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Catalytic dehydrogenation of light alkanes may offer more efficient routes to selectively producing light olefins, which are some of the most important chemical building blocks in the industry, in terms of scale. We present a descriptor based micro-kinetic model of the trends in selectivity and activity of the non-oxidative dehydrogenation of ethane over the close-packed metal facets and through varied thermodynamic conditions. Our model predicts and explains the experimentally observed promotion effect on turnover rate from co-feeding hydrogen as an effect of the shifting equilibria in steady state. Our model predicts platinum group metals to have the most intrinsically active close-packed facets for ethane dehydrogenation and adding small amounts of tin to platinum is predicted to promote selectivity through a purely electronic effect. The trend in selectivity is understood through linear scaling relations and it is due to the re-action mechanism predicted by the model, which shows the path to ethene going through ethane dehydrogenation to ethyl, CH_3CH_2^* , then to ethene. The non-selective pathway to methane and deeply dehydrogenated species is predicted to go through dehydrogenation via CH_3CH^* . This implies that the desorption step of ethene is not the limiting step for selectivity and that geometric effects that stabilize CH_2CH_2^* compared to CH_3CH^* are desirable properties of a better catalyst. Removing reactive bridge and 3-fold sites facilitates this, which may be achievable by sufficient concentrations of tin in platinum. The included model code furthermore provides a base for easy tuning and reproduction and for expanding the study to other thermodynamic conditions, other facets, alloys or the reaction network to longer hydrocarbons or to oxidative pathways.

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First Principles Micro-kinetic Model of Catalytic Non-oxidative Dehydrogenation of Ethane over Close-packed Metallic Facets

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Abstract

Catalytic dehydrogenation of light alkanes may offer more efficient routes to selectively producing light olefins, which are some of the most important chemical building blocks in the industry, in terms of scale. We present a descriptor based micro-kinetic model of the trends in selectivity and activity of the non-oxidative dehydrogenation of ethane over the close-packed metal facets and through varied thermodynamic conditions. Our model predicts and explains the experimentally observed promotion effect on turnover rate from co-feeding hydrogen as an effect of the shifting equilibria in steady state. Our model predicts platinum group metals to have the most intrinsically active close-packed facets for ethane dehydrogenation and adding small amounts of tin to platinum is predicted to promote selectivity through a purely electronic effect. The trend in selectivity is understood through linear scaling relations and it is due to the reaction mechanism predicted by the model, which shows the path to ethene going through ethane dehydrogenation to ethyl, CH_3CH_2^* , then to ethene. The non-selective pathway to methane and deeply dehydrogenated species is predicted to go through dehydrogenation via CH_3CH^* . This implies that the desorption

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step of ethene is not the limiting step for selectivity and that geometric effects that stabilize CH_2CH_2^* compared to CH_3CH^* are desirable properties of a better catalyst. Removing reactive bridge and 3-fold sites facilitates this, which may be achievable by sufficient concentrations of tin in platinum. The included model code furthermore provides a base for easy tuning and reproduction and for expanding the study to other thermodynamic conditions, other facets, alloys or the reaction network to longer hydrocarbons or to oxidative pathways.

Keywords: Surfaces, Density Functional Theory, BEEF-vdW, Micro-kinetic model, Olefins, Alkenes, Paraffins, Alkanes, Transition Metals, Tin

1. Introduction

Catalytic dehydrogenation of light alkanes into light alkenes is receiving increased interest due to the growth in available ethane and propane feedstocks from shale gas, which has expanded rapidly, particularly in the United States. Development of hydraulic fracturing techniques for extraction is the cause of the rapid rise of shale gas, and the growth of natural gas resources is expected to continue for decades to come.[43, 20] Light alkenes are mainly used as precursors for polymers and they are primarily being produced by cracking oil products.[6] Current commercialized processes for catalytic dehydrogenation primarily focus on producing propene or butene rather than ethene,[37] which is due to demand on ethylene being met by existing steam crackers, while the propylene demand is not.[36]

Catalytic ethane dehydrogenation is interesting for several reasons: 1) Steam crackers, which are the conventional source of ethene, produce a mix of products and ethane dehydrogenation catalysts would be useful in applications, where high selectivity to ethene is needed. 2) A catalytic process would ideally be more energy efficient than steam cracking.[33] 3) From a first principles modelling aspect, reaction networks including oxygenated pathways or C_3 and heavier species are potentially so complex, that a higher level framework will be more feasible for constructing the model pathways and intermediates,[41, 15] but that

is beyond the scope of the present work. Meanwhile, ethane dehydrogenation have mechanistic parallels to propane dehydrogenation, and they show similar trends in activity and selectivity, over catalyst materials.[12, 48, 55, 45]

25 Commercialized catalysts for the light alkane dehydrogenation reactions can be classified into oxide based catalysts and metallic platinum based catalysts.[37] Within the metallic class, patents can be found relying on platinum and all the other VIIIb group metals in combination with tin, as catalysts.[6, 11, 31] Platinum in alloys with tin are, however, the only industrially used catalyst in the
30 metallic class, due to their favorable attributes in activity, selectivity, stability, cycle time and favourable properties for regeneration to burn off carbon deposits.[6, 37]

Dehydrogenation reactions are usually considered structure-insensitive re-
35 actions due to high activities regardless of catalyst morphology. C-C bond breaking and making reactions lead to undesired side pathways in dehydrogenation processes, and they are widely regarded as structure-sensitive and to take place on under-coordinated sites such as steps and on large ensembles of reactive atoms.[6] Growth of graphitic carbon is a thermodynamic sink under operating
40 conditions and steps are attributed to facilitate this process, as explained in detail in the following.

Measurements of ethane conversion rates over platinum nano particle catalysts show an initialization phase, where the conversion is high but the selectivity
45 towards ethene is low, compared to the following steady state phase, where conversion is lower, but selectivity is higher.[12, 48] Yang et al. furthermore did experiments comparing activity and selectivity for propane dehydrogenation over octahedral nanoparticles exposing Pt(111) facets versus cubic nanoparticles exposing Pt(100). Pt(111) was clearly more selective but less active, compared to
50 Pt(100), and this trend could be explained by density functional theory (DFT) calculations.[54] Other DFT calculations of the dehydrogenated intermediate

adsorption energies, and of activation energies indicate step sites to facilitate C-C and C-H bond breaking, with lower activation energies than on (111) facets of Pt[7, 52] and the same is the case for Pd.[3] These results in combination
55 indicate that the reactions may occur with high turnover, but lower selectivity, on steps or other under coordinated sites during initialization, which are then rapidly blocked and inactive during the steady state phase.

If reactive step sites exist, they may also serve as nucleation sites for graphitic
60 coke, which can grow to deactivate the otherwise active facets. This picture is shown by DFT calculations which explain that the minimum energy for forming a critical graphite sheet nucleus on a metal is determined by the graphite/metal edge energy.[35] The edge energy is lower on steps than facets, and it scales with the reactivity of a metal towards carbon-binding adsorbates.[5, 35] In agreement
65 with this model, Wu et al. showed that 1-2 nm Pt particles had higher coking resistance under ethane dehydrogenation conditions,[48] which may relate to either the lack of long steps on the smallest particles, or to a lack of support for a critical nucleus size for graphitic coke.

70 Co-feeding a controlled amount of sulfur is practiced in existing dehydrogenation processes to minimize coke formation, most likely because a small amount of sulfur will block reactive sites such as steps.[6] Co-feeding extra hydrogen to shift the equilibrium towards more hydrogenated species has also been shown to improve coking resistance as well as turnover frequency.[12, 48] Raybaud
75 et al. calculated the free state energy landscape of ethane dehydrogenation of ethylene over Pt(111) and concluded that a high hydrogen/hydrocarbon ratio in the stream would destabilize CH_3C^* and promote selectivity to ethene from the facet, providing a qualitative explanation of the effect of hydrogen from a thermodynamic argument.[32]

80 Tin or other additives are also contributing to the necessary step blocking effect for platinum group metallic catalysts. This was shown by IR experiments due to a peak assigned to CO on steps, which was present in spectra from Pt

samples but not from Sn/Pt alloy samples.[42] It is also noteworthy that even amounts below 5% of Tin added in Pt nano particles was reported to improve
85 coking resistance,[12, 48] suggesting that blocking of a minority of under coordinates sites is an important factor. Nykänen and Honkala reported calculations of propylene adsorption and propylene dehydrogenation intermediates on Pt FCC (211) and Pt₃Sn FCC (211), which suggest tin at the step edge suppresses deep dehydrogenation of propylene, by making the step sites inert.

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Based on these reports we assumed that an effective step blocking additive must be required, but not necessarily sufficient for selectivity on all the metallic catalysts and we focused on modelling the reaction over the close packed metallic facets. Reported DFT calculations comparing close packed platinum surfaces
95 with various concentrations of tin, show that tin shifts down the d-band center and makes the surface less reactive towards carbon, and it has been concluded, based on comparison of trends in the activation energies, that tin decreases activity but improves selectivity towards alkenes on the facets alone.[29, 53, 19]

100 Since the pure Pt (111) facet may by itself be non-selective, even if the steps are blocked, we turned our attention on modelling the reaction over close packed facets in a range of metals, leveraging scaling relations[1] to establish the overall trends in selectivity and activity. A few references exist on DFT calculations on other host metals than Pt for ethane decomposition. On palladium (111) Moskaleva et al. calculated the potential energy landscape of ethene
105 decomposition to through vinyl CH₂CH and ethylidene CH₃CH to CH₃C and showed that the isomerization pathway between CH₂CH₂* and CH₃CH* has a transition state energy on the order of 1 eV higher than the dehydrogenation reactions.[28] Chen et al. calculated a larger reaction network on Pd(111) and showed that the C-C bond breaking reactions have higher barriers than
110 C-H bond breaking reactions for all species, except in the case of the CHC intermediate, which was concluded to be the likely precursor for C₁ species.[8] Ande et al. mapped out the potential energy landscape of ethene hydrogenation

tion/dehydrogenation intermediates on Ru HCP(0001), which generally showed
 115 similar trends as on Pt(111) and Pd(111), but notably that the barrier from
 ethyl CH_3CH_2 to CH_2CH_2 is 0.03 eV higher than the barrier from CH_3CH_2^*
 to CH_3CH^* , suggesting this facet is non-selective for ethene.[2] Hook and Celik
 calculated the trends in the free energy landscape of the dehydrogenation inter-
 mediates on platinum alloy FCC(111) facets and showed that a single reactivity
 120 parameter can predict selectivity enhancement relative to platinum while vary-
 ing the ligand.[18] Xu et al. presented a screening study of a broader set of
 alloys using the difference between the C_2H_4 desorption transition state energy
 and the CH_3CH_2 dehydrogenation transition state energy as a descriptor for
 selectivity.[51] Contrary to Xu et al., we will show that the desorption transi-
 125 tion state is not a relevant descriptor in low conversion conditions, but that the
 different CH_3CH_2 dehydrogenation transition states are. Shi et al. calculated
 the reaction network energy landscape on Ir(111) and constructed a two-step
 micro-kinetic model for ethene hydrogenation to ethane, which showed the re-
 lation between activity and reactivity of Pd(111), Rh(111) and Pt(111) using
 130 energetics based on scaling relations.[38]

Generally, these studies show that the dehydrogenation transition state ener-
 gies are often close and that several pathways are in competition. The reaction
 mechanism therefore varies by both reaction conditions and by surface compo-
 sition. The balance between the production of alkenes and production of side
 135 products, such as methane, thus sensitively depends on the surrounding par-
 tial pressures and on temperature.[37] A full micro-kinetic model treatment is
 therefore necessary for predicting trends in selectivity and rates. None of the
 previous studies on dehydrogenation reactions attempt to quantify activity and
 selectivity using micro-kinetic modelling across the full C_1 and C_2 across the
 140 surrounding thermodynamic conditions as well as over descriptors of catalyst
 reactivity. Traditional micro-kinetic models can contain a lot of uncertain pa-
 rameters, which are more than plenty to fit and over-fit any experimental data,
 whereas first-principles micro-kinetic models rely on energetics from DFT cal-
 culations and provide physical predictions with zero free parameters.

Figure 1: The full reaction network including species containing up to two carbon atoms and up to 6 hydrogen atoms. All (de)hydrogenation (Solid black arrows) and C-C scission (Solid gray arrows) reactions are included in the network. Isomerization reactions are shown by dotted arrows, but only the one in black was included in the model. Adsorbed species are denoted by an asterisk, *.

To improve our understanding of this reaction and to create a base model for future studies of C_1 and C_2 hydrogenation/dehydrogenation across surface composition and across thermodynamic conditions, we therefore calculated energies and transition states on the FCC(111) facets of Au, Ag, Cu, Pt, Pd, Ir, Rh, Co, Ni and the HCP(0001) facets of Ru, Re and Zn, such that the energetics of the entire network can be predicted using linear scaling relations.[1] Then we set up a micro-kinetic model of the reaction network shown in Fig. 1. This model provides quantification of selectivity and activity as a function of the thermodynamic conditions and across reactivity descriptors spanning that range of metal facets and thereby forms a unified model of this reaction on close-packed metal facets.

2. Results and discussion

First we present the most important part of the free energy landscape at low conversion conditions, which we calculated by DFT with BEEF-vdW exchange-correlation.[47] Thereafter, the results of the micro-kinetic model will follow.

Figure 2: Free energy diagrams for the most relevant pathway in conversion of C_2H_6 (g) to C_2H_4 (g) in solid lines, plotted with the branching elementary step to CH_3CH^* in dotted lines. Both pathways are plotted for Pt, Pt_3Sn and for Cu. The free energies are plotted at 873 K, 0.2 bar C_2H_6 , $2 \cdot 10^{-4}$ bar C_2H_4 (0.1% carbon conversion) and 0.6 bar H_2 . Atomic structure models of key intermediates are rendered in the right panel, where large gray spheres represent surface atoms, black spheres represent C and small white spheres represent H.

Fig. 2 shows the free energy landscape of a pathway from ethane to ethene on Pt(111), Pt_3Sn (111) and Cu(111). The first reaction step is dehydrogenation of ethane C_2H_6 (g) to ethyl $CH_3CH_2^*$. In the second step, either of the two carbon groups may dehydrogenate leading to either ethene $CH_2CH_2^*$ or ethylidene CH_3CH^* (See the atomic geometries in Fig. 2, right panel). The transition state energy for desorption of ethene was found to be well within $k_B T$ of the energy of a relaxed physisorbed state.

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All net rates of dehydrogenation reactions, calculated from our steady-state micro-kinetic model on Pt (111) and Pt_3Sn (111) are presented in table 1. The net rates are defined as the forward rate minus the reverse rate, thus negative value indicate the reverse direction relative to the reaction expression in tables 1 and 2. The direct pathway through $CH_3CH_2^*$ and $CH_2CH_2^*$ has the highest reaction flux for Pt(111), while a second pathway goes through $CH_3CH^* \rightarrow$

175

$\text{CH}_3\text{CH}^* \rightarrow \text{CH}_2\text{CH}_2^* \rightarrow \text{C}_2\text{H}_4 \text{ (g)}$. We find the transition state of $\text{CH}_2\text{CH}_2^* + \text{H}^*$ formation from CH_3CH_2 to be rate determining for production of ethene of Pt (111), with a degree of rate control[39] ≈ 1 , (See supplementary information
180 (SI) Fig. S.15), showing that this pathway does not contribute to the overall rate.

