Electronic Supplementary Information

for

Reaction Mechanism and Selectivity of Acetylene Hydrogenation over Ni-Ga Intermetallic Compound Catalysts: A Density Functional Theory Study

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1. Structural details and surface energies

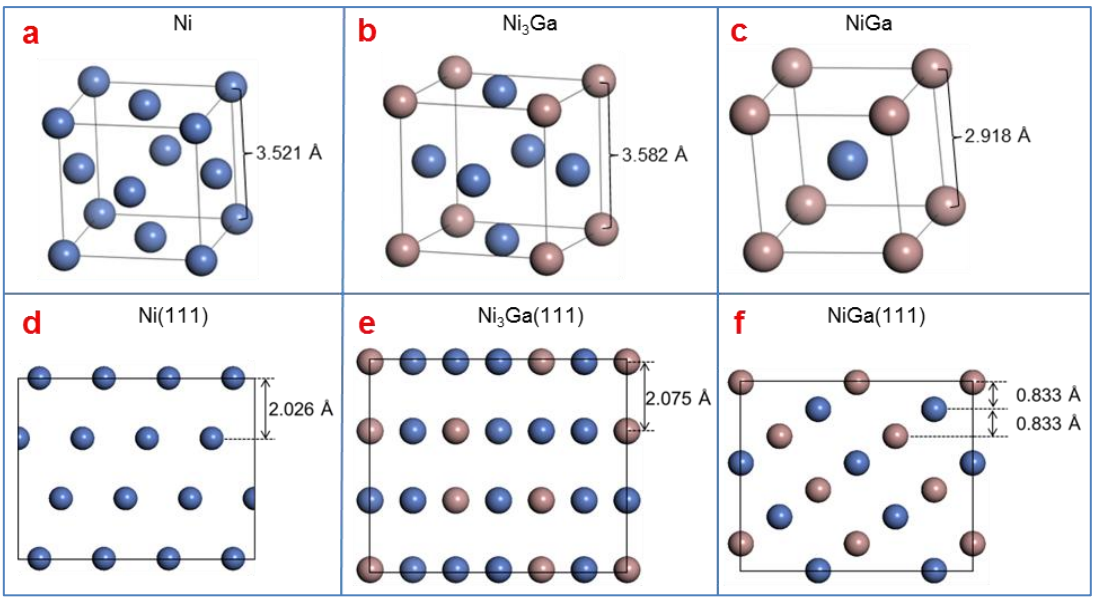

Fig. S1. Structure details of a) bulk Ni, b) bulk Ni_3Ga, and c) bulk NiGa with their corresponding (111) surfaces cleaved from bulk truncation d) Ni(111), e) Ni_3Ga(111), and f) NiGa(111),

respectively (Ni: blue; Ga: rufous), along with the interplanar distances after relaxation displayed.

Table S1. Computation tests for slab-thickness (column I-III), and constrained layers (column IV-VIII) on Ni(111), Ni_3Ga(111) and NiGa(111) surfaces. For instance, "C_2H_2-3L" means C_2H_2 adsorbs on a 3-layer slab, "C_2H_3-4L" means C_2H_3 adsorbs on a 4-layer slab, and so on.

	Bottom-layer fixed (eV)					Full relaxed (eV)		
	I	II	III	IV	V	VI	VII	VIII
	C_2H_2-3L	C_2H_2-5L	C_2H_2-4L	C_2H_3-4L	C_2H_4-4L	C_2H_2-4L	C_2H_3-4L	C_2H_4-4L
Ni	−2.43	−2.52	−2.56	−2.78	−0.75	−2.57	−2.78	−0.76
Ni_3Ga	−2.22	−2.28	−2.24	−2.86	−0.91	−2.24	−2.86	−0.91
NiGa	−1.40	−1.50	−1.55	−2.41	−0.04	−1.53	−2.40	−0.07

Table S2. Total Energies (E), total Energies with entropy effect correction ($E_{entropy}$) and total Energies with entropy effect and Zero-Point Energy Correction ($E_{entropy+ZPE}$) of the reaction intermediates.

		E (eV)	$E_{entropy}$ (eV)	$E_{entropy+ZPE}$ (eV)
Ni(111)	H+C_2H_2 (IS1)	−218.34269	−218.36725	−216.71409
	TS1	−217.28800	−217.31651	−215.70271
	H+C_2H_3 (IS2)	−221.67994	−221.71145	−219.78957
	TS2	−221.05966	−221.09349	−219.20775
	H+C_2H_4 (IS3)	−225.49327	−225.52783	−223.31511
	TS3	−225.05405	−225.09104	−222.92478
	H+CH_2CH (IS4)	−221.28176	−221.31579	−219.57314
	TS4	−221.06277	−221.09544	−219.26418
	H+$CHCH_3$ (IS5)	−225.59784	−225.62546	−223.96589
	TS5	−224.87341	−224.90146	−223.20407
Ni_3Ga(111)	H+C_2H_2 (IS1)	−265.89404	−266.43749	−264.73498
	TS1	−264.97220	−265.51485	−263.86041
	H+C_2H_3 (IS2)	−269.59546	−270.14270	−268.17417
	TS2	−268.96069	−269.49954	−267.56708
	H+C_2H_4 (IS3)	−273.57920	−274.11702	−271.86530
	TS3	−273.03807	−273.57961	−271.35798
	H+CH_2CH (IS4)	−269.57004	−270.11576	−268.18654

	TS4	−268.98408	−269.52958	−267.60530
	H+$CHCH_3$ (IS5)	−273.44894	−273.99699	−271.88582
	TS5	−272.78348	−273.33004	−271.21689
NiGa(111)	H+C_2H_2 (IS1)	−165.48232	−165.48699	−163.80919
	TS1	−164.35225	−164.35558	−162.75162
	H+C_2H_3 (IS2)	−169.30224	−169.48490	−167.75398
	TS2	−168.31647	−168.49800	−166.75957
	H+C_2H_4 (IS3)	−173.09711	−173.11581	−170.91086
	TS3	−172.42378	−172.44127	−170.23696
	H+CH_2CH (IS4)	−168.83081	−168.84481	−166.69487
	TS4	−168.64303	−168.65438	−166.48483
	H+$CHCH_3$ (IS5)	−173.30614	−173.31136	−171.11892
	TS5	−171.22819	−171.24043	−169.04794

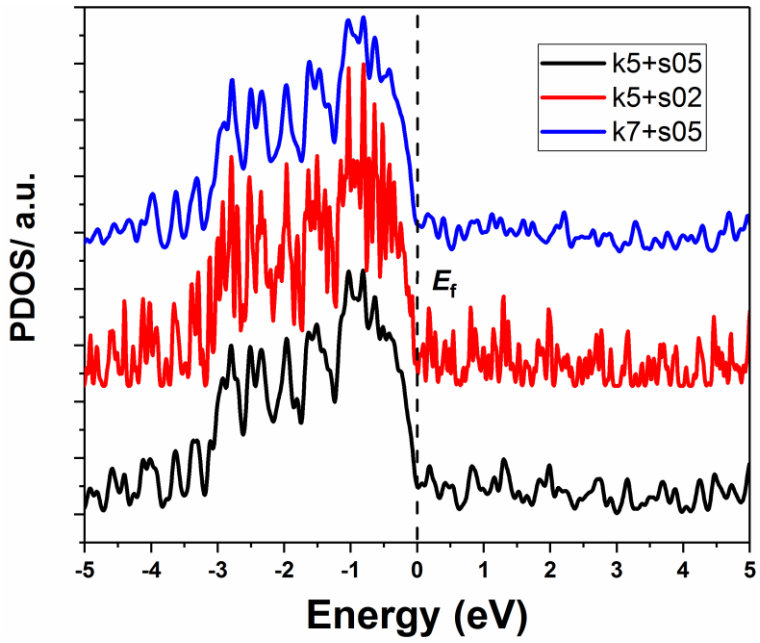

Fig. S2. Convergence tests of PDOS with respect to the *k*-point and smearing, "k5+s05" in the label means a 5 × 5 × 1 *k*-point with smearing value of 0.05, others can be understand in the same manner. The dashed vertical line stands for the Fermi level.

Table S3. Surface energies (γ) of NiGa with different compositions. $\gamma = (E_{slab} - NE_{bulk})/2A$. where E_{slab} and E_{bulk} are the total energies of the slab and one bulk unit cell, respectively, N is the number

of bulk units in the slab, and *A* is the surface area of the slab, according to the reference[S1].

