Ethylene Dissociation on Ni_3Al (111)

Junning Li[1], *Yu Wang*[1*], *Davide Curcio*[2], *Silvano Lizzit*[3], *Alessandro Baraldi,*[2,3,4], *Lev Kantorovich*[5*] and *Andrea Floris*[6*]

[1]School of Physics and Technology, Wuhan University, Wuhan 430072, China
[2]Physics Department, University of Trieste, Via Valerio 2, 34127 Trieste, Italy
[3]Elettra-Sincrotrone Trieste S.C.p.A., Strada Statale 14 Km 163.5, 34149 Trieste, Italy
[4]IOM-CNR, Laboratorio TASC, AREA Science Park, S.S. 14 Km 163.5, 34149 Trieste, Italy
[5]Department of Physics, King's College London, London, Strand WC2R 2LS, United Kingdom
[6]School of Mathematics and Physics, University of Lincoln, Brayford Pool, LN6 7TS Lincoln, United Kingdom.

*afloris@lincoln.ac.uk; *lev.kantorovitch@kcl.ac.uk; *yu.wang@whu.edu.cn

CORRESPONDING AUTHORS
Andrea Floris, School of Mathematics and Physics, University of Lincoln, Brayford Pool, LN6 7TS Lincoln, United Kingdom, phone: +44 1522 83 5884.
Lev Kantorovich, Department of Physics, King's College London, London, Strand WC2R 2LS, United Kingdom, phone: +44 020 7848 2160.
Yu Wang, School of Physics and Technology, Wuhan University, Wuhan 430072, China, phone: +86 1587 135 1027.

Supporting Information

1 Hydrogen adsorption sites on Ni_3Al (111)

In dehydrogenation reactions, hydrogen atoms will dissociate from the hydrocarbon molecule and adsorb on the surface. We investigated the adsorption of an H atom on Ni_3Al (111), by identifying all the most stable adsorption sites. We found that hydrogen atoms only adsorb in hollow positions among three atoms. Three out of four possible hollow sites are able to capture hydrogen atoms (see Fig. S1). Configuration H1 the most stable site for H atom adsorption, with a calculated adsorption energy of -4.04 eV.

The behavior of a H_2 molecule on Ni_3Al (111) was also explored. We found that the molecule detaches from the surface and goes in the gas phase.

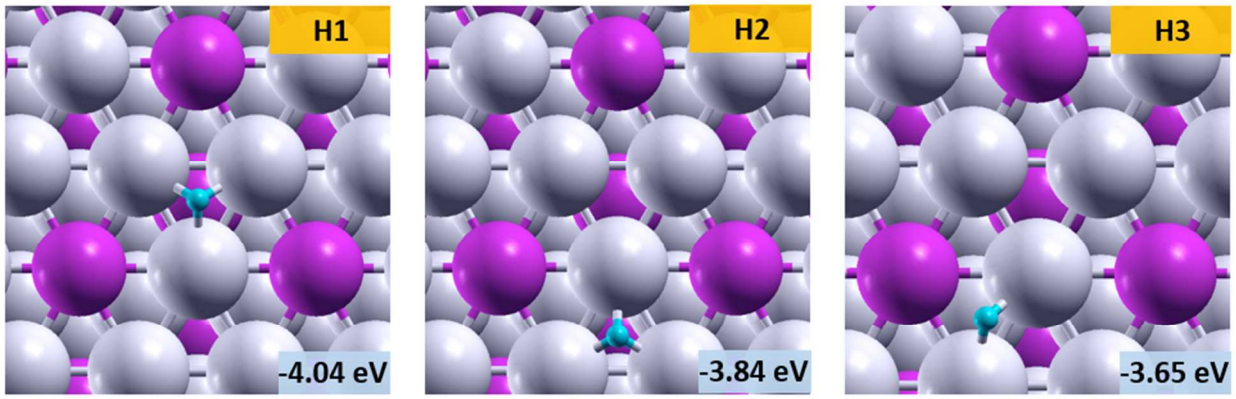
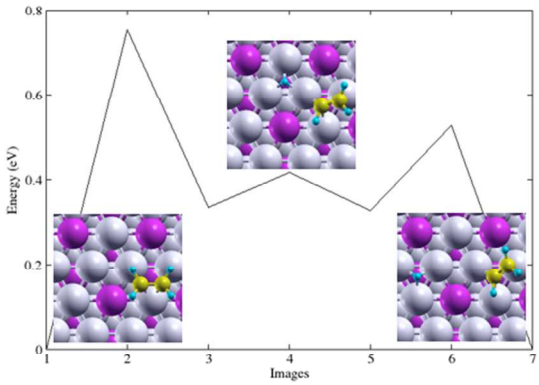


