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Catalytic properties of $Al_{13}Co_4$ studied by ab initio methods

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While the surfaces of ordinary crystals provide only a few inequivalent adsorption sites, the complex landscape of the surfaces of quasicrystals and their approximants provides a rich variety of different adsorption sites. Recently Armbrüster et al. [1] reported that $Al_{13}Co_4$ whose structure is closely related to decagonal Al-Ni-Co quasicrystals is an efficient and selective hydrogenation catalyst for alkynes. In the present work the hydrogenation of acetylene to ethylene on the (100) surface of $Al_{13}Co_4$ has been studied using *ab initio* density-functional simulations. Surprisingly the stable cleavage surface of $Al_{13}Co_4$ is strongly corrugated. The surface is covered by zig-zag chains of edge-sharing Al pentagons, each centered by a Co atom and separated from neighboring chains by wide troughs. The binding energies for adsorption and coadsorption of H_2 and C_2H_2 molecules at various surface sites have been calculated. Surprisingly, in the energetically most favorable configuration acetylene is bound in a di- σ configuration to two Al atoms, not to the Co atom. We have searched for the optimal reaction pathway for the dissociative adsorption of hydrogen and for the hydrogenation of acetylene to vinyl, ethylene by a Langmuir-Hinshelwood mechanism. The energetic barriers for all reaction steps were calculated by the nudged-elastic-band method. It was found that the energetic barrier of any reaction step does not exceed 0.65 eV (63 kJ/mol). This value is lower than the activation energies for acetylene to ethylene hydrogenation over a Pd catalyst where barrier of 78 kJ/mol and 85 kJ/mol were reported for the rate-determining steps.

Keywords: $Al_{13}Co_4$ surface; catalytic reactions; acetylene hydrogenation;

1. Introduction

Recently significant progress has been achieved in experimental and theoretical investigations of surfaces of complex metallic alloys. Surfaces of quasicrystals and their approximants have attracted particular attention. One of the reasons for this interest is that surfaces of quasicrystals and their approximants have extraordinary adsorption properties. While the surfaces of ordinary crystals provide only a few inequivalent adsorption sites, the complex landscape of quasicrystalline surfaces provides a rich variety of different adsorption sites. Co-adsorption of atoms and molecules on complex metallic surfaces offers the possibility of to design novel types of catalytic reactions. Recently Armbrüster et al. [1, 2] reported that the complex intermetallic compound $Al_{13}Co_4$ is an efficient and highly selective hydrogenation catalyst for alkynes. The hydrogenation of acetylene to ethylene is an important step in the industrial production of the polyethylene. This process is generally carried out using Pd catalysts, doped with other metals such as Ag to improve the selectivity for ethylene and to avoid further hydrogenation. The possibility to

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1 replace an expensive Pd-catalyst by an Al-based transition-metal alloy is highly
2 intriguing. In the present contribution the hydrogenation of acetylene to ethylene on
3 the surface of $\text{Al}_{13}\text{Co}_4$ has been studied using *ab initio* density-functional methods.
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6 2. Computational methods

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8 Total-energy and force-calculations have been performed using the Vienna *ab*-
9 initio simulation package (VASP) [3, 4]. We used the semilocal exchange-correlation
10 functional in the generalized gradient approximation (GGA) proposed by Perdew
11 et al. [5]. VASP allows to calculate the Hellmann-Feynman forces acting on atoms.
12 The equilibrium geometries of the surface and of the adsorbates/substrate complex
13 have been determined by a conjugate gradient minimization of the forces acting
14 on the atoms. The energetic barriers of the reaction steps were calculated by the
15 nudged-elastic-band method (NEB) [6].
16

17 The structural model of the (100) surface of orthorhombic $\text{Al}_{13}\text{Co}_4$ is presented in
18 Sec. 3. The large dimensions of the computational cell allow to perform structural
19 optimizations using the Γ -point only, but the accuracy of the energies of reac-
20 tants, transition states, intermediates and products were improved by calculations
21 using a $2 \times 2 \times 1$ \mathbf{k} -point mesh. The basis set contained plane waves with a kinetic
22 energy up to $E_{\text{cutoff}} = 600$ eV, but for the transition-state searches the forces were
23 evaluated with increased accuracy and a cut-off of $E_{\text{cutoff}} = 700$ eV.
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25