In Fig. 2, we see that on Pt_3Sn and Cu the barrier for forming CH_3CH^* is larger than the barrier to form ethene, but on Pt they are almost equal, which
185 would result in a lack of ethene selectivity on pure Pt(111).

A third pathway from CH_3CH^* can proceed via dehydrogenation through CH_3C^* and CH_2C^* and hydrogenation to CH_2CH^* and CH_2CH_2^* . The latter pathway is two orders of magnitude slower than the first and most direct path
190 to $\text{C}_2\text{H}_4 \text{ (g)}$. Finally, we calculated the barrier for a hydrogen attack $\text{CH}_3\text{CH}_2^* + \text{H}^* \leftrightarrow \text{H}_2 + \text{CH}_2\text{CH}_2^*$ elementary reaction, hypothesized by Galvita et al.[12] and found that it has a high activation energy (See transition state scaling relations in the SI Fig. S.8), which is reflected by the extremely low net rate, (See second row in table 2). The degree of rate control[39] for ethene production is
195 ≈ 0 for all intermediates unique to third pathway (involving CH_3C^*) and the final pathway (involving the hydrogen attack step), over Pt (111).

In summary, we see in contrast to some of the existing theory,[51] that the key to selectivity is not by destabilising the alkene to drive desorption, but rather
200 by promoting the second dehydrogenation step towards the alkene as opposed to the competing CH_3CH^* . This situation may depend on the reaction conditions, in particular on the carbon conversion, as discussed later in this section.

Methane is the side product from the ethane dehydrogenation reaction[12]
205 and we therefore show the main pathway to C_1 species on Pt(111) and $\text{Pt}_3\text{Sn}(111)$ in Fig. 3. The first elementary step is again the activation of ethane to form CH_3CH_2^* . The pathway proceeds via dehydrogenation steps through CH_3CH^*

Table 1: Elementary X-H reactions and net rates, r , calculated over Pt(111) and Pt₃Sn (111) at 0.2 bar C₂H₆, $2 \cdot 10^{-4}$ bar C₂H₄ (0.1% carbon conversion), 0.6 bar H₂, 10^{-6} bar CH₄ and 10^{-9} bar C₂H₂. All rates have been rounded to two significant digits in this table.

Reaction	r [s ⁻¹] @ Pt	r [s ⁻¹] @ Pt ₃ Sn
C ₂ H ₆ (g) + 2* $\leftrightarrow$ CH ₃ CH ₂ * + H*	2100.0	60.0
CH ₃ CH ₂ * + H* $\leftrightarrow$ CH ₂ CH ₂ * + H ₂ (g) + *	$4.2 \cdot 10^{-7}$	$1.4 \cdot 10^{-7}$
CH ₃ CH ₂ * + * $\leftrightarrow$ CH ₂ CH ₂ * + H*	1200.0	59.0
CH ₃ CH ₂ * + * $\leftrightarrow$ CH ₃ CH* + H*	820.0	1.4
CH ₃ CH* + * $\leftrightarrow$ CH ₂ CH* + H*	310.0	0.23
CH ₃ CH* + * $\leftrightarrow$ CH ₃ C* + H*	510.0	1.1
CH ₃ C* + * $\leftrightarrow$ CH ₂ C* + H*	510.0	1.1
CH ₂ CH ₂ * + * $\leftrightarrow$ CH ₂ CH* + H*	-390.0	-0.9
CH ₂ CH* + * $\leftrightarrow$ CH ₂ C* + H*	-0.083	-0.0041
CH ₂ CH* + * $\leftrightarrow$ CHCH* + H*	-78.0	-0.66
CH ₂ C* + * $\leftrightarrow$ CHC* + H*	500.0	1.1
CHCH* + * $\leftrightarrow$ CHC* + H*	-84.0	-1.1
CHC* + * $\leftrightarrow$ CC* + H*	0.097	$5.7 \cdot 10^{-7}$
CH ₃ * + H* $\leftrightarrow$ CH ₄ (g) + 2*	860.0	0.019
CH ₃ * + * $\leftrightarrow$ CH ₂ * + H*	-860.0	-0.016
CH ₂ * + * $\leftrightarrow$ CH* + H*	-850.0	-0.016
CH* + * $\leftrightarrow$ C* + H*	-420.0	-0.005
2H* $\leftrightarrow$ H ₂ (g) + 2*	1200.0	60.0

→ CH₃C* → CH₂C* → CHC*, which cracks into C* + CH*. The rate determining step for methane production over Pt (111) is suggested to be the C-C scission transition state in CHC* with a degree of rate control[39] ≈ 1 , (See 210 SI Figure S.15) Table 2 furthermore shows that the C-C scission step with the highest rate is from the CHC* intermediate. This in agreement with conclusions in previous DFT studies on Pd.[8]

Table 2: Elementary reactions other than X-H and net rates, r , over Pt(111) and over Pt₃Sn (111) calculated at 0.2 bar C₂H₆, $2 \cdot 10^{-4}$ bar C₂H₄ (0.1% carbon conversion), 0.6 bar H₂, 10^{-6} bar CH₄ and 10^{-9} bar C₂H₂. The reactions are grouped by type using horizontal dividers. All rates have been rounded to two significant digits in this table.

Reaction	r [s ⁻¹] @ Pt	r [s ⁻¹] @ Pt ₃ Sn
CH ₂ CH ₂ * $\leftrightarrow$ C ₂ H ₄ (g) + *	1600.0	60.0
CHCH* $\leftrightarrow$ C ₂ H ₂ (g) + *	0.11	0.46
C ₂ H ₆ (g) + 2* $\leftrightarrow$ 2CH ₃ *	$1.9 \cdot 10^{-6}$	$7.6 \cdot 10^{-8}$
CH ₃ CH ₂ * + * $\leftrightarrow$ CH ₃ * + CH ₂ *	$4.8 \cdot 10^{-4}$	$1.6 \cdot 10^{-6}$
CH ₃ CH* + * $\leftrightarrow$ CH ₃ * + CH*	0.28	0.0024
CH ₃ C* + * $\leftrightarrow$ CH ₃ * + C*	0.052	$5.4 \cdot 10^{-5}$
CH ₂ CH ₂ * + * $\leftrightarrow$ 2CH ₂ *	$3.1 \cdot 10^{-4}$	$1 \cdot 10^{-5}$
CH ₂ CH* + * $\leftrightarrow$ CH ₂ * + CH*	0.18	$4.0 \cdot 10^{-4}$
CH ₂ C* + * $\leftrightarrow$ CH ₂ * + C*	1.8	$1.6 \cdot 10^{-4}$
CHCH* + * $\leftrightarrow$ 2CH*	6.2	0.0014
CHC* + * $\leftrightarrow$ CH* + C*	420.0	0.0048
CC* + * $\leftrightarrow$ 2C*	0.097	$5.7 \cdot 10^{-7}$
CH ₃ CH* + * $\leftrightarrow$ CH ₂ CH ₂ *	$3 \cdot 10^{-6}$	$3.5 \cdot 10^{-7}$

215 C-H breaking reactions are generally faster on the Pt facet, as seen from the net rates in table 1, when comparing to C-C breaking reactions of hydrogenated species. This trend is also clear from calculated activation energies presented in previous computational studies of dehydrogenation on platinum.[4, 52, 53]

220 The fastest pathway to methane branches off from the fastest ethene pathway, already when CH₃CH* is formed. The barrier for ethene desorption is smaller than the dehydrogenation barriers (See Fig. 2), thus obtaining selectivity towards C₂H₄ (g) on the facets can be a matter of suppressing CH₃CH* formation. Fig. 3 furthermore shows, that on Pt(111), forming CH₃CH* is predicted to have a higher barrier than the C-C scission reaction in CHC*, whereas 225 the predicted barrier on the less reactive Pt₃Sn(111) surface is higher for C-C scission in CHC*, than any of the dehydrogenation barriers.

Figure 3: Free energy diagrams for deep dehydrogenation of ethane and a final cracking step on Pt (111) (black line) and on Pt₃Sn (111) (blue line). The numbers of adsorbed H* are tracked above the frame and the species in the gas phase are tracked in the below the frame. The free energies are plotted at 873 K, 0.2 bar C₂H₆, $2 \cdot 10^{-4}$ bar C₂H₄ (0.1% carbon conversion) and 0.6 bar H₂. Atomic structure models of key intermediates are rendered in the right panel, where large gray spheres represent surface atoms, black spheres represent C and small white spheres represent H.

The above results are all evaluated at a low carbon conversion of 0.1%. In the following we show the results from our micro-kinetic model at varying carbon conversion by showing the turnover rates, coverages and carbon selectivity *versus* $p_{C_2H_4}$, (See Fig. 4). We define the carbon selectivity by equation 1.

$$s_{C_2H_4} = \frac{r_{C_2H_4}/2}{r_{CH_4} + r_{C_2H_2}/2 + r_{C_2H_4}/2} \quad (1)$$

Under steady state conditions at 873 K, the coverages of all species are below 0.1 on the Pt (111) facet, as indicated in Figures 4 and 5. Therefore adsorbate interactions are omitted in this model. At high temperature, diffusion tends to be fast on the metals and mean-field approximation for the rate equations was assumed sufficient.[17]

Figure 4: **Top left:** Net rates on platinum plotted on a log scale vs. ethene partial pressure, implying the reaction orders with respect to ethene partial pressure. **Top right panel:** Selectivities (Defined by Eqn. 1) on a linear scale. **Bottom left:** Selected coverages vs. ethene partial pressure. **Bottom right:** Computed free energies for the reactions C_2H_6 (g) $\rightarrow$ C_2H_4 (g) + H_2 (g) in green, C_2H_2 (g) + H_2 (g) $\rightarrow$ C_2H_4 (g) in red and C_2H_4 (g) + 2 H_2 (g) $\rightarrow$ CH_4 (g) in black. Other gas partial pressures were set to 0.2 bar C_2H_6 , 0.6 bar H_2 , 10^{-9} bar CH_4 and 10^{-12} bar C_2H_2 and the temperature was 873 K. The gray vertical line denotes 1% carbon conversion.

Fig. 4 lower right shows the driving force of the gas phase reactions involving C_2H_4 . We can compare the equilibrium partial pressure for C_2H_4 production, where ΔG crosses 0 in Fig. 4 lower right, with the turnover rates in Fig. 4 upper left. Here it shows that the onset of the elementary reaction $CH_2CH_2 \rightarrow CH_2CH^* + H^*$ only occurs as the equilibrium is approached and the overall ethene production reaction has begun to decrease. This result is consistent with Galvita et al.,[12] who fed isotope-labeled $^{13}C_2H_4$ and observed production of $^{13}CH_4$ and $^{13}C_2H_6$ when the driving force for ethene production was decreased by co-feeding hydrogen, while keeping the ratio of $C_2H_4 / C_2H_6 = 8.4\%$. Fig. 4

upper right shows that the selectivity towards ethene remains constant versus conversion until the equilibrium point is approached, where methane production
 245 becomes dominant. The lower left plot shows that CH_2CH_2^* and CH_2CH^* coverages are very low at all conversions, but that there are two plateaus, a lower coverage at low $p_{\text{C}_2\text{H}_4}$ and a higher coverage plateau at high $p_{\text{C}_2\text{H}_4}$. From these observations we conclude the $\text{CH}_2\text{CH}_2 \rightarrow \text{CH}_2\text{CH}^* + \text{H}^*$ reaction to be unimportant at low conversion conditions, where the pathway towards methane goes
 250 through the $\text{CH}_3\text{CH}_2 \rightarrow \text{CH}_3\text{CH}^* + \text{H}^*$ elementary reaction. At high conversion conditions we can qualitatively infer that the $\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_2\text{CH}^* + \text{H}^*$ reaction may be a relevant side reaction. In this case, mass transport limitations, which are not captured by the present model, are also expected to further increase the local chemical potentials of the product.

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It is also interesting to return to low conversion conditions and evaluate the micro-kinetic model while varying the hydrogen partial pressure, as shown in the following. Our kinetic model predicts that increasing the hydrogen partial pressure, p_{H_2} , caused increased C_2H_4 (g) production from the Pt (111) facets,
 260 as shown in Fig. 5, until the point where the gas mix approaches the equilibrium. Our micro-kinetic model results on coverages *versus* p_{H_2} , presented in the lower left panel of Fig. 5, show that increasing p_{H_2} decreases CH_2C^* coverage and increases CH_2CH_2^* coverage. The higher chemical potential of hydrogen stabilizes more hydrogenated intermediates on the surface, including CH_3CH_2^*
 265 and CH_2CH_2^* , relative to deeply dehydrogenated species, thereby shifting all the equilibria and increasing the steady state coverage of ethene. It is important to note that this effect is apparent without direct interactions between H^* and other adsorbates, since we are low coverage conditions and adsorbate-adsorbate interactions are not included. The forward rate of the desorption reaction to
 270 C_2H_4 (g) production is first order in the coverage of CH_2CH_2^* in the model, and more importantly the forward rate of the CH_3CH_2 dehydrogenation step is first order in the coverage of CH_3CH_2 , which are the apparent reasons for the increased rate.

Figure 5: **Top left:** Computed production rates on Pt (111) plotted on a log scale vs. hydrogen partial pressure, implying the reaction orders with respect to hydrogen partial pressure. The green circles show experimental rates, normalized to Pt atoms in the sample, from Galvita et al.[12], where the experimental data point at 0 hydrogen partial pressure has been placed at the point corresponding to 0.01% ethane conversion, which was the background conversion of the reactor in that study. **Top right panel:** Computed selectivity towards ethene (Defined by Eqn. 1), acetylene and methane on a linear scale, co-plotted with the experimental data on C_2H_4 selectivity from the same reference.[12] **Bottom left:** Computed coverages on a log scale vs. hydrogen partial pressure. **Bottom right:** Computed free energies for the reactions $C_2H_6 (g) \rightarrow C_2H_4 (g) + H_2 (g)$ in green, $C_2H_6 (g) + H_2 (g) \rightarrow CH_4 (g)$ in black and $C_2H_4 (g) + 2H_2 (g) \rightarrow CH_4 (g)$ in red. Other gas partial pressures were set to 0.2 bar C_2H_6 , $2 \cdot 10^{-3}$ bar C_2H_4 (1% carbon conversion), 10^{-6} bar CH_4 and 10^{-9} bar C_2H_2 and the temperature was 873 K.

275 The free energy of reaction, ΔG , for $C_2H_6 (g) \rightarrow C_2H_2 (g) + H_2 (g)$ is shown
in Fig 5, at the lower right, along with ΔG for $C_2H_6 (g) + H_2 (g) \rightarrow CH_4 (g)$
and ΔG for $C_2H_4 (g) + 2H_2 (g) \rightarrow CH_4 (g)$. The driving force for methane pro-
duction increases as the hydrogen partial pressure is increased, and our model
also shows an increased methane production rate in Fig. 5 upper left. Our
280 model (Fig. 5 upper right) predicts an initial increase in ethene selectivity (de-

finied by equation 1), as p_{H_2} increases, and only a decrease in selectivity above $p_{H_2} = 10^{-3}$ bar, due to increasing methane production.