Surface	Composition	Absolute energy (eV)	Surface energy (J/m^2)
Bulk NiGa	Ni_8Ga_8	−74.26086	
NiGa(110)	$Ni_{32}Ga_{32}$	−283.95046	1.087
NiGa(111)	$Ni_{16}Ga_{16}$	−137.51574	1.526
NiGa(111)'	$Ni_{16}Ga_{16}$	−136.18695	1.527

2. Determination of the effective barriers

The *TOF* can be simulated according to the energetic span theory[S2-S5] as follows:

$$TOF \approx \frac{k_B T}{h} e^{-E_a^{eff}/RT} \quad \text{(S1)}$$

where k_B stands for the Boltzmann constant, *T* is the reaction temperature, and *h* is the Planck constant; E_a^{eff} is defined as an effective barrier of a catalysis process, based on the previous reports[S6, S7]:

$$E_a^{eff} = \begin{cases} E_{TDTS} - E_{TDI} & \text{if TDTS appears after TDI} \quad \text{(a)} \\ E_{TDTS} - E_{TDI} + \Delta E & \text{if TDTS appears before TDI} \quad \text{(b)} \end{cases} \quad \text{(S2)}$$

TDTS is the *TOF* determining transition state related to the hydrogenation step with the highest hydrogenation barrier; and TDI stands for the *TOF* determining intermediate, which is the most stable adsorption state along the energy profile, and ΔE is the reaction heat from reactant to TDI.

We hereby take the hydrogenation of C_2H_2 on Ni(111) surface as an example to show how to obtain the E_a^{eff} from the energy profiles (Fig. 7). The essential aim here is to find a transition state (TS) - intermediate (I) pair with the largest energetic span (E_a^{eff}). The first step is to find the TDI, which should be first checked with the most

stable adsorption state along the energy profile. For the hydrogenation of C_2H_2 on Ni(111) surface, the TDI is found to be the adsorption state of C_2H_2+2H. The TDTS is found to be the transition state of the C_2H_3 hydrogenation. (Fig. 7) As TDTS appears after TDI, we can calculate the E_a^{eff} with the eqn. S2(a). The value of E_a^{eff} is calculated to be 1.33 eV.

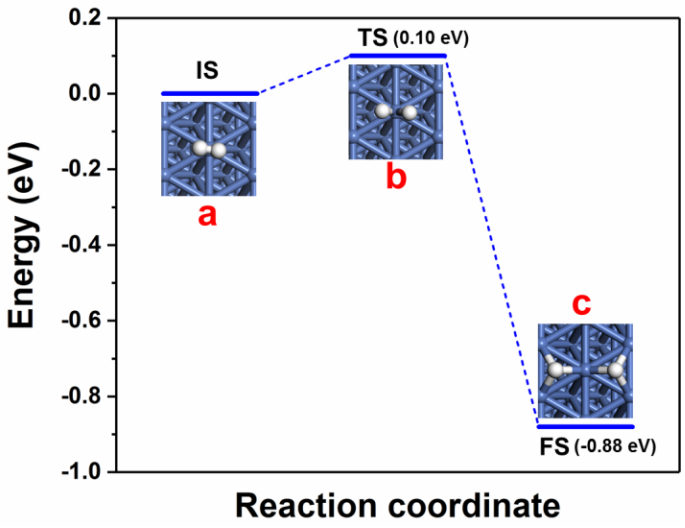

Fig. S3. H_2 dissociation into H atoms on Ni(111) surface.

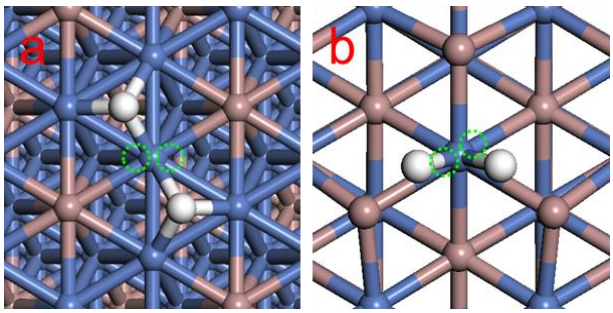

Fig. S4 Adsorption structures of dissociated H atoms on a) Ni_3Ga(111) and b) NiGa(111) surfaces, respectively. The green circles stand for the locations of pre-placed H_2 molecules. (H: white; Ni: blue; Ga: rufous).

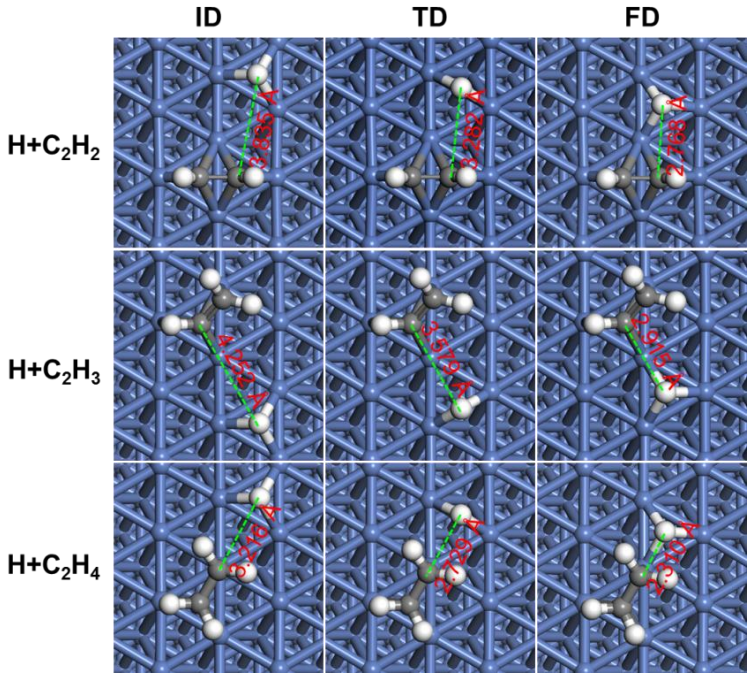

Fig. S5. Hydrogen diffusion with the changes of distance to the acceptor carbon atoms in the presence of C_2 species over Ni(111) surface. "ID", "TD" and "FD" stands for the initial states, transition states the final states of the diffusion processes, respectively. This definition mode will also be used in the following contents.

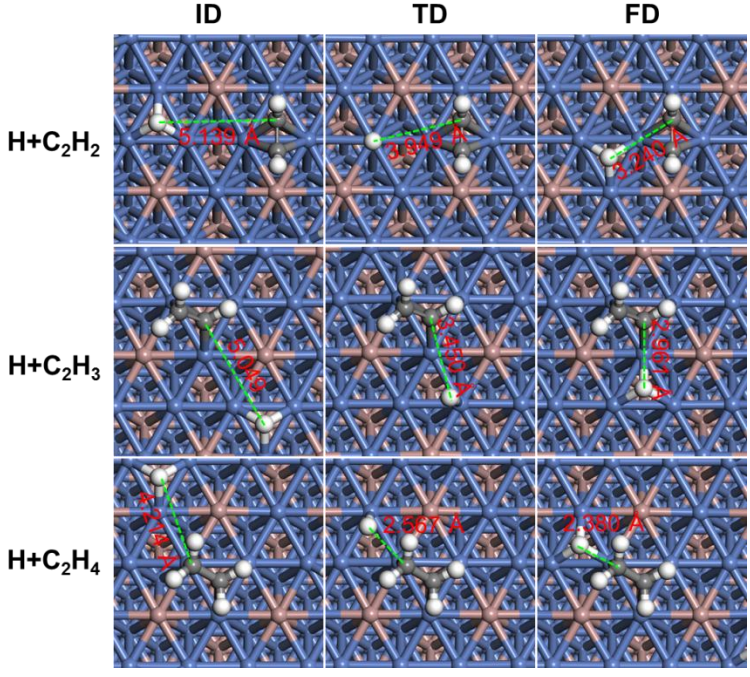

Fig. S6. Hydrogen diffusion with the changes of distance to the acceptor carbon atoms in the

presence of C_2 species over $Ni_3Ga(111)$ surface.