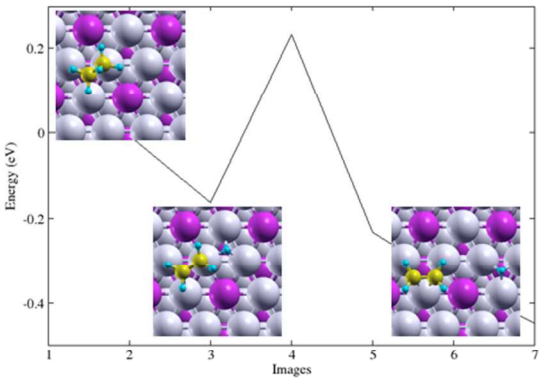
Figure S1. Three stable sites for a hydrogen atom on Ni_3Al (111), with the corresponding adsorption energies. Configuration H1 (left panel) is the most stable found.

2 Energy barriers and reaction paths

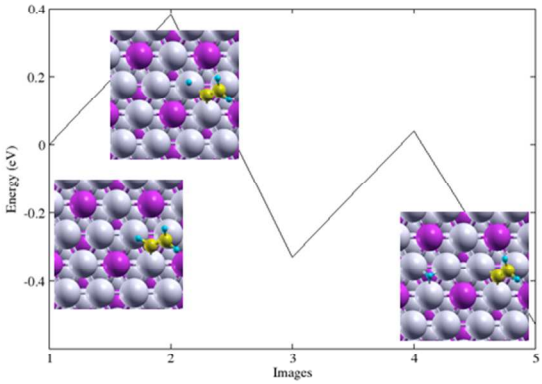
In NEB calculations, energy barriers are highly dependent on the initial and final states chosen (ISs and FSs). Given a specific reaction, we consider various combinations of (stable) ISs and FSs. As an example, the procedure to calculate the barrier corresponding to the dehydrogenation of ethylene (CH_2-CH_2 → CH_2-CH + H) is described. We used the relaxed ethylene molecule on the surface as the IS. In order to obtain a specific FS, we added one H atom in one of the most stable sites (see Fig. S1) into the system of relaxed CH_2-CH and then relaxed the (CH_2-CH + H) system. Different possibilities related to different H adsorption represent different FSs. After calculating the path corresponding to each possibility, we chose the lowest barrier and we associate it to the reaction process. The details of each reaction are shown in the panels of Fig. S2.



