Title

Evaluating the Risk of C–C Bond Formation during Selective Hydrogenation of Acetylene on Palladium

Authors

Vignola, Emanuele
Steinmann, Stephan N
Farra, Ahmad Al
et al.

Evaluating the Risk of C-C Bond Formation during Selective Hydrogenation of Acetylene on Palladium

Emanuele Vignola,[†‡] Stephan N. Steinmann,[†]* Ahmad Al Farra,[‡] Bart D. Vandegehuchte,[§] Daniel Curulla,[§] and Philippe Sautet[†&ç]*

[†]Univ Lyon, ENS de Lyon, CNRS, Université Lyon 1, Laboratoire de Chimie UMR 5182, F-69342, Lyon, France

[‡]Total Research and Technology Gonfreville, BP 27, F-76700 Harfleur, France

[§]Total Research and Technology Feluy, Zone Industrielle Feluy C, Seneffe, Belgium

[&]Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, Los Angeles, CA 90095, United States

[ç]Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, CA 90095, United States

*e-mail: stephan.steinmann@ens-lyon.fr; tel.: 0033-4-72-72-81-55

*e-mail: sautet@ucla.edu; tel.: 1-310-825-8485

ABSTRACT: Palladium-based catalysts are known to promote the selective hydrogenation of acetylene to ethylene. Unfortunately, coupling reactions between the numerous surface intermediates generated in this process occur alongside. These side reactions are undesired, generating the so-called "green oil", i.e., C_4+ hydrocarbons that poison the active sites of the catalyst. The current work assesses the energetic and kinetic aspects of C_4 side products formation from the standpoint of computational chemistry. Our results demonstrate that the C-C coupling of common surface species, in particular acetylene, vinylidene and vinyl, are competitive with selective hydrogenation. These C-C couplings are particularly easy for intermediates where the C-Pd bond can largely remain intact during the coupling. Furthermore, the thus formed oligomers tend to be hydrogenated more easily, consuming hydrogen normally spent on acetylene hydrogenation. The analysis of site requirement suggests that isolated Pd_2 ensembles are sufficient for selective hydrogenation and would suppress oligomerization. However, upon aging, the PdAg alloy is likely to undergo reverse segregation and in this case, our computations suggest that the selectivity of the catalyst is lost, with enhanced C-C couplings interfering even more strongly. Hence, small Pd ensembles are crucial to avoid oligomerisation side reactions of acetylene.

Introduction

Carbon-carbon coupling reactions are among the most useful transformations in organic chemistry.[1] They allow chemists to build complex carbon frameworks from their reagents, thereby achieving products of greater complexity, spreading benefits from daily laboratory practice to the pharmaceutical, the biochemical and the polymer industry. Palladium is at the core of this chemistry for fine chemicals, since it is the elected metallic catalyst promoting carbon-carbon coupling.[2] Although the majority of catalysts are homogeneous palladium complexes to be used in solution phase reactions, supported heterogeneous palladium catalysts start to attract interest as a promising alternative. Today, Pd-based heterogeneous catalysts are particularly important in the industrial production of polyethylene. Ethylene streams from oil refineries contain about 1% acetylene. Leaving acetylene in the ethylene feedstock for polyethylene would lead to deteriorated material properties and decreased catalyst lifespans. Therefore, the ethylene stream is subjected to a partial hydrogenation process,[3] where acetylene is selectively hydrogenated to ethylene, while avoiding over-hydrogenation towards ethane. This selective hydrogenation is carried out over Pd alloy catalysts,
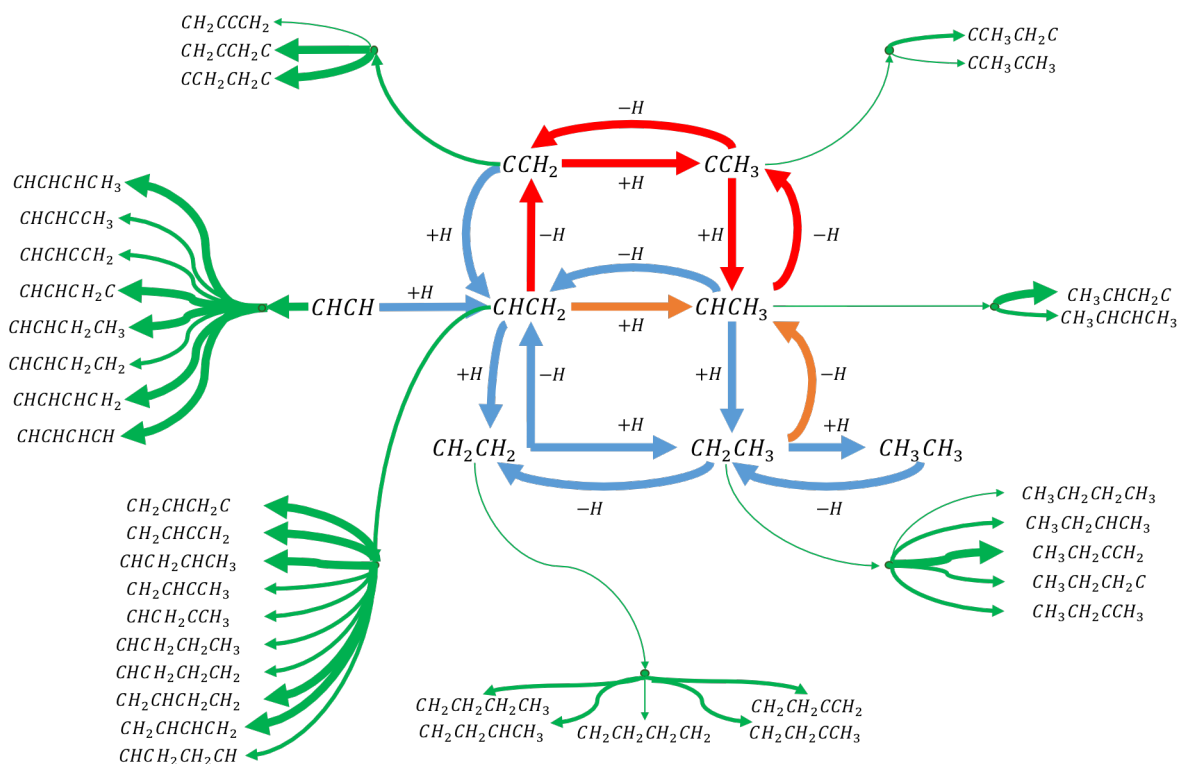
Figure 1 Reaction Scheme considered. The green arrows indicate unwanted oligomerization, the blue ones indicate the "direct" hydrogenation of acetylene and the red ones refer to the isomerization process to asymmetric C_2 species. Arrows in thin, medium and bold lines represent activation energies < 1.5 eV, between 1.5 and 2.0 eV and > 2 eV respectively. For the various hydrogenation elementary reactions of C_4 species considered, the reader is referred to Figure 5.

with Pd surface atoms constituting the active sites.