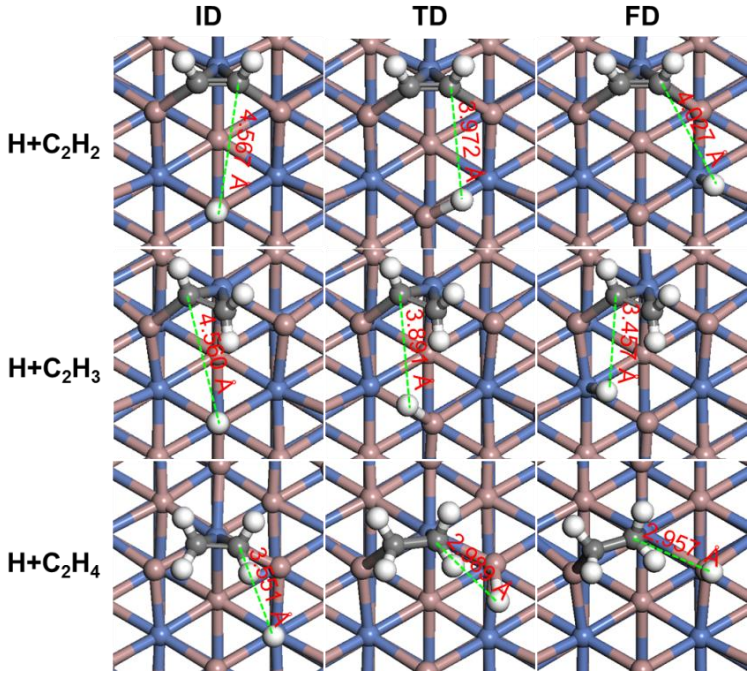

Fig. S7. Hydrogen diffusion with the changes of distance to the acceptor carbon atoms in the presence of C_2 species over NiGa(111) surface.

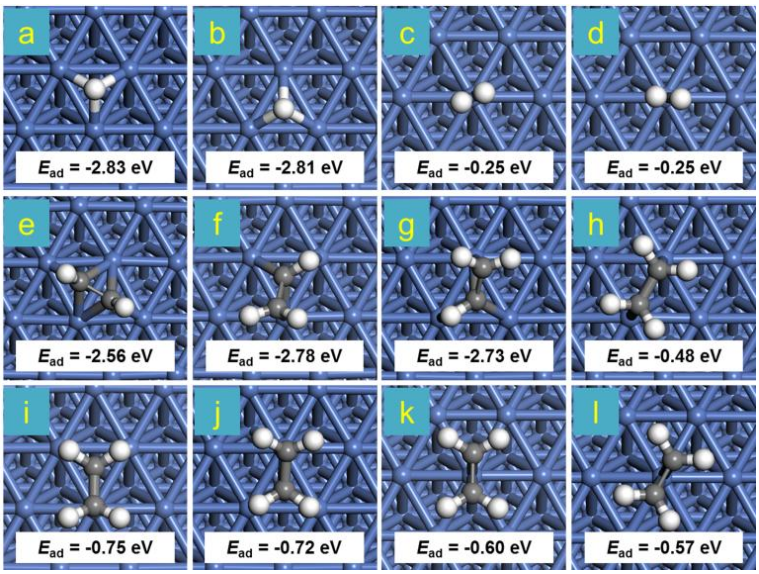

Fig. S8. Summary of the possible adsorption structures of H (a, b), H_2 (c, d), C_2H_2 (e), C_2H_3 (f, g), and C_2H_4 (h-l, including bridge, fcc, hcp and atop sites) on Ni(111) surface. H, C and Ni atoms are

represented by white, gray and blue balls, respectively.

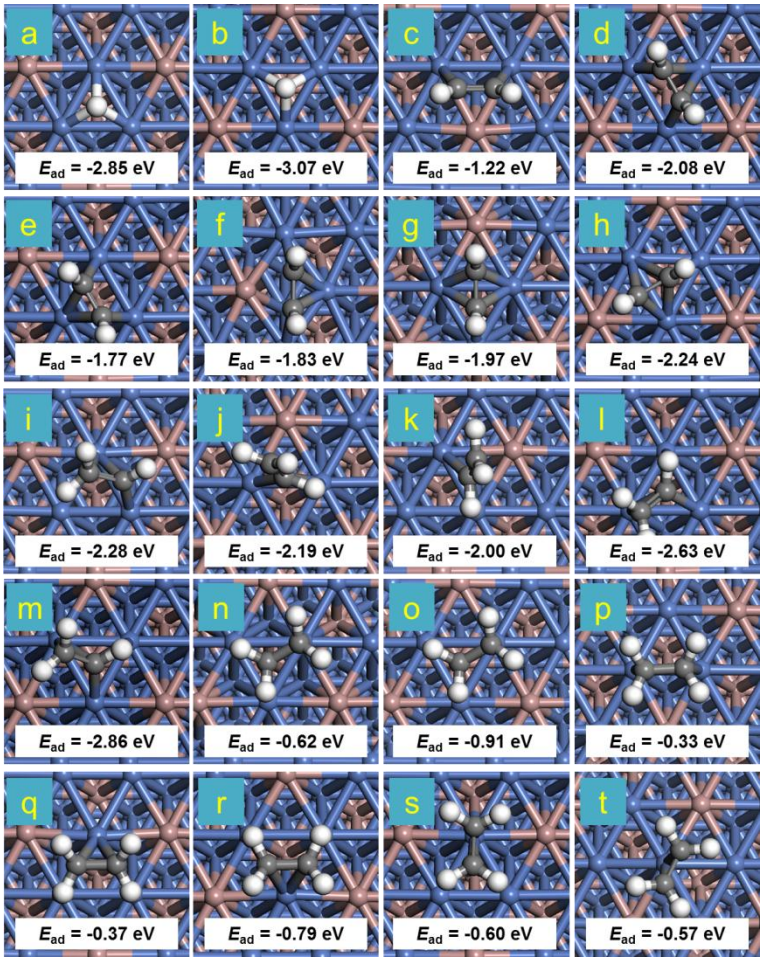

Fig. S9. Summary of the possible adsorption structures of H (a, b), C_2H_2 (c-h, including μ-bridge, parallel-bridge, perpendicular-bridge and triangle sites), C_2H_3 (i-m, including bridge, fcc, and hcp sites), and C_2H_4 (n-t, including fcc, hcp, bridge, parallel-bridge and atop sites) on $Ni_3Ga(111)$ surface. H, C, Ni and Ga atoms are represented by white, gray, blue and rufous balls, respectively.

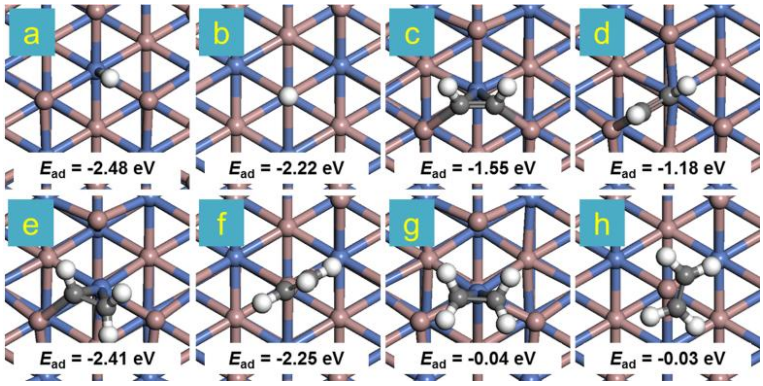

Fig. S10. Summary of the possible adsorption structures of H (a, b), C_2H_2 (c, d), C_2H_3 (e, f), and

C_2H_4 (g, h) on NiGa(111) surface. Atom label codes are the same as **Fig. S8**.