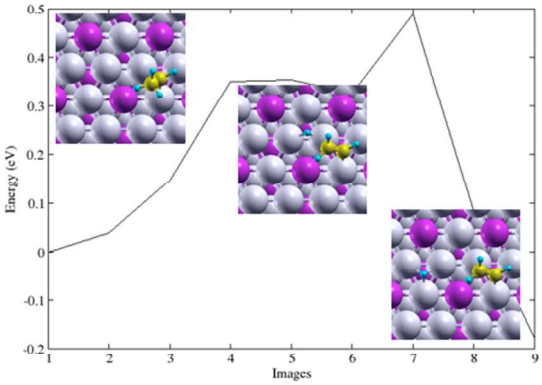
Reaction 1: CH_2-CH_2 → CH_2-CH + H



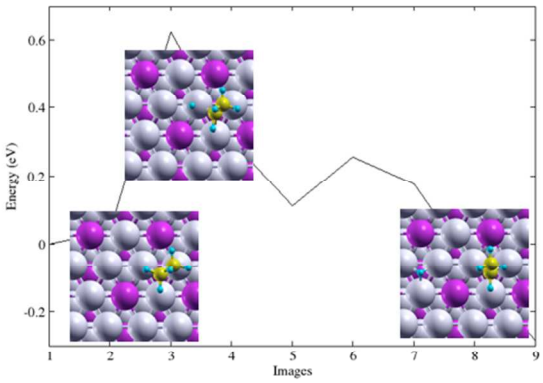
Reaction 2: CH_3-CH_2 → CH_2-CH_2 + H



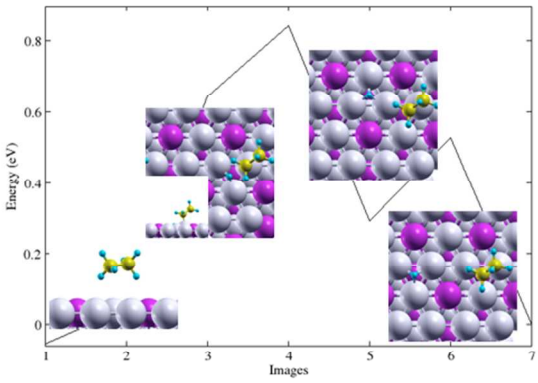
Reaction 3: CH_2-CH → CH_2-C + H



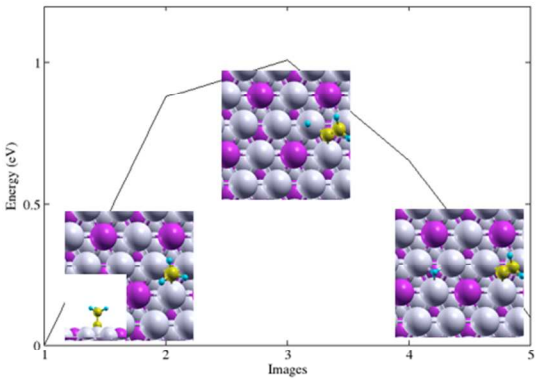
Reaction 4: CH_3-CH → CH_2-CH + H



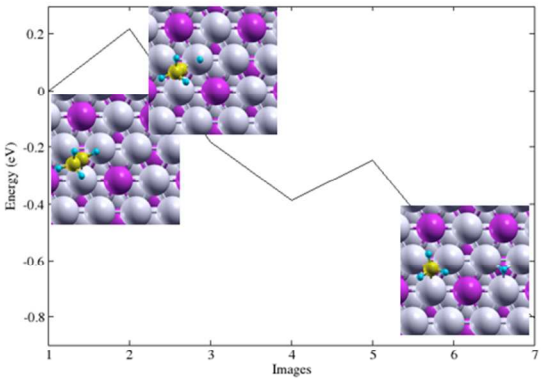
Reaction 5: CH_3-CH_2 → CH_3-CH + H



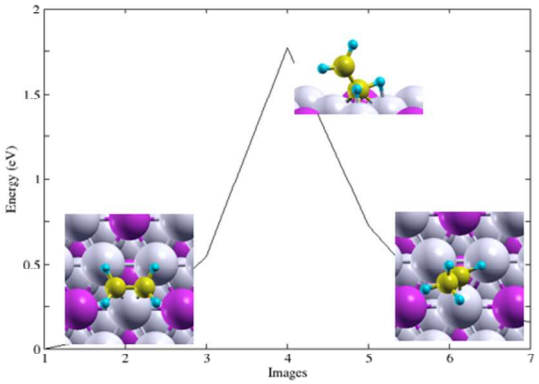
Reaction 6: CH_3-CH_3 → CH_3-CH_2 + H