Unfortunately, during this process Pd can also catalyse oligomerization of hydrogenation intermediates. Indeed, Pd acts as a C-C coupling catalyst, producing complex mixtures of oligomeric compounds.[4] This mixture contains three main fractions: a light end fraction which remains in the gas phase, a liquid portion that is entrained by the gas in the form of fine droplets (denoted as "green oil"), and a heavy fraction, the "sticky green oil". These oligomeric species have several deleterious effects: first, they reduce the atom efficiency of the process, since the carbon contained in green oil cannot be valorized. Second, the sticky green oil blocks active sites and therefore slowly deactivates the catalyst. Therefore, the catalyst needs to be regenerated periodically by oxidation followed by re-activation through reduction. High-temperature reduction has been found to be especially crucial for Pd alloy catalysts, most likely since the high temperature favors solid solution, rather than segregation of the two metals.[5,6] However, green oil is not only present on the catalyst, but also on the support.[7] This leads to an increased mobility of the catalyst and, therefore, to an accelerated sintering during the regeneration process. Hence, suppressing green-oil formation would improve catalyst life span and increase atom efficiency at the same time. While alloying Pd with Ag, Cu or Au either keeps the amount of green oil produced constant or reduces it somewhat, it clearly does not completely suppress it.[8–10] On the one hand, even on pure Ag some green oil formation is observed,[11] on the other hand, some supports, such as γ-alumina catalyze part of the C-C couplings leading to the heavier fractions.[12] Nevertheless, the secondary metal not only forms C-C bonds more slowly, but it also binds the intermediates less strongly and thus favours desorption of the intermediates into the gas-phase, leading to less heavy green oil.[13]

The characterization of these coupling derivatives is not a trivial task. Few groups have tried to analyse the carbonaceous deposits, and their results are not always in agreement.[14] While it is commonly agreed that the gaseous fraction is prevalently composed of C_4 and C_6 hydrocarbons,[4] discrepancies are more obvious regarding the composition of green oil. Yayun *et al.*[15] reported that the liquid heavy polymers have an average composition of $C_nH_{(1.8-1.9)n}$ with a number of carbon

atoms between 14 and 17, and an olefin/paraffin ratio between 0.1 and 0.4. Most remarkably, no aromatics were detected although palladium is renowned to boost acetylene trimerization.[16] Gandman et al.[17] have presented a different green oil composition, with a content of aromatic compounds as high as 74.5% in weight, 23.0% of olefins, and a small fraction of diolefins. The origins of the oligomers is also controversial. Most authors agree that the oligomers are exclusively derived from acetylene. Nevertheless, according to the results obtained by Yayun et al.[15], ethylene in the feed participates in the process as well. The influence of the hydrogen partial pressure is rather complex: oligomerization only occurs in the presence of adsorbed hydrogen. Therefore, the reaction is often referred to as acetylene hydro-oligomerization. At high H_2 partial pressures, the formation of green oil decreases, however at the cost of a lack of selectivity towards ethylene.[18,19] According isotopic labelling and spectroscopic techniques, the most likely molecular precursors for green oil are acetylene, CCH_2 (vinylidene) and $CHCH_2$ (vinyl).[14,20]

In addition to C-C coupling, C-C decomposition products are expected as well. In particular, carbon atoms penetrate the surface layer and preferentially occupy the octahedral vacancies of the lattice to form an interstitial alloy.[21,22] This Pd/C phase crucially alters the adsorption energetics of the reagents,[23] thereby lowering acetylene conversion but improving the selectivity towards ethylene as it weakens ethylene adsorption and hinders the kinetics of subsurface hydrogen diffusion in model catalysts.[3] However, the hydrides and carbide phases are largely suppressed by the industrially relevant addition of CO, which has been shown to be a beneficial additive.[24,25] Since these C_1 species, have been extensively investigated by Mei et al,[26] and are, according to isotopic labelling studies,[20] not expected to play a major role in C-C coupling reactions, we do not re-investigate them in this paper.

The complete reaction network encompasses Horiuti-Polanyi additions of hydrogen atoms to acetylene[27], as well as oligomerization by C-C bond formation and decomposition of intermediates into carbon and hydrogen. Consecutive hydrogenation and dehydrogenation lead to ethylidyne (CCH_3) as an asymmetric side-intermediate, either via vinyl ($CHCH_2$) or ethylidene ($CHCH_3$) (see Figure 1). Ethylidyne has been identified experimentally as early as 1986 and its hydrogenation is significantly slower than the direct hydrogenation of ethylene.[28] The interconversion of ethylidyne, ethylene and acetylene was computationally investigated in 2002.[29] A later refinement was proposed by Moskaleva et al.[30] and IR measurements finally complemented the understanding of the role of this intriguing species.[31] Ethylidene formation seems to be kinetically preferred when subsurface hydrogen is allowed to take part to vinyl hydrogenation,[24] but otherwise acts as a pure spectator of the reaction. Herein, we consider only C_2 and C_4 species, in order to focus on the competition between oligomerization and selective hydrogenation of acetylene. The elementary steps considered herein are shown in Figure 1, where the hydrogenation reactions converting C_4 species into each other are excluded for sake of clarity (see Figure 5 for the C_4 species).

Even though the C-C coupling is a very important reaction for side-product formation, only very few theoretical studies have tackled this complex reaction network. Based on the accepted view that butadiene is involved in the formation of the heavy hydrocarbons, Lopez and Vargas-Fuentes proposed[32] an acetylene-acetylene cis coupling step to C_4H_4 requiring an ensemble of at least 4 active metal atoms. Yang et al.[33] compared three paths to 1,3-butadiene on plain and stepped surfaces in the presence of subsurface carbon and alloyed silver atoms; they proposed that, on a clean Pd(111) surface, acetylene-acetylene coupling followed by hydrogenation is the preferred road to butadiene, while the Pd(211) stepped surface favours vinyl-vinyl coupling. The presence of subsurface carbon or small amounts of alloy metals reduces the adsorption energies for all intermediates and slightly (~0.1 eV) raises activation energies. The effect of molecular spacers on the selectivity versus oligomers formation was also explored for the case of carbon monoxide. Computations showed[24,25] that this adsorbate reduces the size of active ensembles available for coupling steps; however, only one oligomerization step (namely, the acetylene-vinyl coupling) was included into the network, and the ethylidyne route was not considered. To the best of our knowledge, even the experimentally proposed pathway involving CCH_2[14] has not yet been investigated computationally. Hence, although there have been valuable first steps, a comprehensive assessment of the various possibilities for C-C bond formation between surface intermediates has been

lacking so far. Figure 1 illustrates the large spectrum of theoretically possible carbon-carbon couplings.

This paper addresses the aspects of acetylene hydrogenation and oligomerization on palladium from first-principle computations. Since CO acts mainly as a molecular spacer and supresses the hydride and carbide phases, we consider a bare Pd surface as a relevant, albeit simplified model. Particular attention has been given to the roles of vinylidene, ethylene and of the ethylidyne-related fragments for green oil formation. The presented detailed mechanistic study emphasizes the role of early hydrogenation intermediates, both responsible for the selectivity towards ethylene, rather than ethane, and of the undesired oligomerization reactions. To put the results into a broader perspective, implications for catalysis on the industrially important Pd-Ag alloy catalysts are discussed. At the extreme of well mixed, solid solutions, we discuss the site and ensemble-requirements for the selectivity-controlling steps. At the other extreme of reverse segregated catalysts, the most salient kinetic and thermodynamic features are compared to those acquired on a Pd-Ag model.

Computational Details

Total energies were computed at the Density Functional level of theory in the PAW formalism,[34,35] with the Vienna Ab Initio Simulation Package.[36,37] The functional of Perdew, Burke, and Ernzerhoff[38] was employed, corrected for intermolecular forces following the scheme of Steinmann and Corminboeuf,[39] which was shown to perform very well for adsorption energies of organic molecules on a closely related system, Pt(111), when compared to experiment.[40] A plane wave basis set was used, with a cut-off energy of 400 eV. Surface models were cut out of the f.c.c. bulk structure along the 111 crystal direction. A p(3x3) unit cell with 4 metallic layers was used for the surface model, keeping the bottom-most two layers fixed, in order to simulate bulk properties. 15 Å of vacuum were inserted between periodic images along the axis normal to the surface, which proved to be sufficient to avoid spurious interactions between repeated images of the cell. Sampling of the Brillouin zone was performed with a Monkhorst-Pack[41] generated 3x3x1 k-points grid. The Methfessel-Paxton[42] smearing scheme was employed in all computations, with a broadening value of 0.2 eV. No normal mode analysis was

performed except for transition states (TS). The transition states have been located as follows: the co-adsorbed state corresponding to the two reacting fragments has been constructed based on the adsorption mode of the individual fragments, moved to neighbouring positions. Then, a nudged-elastic band (NEB)[43] computation with 8 images between the initial and final state was performed, seeded by interpolations between the two states obtained by the Opt'n Path code,[44] which uses a combination of internal and Cartesian coordinates. After about 50 cycles of NEB, the improved guess for the transition state was fully optimized to a first order saddle point by the dimer method[45] and the normal modes checked to contain only one imaginary frequency corresponding to the bond formation process.