We now discuss how the effect of varying p_{H_2} in relation with previous experi-
 285 mental studies on ethane dehydrogenation over Pt-based catalysts, which report
 that co-feeding hydrogen has a beneficial effect on activity.[12, 48] Experimen-
 tally measured rates from Galvita et al. are co-plotted in Fig. 5 which shows
 an increase in C_2H_4 (g) production rate from 1 to 2 nm Pt particles supported
 on Mg(Al)O by approximately 1 order of magnitude as the H_2 concentration
 290 was increased from 0 up to 0.58,[12] in agreement with our calculation. The
 experiments by Galvita et al., show a 20% increased methane production rate
 and an associated decrease in ethene selectivity from 80% down to 20% when
 increasing the $H_2 : C_2H_6$ ratio from 0 to 0.58, which is also in strong agreement
 with our model.

295

In the following we proceed with the dimensionality reduction to show the
 general trends in ethane turnover frequency and selectivity across the transition
 metals.

300 2.1. General trends for transition metals

Our computed formation energies of most the adsorbates are linearly cor-
 related with each other, as the surface is varied through the transition metals
 FCC (111) facets. The squared Pearson correlation coefficients, R^2 , of the linear
 correlations between all pairs of chemisorbed species in the model are shown in
 305 Fig. 6. Such linear relations are expected from the d-band model,[16, 1] due
 to the adsorption energy of each species correlating strongly with the d-band
 of the metal surface. In the following, we utilize these trends to reduce the
 dimensionality and define two descriptors as design parameters for selective and
 active catalytic sites on the close-packed metal facets.

310

Figure 6: Correlation matrix for calculated formation energies of chemisorbed species. The color scale denotes the squared Pearson correlation coefficient, R^2 , of the linear scaling relation between the formation energies of each pair of adsorbate species, as the surface element is varied.

Site specific energies, where adsorbates are most stable in geometrically identical sites (site-specific scaling), have in the case of CH_3^* *versus* C^* been reported to correlate better than if they were kept constrained to the top site.[1] This tendency is also seen in Fig. 6, where CH_3^* scale well with CH_3CH_2^* ,
 315 being the only two species in the dataset, which tend to bind in a the top site geometry. Meanwhile, the scaling of CH_3^* versus CH^* has been found to correlate better in their respective most stable sites.[26] Scaling between adsorbates in their most stable site have been reported to scale well more generally, as long as the surfaces are not highly inhomogenous.[27]

320

To visualize the results of the micro-kinetic model, we reduce the dimensionality to two descriptors using the CatMAP[25] linear scaler on the homogeneous close packed metal facets, using the most stable site for each species ("min-min scaling"). The best two descriptors are chosen with the consideration, that we
 325 are interested in the most accurate scaling for all species, but that CH_2CH_2^* , CH_3CH^* are the most decisive for calculating selectivity. CH_2CH_2^* is a critical intermediate, which according to Fig 6 has relatively poor correlation with

many other species. The reason for the poor linear correlation may be its particular π bonding geometry, bridging two top sites. Furthermore, it does not chemisorb on the noblest metal surfaces including Cu, Au, Ag, In and Zn. We show CH_3CH^* as the second descriptor because it is correlated highly with most species, including H^* , and it is deciding for selectivity. The consequence of choosing any descriptor, on accuracy of predictions of the remaining species is summarized by the R^2 shown in Figure 6. All the individual linear relations are shown in the SI Fig. S.8.

Figure 7: Activity volcano for ethene production at 873 K, 0.2 bar C_2H_6 (g), $2 \cdot 10^{-4}$ bar C_2H_4 (1% carbon conversion), 0.6 bar H_2 (g), 10^{-9} bar CH_4 and 10^{-12} bar C_2H_2 . The red dashed line shows the scaling between the descriptors (Eqn 2), the vertical and horizontal error bars are the ± 1 BEEF standard deviations on the descriptors and the ellipses show the covariances of the BEEF ensemble between the descriptors. $\text{Pt}_5\text{Sn}/\text{Pt}$ denotes a surface with termination Pt_5Sn and bulk Pt.

To be able to compare the results with reported experiments on various metals and alloys,[48, 50] we show the micro-kinetic model in Fig. 7 at 873 K, 0.2 bar ethane, and a 1 : 3 ratio of C_2H_6 to H_2 , and at low carbon conversion (0.1 %). Under these low pressures and high temperatures, we generally find the surfaces at low coverages of all species (See SI for coverage maps). Notably our model predicts the coverage of CH_2CH_2^* to be lower than 10^{-6} under these conditions on all of the metals.

Fig. 7 shows the top of the activity volcano slightly below the scaling line (Eqn 2) of chemisorbed CH_2CH_2^* *versus* CH_3CH^* .

$$E_{\text{CH}_2\text{CH}_2^*} \approx 0.5 \cdot E_{\text{CH}_3\text{CH}} + 0.65\text{eV} \quad (2)$$

345 Note that Au, Ag, Cu, In and Zn follows a different scaling line, which has slope ≈ 0 and an offset ≈ 2.15 eV, since CH_2CH_2^* is only physisorbed and does not form a bond with these surfaces.

Our model shows most of the FCC metals (111) facets on the weak binding
 350 slopes of the activity volcano with low coverages of all species, due to the high temperature and low partial pressures. Cu, Au and Ag (111) facets are predicted to be far too noble to yield any significant rate due to the high barrier of dehydrogenating CH_3CH_2^* , whereas Pt, Pd, Rh, Ir, Ru and are all predicted to be active. Re binds stronger than the other platinum group metals and the
 355 activation barriers are therefore also lower, but the coverages on Re are predicted to be too high at steady-state, leaving no free sites for dehydrogenation reactions. The present model does not include adsorbate-adsorbate interactions, which presumably would lead to lower coverages on the strong binding side of the volcano and therefore predict higher rates for Re in particular, but they
 360 would not change the results of weaker binding metals (See SI Fig. S.10 for a coverage map).

The selectivity map in Fig. 8a shows a boundary between the selective region where CH_3CH_2^* dehydrogenates most selectively to CH_2CH_2^* and the non-
 365 selective region, where CH_3CH_2^* dehydrogenates more selectively to CH_3CH^* , as described above in the case of platinum. In the following we show the descriptors for selectivity by deriving the origin of this boundary from the scaling relations. The scaling relations for the transition state energies towards CH_2CH_2^* and towards CH_3CH^* , both from CH_3CH_2^* are written in Eqn. 3 and Eqn. 4,

(a) Map of carbon specific selectivity defined analogous to equation 1. The red dashed line shows the scaling between the descriptors, written in Eqn. 2 and the ellipses denote ± 1 standard deviation of the BEEF ensemble energies. The red dotted line is where the transition state energies of CH₃CH* formation and CH₂CH₂* formation are equal (from Eqn. 5).

(b) Catalyst specific activities vs. selectivities towards C₂H₄ (g) predicted by the descriptor-based micro-kinetic model at 873 K, 0.2 bar C₂H₆ (g), 0.6 bar H₂, $2 \cdot 10^{-4}$ bar C₂H₄ (0.1% carbon conversion), 10^{-9} bar CH₄ and 10^{-12} bar C₂H₂. Pt₅Sn/Pt denotes a surface with termination Pt₅Sn and bulk Pt.

370 respectively.

$$E_{CH_3CH-H} \approx 1.33 \cdot E_{CH_3CH*} - 0.2eV \quad (3)$$

$$E_{CH_2CH_2-H} \approx 0.59 \cdot E_{CH_2CH_2*} + 0.28 \cdot E_{CH_3CH*} + 0.6eV \quad (4)$$

From Eqn. 3 and Eqn. 4 we find the crossing line in descriptor space between the planes of the transition state energies and write it in Eqn. 5. The intersection line is where the transition state energies are equal, thus it is determining for the relative differences in rate between the dehydrogenation reaction towards CH₂CH₂* and the dehydrogenation reaction towards CH₃CH*, both from CH₃CH₂*.

$$E_{CH_2CH_2*} \approx 1.78 \cdot E_{CH_3CH*} - 1.36eV \quad (5)$$

This line is plotted as the red dotted line in Fig. 8a, where it falls exactly on the

boundary and thus shows that these transition states are decisive for selectivity, not just for Pt and Pt₃Sn, but throughout the descriptor region in the model. The degree of rate control for methane production goes to 1 with respect to CH₃CH* in the region of descriptor space where $E_{CH_3CH-H} > E_{CH_2CH_2-H}$, confirming that this transition state energy indeed becomes rate limiting (See SI Fig. S.16). The precise location of the boundary and the precise descriptor energies of individual catalysts near the boundary line may be somewhat sensitive to uncertainties on the calculated electronic energies, but conclusions on the trend lines are more robust.

We can also infer from this understanding of the trends, that a shift to the scaling line Eqn. 2, that stabilizes CH₂CH₂ and CH₃CH₂ while destabilizing CH₃CH, would promote selectivity beyond the purely electronic effect. Selectivity and coking resistance are often attributed to ensemble effects,[9, 6] since smaller ensembles are expected to block hydrogenolysis or polymerization pathways. In the context of this model, that would correspond to creating a down-shifted scaling line, as described above, by creating isolated reactive atom geometries, stabilizing CH₃CH₂*, CH₂CH₂* and CH₃* relative to all other species due to their preference for a top site geometry.

In the following we discuss the calculated effects of introducing an alloy element, e.g. tin in Pt. Alloys generally tend to introduce more scatter in the linear scaling relations compared to pure metals. Nevertheless, the linear scaler[25] overall reduces the dimensionality of the problem from 44 parameters per surface to just 2 design parameters. In order to detect any deviations from the scaling relations, we consult the overview of the scaling relations (SI Fig. S.8). To understand the consequence of such a deviation on predicted activity and selectivity of a particular alloy, one should consult the degree of rate control with respect to the free energy of the relevant intermediate, to understand if such an outlier affects the rate and selectivity.

By increasing the amount of tin in the modelled platinum surfaces, we move in descriptor space along the scaling relation (Eqn. 2) to a more noble surface and achieve higher selectivity. Observing the geometries of all the chemisorbed C₂ intermediates, there are no geometric limitations on Pt₃Sn, and therefore it is likely that the step blocking effect and the electronic effect alone is the cause of improved selectivity on the Pt-Sn alloys in the low Sn concentration range, while higher Pt : Sn ratios than 3 : 1 are likely to introduce geometric or ensemble effects.

The model also predicts a compromise in specific activity when the tin content is increased as seen in Fig. 7, where the scaling line crosses the ridge of the volcano near Pt₅Sn/Pt, which is a Pt(111) slab where every 6th surface atom has been replaced by a Sn atom. This compromise in activity *versus* selectivity on the facets is also seen in Fig. 8b.

We now compare the calculated trends to experimental trends in activity. Experimental literature reports that the platinum group metals in general are most active,[6] which is in agreement with our results. The strong reactivity of Re is consistent with experiments on C-H activation in heavier hydrocarbons (n-hexane, 2,2-dimethylbutane and methylcyclopentane),[23] which report that even small amounts of Re added to Pd increase C-H bond breaking activity compared to pure Pd and that pure Re is more active than the Pd-Re alloys.

Wu et al. reports initial selectivities around 85% from Pt and 95% from Pt-Sn nano particles for dehydrogenation of ethene at 873 K, and they report increasing activity as the tin content increases up to a molar concentration of tin around 0.4.[48] Galvita et al. reported tests on ethane dehydrogenation, while varying the tin content in the platinum catalyst from 0 to 70% in molar concentration. Addition of tin increased the activity by up to 30% at an optimum Sn:Pt ratio of 1:3, above which the activity decreases again. Meanwhile selectivity increased monotonically from 60% to over 99%.[12] This behaviour of

selectivity and activity *versus* tin content is in qualitative agreement with the
435 predictions along the trend line in our volcano plot in Fig 7 and the selectivity
maps in Fig. 8a. The volcano plots shows a 2 orders of magnitude higher activ-
ity from Pt (111) than from Pt₃Sn (111), which suggests that the experimental
benchmarks are not observing the full intrinsic activity from the pure Pt (111)
facets, possibly due to deactivation from blocking carbonaceous species being
440 produced by edges or undercoordinated sites.

Wu et al. also report ethane dehydrogenation tests on alloys of Pt and Pd
with indium.[46, 50] From both Pt-In and Pd-In alloys, 98% selectivity was
obtained, whereas the pure Pt was 73% selective and the pure Pd was 53%
445 selective. Turnover rates were also improved by alloying, and in both cases an
optimum was found in the indium concentration. The position of InPd₃ in our
descriptor space predict the close-packed facet to be selective, but weak binding
and therefore less active than Pd. As in the case of pure Pt, the pure Pd, does
not have a step blocking element which means that the steps may be forming
450 blocking species that diffuses onto the facets, making it impossible to observe
the full intrinsic activity of the pure Pd (111) facets. The hydrogen binding
energy on this alloy is an outlier below the scaling relation, which may explain
that it is active. We find InPt₃ close to Pt₃Sn in the descriptor space, suggesting
that In has a similar effect on Pt as Sn does at this concentration.

455

The same authors also reported alloying Pt with iridium, which yielded se-
lectivity up to 95% towards ethene and a turnover rate enhancement of around
30% relative to Pt, at low residence time, similar to a Pt-Sn alloy. Furthermore
the Pt-Ir catalysts were also tested for propane dehydrogenation, which showed
460 correlation between trends in selectivity and turnover rate between ethane and
propane dehydrogenation.[49] They reported a test on a pure Ir catalyst to yield
only 19% selectivity towards ethene. Our calculations of the descriptor values
for IrPt₃ predict the material to be very similar to pure Pt, while the poor ex-
perimentally observed selectivity of the pure Ir sample is in agreement with the

465 location of Ir in our selectivity map, in the area where the scaling line between
the energies of CH_2CH_2^* and CH_3CH crosses into a region of high selectivity
towards methane, (See SI Figure S.9a).

Cybulskis et al. tested and characterized PtZn alloys, that showed over 99%
470 selectivity and a factor of 10 enhancement of the turnover rate compared to pure
platinum. They identified a crystal structure from X-ray diffraction, which dif-
fers from FCC. Geometric effects may therefore play a role, which our model
can not explicitly show. From this phase of PtZn Cybulskis et al. calculated a
d-band down shift of 0.1 eV using DFT. Such a d-band down shift would cor-
475 relate with a more noble surface, corresponding to moving up along the scaling
line (Eqn. 2) in our model, and the improved activity and selectivity is thus
in accordance with the micro-kinetic model, which predicts both high activity
and high selectivity for Pt_3Zn (See Fig. 8b). We calculated the descriptors for
 Pt_3Zn FCC (111), which show that a smaller concentration of Zn does shift the
480 reactivity in the more noble direction, similarly to InPt_3 and Pt_3Sn .

3. Conclusions

Our micro-kinetic model on metallic facets under varied partial pressures
reveals that the mechanism of forming side-products, including methane, goes
485 through CH_3CH in the low conversion limit, and it may involve dehydrogena-
tion of adsorbed ethene only at higher conversion on platinum. It also predicts
that co-feeding an optimal amount of hydrogen increases the turnover rate by
shifting elementary reaction equilibria and increasing the coverages of more hy-
drogenated intermediates, relative to the deeply dehydrogenated intermediates,
490 thereby explaining previous experimental reports.