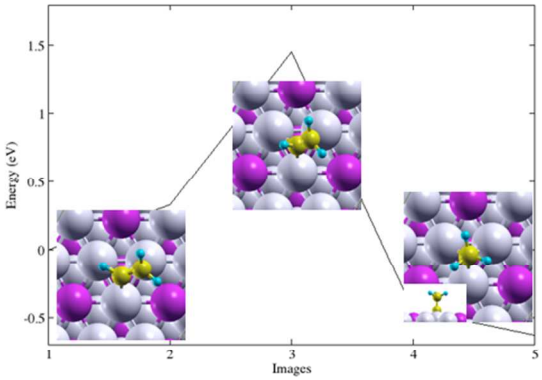
Reaction 7: CH_3-C → CH_2-C + H



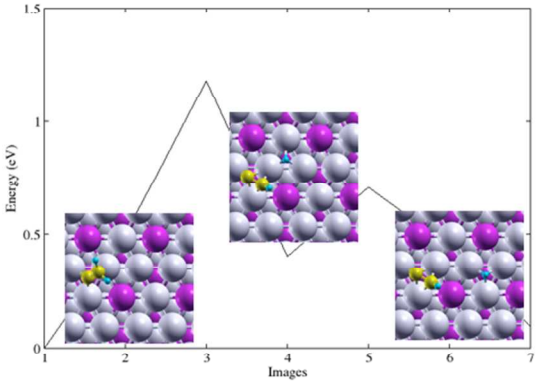
Reaction 8: CH_3-CH → CH_3-C + H



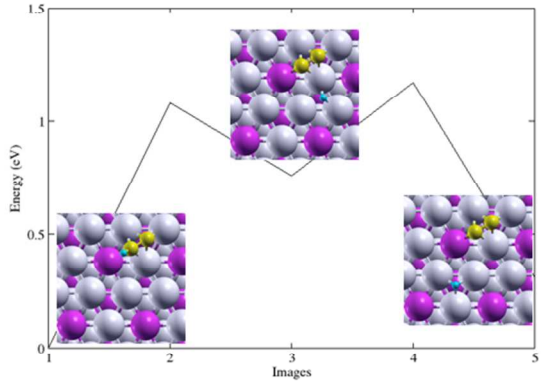
Reaction 9: CH_2-CH_2 → CH_3-CH



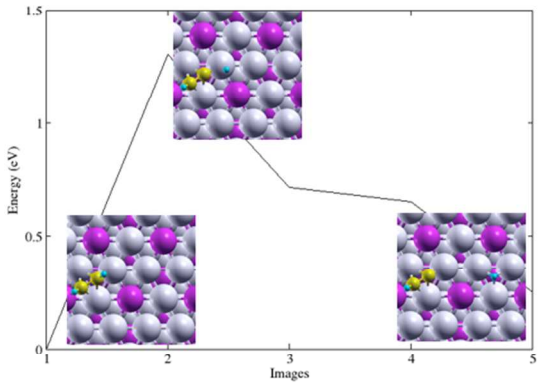
Reaction 10: CH_2-CH → CH_3-C



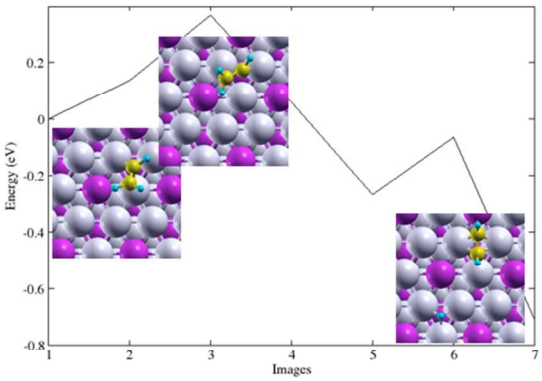
Reaction 11: CH_2-C → CH-C + H



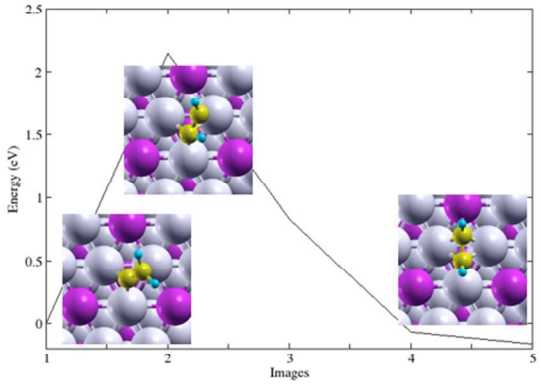
Reaction 12: CH-C → C-C + H