Chemical potentials of gaseous species were calculated from statistical mechanics,[46] ignoring the vibrational contributions to partition functions, at 300 K and 1 bar.

Results and Discussions

Hydrogenation of C_2 species. We first present the thermodynamics and kinetics for the hydrogenation/dehydrogenation steps of C_2 intermediates derived from acetylene.

Industrially, the reaction is carried out on Ag-Pd based catalysts in the range of 300 to 380 K in a large excess of ethylene. For this model study on Pd(111), we have chosen standard conditions to reduce the complexity, i.e., 300 K and 1 bar for all gases. Figure 2 shows the free energy profile for the C_2 hydrogenation reaction network subset of Figure 1. The adsorption free energy of acetylene on Pd(111) is determined to -1.95 eV. Addition of a surface hydrogen (referenced as ½ H_2), leads to vinyl ($CHCH_2$) corresponding to a barrier of 1.08 eV. At this point, the system may evolve along two different pathways (red and blue in Figure 2). On the one hand, an additional atom of hydrogen results in ethylene requiring an activation energy of 0.96 eV. Either ethylene desorbs quickly (the process is non-activated but endergonic by 0.7 eV), or hydrogenates further to ethyl with an activation energy of 1.00 eV. Note, that the difference in adsorption energy between acetylene and ethylene, which has been used as a primer for the selectivity of the hydrogenation[47], is only affected by 0.1 eV when accounting for dispersion interactions, since the adsorption of acetylene and ethylene are more
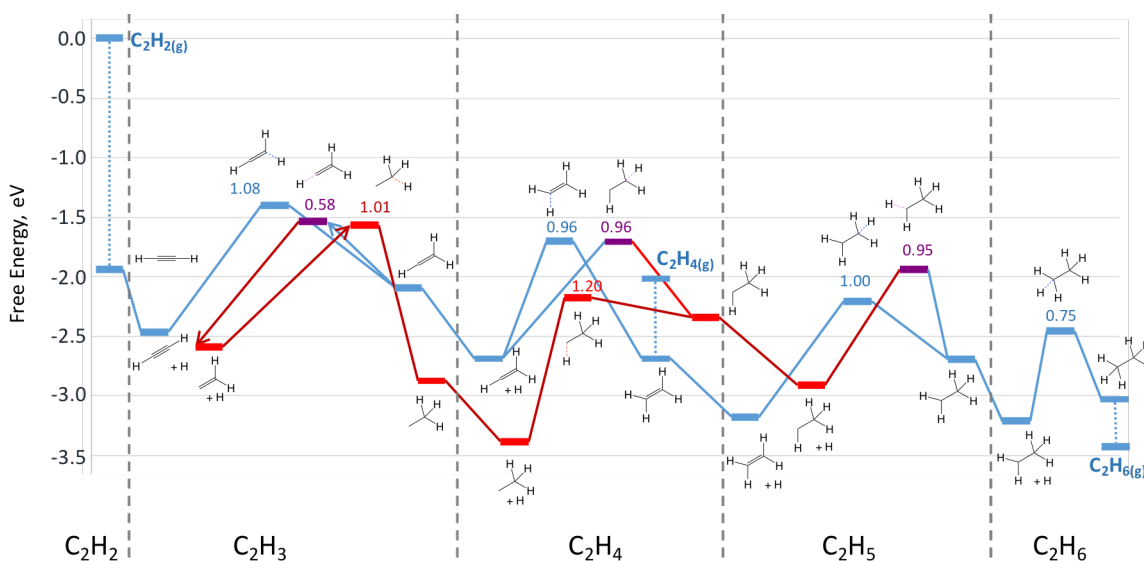
Figure 2. C₂ hydrogenation network free energy (eV) on Pd(111) at standard conditions. The path in blue is the "direct" hydrogenation path to ethylene and ethane. The path in red involves a rearrangement of hydrogen atoms, leading to the asymmetric ethylidyne intermediate. In purple are the transition states that connect the two pathways. All depicted intermediates are chemisorbed on the surface. Numbers indicate the activation energies of the elementary steps.

exothermic by 0.3 and 0.4 eV, respectively. On the other hand, vinyl may dissociate relatively fast (barrier of 0.58 eV) to atomic hydrogen and vinylidene, CCH₂. Vinylidene may be hydrogenated to ethylidyne, CCH₃ with an activation energy of 1.01 eV (the reverse barrier is 1.26 eV). Ethylidyne plus hydrogen is a particularly interesting intermediate, being both the global free energy minimum and the kinetically most inert point. The activation energy of CCH₃ to CHCH₃ is 1.20 eV, while the reverse barrier is only 0.17 eV). In any event, if CHCH₃ is produced, its hydrogenation to CH₂CH₃ can proceed with an activation energy of 0.95 eV. Ethyl can be finally hydrogenated to ethane with a barrier of only 0.75 eV, and the weakly bound ethane product quickly desorbs. An additional interconnection between the "direct" (in blue) and the "asymmetric" (in red) pathways comes from the asymmetric hydrogenation of vinyl. Here, vinyl goes directly into CHCH₃ by an activation energy of 0.95 eV.

5

From these free energy pathways, the experimentally observed CCH$_3$ can either be formed from CCH$_2$ (barrier of 1.01 eV) or by the dehydrogenation of CHCH$_3$ (ΔE‡=0.17 eV), which converts an ethane precursor into an inert spectator. The hydrogenation of CHCH$_2$ is found to be the most critical step for ethylene selectivity, since the barriers towards ethylene and towards the unwanted CHCH$_3$ are found to be equivalent (0.96 eV). Once ethylene is formed, its desorption is easier than its further hydrogenation implying that little ethane should be formed this way. Based on the stability of intermediates and the energy barriers, we expect that the surface would be predominantly covered by hydrogen, C$_2$H$_2$ and CCH$_3$. This predicted state of the surface constitutes a first approximation to a more realistic state to be determined by atomically detailed kinetic simulations.