26 3. $\text{Al}_{13}\text{Co}_4$ surface

27
28 The orthorhombic $\text{Al}_{13}\text{Co}_4$ phase belongs to a family of $\text{Al}_{13}\text{TM}_4$ compounds with
29 interesting physical properties [7]. It can be considered as an approximant to the
30 Co-rich decagonal Al-Co-Ni quasicrystal. The structure of orthorhombic $\text{Al}_{13}\text{Co}_4$
31 compound has been determined by Grin et al. [8, 9] using X-ray single crystal and
32 powder diffraction methods. The structure and stability of $\text{Al}_{13}\text{Co}_4$ and related
33 phases has been studied recently also by Mihalkovič and Widom [10] using *ab*
34 *initio* density-functional method (DFT). We briefly summarize the main structural
35 data. The orthorhombic unit cell consists of 102 atoms (Pearson's symbol oP102,
36 space group $Pmn2_1$, No. 31), out of them 78 are Al and 24 Co atoms. The lattice
37 parameters reported by Grin et al. [8] are $a=8.158$ Å, $b=12.342$ Å, and $c=14.452$ Å.
38 The bulk structure of $\text{Al}_{13}\text{Co}_4$ can be considered as a stacking in (100) direction
39 of two kinds of atomic layers, a flat layer (F) and a puckered one (P). The unit
40 cell consists of 2 F and 2 P layers. The distance between the alternating F and P
41 layers is $a/4=2.04$ Å.
42

43 One could expect that cleavage plane of $\text{Al}_{13}\text{Co}_4$ is located between the atomic
44 layers and that therefore the surface exposes either an F or a P layer. However,
45 quite surprisingly, the cleavage process is more complex. The P layer is split into
46 two complementary parts and the strongly corrugated surface is covered by a part
47 of the P layer only. This peculiar surface structure has recently been confirmed
48 by scanning tunneling microscopy (STM) [11]. Henley [12] recognized that the
49 structure of $\text{Al}_{13}\text{Co}_4$ can be considered as a packing of elementary clusters having
50 the form of pentagonal bipyramids. A pentagonal bipyramid (PB) consists of an
51 equatorial plane and two Al pentagons centered by Co atoms on each side, see Fig.
52 3 in Ref. [10], or Fig. 1c in Ref. [11]. The Co atoms centering the pentagonal rings
53 of Al are slightly above or below the Al plane and form the tips of the BP. In the
54 equatorial plane the BP has a decagonal ring of alternating Al and Co atoms and
55 one Al atom in the center of the ring.
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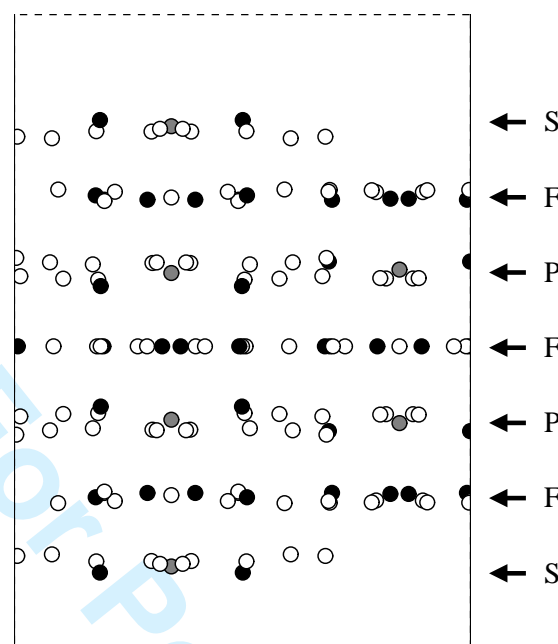


Figure 1. Side view of the slab-model of the (100) surface of orthorhombic $\text{Al}_{13}\text{Co}_4$. The surface layer S is composed by one half of a puckered layer P, the slab is symmetric with respect to the central flat F layer. Cf. text.

We have simulated the cleavage process by *ab initio* calculations. The unit cell was extended in the (100) direction first by $a/2$, the forces were relaxed and then extended again by $a/2$. The tensile deformation induces cleavage by splitting the puckered layer such that the integrity of the elementary PB clusters is preserved. Alternatingly PB clusters remain attached to the upper or lower surface on both sides of the cleavage plane. The PB clusters are connected by junction layers [10]. The surface is formed by the upper parts of the PB clusters in the P layer and the junction layers in F plane located 2.04 \AA below the surface, see Fig. 1.

The formation of a strongly corrugated surface formed by the incomplete P layer is thus a consequence of the strong, partially covalent binding within the PB clusters and the shift of one pair of the PB clusters with respect to the other by $a/2$. We have denoted the incomplete P layer by the S. Two complementary S layers thus form together the P layer.