As the catalyst composition is varied through the transition metals, the
scaling relations impose a compromise between activity and selectivity on the

close-packed facets, where selectivity is only achieved by moving to a more noble
495 surface, which also results in moving down the weak binding slope of an activity
volcano. From projecting the energies onto two descriptors, we can infer how
the scaling line between them could be shifted by a geometric effect. This would
improve activity and/or stability, thus suggesting a strategy for searching for
new catalyst materials. Experimental reports on metallic alloys agree well with
500 the general trends in intrinsic activity on the close packed facets. The activity
of some stronger binding pure metals including Pt will appear over-predicted on
the volcano plot, which is due to a fast partial deactivation of the pure facets,
possibly by coking or green oil formation, so their intrinsic specific activity is
never observed in experiments.

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This model of the C_1 and C_2 reaction network can serve as a convenient
base for future extensions including more alloys, facets, other thermodynamic
conditions and reaction directions, or expanding the reaction network to larger
hydrocarbons or oxidative pathways.

510

4. Method

All adsorbate formation energies (ΔE^{int}) in this paper are defined with
reference to CH_4 (g) and H_2 (g) as follows:

$$\begin{aligned}\Delta E_{C_x H_y^*}^{int} &= E(n_C = x, n_H = y) - E(0, 0) \\ &- n_C(E_{CH_4} - 2E_{H_2}) - n_H E_{H_2}/2\end{aligned}\quad (6)$$

$$\Delta G_{C_x H_y^*}^{int} = \Delta E_{C_x H_y^*}^{int} + \Delta ZPE - T\Delta S \quad (7)$$

where $E(n_C = x, n_H = y)$ is the electronic energy of the slab with adsorbates
515 and $E(0,0)$ is the energy of the clean slab. The difference in zero point energy
 ΔZPE and entropy of formation ΔS were calculated in the harmonic approx-
imation for surface species and in the ideal gas approximation for gas phase
species. The free energy of H_2 (g) was corrected by addition of 0.09 eV as

recommended by Studt et al.,[40] which improves the agreement of gas phase
 520 reactions ΔG with the standard experimental references.[34] After this correc-
 tion all ΔG of reaction agree with experimental values within an error of ± 0.06
 eV at temperatures 298 K and 873 K (See SI section 0.3).

The DFT calculations were carried out using Quantum Espresso[14] in which
 525 the atomic cores were represented by the pseudo potentials GBRV[13] version
 1.5 and the single electron wave functions were expanded in plane waves with
 an energy cut-off at 500 eV and the electron density cut-off was 5000 eV. The
 k-point sampling was a $4 \times 6 \times 1$ mesh. The exchange correlation contribution
 to the electronic energy was approximated using the BEEF-vdW[47] functional
 530 which provides a Bayesian error estimate based on perturbations to the GGA
 functional parameters.

Atomic structures were set up using the Atomic Simulation Environment,
 ASE.[24] The close packed facets were modelled using 3×2 supercells with
 535 five atomic layers, where the two outermost layers were relaxed or 4×2 super
 cells with three atomic layers, where the outermost layer was relaxed. Finite
 size errors in 2×2 supercells were up to 0.1 eV for CH_2CH_2 . The structures
 were centered in the out-of-plane direction with at least 8 Å of vacuum on each
 side. The reaction barriers were calculated using the fixed bond length ("drag")
 540 method for reactions involving C_2 species. Transition state energies for C_1H_x
 dehydrogenation and H_2 dissociation were obtained from scaling relations re-
 ported by Wang et al.[44]

Initial guesses for adsorption geometries included previously reported structures,[28,
 545 7, 8, 29, 52, 53, 30, 2] and other hand-picked starting guesses aiming at satis-
 fying the bond order of 4 for the carbon atoms. All adsorbates were treated in
 single sites, with no adsorbate-adsorbate interactions. Ideally, each geometry
 would have it's own site and associated scaling line and the energies would be
 parametrized as functions of coverages including cross interactions with other

550 adsorbates, but that would require several times more electronic structure optimizations, than the present model includes.

The many DFT calculations needed for this model were managed on three computing clusters using the Fireworks work flow manager,[21] and the atomic
555 structures, energies and meta data were stored in ASE database SQLite3 files, which are available as supplementary material.

There are 31 elementary reactions, for which the descriptor-based micro-kinetic model was set up in the steady-state approximation using the CatMAP
560 python module.[25] This code represents individual rates of surface reactions using as Arrhenius expressions, where the pre-factors represent vibrational attempt frequencies, which are obtained from the harmonic approximation, and the surface coverages are represented in the mean-field approximation. CatMAP solved the system of rate equations with a Newton’s method numerical solver, to
565 a tolerance of 100 decimals using the arbitrary precision floating point numerics package *mpmath*[22]. The input data and the scaling relations are printed in the SI Section 0.5. Hydrogen was given a separate site and all other species were kept on the same site one site. No other adsorbate interactions were included in the model. A python module, outlined in Fig. 9, was written and included
570 in CatMAP, which can convert the raw data from ASE database files, calculate formation free energies, BEEF standard deviations and covariance ellipses and convert them to the CatMAP input format.

ASE databases contain the essential raw data from the electronic structure
575 calculations, including geometries of the atomic structures, so that it is always transparent whether the most stable state or relevant saddle point has really been found. This kind of functionality is very useful for easy updates to the model free energy landscape and thereby for developing more complicated reaction networks in CatMAP. The model can be reproduced and extended using
580 CatMAP version 0.3.0 along with the supplementary files.

Figure 9: Schematic of the information flow from atomic models and electronic structure calculations through the EnergyLandscape class within CatMAP. This class searches the ASE database files, calculates the formation energies and stores the data in the usual CatMAP file format. The subsequent CatMAP work flow is as before.

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Supplementary Information
First Principles Micro-kinetic Model of Catalytic Non-oxidative
Dehydrogenation of Ethane over Close-packed Metallic Facets

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December 7, 2018

0.1 Code

Requirements:

- Atomic Simulation Environment (ASE) version 3.16.2 or above.
- CatMAP version 0.3.0 or above.

For reproducibility of the micro-kinetic model, an attached zip file contains python scripts and atomic structure data. The python files are named with an integer prefix, to guide the user through the workflow.

- 1 reads raw data from the .db files and exports formation energies to EDH_CH3CH.CH2CH2.txt.
- 2 reads formation energies from 'EDH_CH3CH.CH2CH2.txt' and the reaction network and model information from 'EDH_CH3CH.CH2CH2.mkm.py', trains the linear scaling relations and solves the microkinetic model in descriptor space. The model is always saved in 'EDH_CH3CH.CH2CH2.T600C.pkl'. It also exports the scaling relations to a json file 'EDH_CH3CH.CH2CH2_scaling.json'. Various flags can be passed to export extra data.
- 3 reads the scaling relations from 'EDH_CH3CH.CH2CH2_scaling.json' and raw data from the .db files and exports 'thermo_<catalyst name>.txt' with all necessary energies for each catalyst.
- 4 iterates and calls 'run_one_mkm_versus_pH2.py', which reads energies from one 'thermo_<catalyst name>.txt' and the reaction model setup from 'thermo_EDH_1site.mkm.py', solves the microkinetic model for one catalyst while varying p_{H_2} , and writes the results to a 'mkm_versus_pH2_<catalyst name>.txt'.
- 4b Repeats 4, only varying $p_{C_2H_4}$ instead of p_{H_2} .
- 5 plots data from 'mkm_versus_pH2_<catalyst name>.txt'.
- 5b plots data from 'mkm_versus_pC2H4_<catalyst name>.txt'.
- 6 reads energies from 'thermo_<catalyst name>.txt' and the reaction model setup from 'setup_vs_totalp_and_temp.mkm.py' and solves the microkinetic model versus total pressure and temperature for one catalyst and exports figures.
- 7 Iterates over each catalyst, loading energy parameters from 'thermo_<catalyst name>.txt' and solves the mkm at a single temperature and pressure, appending the results to 'mkm_single_cat_all.txt'
- 8 Loads 'mkm_single_cat_all.txt' and plots selectivity versus activity of various catalysts at fixed conditions.

0.2 Elementary Reactions

0.3 Reaction free energy benchmark

ethane_dehydrogenation

September 10, 2018

1 Benchmarking reaction energies from DFT

```
In [1]: import numpy as np
import pandas as pd
from scipy import constants
from scipy.optimize import curve_fit, newton
from ase.units import kJ, mol, invcm
import copy
from collections import Sequence
kB = constants.k / constants.e

from catmap.data.parameter_data import ideal_gas_params
```

1.1 Tabulated data

Standard thermodynamic properties from CRC and Shomate parameters from NIST.

```
In [2]: # Data from CRC handbook and NIST.
```

```
T_standard = 298.15
```

```
dat = {'C2H4': {'H': 52.4, 'G': 68.4, 'S': 219.3, 'C_p': 42.9,
               'shomateA': -6.38788, 'shomateB': 184.4019,
               'shomateC': -112.9718, 'shomateD': 28.49593,
               'shomateE': 0.315540, 'shomateF': 48.17332,
               'shomateG': 163.1568, 'shomateH': 52.46694},
       'C2H2': {'H': 227.4, 'G': 209.9, 'S': 200.9, 'C_p': 44.0,
               'shomateA': 40.68697, 'shomateB': 40.73279,
               'shomateC': -16.17840, 'shomateD': 3.669741,
               'shomateE': -0.658411, 'shomateF': 210.7067,
               'shomateG': 235.0052, 'shomateH': 226.7314},
       # NIST webbook is missing Shomate parameters for ethane.
       'C2H6': {'H': -84.0, 'G': -32.0, 'S': 229.2, 'C_p': 52.5},
       'CH4': {'H': -74.6, 'G': -50.5, 'S': 186.3, 'C_p': 35.7,
               'shomateA': -0.703029, 'shomateB': 108.4773,
               'shomateC': -42.52157, 'shomateD': 5.862788,
               'shomateE': 0.678565, 'shomateF': -76.84376,
```

```

        'shomateG': 158.7163, 'shomateH': -74.87310},
'H2': {'H': 0., 'G': 0., 'S': 130.7, 'C_p': 28.8,
        'shomateA': 33.066178, 'shomateB': -11.363417,
        'shomateC': 11.432816, 'shomateD': -2.772874,
        'shomateE': -0.158558, 'shomateF': -9.980797,
        'shomateG': 172.707974, 'shomateH': 0.0}}

```

In [3]: *# Constant pressure heat capacities data for C2H6 from NIST.*

```

nist_data = np.reshape([35.70,100.,
42.30,200.,
52.49,298.15,
52.71,300.,
65.46,400.,
77.94,500.,
89.19,600.,
99.14,700.,
107.94,800.,
115.71,900.,
122.55,1000.,
128.55,1100.,
133.80,1200.,
41.66,189.20,
43.25,209.30,
45.08,229.65,
47.27,249.90,
47.17,250.15,
49.68,272.00,
49.51,272.07,
50.66,279.00,
52.14,292.00,
53.27,302.70,
57.40,335.82,
58.91,347.65,
60.38,359.75,
61.04,364.78,
62.10,373.60,
63.89,387.55,
72.43,451.95,
80.08,520.55,
86.27,561.65,
90.46,603.25], [33, 2])

```

```

# Constant pressure heat capacity versus temperature.
def cp_shomate(x, a, b, c, d, e):
    if isinstance(x, Sequence):
        x = np.array(x)

```



```

t = x/1000.
return a + b * t + c * t ** 2 + d * t ** 3 + e / (t ** 2)

# Enthalpy change versus temperature
def h_shomate(x, a, b, c, d, e, f, h):
    if isinstance(x, Sequence):
        x = np.array(x)
    t = x/1000.
    H = a * t + (b/2.) * t ** 2 + (c/3.) * t ** 3 + \
        (d/4.) * t ** 4 - e / t + f - h
    return H

# Entropy as a function of temperature
def s_shomate(x, a, b, c, d, e, g):
    if isinstance(x, Sequence):
        x = np.array(x)
    t = x/1000.
    S = a * np.log(t) + b * t + (c/2.) * t ** 2 + \
        (d/3.) * t ** 3 - e / (2 * t ** 2) + g
    return S

# Reorder parameters in order to run root finding.
def fit_h(f, x, a, b, c, d, e, h):
    return h_shomate(x, a, b, c, d, e, f, h)

# Reorder parameters and subtract offset in order to run root finding.
def fit_s(g, x, a, b, c, d, e):
    return s_shomate(x, a, b, c, d, e, g) - 229.2

# Fit Shomate parameters for ethane.
popt, pcov = curve_fit(cp_shomate, nist_data[:, 1], nist_data[:, 0])
print(popt)

# Root finding for shomate parameter g.
root_g = newton(fit_s, x0=-300, args=((298.15),)+tuple(popt))
print(root_g)

# Root finding for shomate parameter f-h.
root_f = newton(fit_h, x0=-300, args=((298.15),)+tuple(popt) + ((0),))
print(root_f)

# Update dictionary with fitted Shomate parameters.
C2H6_dict = dat['C2H6']

```

```

C2H6_dict.update({'shomateA': popt[0], 'shomateB': popt[1],
                  'shomateC': popt[2], 'shomateD': popt[3],
                  'shomateE': popt[4], 'shomateF': root_f,
                  'shomateG': root_g, 'shomateH': 0})

# Make pandas dataframe.
df = pd.DataFrame(dat).transpose()
# Save file in case it's needed elsewhere.
df.to_pickle('crc_data.pkl')
print('Standard thermodynamic properties and shomate parameters.')
df

[ 9.27309365e+00  1.50784214e+02 -2.28933230e+01 -1.40195759e+01
  1.19966020e-01]
197.2817638125341
-8.834319868002734
Standard thermodynamic properties and shomate parameters.

Out[3]:
      C_p      G      H      S  shomateA  shomateB  shomateC  shomateD \
C2H2  44.0  209.9  227.4  200.9  40.686970  40.732790 -16.178400  3.669741
C2H4  42.9   68.4   52.4  219.3  -6.387880 184.401900 -112.971800 28.495930
C2H6  52.5  -32.0  -84.0  229.2   9.273094 150.784214 -22.893323 -14.019576
CH4   35.7  -50.5  -74.6  186.3  -0.703029 108.477300 -42.521570  5.862788
H2    28.8   0.0   0.0  130.7  33.066178 -11.363417  11.432816 -2.772874

      shomateE  shomateF  shomateG  shomateH
C2H2 -0.658411 210.706700 235.005200 226.73140
C2H4  0.315540  48.173320 163.156800  52.46694
C2H6  0.119966 -8.834320 197.281764  0.00000
CH4   0.678565 -76.843760 158.716300 -74.87310
H2   -0.158558 -9.980797 172.707974  0.00000

In [4]: # At temperature.
T = 873.15
df_T_chem_units = copy.deepcopy(df)
df_T_chem_units['C_p'] = cp_shomate(T, df['shomateA'], df['shomateB'],
                                     df['shomateC'], df['shomateD'], df['shomateE'])
dH = h_shomate(T, df['shomateA'], df['shomateB'], df['shomateC'],
               df['shomateD'], df['shomateE'], df['shomateF'], df['shomateH'])
df_T_chem_units['H'] += dH
dS = s_shomate(T, df['shomateA'], df['shomateB'], df['shomateC'],
               df['shomateD'], df['shomateE'], df['shomateG'])
df_T_chem_units['S'] = dS
df_T_chem_units['G'] += dH
df_T_chem_units['G'] -= (T * dS / 1000. - T_standard * df['S'] / 1000.)
print('Thermodynamic properties at ' + str(T) + 'K')
df_T_chem_units