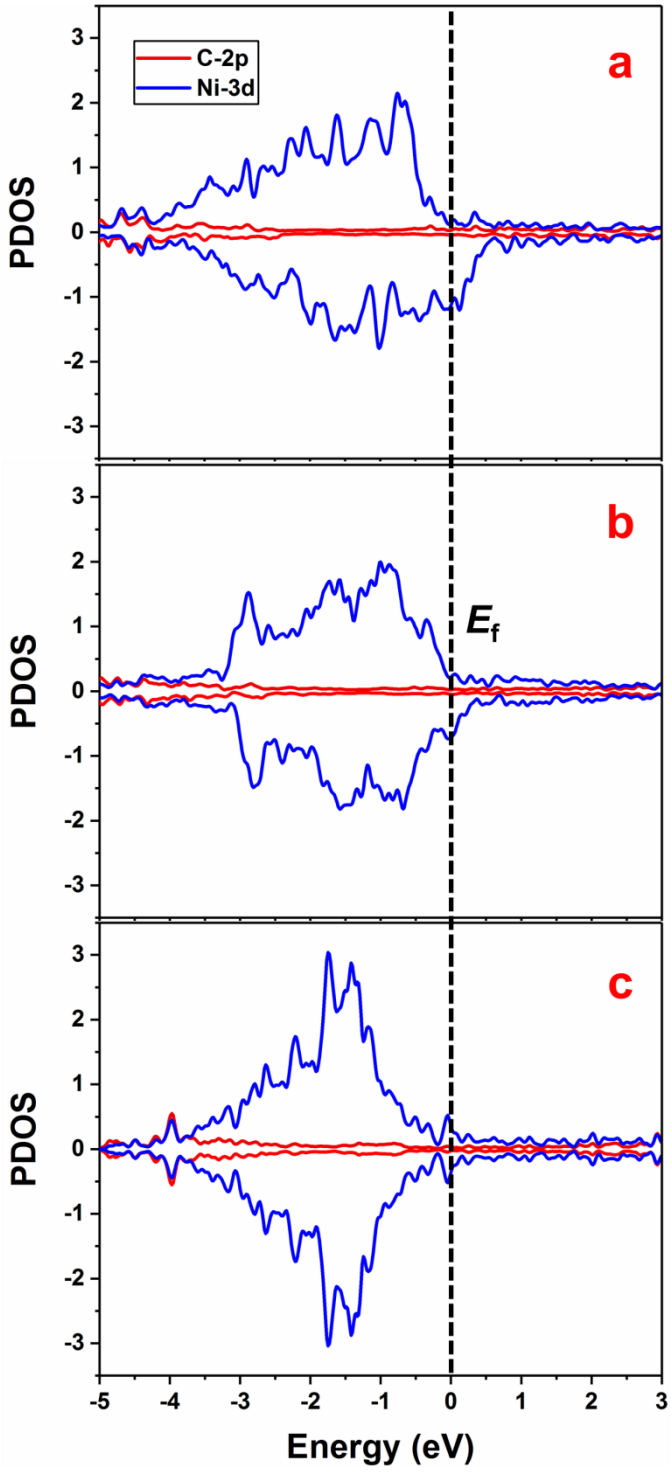

Fig. S11. PDOS of the acetylene adsorption on a) Ni(111), b) $Ni_3Ga(111)$ and c) NiGa(111) surfaces. The Fermi level (E_f) has been set to be zero.

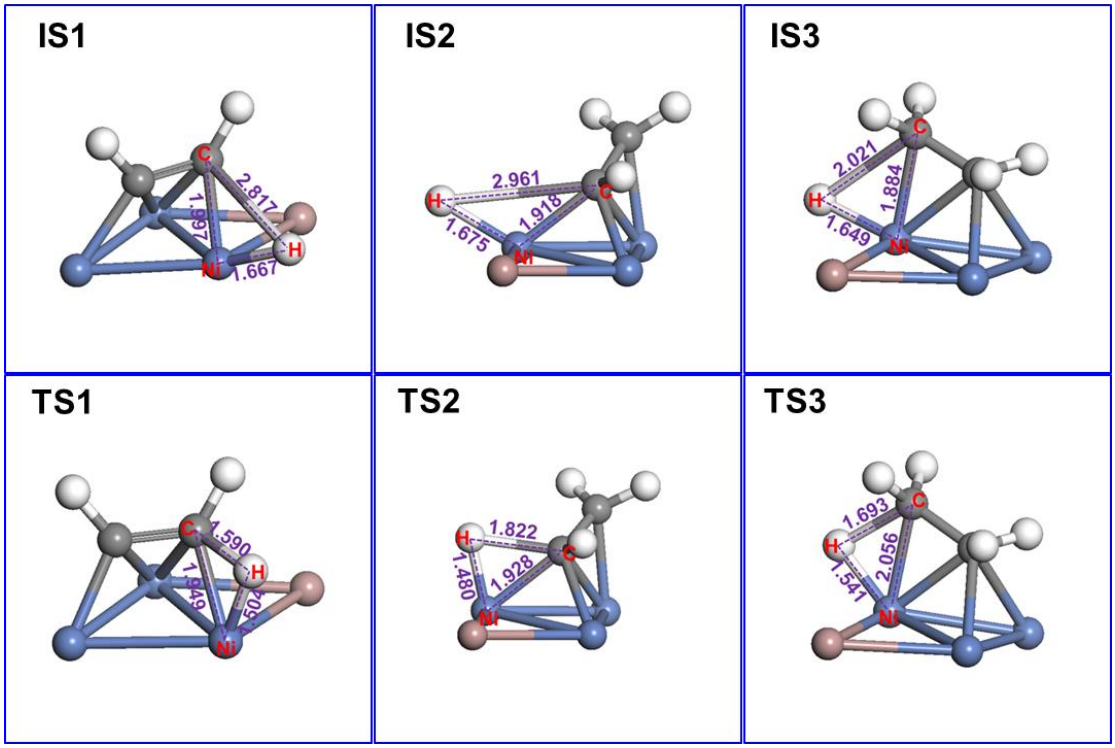

Fig. S12. The structures of the co-adsorbed initial states (ISs) and the corresponding transition states (TSs) over $Ni_3Ga(111)$ surface, only the atoms on the surfaces which bonded to the reactants are displayed (H: white; C: gray; Ni: blue; Ga: rufous). The unit of the data is angstrom (Å).

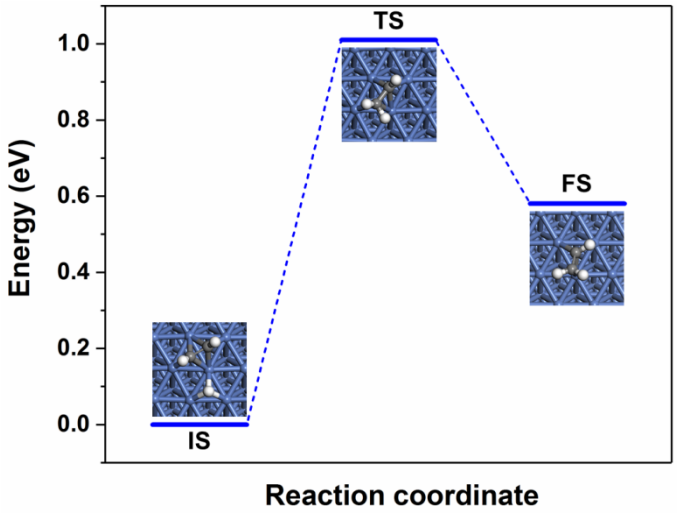

Fig. S13. $C_2H_2+H \rightarrow C_2H_3$ on Ni(111): The hydrogen attacks the acetylene (initial state before hydrogenation, IS) to form vinyl (final state after hydrogenation, FS) via the transition state (TS)

with a barrier of 1.01 eV.

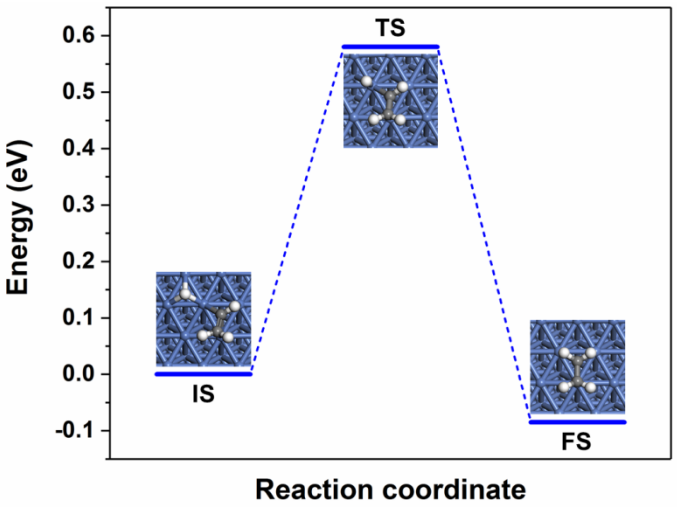

Fig. S14. C_2H_3+H→C_2H_4 on Ni(111): The hydrogen attacks the vinyl (initial state before hydrogenation, IS) to form ethylene (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 0.58 eV.