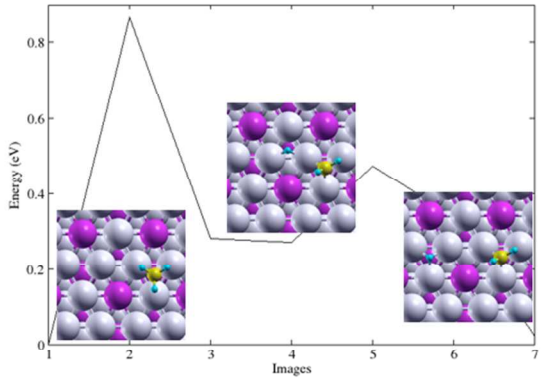
Reaction 13: CH-CH → CH-C + H



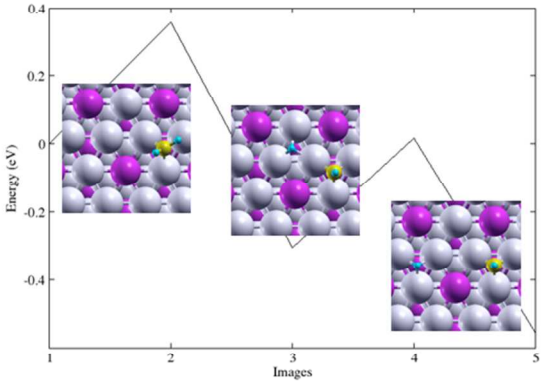
Reaction 14: CH_2-CH → CH-CH + H



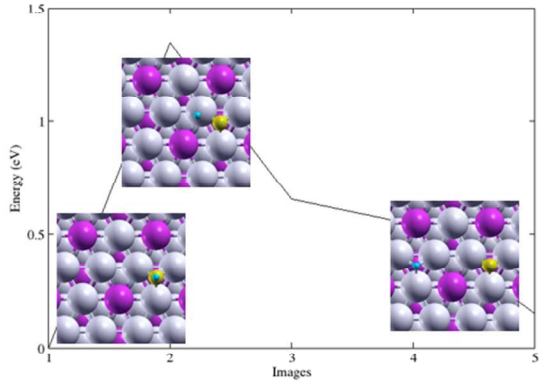
Reaction 15: CH_2-C → CH-CH



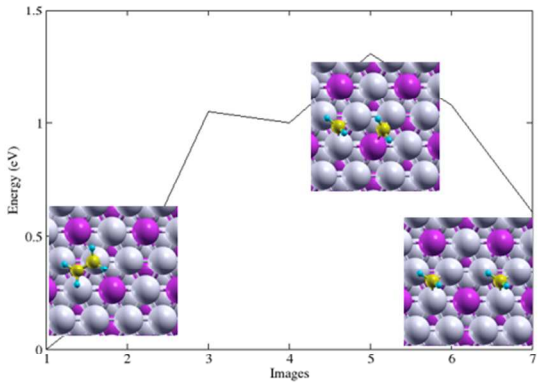
Reaction 16: CH_3 → CH_2 + H



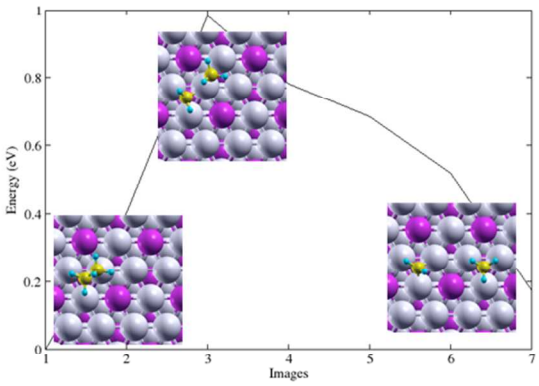
Reaction 17: CH_2 → CH + H



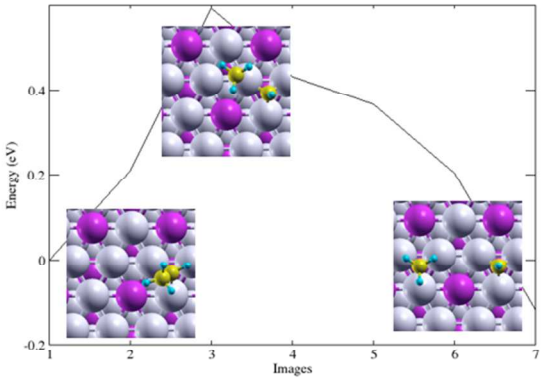
Reaction 18: CH → C + H