C$_4$ derivatives formation. Figure 2 only includes reactions leading to the hydrogenation and isomerization of C$_2$ species. We include now the elementary steps involved in oligomerization. All C$_2$ coupling reactions were considered, since an *a priori* identification of thermodynamic and kinetic restrictions is difficult. Most of the C$_2$ intermediates are asymmetric and therefore have two non-equivalent carbons that can form a new C-C bond. A convenient way to classify these chemical functionalities is to count the number of hydrogens bound to the carbon atom. If S stands for the catalytic surface, C for the carbon atom involved in the coupling and R for the second carbon fragment of the C$_2$ intermediate, the chemical functions available for C-C coupling are the carbyne group, R-C$\equiv$S, the methylidyne group, R-CH=S, and the methylene group, R-CH$_2$-S. Following this logic, acetylene has only one functional group, S=CH-CH=S, while vinyl has two, i.e., R-CH=S and S-CH$_2$-R. Applying these rules leads to a total of 58 distinct C$_4$ intermediates. On top of that, E/Z isomers may exist and the activation energy might depend on
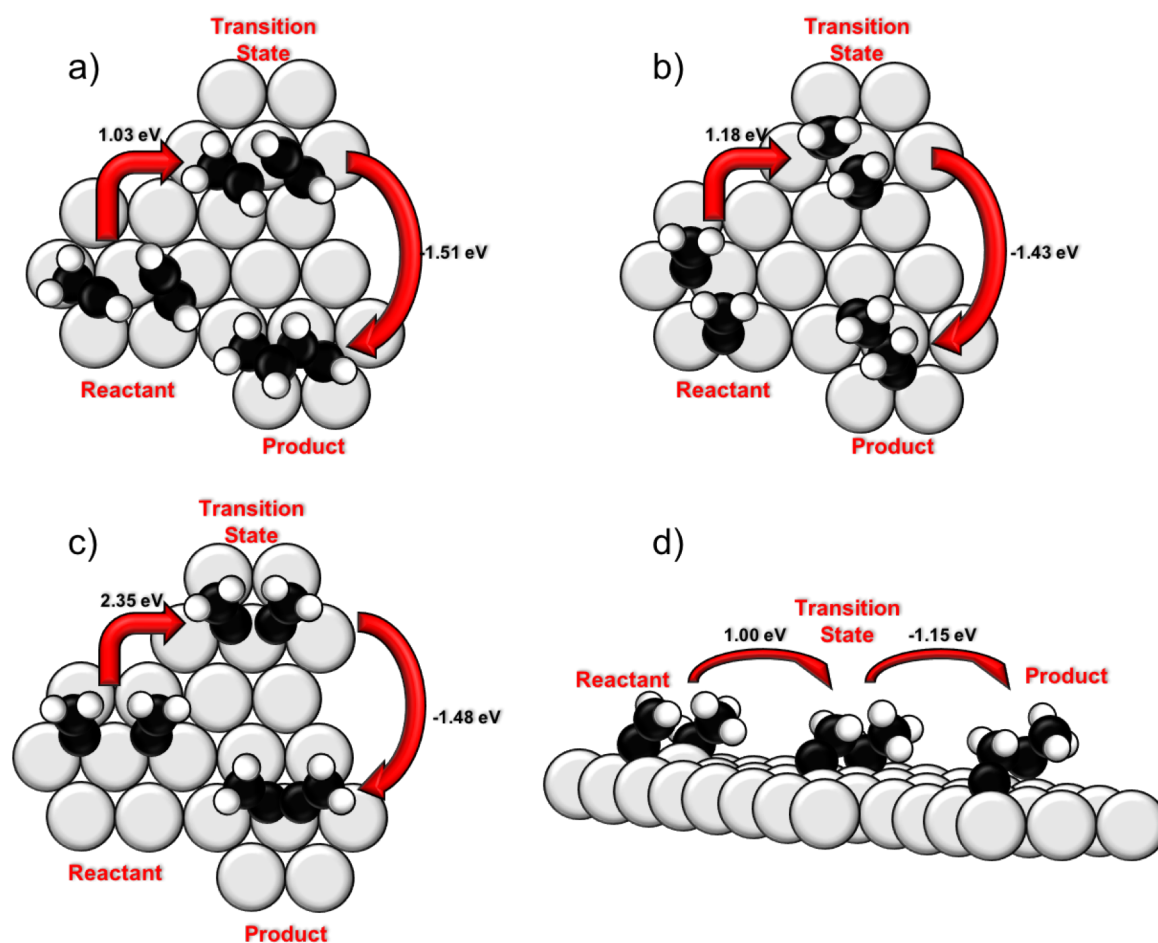

Figure 3. Selected, typical C-C coupling steps between C$_2$ surface species. a) CHCH+CHCH$_2$ to give CHCHCHCH$_2$; b) and CCH$_2$+CCH$_2$ to give CCH$_2$CH$_2$C; c) CCH$_2$+CCH$_2$ to give CH$_2$CCCH$_2$; d) CHCH$_3$+CCH$_2$ to give CH$_3$CHCH$_2$C.

the type of surface site (top, hollow etc). We explored all the possible intermediates and, for the stable ones, located the E or Z transition state, considering three possibilities for the newly formed C-C bond: top, bridge and hollow. With this approach, we were able to identify 50 reaction steps as reported in Table S2 in the SI.

Figure 3 illustrates four distinct C-C couplings. Figure 3a shows the *trans* acetylene-vinyl coupling on a surface top site, which activation energy amounts to a low value of 1.03 eV. It can be seen how closely the reactant positions and especially the transition states resemble the final product structure. The acetylene carbon-carbon axis stays nearly parallel to the Pd-Pd bond and the methylidyne group in vinyl remains completely unperturbed on top of one Pd atom. Only the methylene group is displaced during the transformation. This mode of C-C coupling is typical for fast reactions during which the π systems remain parallel to the surface.

Coupling carbon atoms showing little or no interaction with the catalytic surface is a process with a moderate barrier. In contrast, those steps requiring strongly bound carbons to be desorbed from the surface are disfavoured (see Table S2). This is demonstrated with the coupling of two CCH_2 species, one of the experimentally proposed precursors of green oil. The coupling leading to CH_2CCCH_2 implies a partial cleavage of both triple bonds between the CCH_2 sp carbon atoms and the catalyst. As shown in Figure 3c, the molecules are coupled on top of a surface Pd atom, resulting in a high activation energy of 2.35 eV. This sharply contrasts with the alternative coupling to CCH_2CH_2C: for the coupling of two vinylidene molecules via their methylene functional groups, an activation barrier of only 1.18 eV is obtained. The spatial arrangement exhibited by this transformation is shown in Figure 3b, confirming that no significant alteration of the adsorbate/surface interaction is necessary for this step.

The reaction of $CHCH_3$ and CCH_2 to give CH_3CHCH_2C has the lowest activation energy, 1.00 eV. Figure 3d shows the transition state, in which $CHCH_3$ is slightly lifted from the surface and couples to the spectating $-CH_2-$ group. Since $CHCH_3$ is rather unstable (it dehydrogenates with a barrier <0.2 eV), its partial desorption is rather easy, agreeing with the fact that weakly bound functional groups are activated more easily.

Regarding thermodynamics on the Pd surface, formation of C_4 molecules such as *cis-* and *trans-*butene, butadiene, and butane are among the most exothermic reactions (see Table S2). The balance between formation of alkyl chains and desorption of strongly bound functional groups drives the formation of less common oligomeric precursors. In this perspective, the most exergonic reaction comes from the coupling of ethyl and vinylidene to give $CH_3CH_2CH_2C$; the gain in free energy is -1.05 eV. Close to this value is the free energy gain for 1,3-butadiene formation, -0.86 eV. Reactions involving ethylene are mostly endergonic,
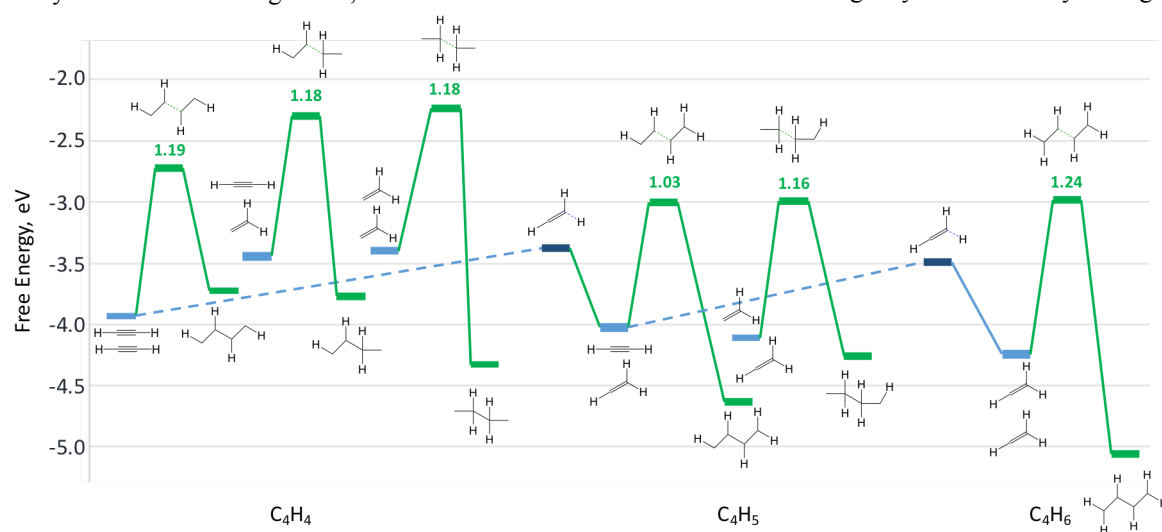

Figure 4. Key oligomerisation steps forming C_4 intermediates by coupling of C_2 fragments. All energies are referenced to acetylene and hydrogen in the gas-phase under standard conditions. For the paths between C_2 intermediates of the same stoichiometry, see Figure 2.

spanning an interval between -0.04 eV and 1.05 eV. Together with the relatively large activation energies for ethylene couplings (>1.3 eV), the absence of a thermodynamic driving force does not support the experimental findings of Yayun *et al.*[15] who suggested that ethylene participates in oligomerization. Again, our results rather support that green oil only involves hydrogen and acetylene derivatives. Similarly, just as for hydrogenations, ethylidyne requires significant activation energies for C-C couplings (>1.6 eV), confirming its role as a spectator in the reaction network.