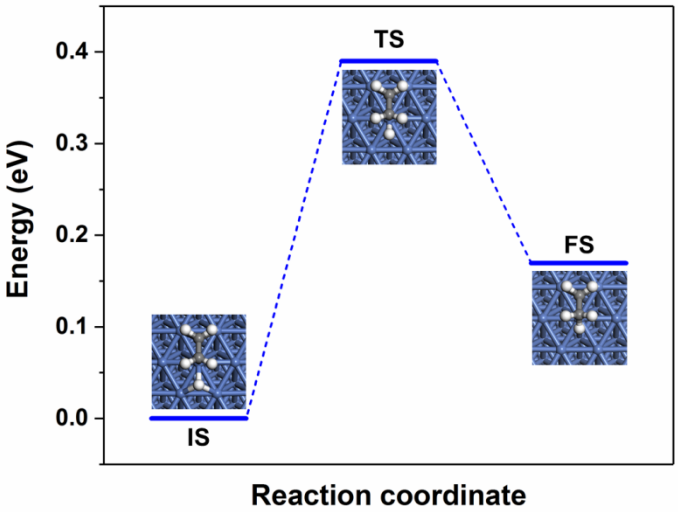

Fig. S15. C_2H_4+H→C_2H_5 on Ni(111): The hydrogen attacks the ethylene (initial state before hydrogenation, IS) to form ethyl (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 0.39 eV.

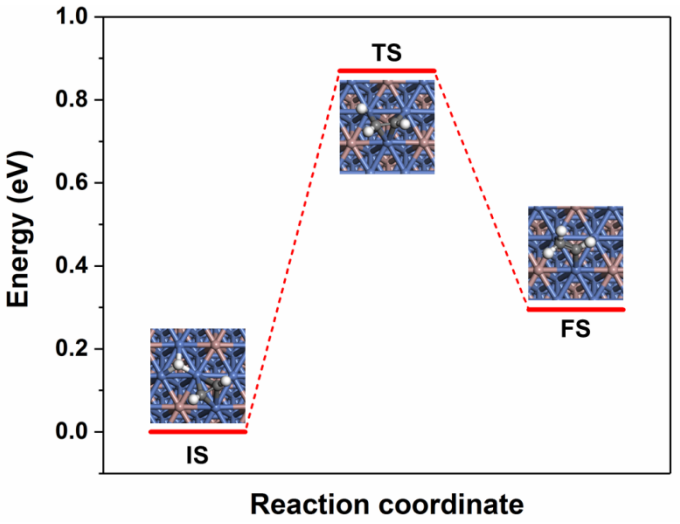

Fig. S16. C_2H_2+H→C_2H_3 on Ni_3Ga(111): The hydrogen attacks the acetylene (initial state before hydrogenation, IS) to form vinyl (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 0.87 eV.

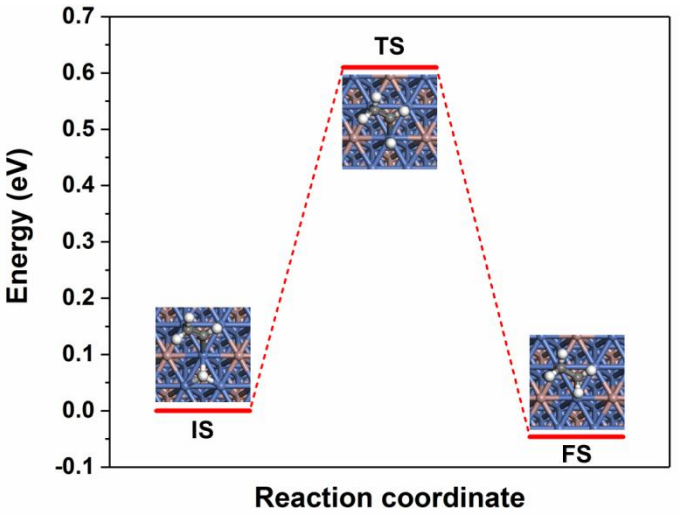

Fig. S17. C_2H_3+H→C_2H_4 on Ni_3Ga(111): The hydrogen attacks the vinyl (initial state before hydrogenation, IS) to form ethylene (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 0.61 eV.

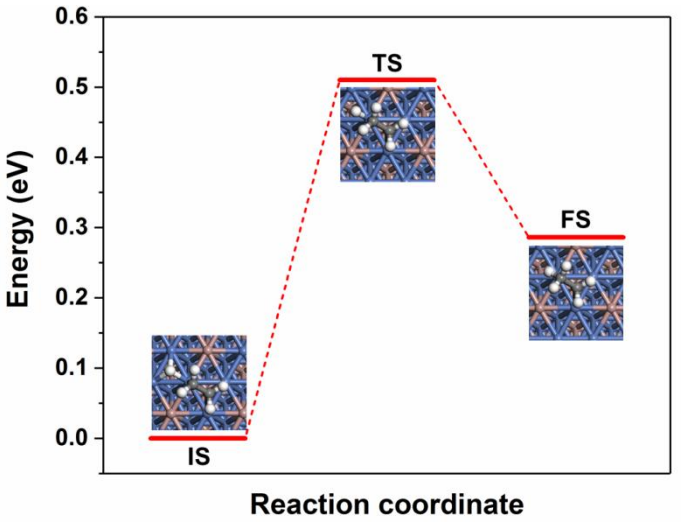

Fig. S18. C_2H_4+H→C_2H_5 on Ni_3Ga(111): The hydrogen attacks the ethylene (initial state before hydrogenation, IS) to form ethyl (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 0.51 eV.

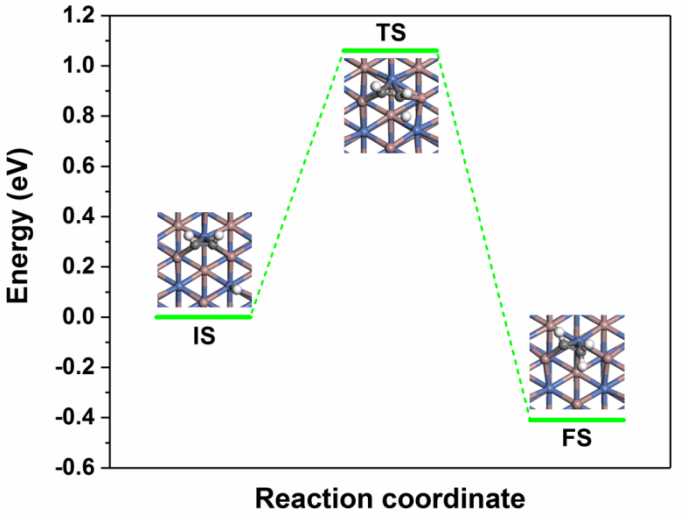

Fig. S19. C_2H_2+H→C_2H_3 on NiGa(111): The hydrogen attacks the acetylene (initial state before hydrogenation, IS) to form vinyl (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 1.06 eV.

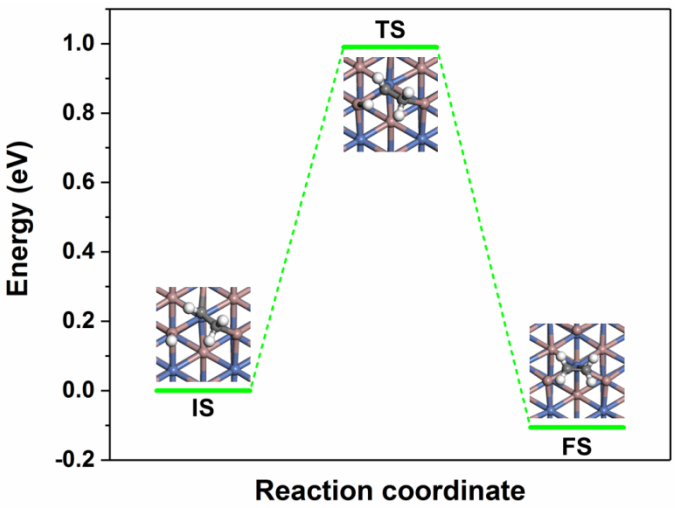

Fig. S20. C_2H_3+H→C_2H_4 on NiGa(111): The hydrogen attacks the vinyl (initial state before hydrogenation, IS) to form ethylene (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 0.99 eV.