The charge density distribution shown in Fig. 2 demonstrates the peculiar character of the $\text{Al}_{13}\text{Co}_4$ surface. One observes a high electron density in zig-zag chains of CoAl_5 pentagons separated by valleys of very low electron density at the place of the missing parts of the P layer. The structure of the surface can be described by a planar tiling consisting of pentagons of with two opposite orientations and thin rhombi. The edge of the tiling is $d=4.73 \text{ \AA}$. Per unit cell there are 4 pentagons and 2 rhombi. Two edge-linked pentagons are decorated by Al and Co atoms from the top S layer, the other two pentagons are at the positions of the junction layers in the F plane 2 \AA deeper. One rhombus is empty, the other is filled by Al atom. This Al site in a bridge position between two Al pentagons is quite special. While according to the original work of Grin et al. [8] all 102 sites of the unit cell have full occupancy, Mihalkovič and Widom [10] have shown that a fractional occupancy ≈ 0.5 of this site increases the thermodynamic stability of the $\text{Al}_{13}\text{Co}_4$ compound. One can assume that if this low-coordinated atom appears at the surface it can easily be removed. This expectation is confirmed by recently published STM im-

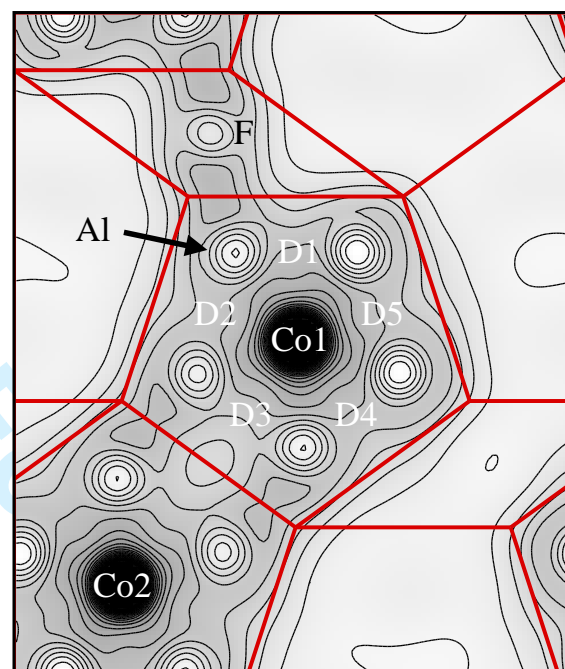


Figure 2. (Color online) Charge density distribution in the surface of $\text{Al}_{13}\text{Co}_4$. Pairs of Co-centered Al pentagons are linked through thin rhombi decorated with a single Al atoms. At the place of missing part of the P layer there are deep charge density troughs. The surface structure may be described in terms of a pentagon-rhombus tiling (red). The Al atoms in the thin rhombi (labeled by F) are only weakly bound, these sites may be only partially occupied, at higher temperatures they desorb. Sites D_i , $i=1, \dots, 5$ are preferable adsorption sites for the acetylene molecule.

ages [11] of the $\text{Al}_{13}\text{Co}_4$ surface where it is clearly seen that after annealing at a high temperature of 1173 K most of these atoms have been removed, probably via desorption into the gas phase.

The model of the surface prepared by simulated cleavage of the bulk structure has the form of a slab consisting of 7 atomic layers - 3 F layers, 2 P layers and the top and bottom S layers, see Fig. 1. The model has a mirror symmetry with respect to the central F layer. The computational cell measures $12.38 \times 14.50 \times 28.66$ Å, separated by a vacuum layer of 16.0 Å. The cell contains 153 atoms plus the adsorbate atoms.

4. Adsorption sites and binding energies

As the transition metals are known to exhibit a significant catalytic activity it is natural to expect that the catalytically active centers on the $\text{Al}_{13}\text{Co}_4$ surface are just the Co sites. On the surface the Co sites occupy the centers of two edge-linked pentagons. The distance between the Co sites in a pair of pentagons is equal to $h=6.51$ Å. Pairs of pentagons are coupled only by the Al atoms decorating the rhombi which can easily desorb (sites F in Fig. 2). Hence the two CoAl_5 clusters in the pentagon-pairs essentially form isolated islands on the surface.

