Supporting Information

Study on Hydrogen Activation Properties of Ni-Based Intermetallics: Relationship between Reactivity and Electronic State

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Experimental details

Catalyst preparation

Ni based intermetallic compounds (Ni_3M, M = Ge, Nb, Sn, Ta, and Ti) were prepared by arc melting of a mixture of Ni (Soekawa Chemical, 99.9%) and the second metal (Soekawa Chemical, 99.9%) under an argon atmosphere. The resultant ingots were crushed in air and filtered into particles with diameters below 25 µm. Powders of pure Ni were also filtered into particles with similar diameters.

Characterization

The crystal structure of the prepared intermetallics was examined by powder X-ray diffraction (XRD) with a Rigaku RINT2400 using an X-ray source of Cu Kα. X-ray photoelectron spectra (XPS) of the intermetallics were recorded with an ULVAC PHI 5000 VersaProbe spectrometer. The catalyst was pressed into a pellet and placed into a quartz reactor, where it was reduced under flowing hydrogen (50 $\mathrm{ml min^{-1}}$) at 873 K for 1 h. The reduced catalyst was transferred to the spectrometer without being exposed to air. Spectra were obtained with an AlKα X-ray source using C 1s as a reference for binding energy. d band center (C_d) was defined as the position of the vertical line bisecting the area of d band. The number of exposed Ni was estimated by CO pulse adsorption. Prior to the measurement, the catalyst was reduced under flowing H_2 (60 $\mathrm{ml min^{-1}}$) at 1073 K for 0.5 h, followed by He (60 $\mathrm{ml min^{-1}}$) at 1073 K for 1 h to remove adsorbed hydrogen. After cooling to room temperature, a specific amount CO(5%)/He pulse was introduced to the catalyst bed and passed (unadsorbed) CO was measured by a TCD detector.

H_2-D_2 equilibration

H_2–D_2 equilibration was carried out with a glass flow and circulation system connected with a quadrupole mass spectrometer (Spectra International, MICROVISION). Prior to each reaction, the catalyst was pretreated under 15 kPa of hydrogen at 873 K for 1 h and evacuated at 298 K for 10 min. A mixture of H_2 (2.5 kPa) and D_2 (2.5 kPa) was then circulated through the catalyst at a certain reaction temperature and the formation of HD was monitored by mass spectrometry. The fraction of HD (f_{HD}) was calculated by the following equation: $f_{HD} = P_{HD} / (P_{H2} + P_{D2} + P_{HD})$. To eliminate the contribution of HD initially contained as an impurity of D_2, f_{HD} was calibrated into Δf_{HD} as follows: $\Delta f_{HD} = f_{HD} - f_{HD}{}^0 = P_{HD} / (P_{H_2} + P_{D_2} + P_{HD}) - P_{HD}{}^0 / (P_{H_2}{}^0 + P_{D_2}{}^0 + P_{HD}{}^0)$, where superscript zero indicates each value at 0 min. The reaction rate (r / $\mathrm{min^{-1}}$) was estimated by the slope of Δf_{HD} (identical to that of f_{HD}) within a linear region. After 10 min of the reaction, the catalyst was evacuated and the temperature was changed, followed by introduction of a mixture of H_2 (2.5 kPa) and D_2 (2.5 kPa) for the next reaction. This procedure was repeated to obtain the Arrhenius plot. Catalyst amount was controlled so that Δf_{HD} reached 0.1~0.4 at 10 min: Ni (10 mg), Ni_3Ge (50 mg), Ni_3Nb (100 mg), Ni_3Sn (100 mg), Ni_3Ta (200 mg), and Ni_3Ti (100 mg).

Table S1. Crystal structure parameters of Ni and Ni_3M intermetallic compounds prepared in this study. [a]