The focus is now turned on oligomerization steps that are competitive with acetylene hydrogenation. Figure 4 summarizes the least activated processes starting from acetylene and vinyl, as certain surface species, and ethylidyne (CCH_2) exhibiting a comparable barrier for coupling and hydrogenation. The coupling of acetylene with another acetylene molecule, which has often be invoked in the literature, last but not least due to the characterization of the corresponding intermediate[48], is 0.1 eV more activated than its hydrogenation. This difference drops to 0.05 eV for the coupling of acetylene with vinyl ($CHCH_2$), a step that is also quite exothermic. Similarly, the hydrogenation of vinyl towards ethylene is only favoured by 0.07 eV over this C-C coupling reaction. Prior to the formation of the "safe" ethylene surface intermediate, oligomerization of C_2

species is probable they approach each other too closely. As discussed below, the required spacing might be provided either by a high hydrogen coverage or by highly dispersed Pd ensembles in PdAg alloys. When ethylene is over-hydrogenated, $CHCH_3$ and CH_2CH_3 constitute an additional pair of intermediates that poses a high risk for oligomerization (see Table S2).

Hydrogenation of C_4 derivatives. Couplings of C_2 species are of crucial importance in identifying the most competitive events generating the components of green oil. However, C_4 species can also be hydrogenated. Hydrogenation pathways were all assumed to be of the Horiuti-Polanyi type at low coverage (only one H atom on the p(3x3) Pd(111) surface). 52 direct hydrogenation steps were identified. These pathways complement the hydrogenation of butadiene ($CH_2CHCHCH_2$), previously published by our group.[49]

Figure 5 and Table S-3 (see SI) indicate that the hydrogenations of C_4 species tend to be less activated (and thus faster) than C_2 hydrogenations. The average activation energy to hydrogenate a C_4 fragment is 0.97 eV, which is competitive with the hydrogenation of acetylene (1.08 eV) and vinyl (0.96 eV). Beyond this average value, we found cases of extremely fast hydrogenations; 22 intermediates are hydrogenated faster than vinyl and six have an activation barrier lying under 0.70 eV.
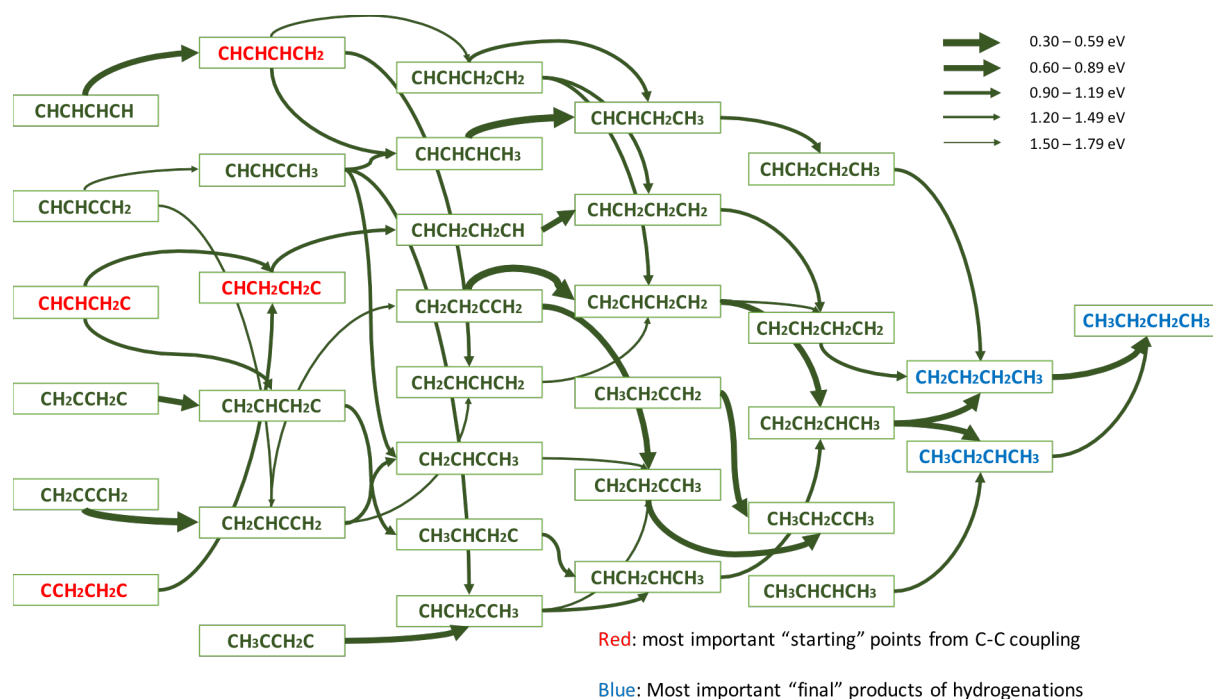

Figure 5. C_4 hydrogenation network. Arrow thicknesses relate to the activation energies.

The fastest C$_4$ hydrogenation is, with $\Delta E^{\ddagger}$=0.31 eV, the hydrogenation of CHCHCHCH$_3$ to CHCHCH$_2$CH$_3$. The C$_4$ coupling products starting from vinylidene (CCH$_2$) most likely go through CHCH$_2$CH$_2$C, followed by the hydrogenation of the terminal carbon, leading to CHCH$_2$CH$_2$CH, which is then converted to CHCH$_2$CH$_2$CH$_2$. The other important route starts with the most commonly formed oligomer, CHCHCHCH$_2$. This species can hydrogenates as quickly at one or the other terminal position. If the methylene carbon atom is hydrogenated, the resulting CHCHCHCH$_3$ intermediate quickly hydrogenates to CHCHCH$_2$CH$_3$. Alternatively, if hydrogenation occurs at the methylidyne end group,[49] butadiene is obtained. Experimentally, butadiene is a commonly observed during acetylene hydrogenation, especially at intermediate stages of catalyst deactivation.[50] According to a previous study of our group,[49] butadiene hydrogenates rather quickly (activation energies of 0.7-0.9 eV) to 1- and 2-butene, both of which are also observed experimentally.

The result that C$_4$ hydrogenations are competitive with C$_2$ hydrogenations is in good agreement with experimental evidence.[14,50] This situation is not only problematic in terms of hydrogen atom efficiency, but also problematic since acetylene and CHCH$_2$ are involved in the oligomerization reaction. Hence, if the C$_2$ species are not hydrogenated fast enough to ethylene, they are more likely to oligomerize. The oligomers in turn increase the hydrogen demand for C$_4$ hydrogenations. Hence, a significant hydrogen partial pressure might be necessary to maintain a sufficient surface hydrogen coverage. The hydrogen coverage might also help to slow down the C-C coupling by isolating C$_2$ species from each other through adsorbed hydrogen atoms. This scenario is in agreement with experimental findings that green oil formation goes through a maximum upon increasing the hydrogen partial pressure.[18,19] Unfortunately, however, too high hydrogen partial pressures diminish the selectivity of acetylene hydrogenation, leading to large amounts of ethane.