The first step towards the exploration of the reaction scenario must be to identify the energetically most favorable adsorption sites of reactants, intermediates and products, via the calculation of the binding energies at specific adsorption

1 sites. Binding energies are defined as the energy difference between the adsor-
2 bate/substrate complex and the energies of the adsorbed species in the gas-phase
3 and of the clean substrate.
4

5 6 7 **4.1. Molecular and dissociative adsorption of hydrogen**

8 The most favorable adsorption site for a H_2 molecule is on top of a Co atoms, with
9 a binding energy of $E_b = -0.47$ eV. The surface has an inversion symmetry with
10 respect to the point I located in the center of the shared edges of two pentagons,
11 see Fig. 3. On top of Al atoms, at bridge positions between Al atoms or in the
12 4-fold hollow at site I a H_2 molecule does not bind at all. A H_2 molecule adsorbed
13 on top of a Co atom can easily dissociate. The activation energy for dissociation
14 is only 0.17 eV. The most favorable adsorption site for a dissociated H atom is a
15 3-fold hollow site between the Co atom and two neighboring Al atoms, see position
16 H1 in Fig. 3, with a binding energy of $E_b = -0.23$ eV. Another (meta)stable site is in
17 a bridge position between Co and a neighboring Al atom, see position H2 in Fig. 3
18 with a binding energy of -0.13 eV. The differences in the binding energies at the
19 bridge and three-fold hollow sites related by approximate five-fold symmetry are
20 very small, hence the dissociated H atoms can easily move around the central Co
21 atom. The adsorption of hydrogen prohibits the adsorption of acetylene at the same
22 $CoAl_5$ pentagon. For the hydrogenation process it is thus very important that mid-
23 way between the coupled $CoAl_5$ clusters an energetically favorable adsorption site
24 for atomic hydrogen exists at a bridge position between two Al atoms (see position
25 H3 in Fig. 3). The binding energy of $E_b = -0.23$ eV at this site is essentially the
26 same as at the H1 site. A symmetry-equivalent site H3' exists in a bridge position
27 between the other two Al atoms forming the four-fold hollow. A H atom can thus
28 move in two diffusion jumps via a H3 or a H3' site from one Co site to the other
29 one within the double pentagon. It is also important that H atoms are not trapped
30 in the four-fold hollow site I.
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36 **4.2. Adsorption of acetylene, vinyl and ethylene**

37 As expected a locally stable adsorption site for the C_2H_2 molecule in a π -bonded
38 configuration exists on top of a Co atom, with a binding energy of $E_b = -0.79$ eV.
39 However, rather surprisingly this is not the energetically most favorable adsorption
40 site on the surface. The energy for binding the C_2H_2 in a di- σ configuration to two
41 Al atoms forming a part of the pentagon around the Co atom is more than 1
42 eV higher. There are five such sites around the Co atom, labelled D_i , $i=1...5$ in
43 Fig. 2. The existence of these adsorption configurations is highly non-trivial, it is
44 one of the main reasons for the high catalytic activity and selectivity of the $Al_{13}Co_4$
45 surface. The high binding capacity of the D_i sites is a consequence of the peculiar
46 topology of the $Al_{13}Co_4$ surface. Because the Al atoms are located at the edges of
47 the chains of $CoAl_5$ pentagons, they have a reduced coordination and, similar to
48 atoms located at the step edges of a vicinal surface, an increased bonding capacity.
49 As the pentagonal symmetry is not perfect the binding energies of acetylene at
50 different D_i sites differ by up to ≈ 0.4 eV. The presence of a bridging Al atom at
51 site F within the adjacent rhombus (see Fig. 3) lowers the binding energy at a
52 neighboring D_i site. The highest binding energy of $E_b = -1.92$ eV was found for the
53 D5 site confronting the wide trough on the surface. A very important observation is
54 that the D_i sites are the preferable adsorption sites for acetylene and vinyl (C_2H_3)
55 formed by the first hydrogenation step, but not for ethylene (C_2H_4) formed by the
56 second hydrogenation step. For vinyl di- σ binding at the D5 site is by 1.24 eV more
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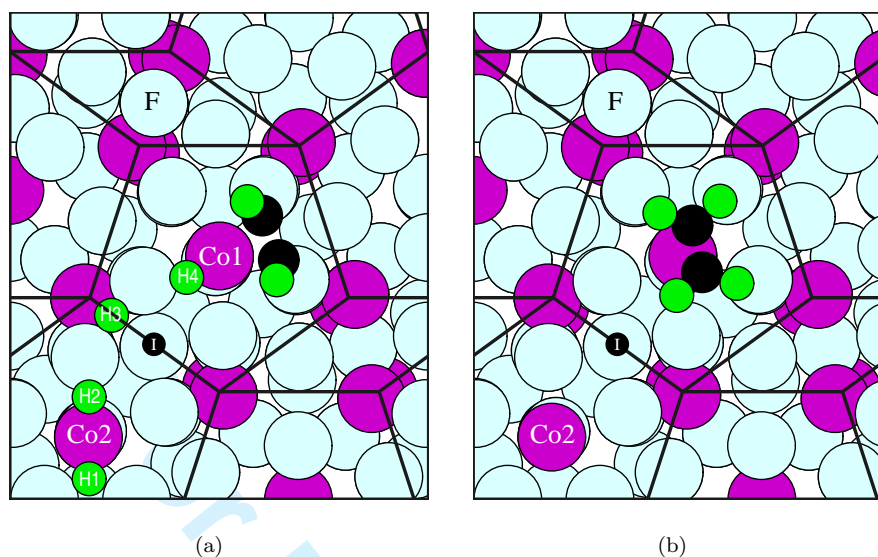