```

Thermodynamic properties at 873.15K

```
Out[4]:
```

	C _p	G	H	S	shomateA	shomateB \
C2H2	65.497806	75.390748	260.125709	260.130900	40.686970	40.732790
C2H4	87.877064	-78.624079	91.533581	288.085616	-6.387880	184.401900
C2H6	114.301450	-189.887746	-34.513727	315.764758	9.273094	150.784214
CH4	66.388665	-173.511533	-45.193956	238.175482	-0.703029	108.477300
H2	29.806660	-85.736083	16.874792	162.147489	33.066178	-11.363417

	shomateC	shomateD	shomateE	shomateF	shomateG	shomateH
C2H2	-16.178400	3.669741	-0.658411	210.706700	235.005200	226.73140
C2H4	-112.971800	28.495930	0.315540	48.173320	163.156800	52.46694
C2H6	-22.893323	-14.019576	0.119966	-8.834320	197.281764	0.00000
CH4	-42.521570	5.862788	0.678565	-76.843760	158.716300	-74.87310
H2	11.432816	-2.772874	-0.158558	-9.980797	172.707974	0.00000

```
In [5]: # Convert to eV.
df_eV = df.loc[:, :'S'] * kJ / mol
df_eV['S'] /= 1000
df_eV['C_p'] /= 1000
print('Standard thermodynamic properties in eV.')
df_eV
```

Standard thermodynamic properties in eV.

```
Out[5]:
```

	C _p	G	H	S
C2H2	0.000456	2.175460	2.356835	0.002082
C2H4	0.000445	0.708916	0.543088	0.002273
C2H6	0.000544	-0.331657	-0.870599	0.002375
CH4	0.000370	-0.523396	-0.773175	0.001931
H2	0.000298	0.000000	0.000000	0.001355

```
In [6]: # At temperature in eV.
df_T = df_T_chem_units.loc[:, :'S'] * kJ / mol
df_T['S'] /= 1000
df_T['C_p'] /= 1000
print('Thermodynamic properties at ' + str(T) + 'K in eV')
df_T
```

Thermodynamic properties at 873.15K in eV

```
Out[6]:
```

	C _p	G	H	S
C2H2	0.000679	0.781370	2.696013	0.002696
C2H4	0.000911	-0.814881	0.948679	0.002986
C2H6	0.001185	-1.968048	-0.357710	0.003273
CH4	0.000688	-1.798320	-0.468402	0.002469
H2	0.000309	-0.888592	0.174895	0.001681

1.2 Thermodynamic properties calculated from DFT

```
In [7]: work_path = '/Users/mhangaard/Documents/arbejde/'
raw = np.genfromtxt(work_path + 'therm/DFT/energies/thermo_Pt.txt',
                    delimiter='\t')
data = raw[np.argsort(raw[:, 1]), :]
x = data[:, 1]
i_p_H2 = np.searchsorted(x, 1.)
# print(i_p_H2, x[i_p_H2], data[i_p_H2, 15])
```

```
In [8]: from ase.vibrations import Vibrations
from ase.thermochemistry import IdealGasThermo
from ase.build import molecule
```

```
In [9]: freq_H2 = [4400]

vib_e_H2 = np.array(freq_H2) * invcm

symmetry, geometry, spin = ideal_gas_params['H2_g']

thermo = IdealGasThermo(vib_energies=vib_e_H2,
                        potentialenergy=0.,
                        atoms=molecule('H2'),
                        geometry=geometry,
                        symmetrynumber=symmetry, spin=spin)
ZPE_H2 = 0.5*(sum(vib_e_H2))
H_H2 = thermo.get_enthalpy(temperature=T)
S_H2 = thermo.get_entropy(temperature=T, pressure=101325.)
G_H2 = thermo.get_gibbs_energy(temperature=T, pressure=101325.)
```

Enthalpy components at T = 873.15 K:

```
=====
E_pot          0.000 eV
E_ZPE          0.273 eV
Cv_trans (0->T) 0.113 eV
Cv_rot (0->T)   0.075 eV
Cv_vib (0->T)   0.000 eV
(C_v -> C_p)    0.075 eV
-----
H              0.537 eV
=====
```

Entropy components at T = 873.15 K and P = 101325.0 Pa:

```
=====
                S                T*S
S_trans (1 bar) 0.0014503 eV/K    1.266 eV
S_rot           0.0002236 eV/K    0.195 eV
S_elec          0.0000000 eV/K    0.000 eV
S_vib           0.0000005 eV/K    0.000 eV
S (1 bar -> P)  -0.0000011 eV/K   -0.001 eV
```

```
-----
S                0.0016733 eV/K        1.461 eV
=====
```

Enthalpy components at T = 873.15 K:

```
=====
E_pot            0.000 eV
E_ZPE            0.273 eV
Cv_trans (0->T)  0.113 eV
Cv_rot (0->T)    0.075 eV
Cv_vib (0->T)    0.000 eV
(C_v -> C_p)     0.075 eV
-----
```

```
H                0.537 eV
=====
```

Entropy components at T = 873.15 K and P = 101325.0 Pa:

```
=====
                        S                T*S
S_trans (1 bar)  0.0014503 eV/K        1.266 eV
S_rot            0.0002236 eV/K        0.195 eV
S_elec           0.0000000 eV/K        0.000 eV
S_vib            0.0000005 eV/K        0.000 eV
S (1 bar -> P)  -0.0000011 eV/K       -0.001 eV
-----
```

```
S                0.0016733 eV/K        1.461 eV
=====
```

Free energy components at T = 873.15 K and P = 101325.0 Pa:

```
=====
H                0.537 eV
-T*S            -1.461 eV
-----
G                -0.925 eV
=====
```

1.2.1 Correction

To apply a correction to the free energy and enthalpy of H2 (g), uncomment the following cell and run all cells.

```
In [10]: H_H2 += 0.09 # 0.09 eV correction from Studt et al.
        G_H2 += 0.09 # 0.09 eV correction from Studt et al.
```

```
In [11]: freq_CH4 = [23.552995581528762, 27.764742563603662, 33.585098005307799,
                    53.406563666871108, 57.897537192848368, 60.177324832107026,
                    1325.8417848412198, 1326.2077585306993, 1326.3096621770933,
                    1544.5344277414026, 1544.619454821669, 3007.1699114446992,
```

3113.831746849025, 3113.9002522596738, 3114.0862738043661]

```
vib_e_CH4 = np.array(freq_CH4) * invcm
```

```
symmetry, geometry, spin = ideal_gas_params['CH4_g']
```

```
thermo = IdealGasThermo(vib_energies=vib_e_CH4,
                        potentialenergy=0.,
                        atoms=molecule('CH4'),
                        geometry=geometry,
                        symmetrynumber=symmetry, spin=spin)
```

```
ZPE_CH4 = 0.5*(sum(vib_e_CH4))
```

```
H_CH4 = thermo.get_enthalpy(temperature=T)
```

```
S_CH4 = thermo.get_entropy(temperature=T, pressure=101325.)
```

```
G_CH4 = thermo.get_gibbs_energy(temperature=T, pressure=101325.)
```

Enthalpy components at T = 873.15 K:

```
=====
E_pot          0.000 eV
E_ZPE          1.204 eV
Cv_trans (0->T) 0.113 eV
Cv_rot (0->T)   0.113 eV
Cv_vib (0->T)   0.105 eV
(C_v -> C_p)    0.075 eV
-----
```

```
H              1.609 eV
=====
```

Entropy components at T = 873.15 K and P = 101325.0 Pa:

```
=====
                        S                T*S
S_trans (1 bar)  0.0017184 eV/K        1.500 eV
S_rot           0.0005777 eV/K        0.504 eV
S_elec          0.0000000 eV/K        0.000 eV
S_vib           0.0001669 eV/K        0.146 eV
S (1 bar -> P)  -0.0000011 eV/K       -0.001 eV
-----
```

```
S              0.0024619 eV/K        2.150 eV
=====
```

Enthalpy components at T = 873.15 K:

```
=====
E_pot          0.000 eV
E_ZPE          1.204 eV
Cv_trans (0->T) 0.113 eV
Cv_rot (0->T)   0.113 eV
Cv_vib (0->T)   0.105 eV
(C_v -> C_p)    0.075 eV
-----
```

```
H              1.609 eV
```

=====

Entropy components at T = 873.15 K and P = 101325.0 Pa:

=====

	S	T*S
S_trans (1 bar)	0.0017184 eV/K	1.500 eV
S_rot	0.0005777 eV/K	0.504 eV
S_elec	0.0000000 eV/K	0.000 eV
S_vib	0.0001669 eV/K	0.146 eV
S (1 bar -> P)	-0.0000011 eV/K	-0.001 eV

S	0.0024619 eV/K	2.150 eV

=====

Free energy components at T = 873.15 K and P = 101325.0 Pa:

=====

H	1.609 eV
-T*S	-2.150 eV

G	-0.540 eV

=====

```
In [12]: freq_C2H4 = [40.262241912411319, 14.033782246299147, 31.618400280955285,
42.157586242962054, 55.677463677951522, 58.662122308615615,
822.31252228222399, 942.23246750833107, 952.39130363498293,
1044.9485310827392, 1227.5224532595853, 1360.0151399884046,
1459.4221113117815, 1655.1029612649604, 3101.0847261440181,
3113.7838179051355, 3172.2538095039035, 3200.2598433642047]
```

```
vib_e_C2H4 = np.array(freq_C2H4) * invcm
```

```
symmetry, geometry, spin = ideal_gas_params['C2H4_g']
```

```
thermo = IdealGasThermo(vib_energies=vib_e_C2H4,
                        potentialenergy=2.328,
                        atoms=molecule('C2H4'),
                        geometry=geometry,
                        symmetrynumber=symmetry, spin=spin)
```

```
ZPE_C2H4 = 0.5*(sum(vib_e_C2H4))
```

```
H_C2H4 = thermo.get_enthalpy(temperature=T)
```

```
S_C2H4 = thermo.get_entropy(temperature=T, pressure=101325.)
```

```
G_C2H4 = thermo.get_gibbs_energy(temperature=T, pressure=101325.)
```

Enthalpy components at T = 873.15 K:

=====

E_pot	2.328 eV
E_ZPE	1.367 eV

Cv_trans (0->T)	0.113 eV
Cv_rot (0->T)	0.113 eV
Cv_vib (0->T)	0.210 eV
(C_v -> C_p)	0.075 eV

H 4.206 eV
=====

Entropy components at T = 873.15 K and P = 101325.0 Pa:

	S	T*S
S_trans (1 bar)	0.0017907 eV/K	1.564 eV
S_rot	0.0008270 eV/K	0.722 eV
S_elec	0.0000000 eV/K	0.000 eV
S_vib	0.0003621 eV/K	0.316 eV
S (1 bar -> P)	-0.0000011 eV/K	-0.001 eV

S 0.0029787 eV/K 2.601 eV
=====

Enthalpy components at T = 873.15 K:

E_pot	2.328 eV
E_ZPE	1.367 eV
Cv_trans (0->T)	0.113 eV
Cv_rot (0->T)	0.113 eV
Cv_vib (0->T)	0.210 eV
(C_v -> C_p)	0.075 eV

H 4.206 eV
=====

Entropy components at T = 873.15 K and P = 101325.0 Pa:

	S	T*S
S_trans (1 bar)	0.0017907 eV/K	1.564 eV
S_rot	0.0008270 eV/K	0.722 eV
S_elec	0.0000000 eV/K	0.000 eV
S_vib	0.0003621 eV/K	0.316 eV
S (1 bar -> P)	-0.0000011 eV/K	-0.001 eV

S 0.0029787 eV/K 2.601 eV
=====

Free energy components at T = 873.15 K and P = 101325.0 Pa:

H	4.206 eV
-T*S	-2.601 eV

G 1.606 eV

=====

```
In [13]: freq_C2H6 = [12.108147923868666, 33.909273195741669, 43.504625999297723,
49.599880989307358, 50.227287410997512, 304.83069072774379,
813.69593133816625, 814.55274958933535, 981.82121707087242,
1203.2577155007673, 1203.4296272289805, 1392.7238071320828,
1400.9497017973126, 1484.2271085954076, 1484.4332700967318,
1488.6917448247164, 1489.0504759635419, 2999.8696255847067,
3001.6179761847134, 3048.0829991962064, 3048.9790623154304,
3072.981935923503, 3073.8959921813162]
```

```
vib_e_C2H6 = np.array(freq_C2H6) * invcm
```

```
symmetry, geometry, spin = ideal_gas_params['C2H6_g']
```

```
thermo = IdealGasThermo(vib_energies=vib_e_C2H6,
                        potentialenergy=0.7597,
                        atoms=molecule('C2H6'),
                        geometry=geometry,
                        symmetrynumber=symmetry, spin=spin)
```

```
ZPE_C2H6 = 0.5*(sum(vib_e_C2H6))
```

```
H_C2H6 = thermo.get_enthalpy(temperature=T)
```

```
S_C2H6 = thermo.get_entropy(temperature=T, pressure=101325.)
```

```
G_C2H6 = thermo.get_gibbs_energy(temperature=T, pressure=101325.)
```

Enthalpy components at T = 873.15 K:

=====

E_pot	0.760 eV
E_ZPE	2.003 eV
Cv_trans (0->T)	0.113 eV
Cv_rot (0->T)	0.113 eV
Cv_vib (0->T)	0.331 eV
(C_v -> C_p)	0.075 eV

H	3.394 eV
---	----------

=====

Entropy components at T = 873.15 K and P = 101325.0 Pa:

=====

	S	T*S
S_trans (1 bar)	0.0017996 eV/K	1.571 eV
S_rot	0.0008446 eV/K	0.737 eV
S_elec	0.0000000 eV/K	0.000 eV
S_vib	0.0006082 eV/K	0.531 eV
S (1 bar -> P)	-0.0000011 eV/K	-0.001 eV

S	0.0032513 eV/K	2.839 eV
---	----------------	----------

=====

Enthalpy components at T = 873.15 K:

```
=====
E_pot          0.760 eV
E_ZPE          2.003 eV
Cv_trans (0->T) 0.113 eV
Cv_rot (0->T)   0.113 eV
Cv_vib (0->T)   0.331 eV
(C_v -> C_p)    0.075 eV
-----
H              3.394 eV
=====
```

Entropy components at T = 873.15 K and P = 101325.0 Pa:

```
=====
                        S                T*S
S_trans (1 bar)  0.0017996 eV/K        1.571 eV
S_rot           0.0008446 eV/K        0.737 eV
S_elec          0.0000000 eV/K        0.000 eV
S_vib           0.0006082 eV/K        0.531 eV
S (1 bar -> P)  -0.0000011 eV/K       -0.001 eV
-----
S              0.0032513 eV/K        2.839 eV
=====
```

Free energy components at T = 873.15 K and P = 101325.0 Pa:

```
=====
H          3.394 eV
-T*S      -2.839 eV
-----
G          0.555 eV
=====
```

```
In [14]: freq_C2H2 = [30.916291535122955, 26.736589038569601, 0.39585013679509395,
0.25965374158359045, 2.0837801993016094, 620.8370312869248,
620.97952652196966, 747.30986688355677, 748.50252105082336,
2056.722043624447, 3449.3659838728395, 3551.1056695728989]
```

```
vib_e_C2H2 = np.array(freq_C2H2) * invcm
```

```
symmetry, geometry, spin = ideal_gas_params['C2H2_g']
```

```
thermo = IdealGasThermo(vib_energies=vib_e_C2H2,
                        potentialenergy=4.4137,
                        atoms=molecule('C2H2'),
                        geometry=geometry,
                        symmetry=symmetry, spin=spin)
ZPE_C2H2 = 0.5*(sum(vib_e_C2H2))
```

```

H_C2H2 = thermo.get_enthalpy(temperature=T)
S_C2H2 = thermo.get_entropy(temperature=T, pressure=101325.)
G_C2H2 = thermo.get_gibbs_energy(temperature=T, pressure=101325.)