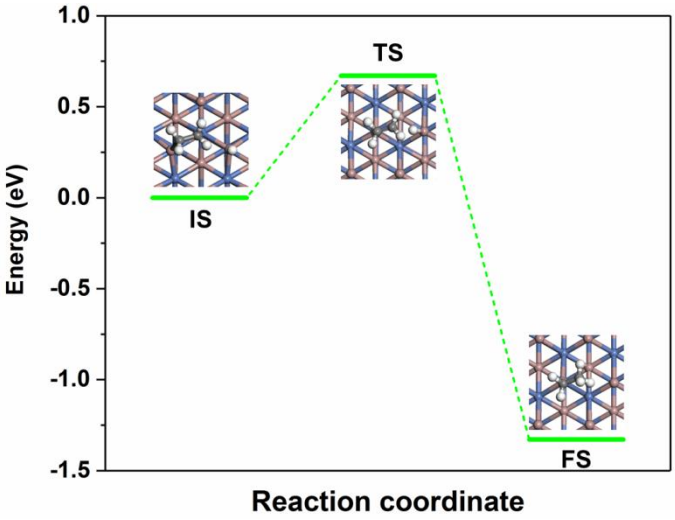

Fig. S21. C_2H_4+H→C_2H_5 on NiGa(111): The hydrogen attacks the ethylene (initial state before hydrogenation, IS) to form ethyl (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 0.67 eV.

Table S4. Reaction heat (ΔE) of the hydrogenation steps over Ni(111), Ni_3Ga(111) and NiGa(111) surfaces. $\Delta E = E_{ad}(C_2H_{y+1}) - E_{ad}(H + C_2H_y)$.

	ΔE/eV		
	$H + C_2H_2 \rightarrow C_2H_3$	$H + C_2H_3 \rightarrow C_2H_4$	$H + C_2H_4 \rightarrow C_2H_5$
Ni(111)	0.58	−0.05	0.17
Ni_3Ga(111)	0.30	−0.05	0.29
NiGa(111)	−0.41	−0.11	−1.33

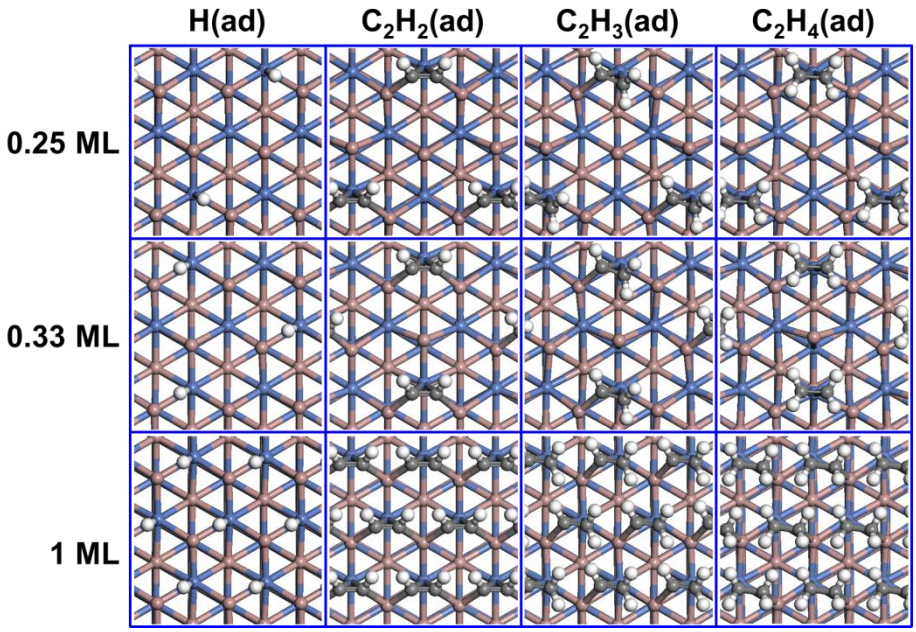

Fig. S22. Adsorption structures of H, C_2H_2, C_2H_3 and C_2H_4 on NiGa(111) surface with different coverage density.

Table S5. Adsorption energies of H, C_2H_2, C_2H_3 and C_2H_4 on NiGa(111) surface with different coverage density.

	Adsorption energy (eV)			
	H	C_2H_2	C_2H_3	C_2H_4
0.25 ML	−0.21	−1.55	−2.41	−0.04
0.33 ML	−0.21	−1.55	−2.39	−0.004
1 ML	−0.18	−1.05	−1.69	0.49

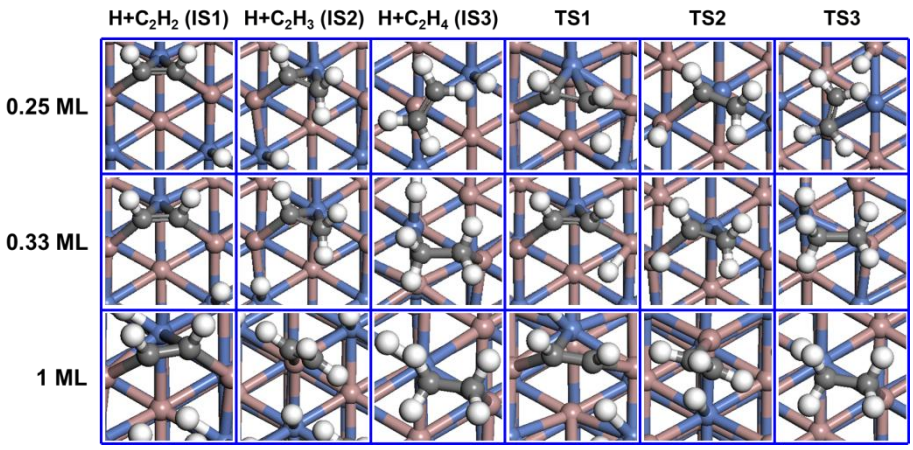

Fig. S23. Co-adsorption structures of C_2H_y (y=2, 3, 4) species with hydrogen atoms before hydrogenation (initial states, ISs), and their corresponding transition states (TSs) on NiGa(111) surface with different coverage density.

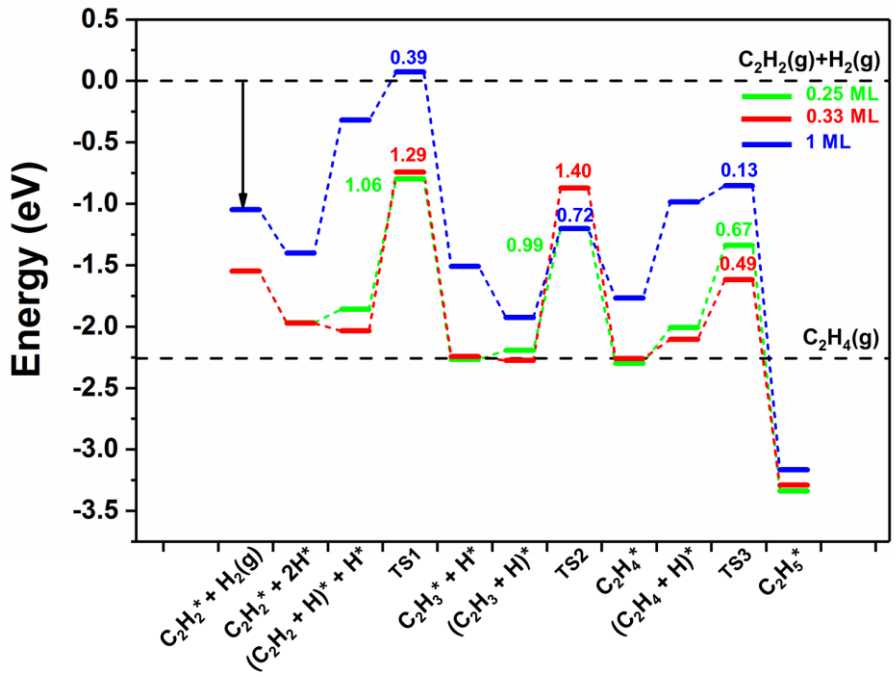

Fig. S24. Energy profiles of overall acetylene hydrogenation reactions over NiGa(111) surfaces via ethylene pathway with different coverage density. The reaction states of the species are labeled below the coordinate, where "(g)" stands for the gas phase and "*" stands for the adsorption state; "TS" stands for the transition state of hydrogenation.