Figure 3. Atomistic scenario for the hydrogenation of acetylene to ethylene. Al atoms are shown in light blue, Co atoms in deep purple. Hydrogen atoms are light green circles, black spheres represent C atoms. (a) The acetylene molecule with sites H1 - H4 for co-adsorbed hydrogen atoms. (b) The ethylene molecule on top of the Co1 atom. Cf. text.

stable than π -binding on top of Co1 atom. For ethylene di- σ binding at the D5 site is unstable, so the molecule moves to the stable position on top of Co atom where it is π -bonded with a binding energy of $E_b = -0.73$ eV. In the following we shall consider a reaction pathway for the hydrogenation of acetylene starting with the molecule adsorbed at the most stable D5 site around the Co1 atom, and molecular hydrogen co-adsorbed on-top of the Co2 atom.

5. Acetylene hydrogenation

Chemical reactions on the surface of a catalyst can proceed either via a Langmuir-Hinshelwood or an Eley-Rideal mechanism. In the former reactants are coadsorbed on the surface, and the reaction proceeds via thermally activated diffusion and reaction steps. The Eley-Rideal mechanism supposes that only acetylene is adsorbed on the surface and reacts directly with hydrogen from the gas phase. This reaction mechanism is disfavored by the strong Pauli repulsion between the H₂ and C₂H₂ molecules, leading to a very high activation energy of 3.4 eV. Hence in the following we will discuss a Langmuir-Hinshelwood reaction starting with co-adsorbed acetylene and hydrogen.

Coadsorption of atoms or molecules is substantially influenced by lateral interactions between the adsorbates. Coadsorption studies show that at distances larger than bonding distances the interaction between H₂ and C₂H₂ is repulsive. Hydrogen and acetylene cannot simultaneously occupy the Co1 (H₂) and the D5 (C₂H₂) sites. Adsorption of acetylene at a D5 site blocks the entire CoAl₅ pentagon for hydrogen adsorption, the dissociative adsorption of hydrogen can take place only at the Co2 atom in the neighboring pentagon. The H₂ molecule adsorbed on top of the Co2 atom dissociates in a slightly endothermic process with a heat of reaction of 0.068 eV and a low activation energy of 0.17 eV. The dissociated H atoms occupy, say, H1 and H2 sites around the Co2 atom. The dissociated H atoms can move towards the co-adsorbed acetylene molecule in several diffusion steps via the H3 or H3' sites and approach the acetylene molecule. The potential-energy profile for the