```

Enthalpy components at T = 873.15 K:

```

=====
E_pot          4.414 eV
E_ZPE          0.731 eV
Cv_trans (0->T) 0.113 eV
Cv_rot (0->T)   0.075 eV
Cv_vib (0->T)   0.174 eV
(C_v -> C_p)    0.075 eV
-----

```

```

H              5.583 eV
=====

```

Entropy components at T = 873.15 K and P = 101325.0 Pa:

```

=====
                S                T*S
S_trans (1 bar) 0.0017810 eV/K    1.555 eV
S_rot           0.0005659 eV/K    0.494 eV
S_elec          0.0000000 eV/K    0.000 eV
S_vib           0.0003394 eV/K    0.296 eV
S (1 bar -> P)  -0.0000011 eV/K   -0.001 eV
-----
S              0.0026852 eV/K    2.345 eV
=====

```

Enthalpy components at T = 873.15 K:

```

=====
E_pot          4.414 eV
E_ZPE          0.731 eV
Cv_trans (0->T) 0.113 eV
Cv_rot (0->T)   0.075 eV
Cv_vib (0->T)   0.174 eV
(C_v -> C_p)    0.075 eV
-----

```

```

H              5.583 eV
=====

```

Entropy components at T = 873.15 K and P = 101325.0 Pa:

```

=====
                S                T*S
S_trans (1 bar) 0.0017810 eV/K    1.555 eV
S_rot           0.0005659 eV/K    0.494 eV
S_elec          0.0000000 eV/K    0.000 eV
S_vib           0.0003394 eV/K    0.296 eV
S (1 bar -> P)  -0.0000011 eV/K   -0.001 eV
-----
S              0.0026852 eV/K    2.345 eV
=====

```

=====

Free energy components at T = 873.15 K and P = 101325.0 Pa:

```
=====
      H          5.583 eV
    -T*S        -2.345 eV
-----
      G          3.238 eV
=====
```

2 Compare ΔG

2.1 $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$

```
In [15]: # CRC
print('CRC \n -----')
print('$\Delta$ TS', T, 'K = ',
      T * ((df_T['S']['C2H4'] + df_T['S']['H2']) - df_T['S']['C2H6']))
print('$\Delta$ H ', T, 'K = ',
      (df_T['H']['C2H4'] + df_T['H']['H2']) - (df_T['H']['C2H6']))
print('$\Delta$ G ', T, 'K ,1bar = ',
      (df_T['G']['C2H4'] + df_T['G']['H2']) - (df_T['G']['C2H6']))
print('$\Delta$ G ', T, 'K ,p = ',
      (df_T['G']['C2H4'] + kB * T * np.log(0.002) + df_T['G']['H2']) -
      (df_T['G']['C2H6'] + kB * T * np.log(0.2)))

# DFT
print('\n DFT \n -----')
print('$\Delta$ TS ', T, 'K = ', T * (S_C2H4 + S_H2) - T*S_C2H6)
print('$\Delta$ H ', T, 'K = ', (H_C2H4 + H_H2) - H_C2H6)
print('$\Delta$ G ', T, 'K,1bar = ', (G_C2H4 + G_H2) - G_C2H6)
p_p0 = kB * T * (np.log(0.002) - np.log(0.2))
print('$\Delta$ G ', T, 'K,p = ', G_C2H4 + G_H2 - G_C2H6 + p_p0)
# print('$\Delta$ G CatMAP 873K,p = ', data[i_p_H2, 15])
```

CRC

```
-----
$\Delta$ TS 873.15 K = 1.216879636166452
$\Delta$ H 873.15 K = 1.4812831719218695
$\Delta$ G 873.15 K ,1bar = 0.2645747534887932
$\Delta$ G 873.15 K ,p = -0.08192847404322912
```

DFT

```
-----
$\Delta$ TS 873.15 K = 1.2230402120950106
$\Delta$ H 873.15 K = 1.4389489175477177
$\Delta$ G 873.15 K,1bar = 0.21590870545270768
```

ΔG 873.15 K, p = -0.13059452207931455

2.2 $C_2H_6 + H_2 \rightarrow 2CH_4$

```
In [16]: # CRC
print('CRC \n -----')
print('$\Delta$ TS', T, 'K = ',
      T * (2 * df_T['S']['CH4'] - (df_T['S']['C2H6'] + df_T['S']['H2'])))
print('$\Delta$ H ', T, 'K = ',
      2 * df_T['H']['CH4'] - (df_T['H']['C2H6'] + df_T['H']['H2']))
print('$\Delta$ G ', T, 'K ,1bar = ',
      2 * df_T['G']['CH4'] - (df_T['G']['C2H6'] + df_T['G']['H2']))
print('$\Delta$ G ', T, 'K ,p = ',
      2 * (df_T['G']['CH4'] + kB * T * np.log(2.e-7)) -
      (df_T['G']['C2H6'] + kB * T * np.log(0.2) + df_T['G']['H2']))

# DFT
print('\n DFT \n -----')
print('$\Delta$ TS', T, 'K = ', T*(2 * S_CH4 - (S_C2H6 + S_H2)))
print('$\Delta$ H ', T, 'K = ', 2 * H_CH4 - (H_C2H6 + H_H2))
print('$\Delta$ G ', T, 'K,1bar = ', 2 * G_CH4 - (G_C2H6 + G_H2))
p_p0 = kB * T * (2 * np.log(2.e-7) - np.log(0.2))
print('$\Delta$ G ', T, 'K,p = ', 2 * G_CH4 - (G_C2H6 + G_H2) + p_p0)
# print('$\Delta$ G CatMAP 873K,p = ', data[i_p_H2, 16])
```

CRC

```
-----
$\Delta$ TS 873.15 K = -0.014128937295745343
$\Delta$ H 873.15 K = -0.7539900048514305
$\Delta$ G 873.15 K ,1bar = -0.7400009333735955
$\Delta$ G 873.15 K ,p = -2.9401179797909798
```

DFT

```
-----
$\Delta$ TS 873.15 K = -0.0007666981609171901
$\Delta$ H 873.15 K = -0.8019106339383648
$\Delta$ G 873.15 K,1bar = -0.8011439357774474
$\Delta$ G 873.15 K,p = -3.001260982194832
```

2.3 $C_2H_6 \rightarrow C_2H_2 + 2H_2$

```
In [17]: # CRC
print('CRC \n -----')
print('$\Delta$ TS', T, 'K = ',
      T * ((df_T['S']['C2H2'] + 2 * df_T['S']['H2']) - df_T['S']['C2H6']))
print('$\Delta$ H ', T, 'K = ',
```

```

        (df_T['H']['C2H2'] + 2 * df_T['H']['H2']) - (df_T['H']['C2H6']))
print('$\Delta$ G ', T, 'K ,1bar = ',
      (df_T['G']['C2H2'] + 2 * df_T['G']['H2']) - (df_T['G']['C2H6']))
print('$\Delta$ G ', T, 'K ,p = ',
      (df_T['G']['C2H2'] + kB * T * np.log(2.e-10) + 2 * df_T['G']['H2']) -
      (df_T['G']['C2H6'] + kB * T * np.log(0.2)))

# DFT
print('\n DFT \n -----')
print('$\Delta$ TS', T, 'K = ', T * ((S_C2H2 + 2 * S_H2) - S_C2H6))
print('$\Delta$ H ', T, 'K = ', (H_C2H2 + 2 * H_H2) - H_C2H6)
print('$\Delta$ G ', T, 'K,1bar = ', (G_C2H2 + 2 * G_H2) - G_C2H6)
p_p0 = kB * T * (np.log(2.e-10) - np.log(0.2))
print('$\Delta$ G ', T, 'K,p = ', (G_C2H2 + 2 * G_H2) - G_C2H6 + p_p0)
# print('$\Delta$ G CatMAP 873K,p = ', data[i_p_H2, 18])

```

CRC

```

-----
$\Delta$ TS 873.15 K = 2.4312654605471087
$\Delta$ H 873.15 K = 3.4035123254480326
$\Delta$ G 873.15 K ,1bar = 0.9722340650279991
$\Delta$ G 873.15 K ,p = -0.5870304588661006

```

DFT

```

-----
$\Delta$ TS 873.15 K = 2.42784305973552
$\Delta$ H 873.15 K = 3.441644196345349
$\Delta$ G 873.15 K,1bar = 1.013801136609829
$\Delta$ G 873.15 K,p = -0.5454633872842711

```

0.4 Trends in total pressure and temperature.

In the following, we present the calculated effects of varying the temperature and the total pressure at low conversion over pure platinum, with energies from the linear scaler (see Fig. S.8).

High temperature increases the driving force for dehydrogenation, but it increases production rates of CH_4 (g) and C_2H_2 (g) relatively more than the increase in ethene production, leading to decreased selectivity with higher temperature as seen in Fig. S.1. Given the trends in selectivity and turnover frequency *versus* temperature and total pressure, it appears beneficial to keep the operating temperature relatively low and instead drive the reaction through an increase in ethane pressure, although this would lower the carbon conversion.

Figure S.1: Thermodynamic maps of selectivity, plotted vs. temperature and total pressure of C_2H_6 and H_2 in a 1 : 3 ratio. Ethane conversion to ethene was set to 0.1% and other molar gas concentrations were 10^{-6} methane and 10^{-9} acetylene. The white symbol denotes 0.2 bar for C_2H_6 partial pressure and temperature conditions, which was used in the following figures and by Wu et al.

The effect on carbon product selectivity of varying the *total* pressure in a 1 : 3 ratio of ethane to hydrogen is plotted in Fig. S.2 and Fig. S.1 (For selectivity towards CH_4 , see the SI Fig. S.1). Raising the C_2H_6 (g) partial pressure alone will increase the coverage of CH_3CH_2 , which is the intermediate reactant of the elementary step, and therefore the rate of production increases for C_2H_4 (g), C_2H_2 (g) and CH_4 (g). As seen in Fig. S.1, selectivity towards ethene may be enhanced by operating at higher total pressures, although this decreases the overall reaction driving force, ΔG .

Figure S.2: Computed ethene production plotted vs. temperature and total pressure of C₂H₆ and H₂ in a 1 : 3 ratio. Conversion to ethene is at 0.1% and other molar gas concentrations were 10⁻⁶ methane and 10⁻⁹ acetylene. The white symbol denotes 0.2 bar for the H₂ and C₂H₆ partial pressure and temperature conditions, which was used in the following figures and by Wu et al.

Figure S.3: Computed coverages vs. temperature and total pressure C₂H₆ and H₂ in a 1 : 3 ratio. Conversion to ethene is at 0.1% and other molar gas concentrations were 10⁻⁶ methane and 10⁻⁹ acetylene. The white symbol denotes 0.2 bar for the H₂ and C₂H₆ partial pressure and temperature conditions, which was used in the following figures and by Wu et al.

Figure S.4: Computed coverages on a log scale vs. temperature and total pressure C₂H₆ and H₂ in a 1 : 3 ratio. Conversion to ethene is at 0.1% and other molar gas concentrations were 10⁻⁶ methane and 10⁻⁹ acetylene. The white symbol denotes 0.2 bar for the H₂ and C₂H₆ partial pressure and temperature conditions, which was used in the following figures and by Wu et al.

Figure S.5: Computed directional rates vs. temperature and total pressure C_2H_6 and H_2 in a 1 : 3 ratio. Conversion to ethene is at 0.1% and other molar gas concentrations were 10^{-6} methane and 10^{-9} acetylene. The white symbol denotes 0.2 bar for the H_2 and C_2H_6 partial pressure and temperature conditions, which was used in the following figures and by Wu et al. The directional rates are the individual rates of all elementary reactions in the model. There are therefore up to two maps per reaction, one for the forward rate and one for the reverse rate.

Figure S.6: Forward net rates vs. temperature and total pressure C_2H_6 and H_2 in a 1 : 3 ratio. Conversion to ethene is at 0.1% and other molar gas concentrations were 10^{-6} methane and 10^{-9} acetylene. The white symbol denotes 0.2 bar for the H_2 and C_2H_6 partial pressure and temperature conditions, which was used in the following figures and by Wu et al. The net rate maps are equal to point-wise subtracting the reverse directional rates from the corresponding forward directional rates, thus there are up to one map per reaction. Maps are generally omitted if their values are below a threshold in all points, e.g. if there are nowhere in the map where the net rate is reverse, then the net reverse map is omitted for that reaction.

Figure S.7: Reverse net rates vs. temperature and total pressure C_2H_6 and H_2 in a 1 : 3 ratio. Conversion to ethene is at 0.1% and other molar gas concentrations were 10^{-6} methane and 10^{-9} acetylene. The white symbol denotes 0.2 bar for the H_2 and C_2H_6 partial pressure and temperature conditions, which was used in the following figures and by Wu et al. The net rate maps are equal to point-wise subtracting the reverse directional rates from the corresponding forward directional rates, thus there are up to one map per reaction. Maps are generally omitted if their values are below a threshold in all points, e.g. if there is nowhere in the map where the net rate is reverse, then the net reverse map is omitted for that reaction.

0.5 Descriptor based MKM

Figure S.8: Scaling analysis showing the individual linear relations between adsorbate and transition state energies. All energies are with respect to CH_4 (g) and H_2 (g) and the respective empty surfaces.