In the following two subsections, we will consider two extreme cases, relevant for AgPd catalysts. On the one hand, we assess well mixed solid solutions, where the ensembles for Pd atoms can be rather small and we therefore might have a chance to largely suppress green-oil formation due to the geometric effect. On the other hand, surface reorganization under reactive conditions might lead to large patches of Pd surrounded by Ag. In such a situation, only the electronic effect of Ag alloying comes into play. As will be shown, this electronic effect might slightly increase green oil formation.

Ensemble Requirements for Key Reaction Steps

A key question for the design of optimal catalysts for hydrogenation of acetylene in order to improve selectivity and avoid unwanted oligomers such as green oil is to determine the ensemble of atoms required for each elementary step in the mechanistic network. One way to depict this active site requirement is to determine the surface atoms that are formally occupied by a given intermediate or transition state. As we have established in a previous study[51] the projection of atomic radii on a graphical lattice including top and 3 fold hollow sites is an accurate method to assign sites to a given adsorbate. Here, we apply this approach to four key species in the mechanism: (a) acetylene, which needs to be adsorbed strongly for hydrogenation (b) CHCH$_2$, which is a certain intermediate in the selective hydrogenation towards ethylene (c) CHCH$_3$, which might proceed to non-selective ethane formation and cause surface poisoning through CCH$_3$ accumulation, and (d) the transition state for the C-C bond formation between acetylene and CHCH$_2$. The latter process has a competitive barrier (1.03 eV) compared to that for the hydrogenation to ethylene (0.96 eV) and represents the path leading to unwanted oligomers. The corresponding site requirements are given in Figure 6.

In agreement with our previous study on the Pd-Ag alloy,[52] Figure 6a indicates that there are two top sites (red circles) which are crucial for the binding energy of acetylene. Furthermore, the C-C bond is close to the hollow site (green circle), defined by a third top site. The latter is, however, not directly occupied by the molecule. This implies that an ensemble of 2 Pd atoms will strongly bind acetylene, with a third surface atom modulating the strength of the interaction (Ag for weaker binding, Pd for strong binding). Two additional hollow sites are blocked by the hydrogen atoms.

Moving to the key intermediate for hydrogenation, CHCH$_2$, only one top site is occupied by the adsorbate (see Figure 6b). However, similarly to acetylene, a hollow site is found below the C-C

a) CHCH

c) CH₃CH
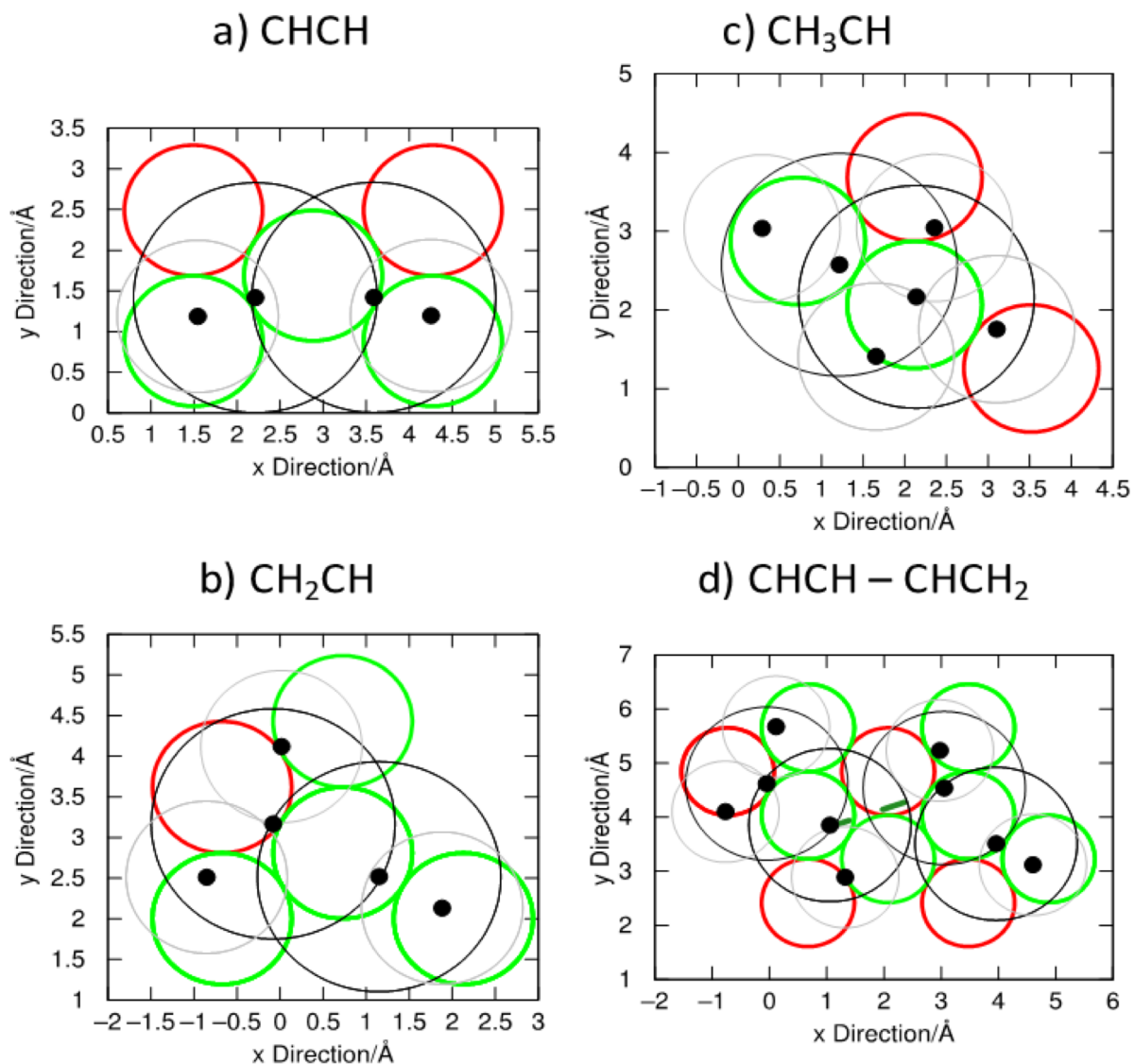

b) CH₂CH

d) CHCH − CHCH₂

Figure 6. Site requirements for key intermediates on a Pd(111) surface. Occupied top sites (in red) and 3-fold hollow sites (in green) are highlighted. The atomic nuclei of the adsorbate are given as black dots and the size of the atoms indicated as black and grey circles for carbon and hydrogen, respectively. The bond being formed in d) is indicated by a dashed green line.

bond. Hence, the neighbouring atoms of this hollow site are predicted to have a strong impact on the stability of this intermediate. Since, however, the site requirements of $CHCH_2$ are rather less (1 instead of 2 top sites) than more stringent compared to acetylene, the first hydrogenation reaction should be able to proceed on the very same ensemble as for acetylene adsorption, implying that surface diffusion is not required for hydrogenation.

