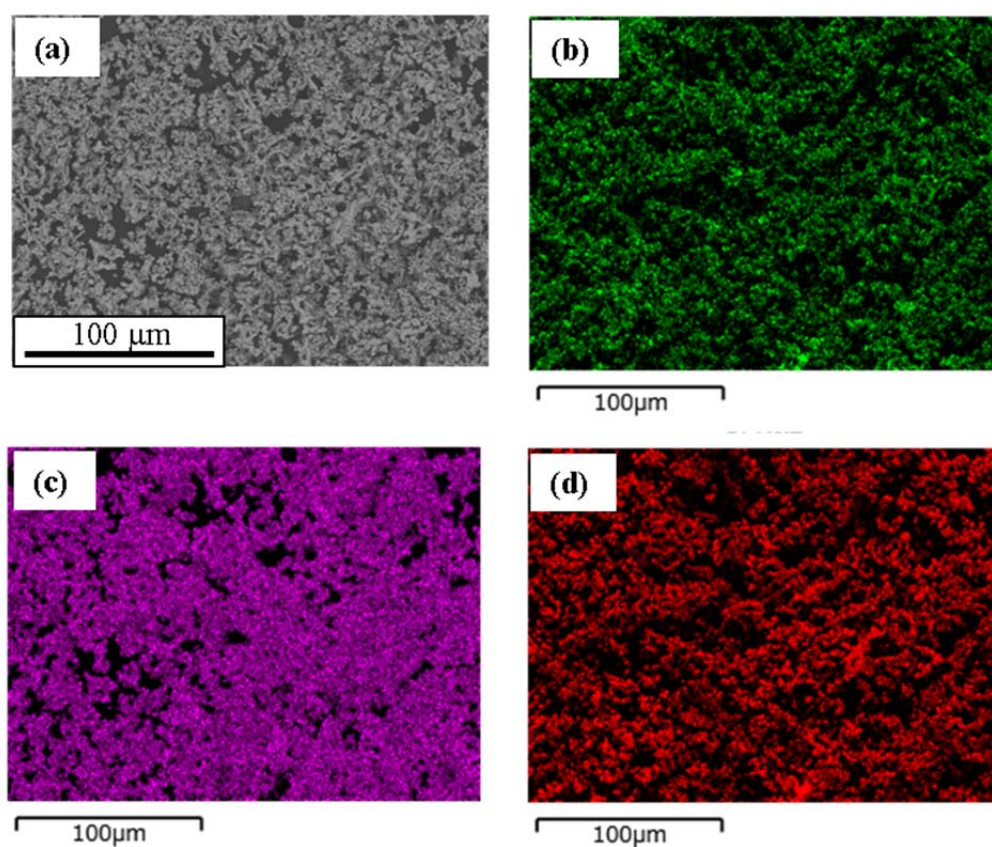

Figure S4. (a) SEM image and SEM-EDX mappings of (b) O, (c) Ni and (d) Si for Ni_3Si powder (synthesized at 1123 K).

(7) XPS spectra of the Si 2p core level of commercial and synthetic Ni₃Si powder

As shown in Figure S5, the synthesized Ni₃Si powder had lower intensity of the peak corresponding to Si-O when compared to commercial Ni₃Si powder.

It is expected that the oxygen in the raw powder or possible unreacted Si was removed by washing because they dissolved in alcohol and water as Na-Si-O or Na-Si. Thus, the synthetic Ni₃Si had a small amount of oxides.
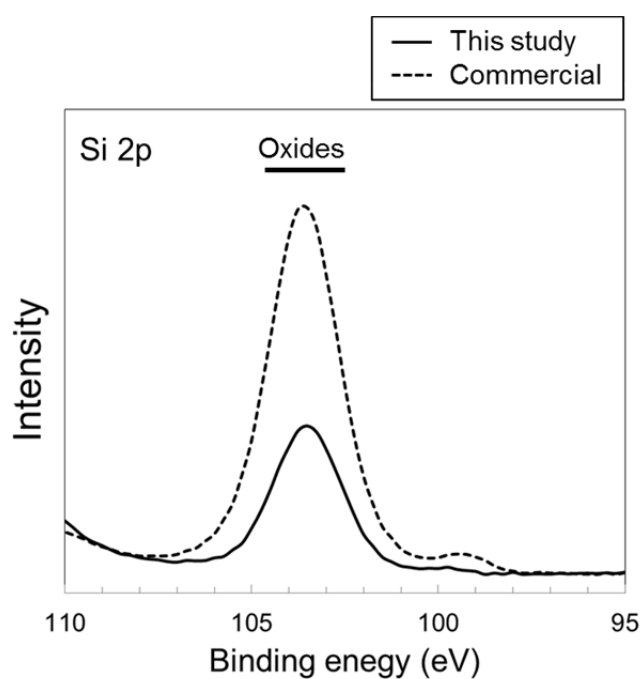

Figure S5.   XPS spectra of the Si 2p core level of commercial and synthetic Ni₃Si powder

(8) Details of the catalytic activities of Ni and Ni$_3$Si

Table S1. Catalytic activities of Ni and Ni$_3$Si in hydrogenation of various hydrocarbons

Reactant	Temp. (K)	Catalyst*	Dispersion (%)	Amount (mg)	Conv. (%)	TOF	Relative activity**	
							Rate	TOF
						(s^{-1})		
ethylene	343	Ni$_3$Si	0.0239	10	25.0	17.8	20.3	8.6
	343	Ni$_3$Si (Commercial)	0	30	0.0	0.0	0.0	0.0
	343	Ni (Commercial)	0.0652	300	37	2.1	1.0	1.0
						(s^{-1})		
acetylene	423	Ni$_3$Si	0.0239	30	6	1.4	20.0	8.5
	423	Ni (Commercial)	0.0652	100	1	0.2	1.0	1.0
						(min^{-1})		
toluene	423	Ni$_3$Si	0.0239	30	23	7.5	38.3	16.3
	423	Ni (Commercial)	0.0652	300	6	0.5	1.0	1.0
						(min^{-1})		
benzene	423	Ni$_3$Si	0.0239	30	12	12.8	10.0	6.4
	423	Ni (Commercial)	0.0652	200	8	2.0	1.0	1.0

* Ni$_3$Si: synthetized at 1123K, Ni$_3$Si (Commercial): see section (3) in the supporting information.

**The catalytic activities (reaction rate or turnover frequency (TOF)) of Ni$_3$Si were the relative values to those of commercial Ni (*i.e.*, relative activity of Ni =1).

References

[S1] E. Ikenaga, M.Kobata, H.Matsuda, T. Sugiyama, H.Daimonand K. Kobayashi, *J. Electron Spectrosc. Relat. Phenom.*, 2013, 190, 180.

[S2] S. Tanuma, C. J. Powell and D. R. Penn, *Surf. Interface Anal.*, 1988, 11, 577.