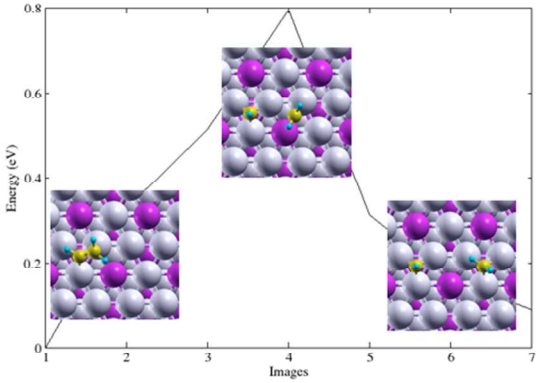
Reaction 19: CH_2-CH_2 → CH_2 + CH_2



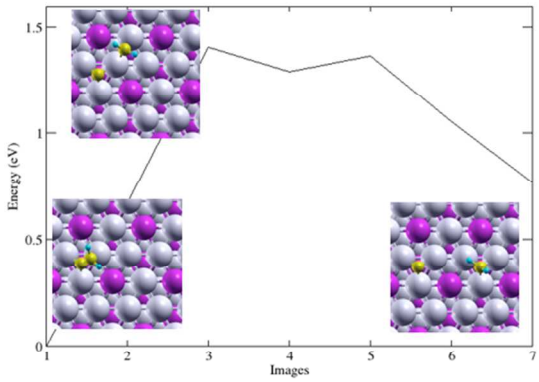
Reaction 20: CH_3-CH_2 → CH_3 + CH_2



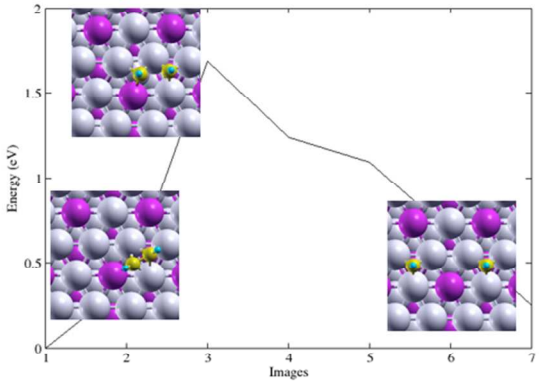
Reaction 21: CH_3-CH → CH_3 + CH



Reaction 22: CH_2-CH → CH_2 + CH



Reaction 23: CH_2-C → CH_2 + C



Reaction 24: CH-CH → CH + CH

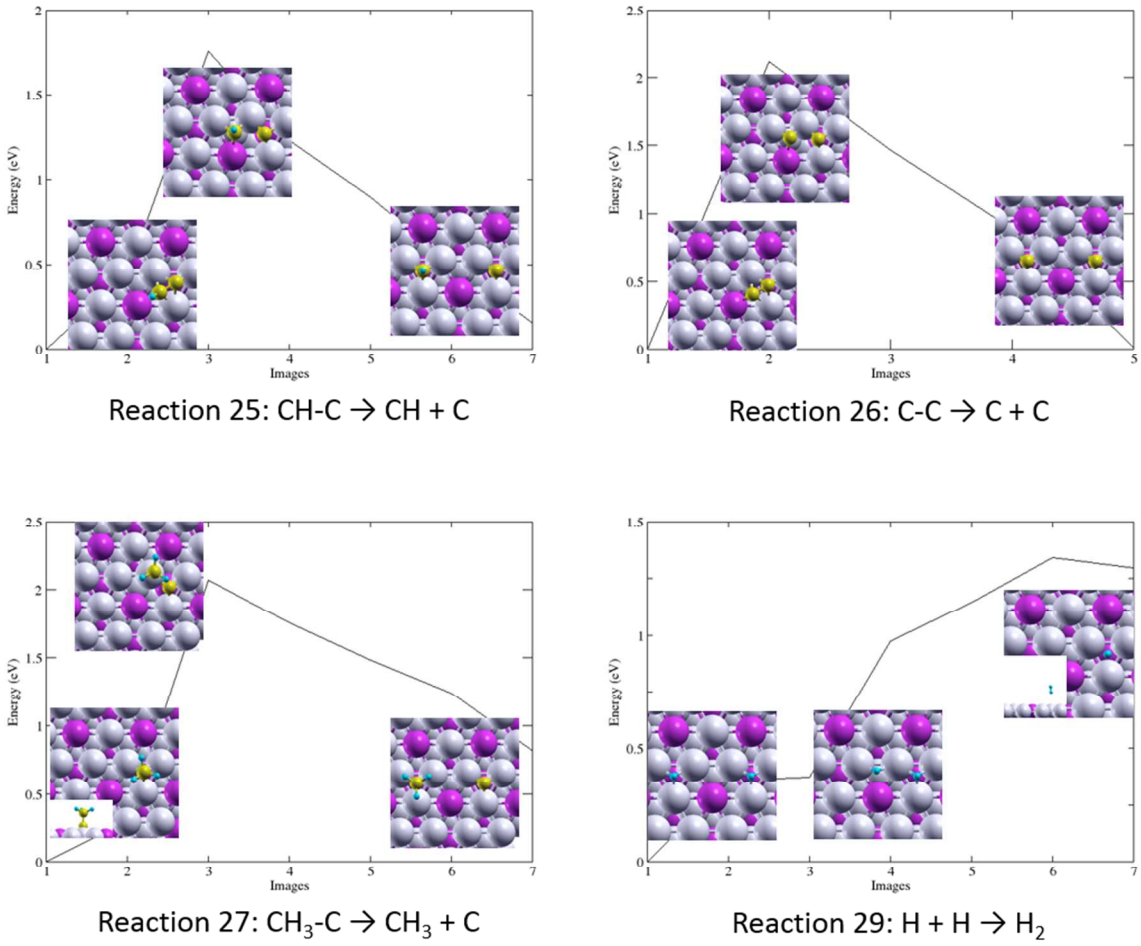


Figure S2. Minimum reaction paths and energy profiles of all processes analyzed in this work.