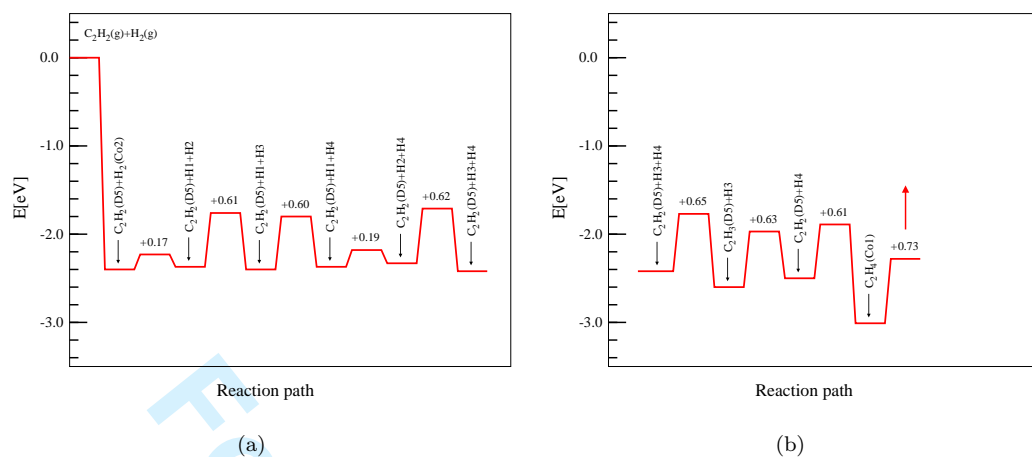


Figure 4. Potential energy profile of the reaction steps. (a) Hydrogen molecule dissociation and diffusion jumps of dissociated hydrogen atoms towards the acetylene molecule. (b) Hydrogenation of acetylene to vinyl and ethylene. The activation energy barriers are in eV. The energy scale is with respect to the reactants in the gas phase. Labels refer to the configurations shown in Fig. 3. Cf. text.

hydrogen-diffusion is shown in Fig. 4(a). The process is essentially thermo-neutral, the highest barrier on the diffusion path is 0.62 eV for the final H-migration step after which the two dissociated H atoms occupy sites H3 and H4, close to the acetylene molecule adsorbed in sites D5 (see Fig. 3).

The hydrogenation can further proceed in the following way. To react with the acetylene molecule the H4 atom first moves around the Co atom until it binds to a carbon atom, forming a vinyl (C_2H_3) molecule. The activation energy for this step is 0.65 eV. The vinyl molecule remains di- σ adsorbed at the D5 site. In the next step the second hydrogen atom has to move from site H3 to H4 (Co-Al bridge site) where it is co-adsorbed close to the vinyl molecule. This requires overcoming a barrier of 0.63 eV. Hydrogenation of vinyl to ethylene occurs by a simultaneous rotation of the C-H group of vinyl around the C-C axis and a movement of the H atom along the valley between the Co atom and the surrounding Al atoms. The activation energy for this step is 0.61 eV. In the final configuration ethylene (C_2H_4) is bound via a π -bond on top of the Co1 atom. The desorption energy of the ethylene molecule bonded to the Co1 site is 0.73 eV. The potential-energy profile for this reaction is shown in Fig. 4(b).

6. Discussion

We have performed an ab-initio DFT study of properties of the $Al_{13}Co_4$ surface as a hydrogenation catalyst. We have determined a detailed atomistic scenario for the hydrogenation of acetylene. We have identified active sites, calculated adsorption energies, identified the reaction mechanism, resolved reaction steps, searched for the optimal reaction channel for the hydrogenation, and calculated all activation energies. We have found that the energetic barriers of all reaction steps does not exceed 0.65 eV (63 kJ/mol). This value is lower than the energetic barrier for acetylene to ethylene hydrogenation over Pd or Pd-Ag catalysts where for the rate determining step activation energies between 78 kJ/mol and 85 kJ/mol were reported [14]. The energy barrier for ethylene desorption is 0.73 eV, however, it can be substantially reduced by co-adsorption of other hydrogen atoms in the vicinity of the ethylene molecule. These data confirm that the $Al_{13}Co_4$ surface can be an efficient catalyst for acetylene to ethylene hydrogenation.

We have explored also alternative reaction channels. For instance, the hydrogenation can start with acetylene adsorbed on top of the Co1 atom and the hydrogen molecule on top of Co2 site. After H₂ dissociation the hydrogen atom attacks C₂H₂ directly from the H3 site. We have found that this simple reaction channel is possible, however, the calculated energetic barrier of 1.38 eV is much higher. An important question is whether under normal conditions ethylene will be further hydrogenated to ethyl and ethane, or whether ethylene will desorb before further hydrogenation. This will require a similar detailed study of the further hydrogenation steps which is now under way. Preliminary results show that the decisive point for the observed selectivity of Al₁₃Co₄ is the change in the adsorption mode from di- σ bonded for acetylene and vinyl to π -bonded for ethylene. Results will be reported soon.