Looking at the third intermediate ($CHCH_3$), leading to total hydrogenation, Figure 6c suggests that it is also stabilized by essentially the same ensemble of sites as the previous intermediates. Hence, it seems difficult to improve the selectivity

towards ethylene, versus ethane, just by controlling the ensemble of Pd atoms: one should rely instead on electronic effects weakening the adsorption of ethylene and favouring its desorption versus further hydrogenation. As one might have expected, the oligomerization process (Figure 6d) requires a larger ensemble of Pd atoms: Four top sites (and six hollow sites) are occupied by the transition state. Hence, if one of the top sites is exchanged for a less reactive metal (e.g., Ag), a significant increase in the activation energy can be expected. This explains the decrease of oligomer production when a PdAg alloy is used, instead of Pd, although other alloys of Pd with less reactive atoms with carbon (as PdAu) should lead to the same effect.[17]

To conclude, the site requirements for the main C_2 species are all quite similar. Hence, only specific electronic effects could affect the relative barriers and intermediate energies and hence the selectivity toward ethylene. The C-C coupling, on the other hand, required a markedly larger ensemble and oligomer formation is likely to be strongly slowed down by catalysts composed of exclusively Pd_2 (or maybe Pd_3) ensembles embedded in a less reactive metal. Our analysis has hence identified the configuration of the sites affecting the stability of intermediates and transition states, which could open to more detailed selective catalyst design using transition metal alloys.

reaction parameters for selected key reaction steps: the hydrogenation of vinyl to ethylene and to ethylidene, of ethylidene to ethyl, and of C_4H_4 on its terminal carbon atom. Subsurface Ag exerts a tensile strain on the Pd surface layer (unit-cell expansion) and modifies the electronic structure of the surface atoms. This causes a general increase in the catalyst's activity towards hydrogenation, with a lowering of activation energy barriers by ~0.1 eV. However, with an activation energy of ~0.5 eV, the unwanted acetylene-vinyl coupling for oligomerization experiences an even more important acceleration. If kinetics does not privilege selective hydrogenation versus oligomerization on this

Table 1. Most salient kinetic features as computed on a reverse-segregated $Pd_{25}Ag_{75}$ alloy model

Reaction Step	R, Å	Freq, cm^{-1}	ΔE_{act}, eV
$CHCH_2 + H \rightarrow CH_2CH_2$	1.82	715.24	0.88
$CHCH_3 + H \rightarrow CH_2CH_3$	1.71	820.38	0.89
$CHCH_2 + H \rightarrow CHCH_3$	1.65	928.46	0.83
$(CHCH)_2 + H \rightarrow CHCHCHCH_2$	1.47	855.51	0.79
$CHCH + CHCH_2 \rightarrow CHCHCHCH_2$	2.15	383.84	0.46

Reverse segregation and its influence on the selectivity

When two different metals are mixed together, those atoms showing the least surface formation energy tends to accumulate at the top of the surface, a phenomenon known as *surface segregation*. Pd-Ag alloys pose no exception to this.[53] In vacuum condition, Ag atoms are seen to accumulate at the surface. However, the presence of adsorbates on the surface may significantly enrich the surface in Pd, as it was predicted for atomic adsorbates,[54,55] and for acetylene.[56] In particular, by exploiting large-scale Monte Carlo simulations, we have predicted that, the equilibrium segregation profile is reversed for a wide range of compositions (0.0-0.7) and temperature (300 K-800 K) in an atmosphere of 1 bar of acetylene, i.e., Pd accumulates at the surface. A comparison between the most striking catalytic features acquired on Pd and the same features as computed on a Pd-Ag model is, therefore, appropriate. We have chosen, a 4-layer slab of $Pd_{25}Ag_{75}$ (111), with all Pd atoms placed on the topmost layer as the most representative model of the thermodynamically most likely surface state after long exposure to the reactive atmosphere.

Table 1 displays activation energy and

catalyst, one might still argue that selectivity is due to a profitable difference between acetylene and ethylene adsorption energy. However, we find that the change between pure Pd and reverse-segregated $Pd_{25}Ag_{75}$ is small, and that the difference in adsorption energy is even slightly decreased (by 0.05 eV) on the alloy model surface.

Both, the ensemble requirements and the unselective reactivity of the reverse-segregated alloy, reinforce the idea that well-mixed catalysts are crucial for selectivity in acetylene hydrogenation. Once the segregation reversal reaches its equilibrium stage, the catalyst is to be considered as aged and formation of oligomers will be favoured kinetically and thermodynamically. An estimate of the timescale of the surface restructuring would be of great benefit, but clearly exceeds the scope of the present work. We are not aware of any data in the literature on the evolution of the green-oil formation and surface structure of AgPd catalysts on an industrially relevant timescale (at least months). Therefore, we cannot compare our theoretical predictions on reverse segregation under relevant reaction conditions with any experimental data at this point. Furthermore, realistic kinetic simulations on a surface of an alloy that can undergo both (reverse) segregation and island formation for such a vast reaction network (roughly 40 intermediates) is

beyond the capabilities of today's simulation techniques. The major challenge for these simulations is to establish the cluster expansion for all the intermediates as a function of the surface state, i.e., the ensemble on which the intermediate is adsorbed and the lateral interactions due to the presence of other intermediates on the surface.

Conclusions

This paper has explored the vast network of chemical reaction steps leading to coupling by-products during selective hydrogenation of acetylene on a Pd(111) surface. Activation and reaction energies for the coupling between all plausible C_2 fragments, their interconversion and the key hydrogenation steps of C_4 intermediates have been computed.

Hydrogenation of C_2 intermediates is in general faster than C-C coupling. Nevertheless, some dimer formation steps are found to compete with hydrogenation, especially those not requiring cleavage of highly stable carbon-surface bonds, such as the coupling of early intermediates, including acetylene (CHCH) and vinyl (CHCH$_2$), and of vinylidene (CCH$_2$) provided the strongly bound carbon atom is not involved in the reaction. Ethylene is found to be kinetically inert towards dimer formation. This suggests that its role in the formation of green oil is of little or no importance. These findings are in good agreement with earlier experimental evidence, that acetylene, vinyl and vinylidene are the fragments which are most likely to participate in the formation of green oil.

Hydrogenation of C_4 intermediates is kinetically favoured on average compared to the hydrogenation of C_2 species, most likely due to an easier deformation of the intermediate, which on a per carbon basis is less strongly bound than, for instance, acetylene. Hence, C_4 intermediates are likely to consume a significant fraction of the surface hydrogen species. This could promote further coupling of early intermediates, which in turn would exhaust the surface from adsorbed hydrogen, decreasing the atom efficiency of the process. This emphasizes the detrimental role of "green oil" beyond catalyst deactivation. In analogy with the easier C-H bond formation in C_4 compared to C_2 species, the C-C coupling between C_4 intermediates or, statistically more likely, chain elongation by adding a C_2 unit to C_4 intermediates,

can also be expected to be faster than the C_2-C_2 couplings. Together, these observations rationalize the accumulation of long, almost completely saturated hydrocarbons as the main constituents of green oil.

Coupling steps were also investigated for their ensemble requirements, i.e., the size and geometry of a surface site required for reaction. Computations showed that an ensemble of 4 sites of Pd is required to permit acetylene oligomerization. Pd-based alloyed catalyst should then really be well-mixed in order to prevent green oil formation. Furthermore, we have demonstrated that once the reversed segregation has taken place, the selectivity of the catalyst is lost and green-oil formation is predicted to be fast. This insight sheds a new light on the design of novel catalysts for acetylene selective hydrogenation, emphasizing the need for stable, small, isolated dimers and trimers of the active metal surrounded by an inactive metal in order to avoid competitive oligomerization pathways.

Supporting Information available

Reaction and activation energies and all geometries are provided.

Corresponding Author

stephan.steinmann@ens-lyon.fr, sautet@ucla.edu

Acknowledgements

References

(1)   Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem. Int. Ed.* **2005**, *44*, 4442-4489

(2)   Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133–137.

(3)   Borodziński, A.; Bond, G. C. *Catal. Rev.* **2006**, *48*, 91–144.

(4)   Bos, A. N. R.; Westerterp, K. R. *Chem. Eng. Process.* **1993**, *32*, 1–7.

(5)   Jin, Y. *J. Catal.* **2001**, *203*, 292–306.

(6)   Friedrich, M.; Villaseca, S. A.; Szentmiklósi, L.; Teschner, D.; Armbrüster, M. *Materials* **2013**, *6*, 2958–2977.

