Electronic Supporting Information

for

Theoretical Study on the Reaction Mechanism and Selectivity of

Acetylene Semi-hydrogenation on Ni-Sn Intermetallic Catalysts

De-Ming Rao^{&a,b}, Tao Sun^{&a}, Yu-Sen Yang^a, Pan Yin^a, Min Pu^a, Hong Yan^{*a} and Min Wei^{*a}

^aState Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

^bInstitute of Science and technology strategy, Jiangxi academy of science, Jiangxi 330000, China

Corresponding Authors

*(H. Y.) E-mail: yanhong@mail.buct.edu.cn

*(M. W.) Tel: +86-010-64412131. E-mail: weimin@mail.buct.edu.cn



Fig. S1. Structure details of a) bulk Ni₃Sn and b) bulk Ni₃Sn₂, and the side view of their corresponding surfaces of c) Ni₃Sn(111), d) Ni₃Sn(001) e) Ni₃Sn₂(101), f) Ni₃Sn₂(001), g) Ni₃Sn₂(101)-2 and h) Ni₃Sn₂(001)-2 surfaces after optimization. (Ni: blue; Sn: dark green)

Table S1. Computational tests for layer-thickness with the adsorption of C_2H_2 as an example. " C_2H_2 -3L" means C_2H_2 adsorbs on a 3-layer slab, " C_2H_2 -4L" means C_2H_2 adsorbs on a 4-layer slab, and so on.

	Ni ₃ Sn(111)	Ni ₃ Sn(001)	Ni ₃ Sn ₂ (101)	Ni ₃ Sn ₂ (001)	Ni ₃ Sn ₂ (101)-2	Ni ₃ Sn ₂ (001)-2
C ₂ H ₂ -3L	-1.79	-0.49	-1.03	-0.68	-2.35	-1.69
C ₂ H ₂ -4L	-1.91	-0.56	-1.12	-0.74	-2.49	-1.80

C_2H_2 -5L	-1.90	-0.58	-1.11	-0.75	-2.47	-1.83

Table S2. Surface energies (γ) of Ni-Sn surfaces with different compositions. $\gamma = (E_{\text{slab}} - NE_{\text{bulk}})/2A$. 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 Ni ₃ Sn	Ni ₃ Sn	-21.369488	
Ni ₃ Sn(111)	Ni ₃₆ Sn ₁₂	-243.97860	1.372
Ni ₃ Sn(001)	Ni ₄₈ Sn ₁₆	-317.28028	1.763
Bulk Ni ₃ Sn ₂	Ni ₃ Sn ₂	-31.056213	
Ni ₃ Sn ₂ (101)	Ni ₂₄ Sn ₁₆	-232.01315	1.246
Ni ₃ Sn ₂ (001)	Ni ₂₇ Sn ₁₈	-253.23837	1.464
Ni ₃ Sn ₂ (101)-2	Ni ₂₄ Sn ₁₆	-232.00692	1.247
Ni ₃ Sn ₂ (001)-2	Ni ₂₇ Sn ₁₈	-256.80077	1.266



Fig. S2. Adsorption structures and energies of a) H_2 molecule and b) H atom on $Ni_3Sn(111)$, $Ni_3Sn(001)$, $Ni_3Sn_2(101)$ and $Ni_3Sn_2(001)$ surfaces.



Fig. S3. Energy profile of H₂ dissociation on Ni₃Sn(111), Ni₃Sn(001), Ni₃Sn₂(101), Ni₃Sn₂(001), Ni₃Sn₂(101)-2 and Ni₃Sn₂(001)-2 surfaces, "TS0" in the reaction coordinate stands for the transition state of H₂ dissociation. (numbers of TS0 indicate the dissociation barriers)



Fig. S4. Summary of the possible adsorption stations of C₂H₂ (a-f) and C₂H₄ (g-l) on

Ni₃Sn(111) surface. H, C and Ni atoms are represented by white, gray and blue balls, respectively, and this color mode is used throughout the context.



Fig. S5. Summary of the possible adsorption stations of C_2H_2 (a, b) and C_2H_4 (c) on $Ni_3Sn(001)$ surface.



Fig. S6. Summary of the possible adsorption stations of C_2H_2 (a-e) and C_2H_4 (f-k) on $Ni_3Sn_2(101)$ surface.



Fig. S7. Summary of the possible adsorption stations of C_2H_2 (a, b) and C_2H_4 (c, d) on $Ni_3Sn_2(001)$ surface.



Fig. S8. Summary of the possible adsorption stations of C_2H_2 (a, b) and C_2H_4 (c-g) on

Ni₃Sn₂(101)-2 surface.



Fig. S9. Summary of the possible adsorption stations of C_2H_2 (a, b) and C_2H_4 (c, d) on





Fig. S10. Co-adsorption structures of H and C₂ species, the initial states (ISs) before hydrogenation.