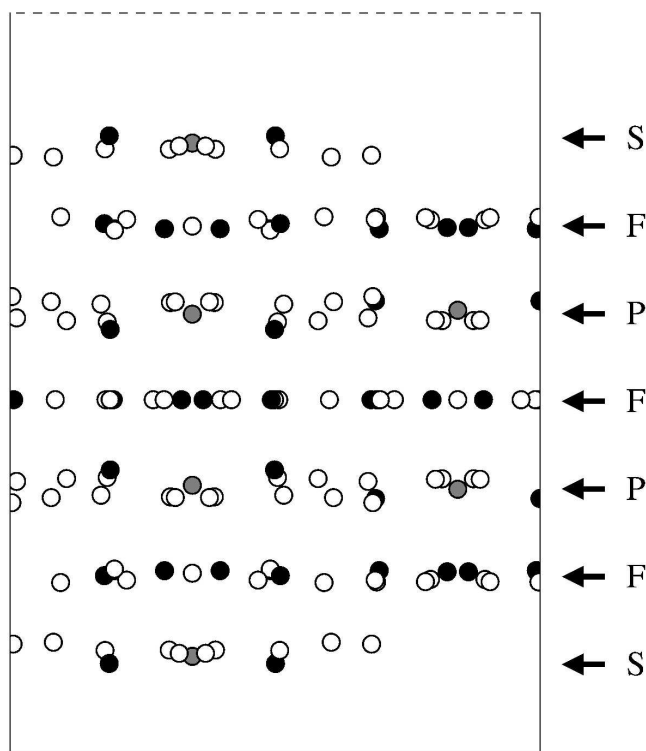
Acknowledgements

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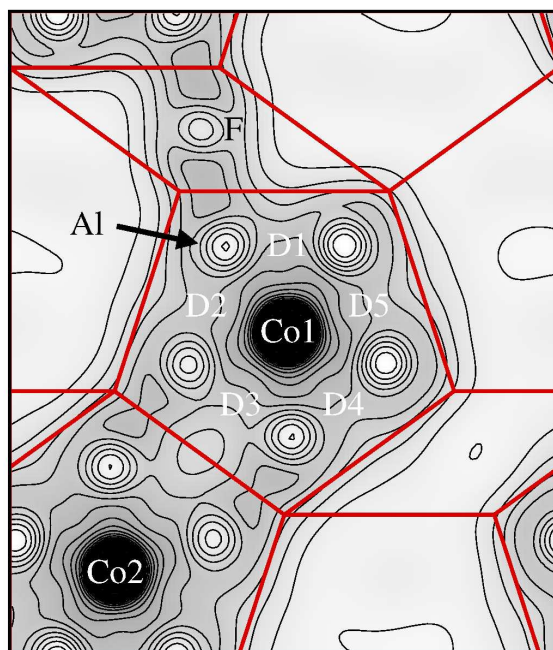
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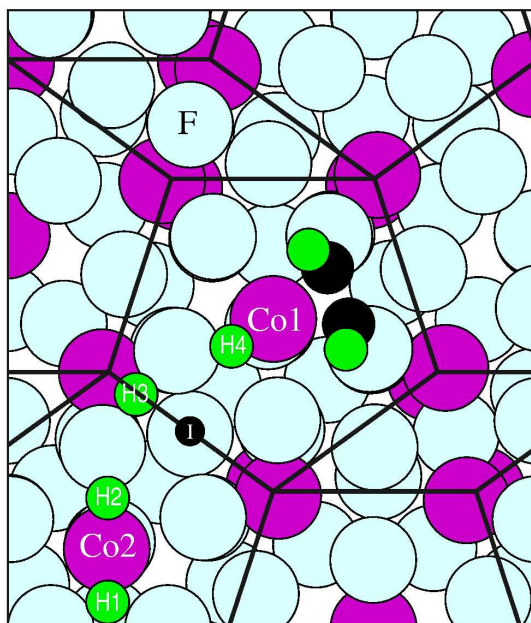
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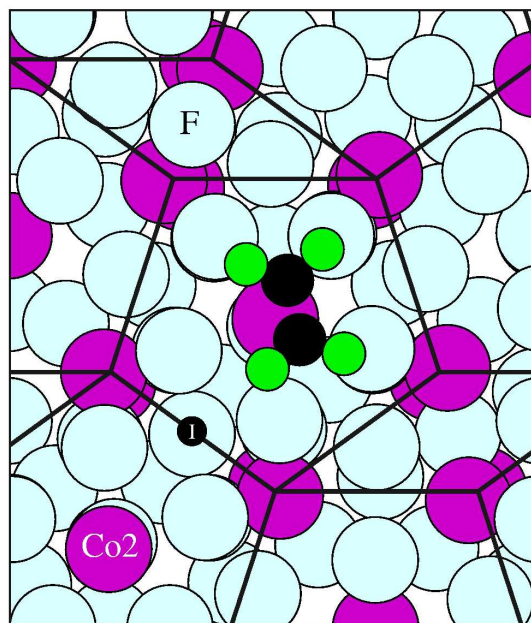
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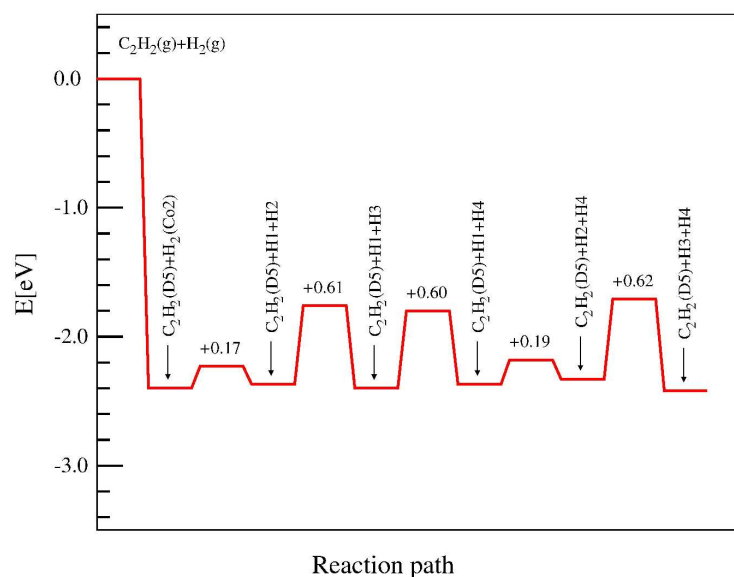
(Color online) Charge density distribution in the surface of $\text{Al}_{13}\text{Co}_4$. Pairs of Co-centered Al pentagons are linked through thin rhombi decorated with a single Al atoms. At the place of missing part of the P layer there are deep charge density troughs. The surface structure may be described in terms of a pentagon-rhombus tiling (red). The Al atoms in the thin rhombi (labeled by F) are only weakly bound, these sites may be only partially occupied, at higher temperatures they desorb. Sites D_i , $i=1, \dots, 5$ are preferable adsorption sites for the acetylene molecule.
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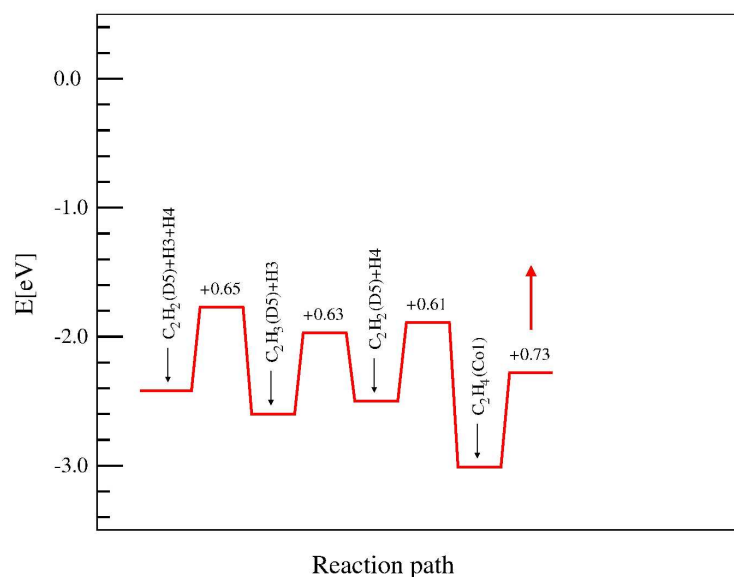
Atomistic scenario for the hydrogenation of acetylene to ethylene. Al atoms are shown in light blue, Co atoms in deep purple. Hydrogen atoms are light green circles, black spheres represent C atoms.
 (a) The acetylene molecule with sites H1 - H4 for co-adsorbed hydrogen atoms. (b) The ethylene molecule on top of the Co1 atom. Cf. text.
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Atomistic scenario for the hydrogenation of acetylene to ethylene. Al atoms are shown in light blue, Co atoms in deep purple. Hydrogen atoms are light green circles, black spheres represent C atoms.
(a) The acetylene molecule with sites H1 - H4 for co-adsorbed hydrogen atoms. (b) The ethylene molecule on top of the Co1 atom. Cf. text.
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Potential energy profile of the reaction steps. (a) Hydrogen molecule dissociation and diffusion jumps of dissociated hydrogen atoms towards the acetylene molecule. (b) Hydrogenation of acetylene to vinyl and ethylene. The activation energy barriers are in eV. The energy scale is with respect to the reactants in the gas phase. Labels refer to the configurations shown in Fig.~\ref{fig:hydro}. Cf. text.
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