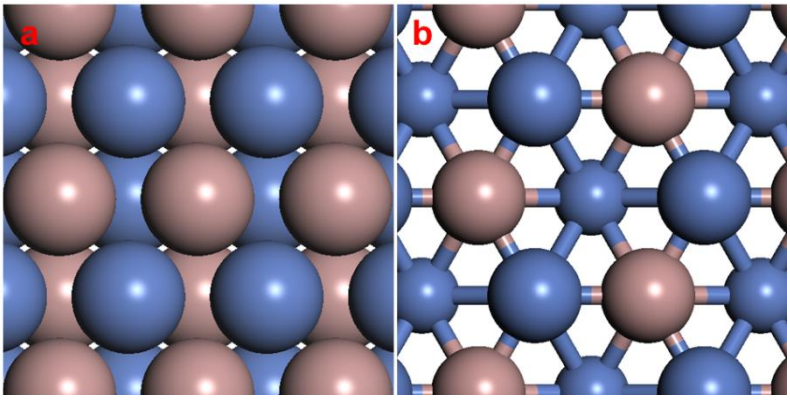

Fig. S25. The topview of a) NiGa(110) and b) NiGa(111)' crystal surfaces (Ni: blue; Ga: rufous).

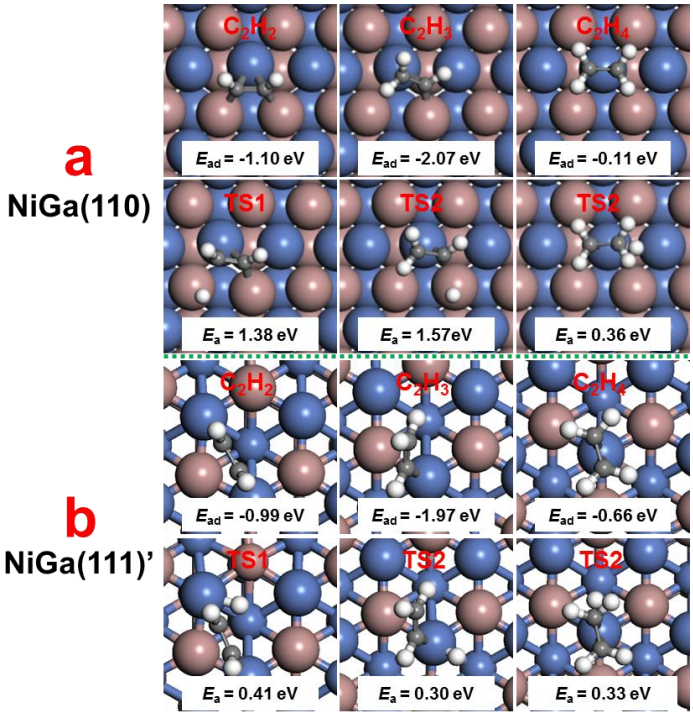

Fig. S26. Adsorption structures and energies (E_{ad}) of C_2H_y together with their corresponding transition states and hydrogenation barriers (E_a) over a) NiGa(110) and b) NiGa(111)' surfaces.

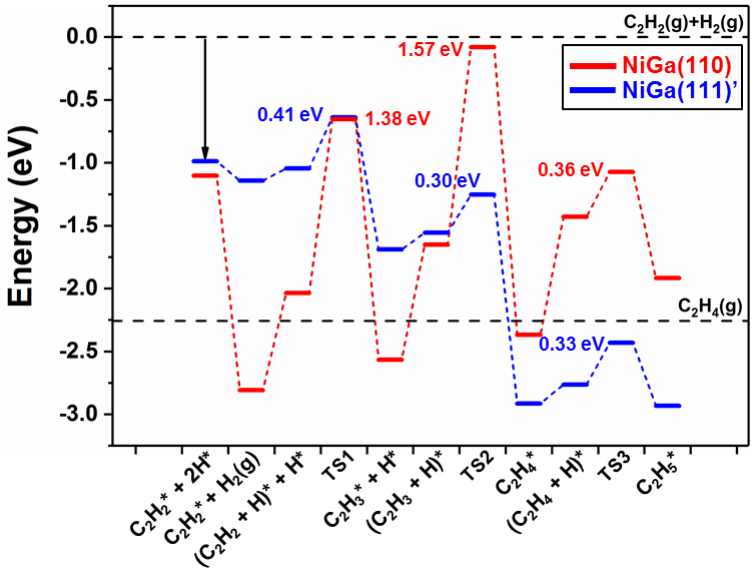

Fig. S27. Energy profiles of overall acetylene hydrogenation reactions over NiGa(110) and NiGa(111)' surfaces via ethylene pathway. The label codes are the same as those in **Fig. S24**.

Table S6. Adsorption energies (E_{ad}) and hydrogenation barriers (E_a) of ethylene on NiGa(110) and NiGa(111)' surfaces, as well as their corresponding ΔE_a calculated by eqn. (2).

	NiGa(110)	NiGa(111)'
ΔE_a (eV)	0.25	−0.33
E_a^{eff} (eV)	2.73	0.50

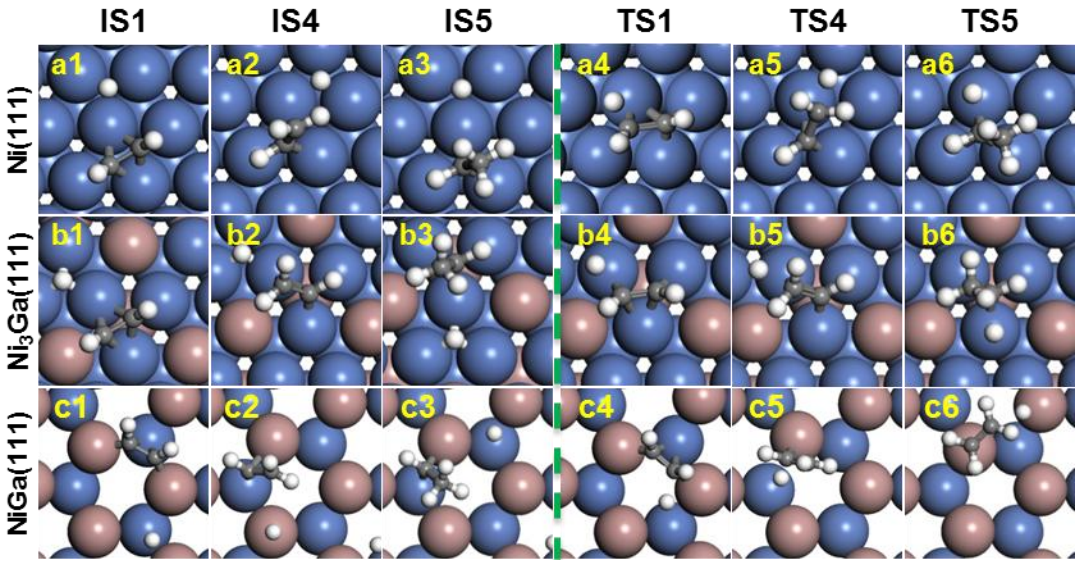

Fig. S28. a) Co-adsorption structures (initial states, ISs) of C_2H_2, C_2H_3 and $CHCH_3$ with hydrogen atoms and b) their corresponding transition states (TSs) on Ni(111), Ni_3Ga(111), and NiGa(111) surfaces.

Table S7. Hydrogenation barrier and the distance between the attacking H atom and the acceptor C atom of each transition state on Ni(111), Ni_3Ga(111) and NiGa(111) surfaces.

	TS1		TS4		TS5	
	E_a (eV)	$d_{H\text{-}C}$（Å）	E_a (eV)	$d_{H\text{-}C}$（Å）	E_a (eV)	$d_{H\text{-}C}$（Å）
Ni(111)	1.01	1.170	0.31	1.673	0.76	1.563
Ni_3Ga(111)	0.87	1.590	0.58	1.834	0.67	1.525
NiGa(111)	1.06	1.660	0.21	1.949	2.07	2.111

Table S8. The states of TDTS and TDI, the energies of TDTS and TDI, and the calculated E_a^{eff} of ethylidene pathway over Ni(111), Ni_3Ga(111) and NiGa(111) surfaces.