Adsorption Scaling Parameters

$$E_{H^*h} = 0.472E_{CH_3CH^*s} - 1.142 \quad (32)$$

$$E_{CC^*s} = 0.993E_{CH_3CH^*s} + 2.597 \quad (33)$$

$$E_{CH_2CH^*s} = 0.369E_{CH_3CH^*s} + 1.163E_{CH_2CH_2^*s} - 0.263 \quad (34)$$

$$E_{CH_2C^*s} = 1.277E_{CH_3CH^*s} + 0.104E_{CH_2CH_2^*s} - 0.081 \quad (35)$$

$$E_{CH_2^*s} = 0.897E_{CH_3CH^*s} + 0.077E_{CH_2CH_2^*s} - 0.496 \quad (36)$$

$$E_{CH_3CH_2^*s} = 0.095E_{CH_3CH^*s} + 0.826E_{CH_2CH_2^*s} - 0.167 \quad (37)$$

$$E_{CH_3C^*s} = 1.463E_{CH_3CH^*s} + 0.16E_{CH_2CH_2^*s} - 1.19 \quad (38)$$

$$E_{CH_3^*s} = 0.346E_{CH_3CH^*s} + 0.249E_{CH_2CH_2^*s} - 0.436 \quad (39)$$

$$E_{CHCH^*s} = 1.236E_{CH_3CH^*s} + 0.171 \quad (40)$$

$$E_{CHC^*s} = 1.128E_{CH_3CH^*s} + 1.1 \quad (41)$$

$$E_{CH^*s} = 1.433E_{CH_3CH^*s} - 1.282 \quad (42)$$

$$E_{C^*s} = 1.751E_{CH_3CH^*s} - 1.016 \quad (43)$$

Transition-state Scaling Parameters

$$E_{H-H^*h} = 0.632E_{CH_3CH^*s} - 0.841 \quad (44)$$

$$E_{C-C^*s} = 2.82E_{CH_3CH^*s} + 0.942 \quad (45)$$

$$E_{C-H^*s} = 2.223E_{CH_3CH^*s} - 1.438 \quad (46)$$

$$E_{CC-H^*s} = 1.458E_{CH_3CH^*s} + 2.335 \quad (47)$$

$$E_{CH-CH^*s} = 2.043E_{CH_3CH^*s} + 0.467 \quad (48)$$

$$E_{CH-C^*s} = 2.693E_{CH_3CH^*s} - 0.0 \quad (49)$$

$$E_{CH-H^*s} = 1.791E_{CH_3CH^*s} - 1.259 \quad (50)$$

$$E_{CH_2-CH_2^*s} = 0.762E_{CH_3CH^*s} + 0.065E_{CH_2CH_2^*s} + 1.907 \quad (51)$$

$$E_{CH_2-CH^*s} = 1.426E_{CH_3CH^*s} + 0.047E_{CH_2CH_2^*s} + 1.096 \quad (52)$$

$$E_{CH_2-C^*s} = 2.218E_{CH_3CH^*s} + 0.064E_{CH_2CH_2^*s} + 0.445 \quad (53)$$

$$E_{CH_2-HCH^*s} = 0.996E_{CH_3CH^*s} + 1.908 \quad (54)$$

$$E_{CH_2-H^*s} = 1.259E_{CH_3CH^*s} + 0.07E_{CH_2CH_2^*s} - 0.707 \quad (55)$$

$$E_{CH_2C-H^*s} = 1.137E_{CH_3CH^*s} + 0.068E_{CH_2CH_2^*s} + 1.614 \quad (56)$$

$$E_{CH_2CH-H^*s} = 0.807E_{CH_3CH^*s} + 1.115E_{CH_2CH_2^*s} - 0.601 \quad (57)$$

$$E_{CH_2CH_2-H^*s} = 0.276E_{CH_3CH^*s} + 0.585E_{CH_2CH_2^*s} + 0.603 \quad (58)$$

$$E_{CH_2CH_2-^*s} = -0.018E_{CH_2CH_2^*s} + 2.189 \quad (59)$$

$$E_{CH_3-CH_2^*s} = 0.974E_{CH_3CH^*s} + 0.255E_{CH_2CH_2^*s} + 1.229 \quad (60)$$

$$E_{CH_3-CH_3^*s} = 0.46E_{CH_3CH^*s} + 0.331E_{CH_2CH_2^*s} + 2.256 \quad (61)$$

$$E_{CH_3-CH^*s} = 1.25E_{CH_3CH^*s} + 0.175E_{CH_2CH_2^*s} + 0.625 \quad (62)$$

$$E_{CH_3-C^*s} = 1.62E_{CH_3CH^*s} + 0.192E_{CH_2CH_2^*s} + 0.841 \quad (63)$$

$$E_{CH_3-H^*s} = 0.548E_{CH_3CH^*s} + 0.167E_{CH_2CH_2^*s} - 0.017 \quad (64)$$

$$E_{CH_3C-H^*s} = 1.716E_{CH_3CH^*s} + 0.142E_{CH_2CH_2^*s} - 1.015 \quad (65)$$

$$E_{CH_3CH-H^*s} = 1.325E_{CH_3CH^*s} - 0.199 \quad (66)$$

$$E_{CH_3CH_2-H^*s} = 0.503E_{CH_3CH^*s} + 0.733E_{CH_2CH_2^*s} - 0.173 \quad (67)$$

$$E_{CHC-H^*s} = 1.658E_{CH_3CH^*s} + 0.836 \quad (68)$$

$$E_{CHCH-H^*s} = 1.524E_{CH_3CH^*s} + 0.413 \quad (69)$$

$$E_{CHCH-*s} = 4.16 \quad (70)$$

$$E_{H-CH_2CH^*s} = 1.038E_{CH_3CH^*s} + 1.434E_{CH_2CH_2^*s} - 1.348 \quad (71)$$

$$E_{H-CH_2C^*s} = 1.927E_{CH_3CH^*s} + 0.114E_{CH_2CH_2^*s} - 0.626 \quad (72)$$

$$E_{H-CH_3CH_2^*s} = 0.151E_{CH_3CH^*s} + 0.22E_{CH_2CH_2^*s} + 2.467 \quad (73)$$