compound	system	space group	*a*	*b*	*c*	*α*	*β*	*γ*
Ni	cubic	Fm−3m	3.5262	3.5262	3.5262	90	90	90
(ref: PDF#00-004-0850)			3.5238	3.5238	3.5238	90	90	90
Ni_3Ge	cubic	Pm−3m	3.5834	3.5834	3.5834	90	90	90
(ref: PDF#00-035-1359)			3.5720	3.5720	3.5720	90	90	90
Ni_3Sn	hexagonal	$P6_3/mmc$	5.2983	5.2983	4.2517	90	90	120
(ref: PDF#00-004-0850)			5.2961	5.2961	4.2481	90	90	120
Ni_3Ti	hexagonal	$P6_3/mmc$	5.1152	5.1152	8.3268	90	90	120
(ref: PDF#03-065-2038)			5.1010	5.1010	8.3067	90	90	120
Ni_3Ta	tetragonal	I4/mmm	3.6341	3.6341	7.4555	90	90	90
(ref: PDF#01-072-2595)			3.6270	3.6270	7.4550	90	90	90
Ni_3Nb	orthorhombic	Pmmn	5.1228	4.2547	4.5439	90	90	90
(ref: PDF#00-015-0101)			5.1060	4.2510	4.5560	90	90	90

[a] Calculated based on their XRD patterns.The reported values are also listed in the lower rows.

Table S2. The number of exposed Ni (N_{Ni}^{ex})[a] and specific surface area of Ni and Ni_3M.

catalyst	N_{Ni}^{ex} / μmol·g^{-1}	relative amount	S_{BET} / m^2·g^{-1}	relative amount
Ni	0.21	1.00	0.92	1.00
Ni_3Ge	0.10	0.48	1.44	1.57
Ni_3Nb	0.054	0.26	0.90	0.98
Ni_3Sn	0.11	0.52	0.86	0.94
Ni_3Ta	0.059	0.28	1.37	1.49
Ni_3Ti	0.10	0.47	0.37	0.41

[a] Measured by CO adsorption.

Figures

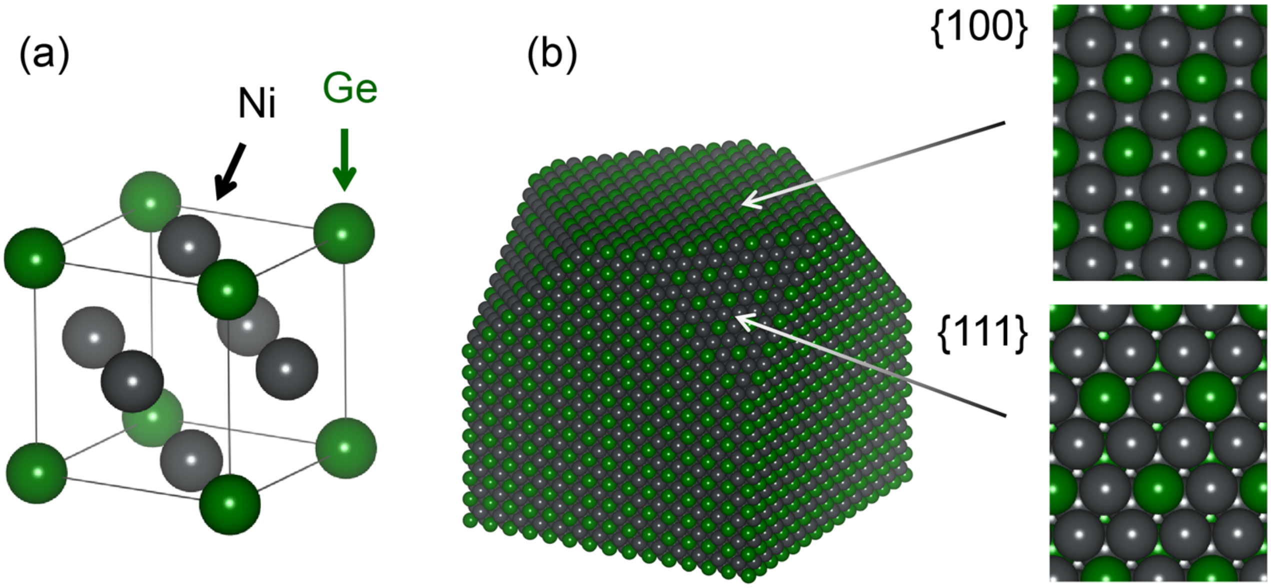

Figure S1. Crystal structure of Ni_3Ge (ICSD: #53745) with (a) a single unit cell and (b) its truncated cube model exposing {100} and {111} planes.