	Ni(111)	Ni_3Ga(111)	NiGa(111)
TDTS	TS3	TS3	TS3
E_{TDTS} (eV)	−2.21	−2.12	−0.42
TDI	C_2H_2*+2H*	C_2H_2*+2H*	$CHCH_3$*
E_{TDI} (eV)	−3.68	−3.85	−2.56
E_a^{eff} (eV)	1.47	1.73	2.14

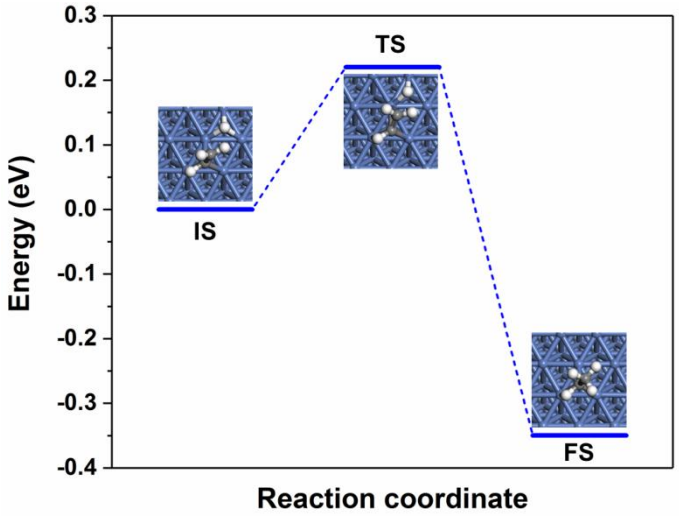

Fig. S29. C_2H_3+H→$CHCH_3$ on Ni(111): The hydrogen attacks the vinyl (initial state before hydrogenation, IS) to form ethylidene (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 0.31 eV.

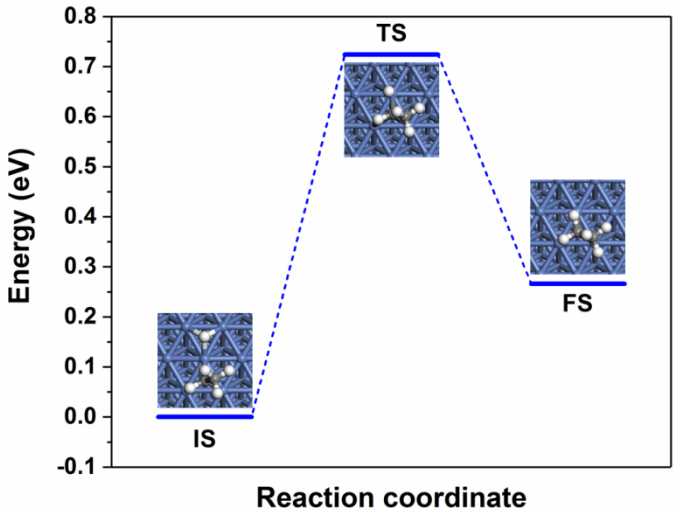

Fig. S30. $CHCH_3$+H→C_2H_5 on Ni(111): The hydrogen attacks the ethylidene (initial state before hydrogenation, IS) to form ethyl (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 0.76 eV.

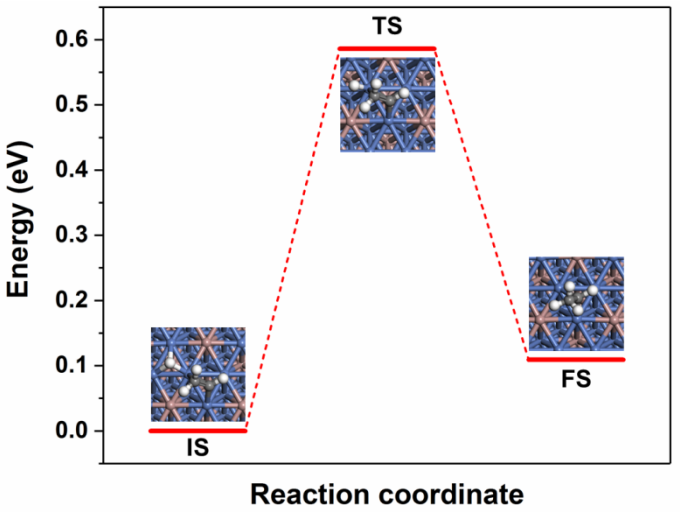

Fig. S31. C_2H_3+H→$CHCH_3$ on Ni_3Ga(111): The hydrogen attacks the vinyl (initial state before hydrogenation, IS) to form ethylidene (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 0.58 eV.

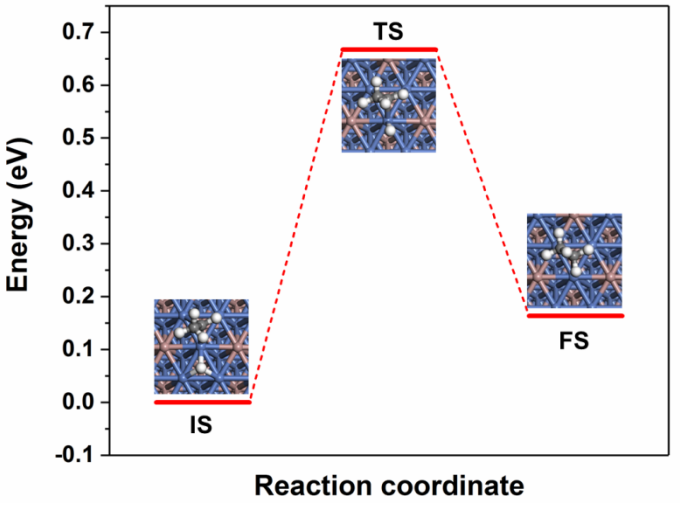

Fig. S32. $CHCH_3$+H→C_2H_5 on Ni_3Ga(111): The hydrogen attacks the ethylidene (initial state before hydrogenation, IS) to form ethyl (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 0.67 eV.

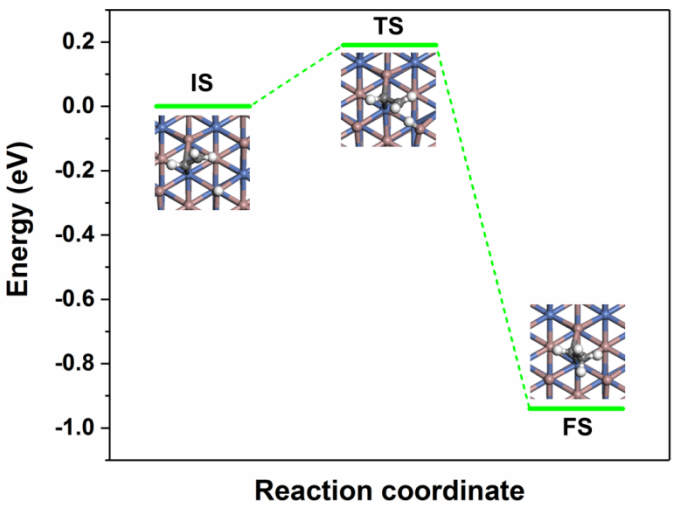

Fig. S33. C_2H_3+H→$CHCH_3$ on NiGa(111): The hydrogen attacks the vinyl (initial state before hydrogenation, IS) to form ethylidene (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 0.21 eV.

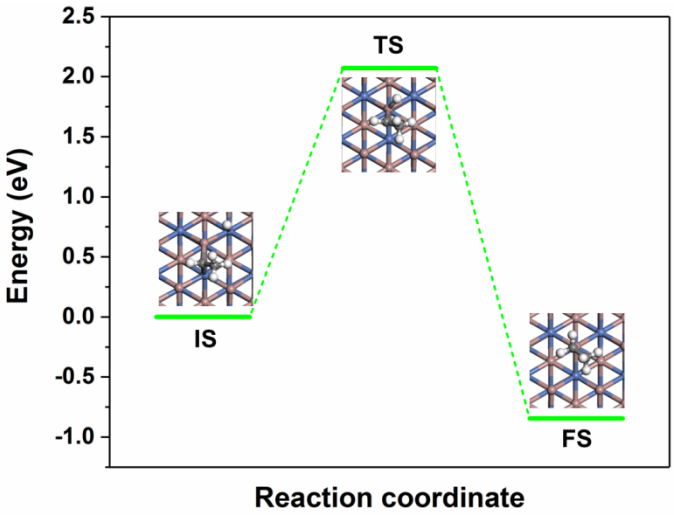

Fig. S34. $CHCH_3$+H→C_2H_5 on NiGa(111): The hydrogen attacks the ethylidene (initial state before hydrogenation, IS) to form ethyl (final state after hydrogenation, FS) via the transition state (TS) with a barrier of 2.07 eV.

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