3 C-C and C diffusion processes on $Ni_3Al(111)$

C-C diffusions are considered in two directions: 1) the C-C molecule diffuses around one Al atom. 2) C-C molecule diffuse between two Al atoms.

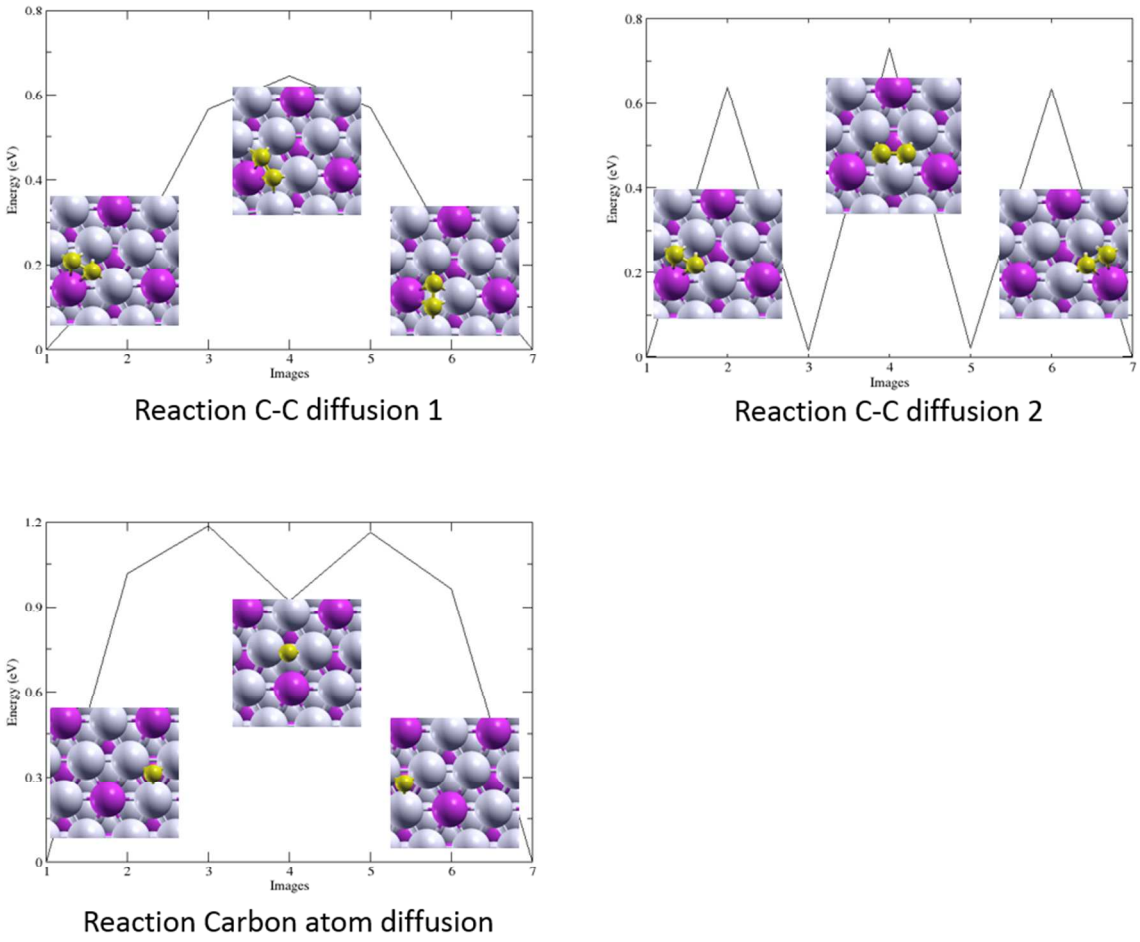


Figure S3. Minimum reaction paths and energy profiles of C-C and C diffusion on $Ni_3Al(111)$.