(7)   Liu, R. J.; Crozier, P. a.; Smith, C. M.; Hucul, D. a.; Blackson, J.; Salaita, G. *Appl. Catal. A Gen.* **2005**, *282*, 111–121.

(8)   Leviness, S.; Weiss, A. H.; Schay, Z.; Guczi, L. *J. Mol. Catal.* **1984**, *25*, 131–140.

(9)   Ahn, I. Y.; Lee, J. H.; Kim, S. K.; Moon, S. H. *Appl. Catal. A Gen.* **2009**, *360*, 38–42.

(10)   Pachulski, A.; Schödel, R.; Claus, P. *Appl. Catal. A Gen.* **2011**, *400*, 14–24.

(11)   Sárkány, A.; Révay, Z. *Appl. Catal. A Gen.* **2003**, *243*, 347–355.

(12)   Asplund, S. *J. Catal.* **1996**, *158*, 267–278.

(13)   Kim, W.-J.; Moon, S. H. *Catal. Today* **2012**, *185*, 2–16.

(14)   Molnár, Á.; Sárkány, A.; Varga, M. *J. Mol. Catal. A Chem.* **2001**, *173*, 185–221.

(15)   Yayun, L.; Jing, Z.; Xueru, M. *Proc. Jt. Meet. Chem. Eng., Chem. Ind. Eng. Soc. China. AIChE. Beijing* **1982**, *2*, 688–702.

(16)   Gentle, M.; Muettertles E., L. *J. Chem. Phys.* **1983**, *87*, 2469–2472.

(17)   Gandman, Z. E.; Aerov, M. E.; Men'shchikov, V. A.; Getmantsev, V. S. *Int. Chem. Eng.* **1975**, *15*, 183–185.

(18)   Kim, W. J.; Shin, E. W.; Kang, J. H.; Moon, S. H. *Appl. Catal. A Gen.* **2003**, *251*, 305–313.

(19)   Zhang, J.; Sui, Z.; Zhu, Y. A.; Chen, D.; Zhou, X.; Yuan, W. *Chem. Eng. Technol.* **2016**, *39*, 865–873.

(20)   Larsson, M.; Jansson, J.; Asplund, S. *J. Catal.* **1996**, *162***,** 365–367

(21)   Sautet, P.; Cinquini, F. *ChemCatChem* **2010**, *2*, 636–639.

(22)   Armbrüster, M.; Behrens, M.; Cinquini, F.; Föttinger, K.; Grin, Y.; Haghofer, A.; Klötzer, B.; Knop-Gericke, A.; Lorenz, H.; Ota, A.; Penner, S.; Prinz, J.; Rameshan, C.; Révay, Z.; Rosenthal, D.; Rupprechter, G.; Sautet, P.; Schlögl, R.; Shao, L.; Szentmiklósi, L.; Teschner, D.; Torres, D.; Wagner, R.; Widmer, R.; Wowsnick, G. *ChemCatChem* **2012**, *4*, 1048–1063.

(23)   Torres, D.; Cinquini, F.; Sautet, P. *J. Phys. Chem. C* **2013**, *117*, 11059–11065.

(24)   García-Mota, M.; Bridier, B.; Pérez-Ramírez, J.; López, N. *J. Catal.* **2010**, *273*, 92–102.

(25)   Bridier, B.; Lopez, N.; Perez-Ramırez, J. *Dalt. Trans* **2010**, *39*, 8412–8419.

(26)   Mei, D.; Sheth, P.; Neurock, M.; Smith, C. *J. Catal.* **2006**, *242*, 1–15.

(27)   Sheth, P. A.; Neurock, M.; Smith, C. M. *J. Phys. Chem. B* **2003**, *107*, 2009–2017.

(28)   Beebe, T. P.; Yates, J. T. *J. Am. Chem. Soc.* **1986**, *108*, 663–671.

(29)   Pallassana, V.; Neurock, M.; Lusvardi, V. S.; Lerou, J. J.; Kragten, D. D.; Santen, R. A. Van. *J. Phys. Chem. B* **2002**, *111*, 1656–1669.

(30)   Moskaleva, L. V.; Chen, Z. X.; Aleksandrov, H. a.; Mohammed, A. B.; Sun, Q.; Rösch, N. *J. Phys. Chem. C* **2009**, *113*, 2512–2520.

(31)   Stacchiola, D.; Tysoe, W. T. *J. Phys. Chem. C* **2009**, *113*, 8000–8001.

(32)   López, N.; Vargas-Fuentes, C. *Chem. Commun.* **2012**, *48*, 1379–1391.

(33)   Yang, B.; Burch, R.; Hardacre, C.; Hu, P.; Hughes, P. *J. Phys. Chem. C* **2014**, *118*, 1560–1567.

(34)   Blochl, P. E. *Phys. Rev. B* **1994**, *50*, 17953–17979.

(35)   Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758–1775.

(36)   Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558–561.

(37)   Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169–11186.

(38)   Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(39)   Steinmann, S. N.; Corminboeuf, C. *J. Chem. Theory Comput.* **2011**, *7*, 3567–3577.

(40)   Gautier, S.; Steinmann, S.; Michel, C.;

Fleurat-Lessard, P.; Sautet, P. *Phys. Chem. Chem. Phys.* **2015**, *17*, 28921–28930.

(41)   Pack, J. D.; Monkhorst, H. J. *Phys. Rev. B* **1976**, *13*, 5188–5192.

(42)   Methfessel, M.; Paxton, A. T. *Phys. Rev. B* **1989**, *40*, 3616–3621.

(43)   Henkelman, G.; Jónsson, H. *J. Chem. Phys.* **2000**, *113*, 9978–9985.

(44)   Fleurat-Lessard, P.; Dayal, P. Opt'n Path http://perso.ens-lyon.fr/paul.fleurat-lessard/ReactionPath.html (accessed 2015).

(45)   Henkelman, G.; Jónsson, H. *J. Chem. Phys.* **1999**, *111*, 7010–7022.

(46)   Hill, T. L. *An Introduction to Statistical Thermodynamics*; Dover Publications, 1960.

(47)   Studt, F.; Abild-Pedersen, F.; Bligaard, T.; Sørensen, R. Z.; Christensen, C. H.; Nørskov, J. K. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 9299–9302.

(48)   Ormerod, R. M.; Lambert, R. M.; Hoffmann, H.; Zaera, F.; Yao, J. M.; Saldin, D. K.; Wang, L. P.; Bennett, D. W.; Tysoe, W. T. *Surf. Sci.* **1993**. *295*, 277–286

(49)   Valcárcel, A.; Clotet, A.; Ricart, J. M.; Delbecq, F.; Sautet, P. *J. Phys. Chem. B* **2005**, *109*, 14175–14182.

(50)   Ahn, I. Y.; Lee, J. H.; Kum, S. S.; Moon, S. H. *Catal. Today* **2007**, *123*, 151–157.

(51)   Vignola, E.; Steinmann, S. N.; Vandegehuchte, B. D.; Curulla, D.; Stamatakis, M.; Sautet, P. *J. Chem. Phys.* **2017**, *147*, 054106

(52)   Vignola, E.; Steinmann, S. N.; Vandegehuchte, B. D.; Curulla, D.; Sautet, P. *J. Phys. Chem. C* **2016**, *120*, 26320−26327.

(53)   Padama, A. A. B.; Kasai, H.; Budhi, Y. W. *Int. J. Hydrogen Energy* **2013**, *38*, 14715–14724.

(54)   Lovvik, O. M.; Opalka, S. M. *Surf. Sci.* **2008**, *602*, 2840–2844.

(55)   Svenum, I. H.; Herron, J. A.; Mavrikakis, M.; Venvik, H. J. *Catal. Today* **2012**, *193*, 111–119.

(56)   Vignola, E.; Steinmann, S. N.;

Vandegehuchte, B. D.; Le Mapihan, K.; Curulla, D.; Sautet, P. *under revision in J. Phys. Chem. C.*

Poisoned Surface

Hydrogenation