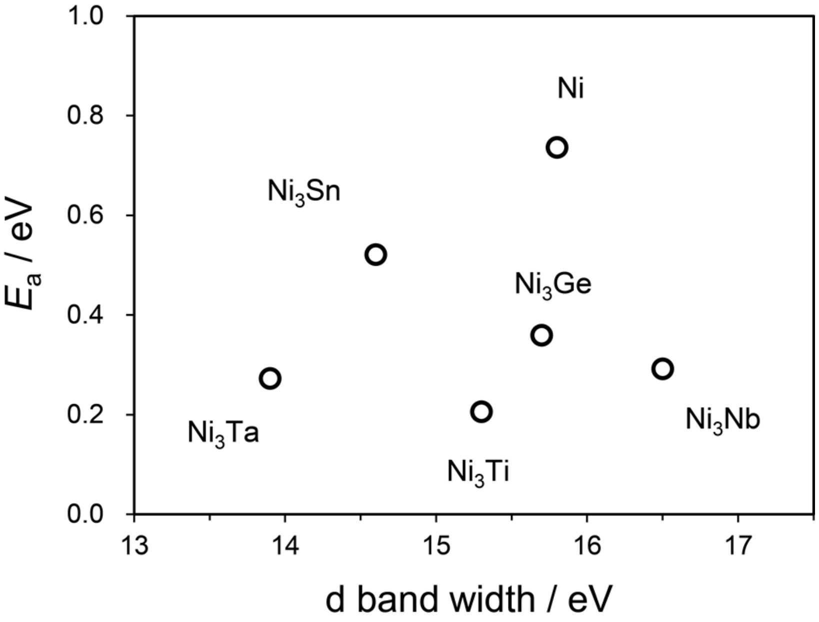

Figure S2. Correlation between E_a and d band width of Ni and Ni_3M intermetallics.

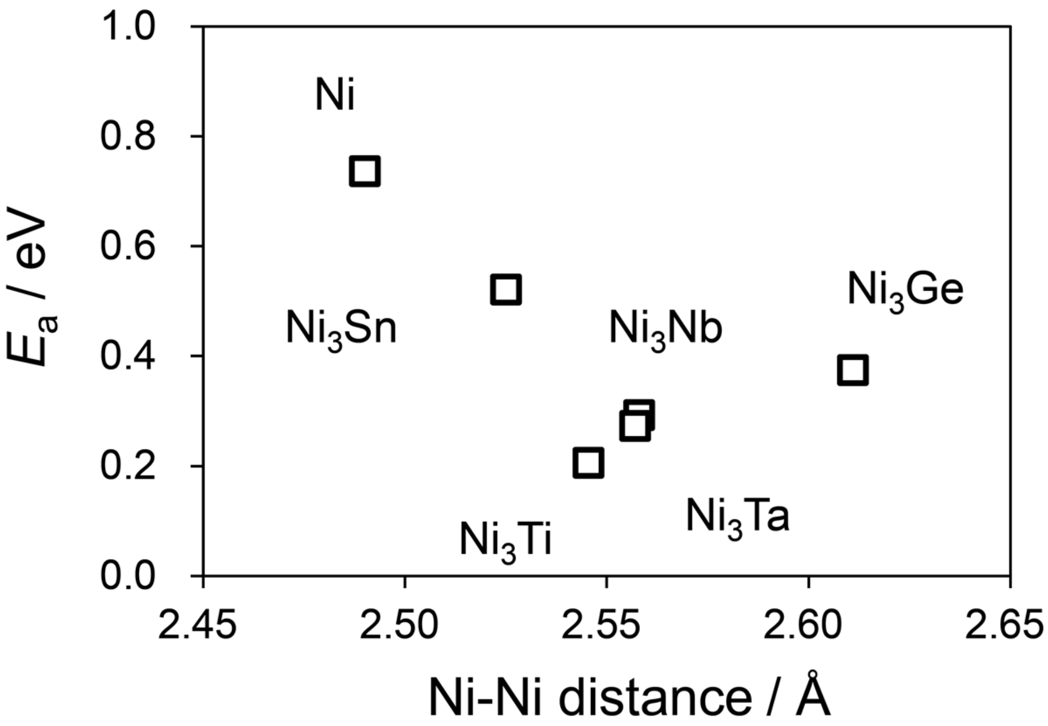

Figure S3. Correlation between E_a and the nearest Ni–Ni distance of Ni and Ni_3M intermetallics.