Fig. S11. $C_2H_2+H\rightarrow C_2H_3$ on Ni₃Sn(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 1.25 eV.



Fig. S12. $C_2H_3+H\rightarrow C_2H_4$ on Ni₃Sn(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 1.11 eV.



Fig. S13. $C_2H_4+H\rightarrow C_2H_5$ on Ni₃Sn(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 1.05 eV.



Fig. S14. $C_2H_2+H\rightarrow C_2H_3$ on Ni₃Sn(001): 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 0.90 eV.



Fig. S15. $C_2H_3+H\rightarrow C_2H_4$ on Ni₃Sn(001): 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 0.86 eV.



Fig. S16. $C_2H_4+H\rightarrow C_2H_5$ on Ni₃Sn(001): 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 0.97 eV.



Fig. S17. $C_2H_2+H\rightarrow C_2H_3$ on Ni₃Sn₂(101): 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 1.23 eV.



Fig. S18. $C_2H_3+H\rightarrow C_2H_4$ on Ni₃Sn₂(101): 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 0.76 eV.



Fig. S19. $C_2H_4+H\rightarrow C_2H_5$ on Ni₃Sn₂(101): 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 0.94 eV.



Fig. S20. $C_2H_2+H\rightarrow C_2H_3$ on Ni₃Sn₂(001): 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 0.45 eV.



Fig. S21. $C_2H_3+H\rightarrow C_2H_4$ on Ni₃Sn₂(001): 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 0.36 eV.



Fig. S22. $C_2H_4+H\rightarrow C_2H_5$ on Ni₃Sn₂(001): 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 0.50 eV.



Fig. S23. $C_2H_2+H\rightarrow C_2H_3$ on Ni₃Sn₂(101)-2: 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 1.24 eV.



Fig. S24. $C_2H_3+H\rightarrow C_2H_4$ on Ni₃Sn₂(101)-2: 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 0.95 eV.



Fig. S25. $C_2H_4+H\rightarrow C_2H_5$ on Ni₃Sn₂(101)-2: 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 1.14 eV.



Fig. S26. $C_2H_2+H\rightarrow C_2H_3$ on Ni₃Sn₂(001)-2: 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 0.28 eV.



Fig. S27. $C_2H_3+H\rightarrow C_2H_4$ on Ni₃Sn₂(001)-2: 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 0.22 eV.



Fig. S28. $C_2H_4+H\rightarrow C_2H_5$ on Ni₃Sn₂(001)-2: 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 0.54 eV.

Table S3. The distance $(d_{C-H} / \text{Å})$ between the attacking H and the acceptor C atoms from the initial state to the transition state.

	Ni ₃ Sn(111)	Ni ₃ Sn(001)	Ni ₃ Sn ₂ (101)	Ni ₃ Sn ₂ (001)	Ni ₃ Sn ₂ (101)-2	Ni ₃ Sn ₂ (001)-2
H+C ₂ H ₂	2.91→1.71	3.15→2.27	2.58→1.76	2.59→2.36	2.62→1.17	2.50→1.70
H+C ₂ H ₃	3.07→1.83	3.76→2.29	2.63→2.33	2.88→2.09	3.44→1.93	2.70→1.94
H+C ₂ H ₄	2.44→1.68	3.39→2.28	2.54→1.54	3.96→1.92	3.50→1.55	3.36→1.58

Determination of the effective barriers

The *TOF* can be simulated according to the energetic span theory^{S2-S5} as follows:

$$TOF \approx \frac{k_{\rm B}T}{h} e^{-E_{\rm a}^{\rm eff}/RT}$$
(S1)

where $k_{\rm B}$ stands for the Boltzmann constant, *T* is the reaction temperature, and *h* is the Planck constant; $E_{\rm a}^{\rm eff}$ is defined as an effective barrier of a catalysis process, based on the previous reports^{S6, S7}:

$$E_{a}^{\text{eff}} = \begin{cases} E_{\text{TDTS}} - E_{\text{TDI}} & \text{if TDTS appears after TDI} & (a) \\ E_{\text{TDTS}} - E_{\text{TDI}} + \Delta E & \text{if TDTS appears before TDI} & (b) \end{cases}$$
(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 Ni₃Sn(111) surface as an example to show how to obtain the E_a^{eff} from the energy profiles (Fig. 3 in the main text). 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 to C_2H_4 on Ni₃Sn(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. As TDTS appears after TDI, we can calculate the E_a^{eff} with the eq. S2(a). The value of E_a^{eff} is calculated to be 1.73 eV.

Table S4. The states of TDTS and TDI, the energies of TDTS and TDI, and the calculated E_{a}^{eff} of ethylene pathway over Ni₃Sn(111), Ni₃Sn(001), Ni₃Sn₂(101) and Ni₃Sn₂(001) surfaces.

	Ni ₃ Sn(111)	Ni ₃ Sn(001)	Ni ₃ Sn ₂ (101)	Ni ₃ Sn ₂ (001)	Ni ₃ Sn ₂ (101)-2	Ni ₃ Sn ₂ (001)-2
TDTS	TS2	TS0	TS1	TS1	TS1	TS3
$E_{\text{TDTS}} (\text{eV})$	-1.83	-0.29	0.69	-0.21	-2.18	-3.01
TDI	$2H^{+}C_{2}H_{2}^{+}$	H ₂ *	C_2H_2*	C_2H_2*	2H*+C ₂ H ₂ *	C_2H_4 *
$E_{\text{TDI}} \left(\text{eV} \right)$	-3.56	-1.18	-1.12	-0.74	-3.60	-2.46
$E_{a}^{eff}(eV)$	1.73	1.47	1.81	0.53	1.42	0.55



Fig. S29. Adsorption sites of C_2H_4 on Ni-Sn surfaces and the Ni-Ni distances of the sites for calculating the average Ni-Ni distance (d_{Ni-Ni}).

Table S5. The average Ni-Ni distance $(d_{\text{Ni-Ni}} / \text{Å})$ of the site for C₂H₄ adsorption on each Ni-Sn surface.

	Ni ₃ Sn(111	Ni ₃ Sn(001)	Ni ₃ Sn ₂ (101)	Ni ₃ Sn ₂ (001)	Ni ₃ Sn ₂ (101)-2	Ni ₃ Sn ₂ (001)-2
)					
$d_{ m Ni-Ni}$ /Å	2.669	3.789	3.576	4.333	2.434	2.454

Table S6. The surface roughness (R) of Ni-Sn surfaces, according to eq. (6) in the main text.

	Ni ₃ Sn(111	Ni ₃ Sn(001)	Ni ₃ Sn ₂ (101)	Ni ₃ Sn ₂ (001)	Ni ₃ Sn ₂ (101)-2	Ni ₃ Sn ₂ (001)-2
_)					
<i>R</i> /10 ⁻³ Å	8.27	7.28	34.79	29.92	14.69	22.83



Fig. S30. Activity and selectivity of Ni₃Sn and Ni₃Sn₂ surfaces for the hydrogenation of acetylene to ethylene plotted as a function of the surface roughness. The activity and selectivity is measured by the values of $-\frac{E_{a}^{eff}}{a}$ and ΔE_{a} , respectively.

Energy decomposition method

An energy decomposition method to quantitively analyze the determining factor of the transition states of C_2H_4 hydrogenation on the Ni-Sn surfaces was used (Scheme S1), which was previously proposed by Liu and Hu.^{S8, S9} The energy barrier (E_a) can be decomposed into three terms, E_{C2H4} , E_H and E_{int} as follows:

$$E_{\rm a} = E_{\rm C2H4} + E_{\rm H} + E_{\rm int} \tag{S3}$$

where E_{C2H4} (E_H) is the energy difference between the surface adsorption state of C_2H_4 (H) and the transition state without H (C_2H_4) and E_{int} is the interaction energy of

the two reactants at the transition state. E_{C2H4} (E_{H}) can be obtained from the single point energy of the transition state, in which only the species H ($C_{2}H_{4}$) was removed without any structural relaxation. By using this energy decomposition method, we can identify which one contributes the most among E_{C2H4} , E_{H} and E_{int} to the reaction barrier E_{a} .



Scheme S1. Reaction barrier (E_a) decomposition, E_a is decomposed into three terms: E_{C2H4} (E_H) is the energy cost for C₂H₄ (H) to move from the initial state (IS) to the transition state (TS) without H (C₂H₄). E_{int} is a measure of the interaction energy between C₂H₄ and H at the TS.

Reference

- S1 Q. Feng, S. Zhao, Y. Wang, J. Dong, W. Chen, D. He, D. Wang, J. Yang, Y. Zhu and H. Zhu, J. Am. Chem. Soc., 2017, 139, 7294-7301.
- S2 S. Kozuch and S. Shaik, J. Am. Chem. Soc., 2006, 128, 3355-3365.

- S3 S. Kozuch and S. Shaik, Acc. Chem. Res., 2010, 44, 101-110.
- S4 S. Kozuch and J. M. L. Martin, ACS Catal., 2011, 1, 246-253.
- S5 S. Kozuch and J. M. L. Martin, Chem. Commun., 2011, 47, 4935-4937.
- S6 B. Yang, R. Burch, C. Hardacre, P. Hu and P. Hughes, J. Phys. Chem. C, 2014, 118, 3664-3671.
- S7 B. Yang, R. Burch, C. Hardacre, G. Headdock and P. Hu, J. Catal., 2013, 305, 264-276.
- S8 Z. P. Liu and P. Hu, J. Chem. Phys., 2001, 114, 8244-8247.
- S9 Z. P. Liu and P. Hu, J. Chem. Phys., 2001, 115, 4977-4980.