$$E_{H-CHC^*s} = 1.583E_{CH_3CH^*s} + 0.925 \quad (74)$$

0.5.1 Solver Summary

```

s = [0]*3
s[0] = (mpf('1.0') - theta[1] - theta[2] - theta[3] - theta[4] - theta[5] - theta[6] - theta[7] - theta[8] -
s[1] = (mpf('1.0') - theta[0])
s[2] = (mpf('0.0'))
r[0] = kf[0]*p[2]*s[0]*s[1] - kr[0]*theta[6]*theta[0]
r[1] = kf[1]*p[2]*s[0]*s[0] - kr[1]*theta[9]*theta[9]
r[2] = kf[2]*theta[6]*theta[0] - kr[2]*p[4]*theta[2]*s[1]
r[3] = kf[3]*theta[6]*s[1] - kr[3]*theta[2]*theta[0]
r[4] = kf[4]*theta[6]*s[1] - kr[4]*theta[7]*theta[0]
r[5] = kf[5]*theta[6]*s[0] - kr[5]*theta[9]*theta[5]
r[6] = kf[6]*theta[7] - kr[6]*theta[2]
r[7] = kf[7]*theta[7]*s[1] - kr[7]*theta[3]*theta[0]
r[8] = kf[8]*theta[7]*s[1] - kr[8]*theta[8]*theta[0]
r[9] = kf[9]*theta[7]*s[0] - kr[9]*theta[9]*theta[12]
r[10] = kf[10]*theta[8]*s[1] - kr[10]*theta[4]*theta[0]
r[11] = kf[11]*theta[8]*s[0] - kr[11]*theta[9]*theta[13]
r[12] = kf[12]*theta[2] - kr[12]*p[1]*s[0]
r[13] = kf[13]*theta[2]*s[1] - kr[13]*theta[3]*theta[0]
r[14] = kf[14]*theta[2]*s[0] - kr[14]*theta[5]*theta[5]
r[15] = kf[15]*theta[3]*s[1] - kr[15]*theta[4]*theta[0]
r[16] = kf[16]*theta[3]*s[1] - kr[16]*theta[10]*theta[0]
r[17] = kf[17]*theta[3]*s[0] - kr[17]*theta[5]*theta[12]
r[18] = kf[18]*theta[4]*s[1] - kr[18]*theta[11]*theta[0]
r[19] = kf[19]*theta[4]*s[0] - kr[19]*theta[5]*theta[13]
r[20] = kf[20]*theta[10] - kr[20]*p[0]*s[0]
r[21] = kf[21]*theta[10]*s[0] - kr[21]*theta[12]*theta[12]
r[22] = kf[22]*theta[10]*s[1] - kr[22]*theta[11]*theta[0]
r[23] = kf[23]*theta[11]*s[1] - kr[23]*theta[1]*theta[0]
r[24] = kf[24]*theta[11]*s[0] - kr[24]*theta[12]*theta[13]
r[25] = kf[25]*theta[1]*s[0] - kr[25]*theta[13]*theta[13]
r[26] = kf[26]*theta[9]*theta[0] - kr[26]*p[3]*s[0]*s[1]
r[27] = kf[27]*theta[9]*s[1] - kr[27]*theta[5]*theta[0]
r[28] = kf[28]*theta[5]*s[1] - kr[28]*theta[12]*theta[0]
r[29] = kf[29]*theta[12]*s[1] - kr[29]*theta[13]*theta[0]
r[30] = kf[30]*theta[0]*theta[0] - kr[30]*p[4]*s[1]*s[1]
dtheta_dt[0] = + 1*r[0] + -1*r[2] + 1*r[3] + 1*r[4] + 1*r[7] + 1*r[8] + 1*r[10] + 1*r[13] + 1*r[15] + 1*r[18] + 1*r[21] + 1*r[24] + 1*r[27] + 1*r[30]
dtheta_dt[1] = + 1*r[23] + -1*r[25]
dtheta_dt[2] = + 1*r[2] + 1*r[3] + 1*r[6] + -1*r[12] + -1*r[13] + -1*r[14]
dtheta_dt[3] = + 1*r[7] + 1*r[13] + -1*r[15] + -1*r[16] + -1*r[17]
dtheta_dt[4] = + 1*r[10] + 1*r[15] + -1*r[18] + -1*r[19]
dtheta_dt[5] = + 1*r[5] + 2*r[14] + 1*r[17] + 1*r[19] + 1*r[27] + -1*r[28]
dtheta_dt[6] = + 1*r[0] + -1*r[2] + -1*r[3] + -1*r[4] + -1*r[5]
dtheta_dt[7] = + 1*r[4] + -1*r[6] + -1*r[7] + -1*r[8] + -1*r[9]

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dtheta_dt[8] = + 1*r[8] + -1*r[10] + -1*r[11]
dtheta_dt[9] = + 2*r[1] + 1*r[5] + 1*r[9] + 1*r[11] + -1*r[26] + -1*r[27]
dtheta_dt[10] = + 1*r[16] + -1*r[20] + -1*r[21] + -1*r[22]
dtheta_dt[11] = + 1*r[18] + 1*r[22] + -1*r[23] + -1*r[24]
dtheta_dt[12] = + 1*r[9] + 1*r[17] + 2*r[21] + 1*r[24] + 1*r[28] + -1*r[29]
dtheta_dt[13] = + 1*r[11] + 1*r[19] + 1*r[24] + 2*r[25] + 1*r[29]

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0.5.2 Input Summary

Table 1: Formation energies input for CatMAP. Adsorbate*slab geometries are stored in the ASE database file 'ads.db' and the last column in this table refers to the corresponding database id in this file.

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$C_2H_{2(g)}$	gas	4.41	3.8, 3.3, 0.0 0.0, 0.3, 77.0 77.0, 92.7, 92.8	19
$C_2H_{4(g)}$	gas	2.33	255.0, 427.7, 440.3 5.0, 1.7, 3.9 5.2, 6.9, 7.3 102.0, 116.8, 118.1 129.6, 152.2, 168.6 180.9, 205.2, 384.5 386.1, 393.3, 396.8	11
$C_2H_{6(g)}$	gas	0.76	1.5, 4.2, 5.4 6.1, 6.2, 37.8 100.9, 101.0, 121.7 149.2, 149.2, 172.7 173.7, 184.0, 184.0 184.6, 184.6, 371.9 372.2, 377.9, 378.0 381.0, 381.1	14
$CH_{4(g)}$	gas	-0.0	2.9, 3.4, 4.2 6.6, 7.2, 7.5 164.4, 164.4, 164.4 191.5, 191.5, 372.8 386.1, 386.1, 386.1	12
$H_{2(g)}$	gas	0.09	545.5	13
H^{*h}	Pt5Sn/Pt	-0.26	(82.9+0j), (85.9+0j), (125.6+0j)	1060
H^{*h}	Pt3Sn/Pt	-0.27	(82.9+0j), (85.9+0j), (125.6+0j)	965
H^{*h}	Pt	-0.33	(82.9+0j), (85.9+0j), (125.6+0j)	581
H^{*h}	Pd	-0.37	(82.9+0j), (85.9+0j), (125.6+0j)	4
H^{*h}	Rh	-0.36	(82.9+0j), (85.9+0j), (125.6+0j)	5
H^{*h}	Ir	-0.33	(82.9+0j), (85.9+0j), (125.6+0j)	587

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
H^{*h}	Ni	-0.34	(82.9+0j), (85.9+0j), (125.6+0j)	290
H^{*h}	Co	-0.34	(82.9+0j), (85.9+0j), (125.6+0j)	260
H^{*h}	Ru	-0.44	(82.9+0j), (85.9+0j), (125.6+0j)	104
H^{*h}	Re	-0.57	(82.9+0j), (85.9+0j), (125.6+0j)	108
H^{*h}	Cu	-0.06	(82.9+0j), (85.9+0j), (125.6+0j)	34
H^{*h}	Au	0.36	(82.9+0j), (85.9+0j), (125.6+0j)	1
H^{*h}	Ag	0.34	(82.9+0j), (85.9+0j), (125.6+0j)	3
H^{*h}	In	0.72	(82.9+0j), (85.9+0j), (125.6+0j)	857
H^{*h}	Zn	0.63	(82.9+0j), (85.9+0j), (125.6+0j)	848
H^{*h}	Pt3Sn	-0.4	(82.9+0j), (85.9+0j), (125.6+0j)	976
H^{*h}	IrPt3	-0.25	(82.9+0j), (85.9+0j), (125.6+0j)	998
CC^{*s}	Pt	4.82	(32.3+0j), (39.5+0j), (42.2+0j), (47.8+0j), (52.7+0j), (186.8+0j)	660
CC^{*s}	Pd	4.92	(32.3+0j), (39.5+0j), (42.2+0j), (47.8+0j), (52.7+0j), (186.8+0j)	623
CC^{*s}	Rh	4.02	(32.3+0j), (39.5+0j), (42.2+0j), (47.8+0j), (52.7+0j), (186.8+0j)	630

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CC^{*s}	Ir	4.2	(32.3+0j), (39.5+0j), (42.2+0j) (47.8+0j), (52.7+0j), (186.8+0j)	619
CC^{*s}	Ni	4.11	(32.3+0j), (39.5+0j), (42.2+0j) (47.8+0j), (52.7+0j), (186.8+0j)	668
CC^{*s}	Co	3.91	(32.3+0j), (39.5+0j), (42.2+0j) (47.8+0j), (52.7+0j), (186.8+0j)	624
CC^{*s}	Ru	3.4	(32.3+0j), (39.5+0j), (42.2+0j) (47.8+0j), (52.7+0j), (186.8+0j)	628
CC^{*s}	Cu	4.98	(32.3+0j), (39.5+0j), (42.2+0j) (47.8+0j), (52.7+0j), (186.8+0j)	975
$CH_2CH_2^{*s}$	Pt5Sn/Pt	1.44	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	1080

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$CH_2CH_2^{*s}$	Pt3Sn/Pt	1.58	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	967
$CH_2CH_2^{*s}$	Pt	1.28	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	641
$CH_2CH_2^{*s}$	Pd	1.57	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	640

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$CH_2CH_2^{*s}$	Rh	1.59	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	92
$CH_2CH_2^{*s}$	Ir	1.46	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	94
$CH_2CH_2^{*s}$	Ni	1.8	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	656

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$CH_2CH_2^{*s}$	Co	1.85	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	644
$CH_2CH_2^{*s}$	Ru	1.53	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	649
$CH_2CH_2^{*s}$	Re	1.36	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	646

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$CH_2CH_2^{*s}$	Cu	2.12	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	642
$CH_2CH_2^{*s}$	Au	2.12	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	95
$CH_2CH_2^{*s}$	Ag	2.15	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	97

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$CH_2CH_2^{*s}$	In	2.18	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	860
$CH_2CH_2^{*s}$	Zn	2.14	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	853
$CH_2CH_2^{*s}$	Pt3Sn	1.55	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	950

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$CH_2CH_2^{*s}$	InPt3	1.21	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	1022
$CH_2CH_2^{*s}$	InPt3	1.6	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	1023
$CH_2CH_2^{*s}$	InPd3	1.9	(12.9+0j), (14.2+0j), (19+0j) (45.9+0j), (59.5+0j), (73.9+0j) (99.3+0j), (112+0j), (115.9+0j) (124+0j), (135+0j), (148.9+0j) (175.1+0j), (179.9+0j), (380+0j) (381.2+0j), (389.3+0j), (392.4+0j)	1030
CH_2CH^{*s}	Pt5Sn/Pt	2.09	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	1075

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CH_2CH^{*s}	Pt	1.89	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	14
CH_2CH^{*s}	Pd	2.42	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	494
CH_2CH^{*s}	Rh	2.16	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	68
CH_2CH^{*s}	Ir	1.85	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	888
CH_2CH^{*s}	Ni	2.69	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	887
CH_2CH^{*s}	Co	2.99	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	496
CH_2CH^{*s}	Ru	1.83	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	507
CH_2CH^{*s}	Re	1.57	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	545
CH_2CH^{*s}	Cu	3.08	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	548
CH_2CH^{*s}	Au	3.35	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	634
CH_2CH^{*s}	Ag	3.64	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	890

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CH_2CH^{*s}	In	3.4	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	855
CH_2CH^{*s}	Zn	3.15	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	955
CH_2CH^{*s}	Pt3Sn	2.3	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	1011
CH_2CH^{*s}	IrPt3	1.72	20.6, 22.9, 43.1 52.8, 53.9, 60.7 79.7, 107.7, 119.9 127.2, 136.5, 172.7 373.4, 375.0, 381.9	1037
CH_2C^{*s}	Pt3Sn/Pt	2.72	10.3, 16.6, 18.6 35.7, 38.9, 43.2 107.3, 116.4, 168.5 188.9, 381.7, 390.3	669
CH_2C^{*s}	Pt	2.06	10.3, 16.6, 18.6 35.7, 38.9, 43.2 107.3, 116.4, 168.5 188.9, 381.7, 390.3	169
CH_2C^{*s}	Pd	2.63	10.3, 16.6, 18.6 35.7, 38.9, 43.2 107.3, 116.4, 168.5 188.9, 381.7, 390.3	74
CH_2C^{*s}	Rh	2.03	10.3, 16.6, 18.6 35.7, 38.9, 43.2 107.3, 116.4, 168.5 188.9, 381.7, 390.3	78
CH_2C^{*s}	Ir	1.79	10.3, 16.6, 18.6 35.7, 38.9, 43.2 107.3, 116.4, 168.5 188.9, 381.7, 390.3	676
CH_2C^{*s}	Ni	2.53	10.3, 16.6, 18.6 35.7, 38.9, 43.2 107.3, 116.4, 168.5 188.9, 381.7, 390.3	482
CH_2C^{*s}	Co	2.59	10.3, 16.6, 18.6 35.7, 38.9, 43.2 107.3, 116.4, 168.5 188.9, 381.7, 390.3	665
CH_2C^{*s}	Ru	2.09	10.3, 16.6, 18.6 35.7, 38.9, 43.2 107.3, 116.4, 168.5 188.9, 381.7, 390.3	671
CH_2C^{*s}	Re	1.79	10.3, 16.6, 18.6 35.7, 38.9, 43.2 107.3, 116.4, 168.5 188.9, 381.7, 390.3	673

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CH_2C^{*s}	Cu	3.61	10.3, 16.6, 18.6 35.7, 38.9, 43.2 107.3, 116.4, 168.5 188.9, 381.7, 390.3	674
CH_2C^{*s}	Au	4.27	10.3, 16.6, 18.6 35.7, 38.9, 43.2 107.3, 116.4, 168.5 188.9, 381.7, 390.3	666
CH_2C^{*s}	Ag	4.6	10.3, 16.6, 18.6 35.7, 38.9, 43.2 107.3, 116.4, 168.5 188.9, 381.7, 390.3	850
CH_2C^{*s}	Zn	4.38	10.3, 16.6, 18.6 35.7, 38.9, 43.2 107.3, 116.4, 168.5 188.9, 381.7, 390.3	1014
CH_2^{*s}	Pt5Sn/Pt	1.21	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	1072
CH_2^{*s}	Pt	1.03	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	917
CH_2^{*s}	Pd	1.37	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	50
CH_2^{*s}	Rh	1.11	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	81
CH_2^{*s}	Ir	0.97	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	433
CH_2^{*s}	Ni	1.31	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	342
CH_2^{*s}	Co	1.61	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	483
CH_2^{*s}	Ru	1.16	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	491
CH_2^{*s}	Re	0.56	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	919
CH_2^{*s}	Cu	2.11	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	49
CH_2^{*s}	Au	2.57	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	17
CH_2^{*s}	Ag	2.99	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	849
CH_2^{*s}	Zn	2.3	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	1009

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CH_2^{*s}	Pt3Sn	1.31	9.4, 43.4, 64.7 65.3, 75.0, 98.4 165.6, 368.8, 378.6	1043
$CH_3CH_2^{*s}$	Pt5Sn/Pt	1.13	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	1073
$CH_3CH_2^{*s}$	Pt3Sn/Pt	1.2	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	969
$CH_3CH_2^{*s}$	Pt	0.99	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	808
$CH_3CH_2^{*s}$	Pd	1.31	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	806
$CH_3CH_2^{*s}$	Rh	1.29	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	40
$CH_3CH_2^{*s}$	Ir	1.14	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	38
$CH_3CH_2^{*s}$	Ni	1.57	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	375

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$CH_3CH_2^{*s}$	Co	1.56	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	705
$CH_3CH_2^{*s}$	Ru	1.32	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	704
$CH_3CH_2^{*s}$	Re	1.26	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	706
$CH_3CH_2^{*s}$	Cu	1.88	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	37
$CH_3CH_2^{*s}$	Au	1.81	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	811
$CH_3CH_2^{*s}$	Ag	2.16	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	812
$CH_3CH_2^{*s}$	In	1.91	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	858

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$CH_3CH_2^{*s}$	Zn	1.71	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	111
$CH_3CH_2^{*s}$	Pt3Sn	1.22	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	959
$CH_3CH_2^{*s}$	IrPt3	0.98	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6	1007
CH_3CH^{*s}	Pt5Sn/Pt	1.68	4.6, 6.6, 7.3 20.9, 27.6, 45.2 68.8, 109.8, 114.7 121.4, 137.8, 151.1 170.6, 176.6, 180.8 181.2, 370.1, 377.1 379.2, 382.2, 384.6 (13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	1076

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CH_3CH^{*s}	Pt3Sn/Pt	1.89	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	972
CH_3CH^{*s}	Pt	1.56	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	41
CH_3CH^{*s}	Pd	1.91	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	44

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CH_3CH^{*s}	Rh	1.68	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	12
CH_3CH^{*s}	Ir	1.55	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	42
CH_3CH^{*s}	Ni	1.95	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	486

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CH_3CH^{*s}	Co	1.99	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	347
CH_3CH^{*s}	Ru	1.58	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	485
CH_3CH^{*s}	Re	1.24	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	493

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CH_3CH^{*s}	Cu	2.83	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	908
CH_3CH^{*s}	Au	3.17	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	909
CH_3CH^{*s}	Ag	3.67	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	910

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CH_3CH^{*s}	In	3.2	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	844
CH_3CH^{*s}	Zn	3.08	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	851
CH_3CH^{*s}	Pt3Sn	1.92	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	946

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CH_3CH^{*s}	IrPt3	1.47	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	996
CH_3CH^{*s}	InPt3	2.11	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	1025
CH_3CH^{*s}	InPd3	2.56	(13.6+0j), (13.7+0j), (19.9+0j) (30.2+0j), (42.9+0j), (53.4+0j) (90.7+0j), (116.5+0j), (121.4+0j) (124.3+0j), (150.4+0j), (169.6+0j) (177.7+0j), (179.2+0j), (367.8+0j) (372+0j), (377.5+0j), (380.2+0j)	1029

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$CH_3C^*_{*s}$	Pt5Sn/Pt	1.47	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	1069
$CH_3C^*_{*s}$	Pt	1.22	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	69
$CH_3C^*_{*s}$	Pd	1.67	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	490
$CH_3C^*_{*s}$	Rh	1.38	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	663
$CH_3C^*_{*s}$	Ir	1.15	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	492
$CH_3C^*_{*s}$	Ni	1.78	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	344
$CH_3C^*_{*s}$	Co	1.94	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	488
$CH_3C^*_{*s}$	Ru	1.57	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	489
$CH_3C^*_{*s}$	Re	1.33	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	71
$CH_3C^*_{*s}$	Cu	3.16	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	487
$CH_3C^*_{*s}$	Au	3.7	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	922

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CH_3C^{*s}	Ag	4.52	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	832
CH_3C^{*s}	In	4.08	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	898
CH_3C^{*s}	Zn	4.03	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	960
CH_3C^{*s}	Pt3Sn	1.97	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	1006
CH_3C^{*s}	IrPt3	1.12	12.6, 15.8, 16.1 45.2, 45.8, 47.0 117.6, 117.8, 133.8 169.0, 176.3, 176.9 372.6, 380.0, 380.4	1035
CH_3^*	Pt5Sn/Pt	0.47	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	1077
CH_3^*	Pt	0.36	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	462
CH_3^*	Pd	0.68	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	51
CH_3^*	Rh	0.64	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	58
CH_3^*	Ir	0.48	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	502
CH_3^*	Ni	0.75	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	504
CH_3^*	Co	0.64	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	503

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$CH_3^*{}_s$	Ru	0.45	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	506
$CH_3^*{}_s$	Re	0.33	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	495
$CH_3^*{}_s$	Cu	1.11	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	464
$CH_3^*{}_s$	Au	1.16	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	466
$CH_3^*{}_s$	Ag	1.44	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	821
$CH_3^*{}_s$	In	1.19	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	829
$CH_3^*{}_s$	Zn	1.0	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	956
$CH_3^*{}_s$	Pt3Sn	0.53	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	997
$CH_3^*{}_s$	IrPt3	0.39	6.6, 10.3, 10.6 54.7, 83.2, 83.7 141.9, 174.3, 174.9 374.2, 387.2, 387.4	1032
$CHCH^*{}_s$	Pt5Sn/Pt	2.64	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	1074
$CHCH^*{}_s$	Pt3Sn/Pt	3.01	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	970
$CHCH^*{}_s$	Pt	2.29	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	15
$CHCH^*{}_s$	Pd	2.74	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	53
$CHCH^*{}_s$	Rh	2.18	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	72

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$CHCH^{*s}$	Ir	1.97	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	56
$CHCH^{*s}$	Ni	2.34	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	683
$CHCH^{*s}$	Co	2.2	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	346
$CHCH^{*s}$	Ru	1.87	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	684
$CHCH^{*s}$	Re	1.16	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	667
$CHCH^{*s}$	Cu	3.51	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	682
$CHCH^{*s}$	Au	4.23	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	65
$CHCH^{*s}$	Ag	4.26	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	55
$CHCH^{*s}$	In	4.27	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	870
$CHCH^{*s}$	Zn	4.26	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	869
$CHCH^{*s}$	Pt3Sn	2.94	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	958
$CHCH^{*s}$	IrPt3	2.03	31.7, 34.0, 35.8 64.2, 73.9, 93.6 105.4, 121.8, 140.9 161.0, 388.1, 390.6	1018
CHC^{*s}	Pt	3.47	8.2, 8.0, 22.8 23.0, 47.3, 76.4 76.8, 248.4, 430.5	899
CHC^{*s}	Pd	3.68	8.2, 8.0, 22.8 23.0, 47.3, 76.4 76.8, 248.4, 430.5	610

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CHC^{*s}	Rh	3.03	8.2, 8.0, 22.8 23.0, 47.3, 76.4 76.8, 248.4, 430.5	621
CHC^{*s}	Ir	2.97	8.2, 8.0, 22.8 23.0, 47.3, 76.4 76.8, 248.4, 430.5	609
CHC^{*s}	Ni	3.14	8.2, 8.0, 22.8 23.0, 47.3, 76.4 76.8, 248.4, 430.5	795
CHC^{*s}	Co	2.99	8.2, 8.0, 22.8 23.0, 47.3, 76.4 76.8, 248.4, 430.5	794
CHC^{*s}	Ru	2.42	8.2, 8.0, 22.8 23.0, 47.3, 76.4 76.8, 248.4, 430.5	617
CHC^{*s}	Re	1.72	8.2, 8.0, 22.8 23.0, 47.3, 76.4 76.8, 248.4, 430.5	891
CHC^{*s}	Cu	4.21	8.2, 8.0, 22.8 23.0, 47.3, 76.4 76.8, 248.4, 430.5	627
CHC^{*s}	Au	5.03	8.2, 8.0, 22.8 23.0, 47.3, 76.4 76.8, 248.4, 430.5	892
CHC^{*s}	Ag	4.76	8.2, 8.0, 22.8 23.0, 47.3, 76.4 76.8, 248.4, 430.5	947
CH^{*s}	Pt5Sn/Pt	1.14	56.5, 57.3, 72.9 97.7, 97.8, 383.5	1068
CH^{*s}	Pt3Sn/Pt	1.46	56.5, 57.3, 72.9 97.7, 97.8, 383.5	966
CH^{*s}	Pt	0.91	56.5, 57.3, 72.9 97.7, 97.8, 383.5	7
CH^{*s}	Pd	1.39	56.5, 57.3, 72.9 97.7, 97.8, 383.5	636
CH^{*s}	Rh	1.0	56.5, 57.3, 72.9 97.7, 97.8, 383.5	10
CH^{*s}	Ir	0.8	56.5, 57.3, 72.9 97.7, 97.8, 383.5	9
CH^{*s}	Ni	1.41	56.5, 57.3, 72.9 97.7, 97.8, 383.5	921
CH^{*s}	Co	1.58	56.5, 57.3, 72.9 97.7, 97.8, 383.5	343
CH^{*s}	Ru	1.17	56.5, 57.3, 72.9 97.7, 97.8, 383.5	394
CH^{*s}	Re	0.57	56.5, 57.3, 72.9 97.7, 97.8, 383.5	904
CH^{*s}	Cu	2.67	56.5, 57.3, 72.9 97.7, 97.8, 383.5	914
CH^{*s}	Au	3.22	56.5, 57.3, 72.9 97.7, 97.8, 383.5	635
CH^{*s}	Ag	3.99	56.5, 57.3, 72.9 97.7, 97.8, 383.5	11
CH^{*s}	In	3.3	56.5, 57.3, 72.9 97.7, 97.8, 383.5	831
CH^{*s}	Zn	3.34	56.5, 57.3, 72.9 97.7, 97.8, 383.5	398

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
CH^*_{s}	Pt3Sn	1.64	56.5, 57.3, 72.9	953
C^*_{s}	Pt5Sn/Pt	2.17	97.7, 97.8, 383.5	1071
C^*_{s}	Pt	1.86	55.9, 72.5, 79.5	598
C^*_{s}	Pd	2.14	55.9, 72.5, 79.5	551
C^*_{s}	Rh	1.91	55.9, 72.5, 79.5	596
C^*_{s}	Ir	1.66	55.9, 72.5, 79.5	607
C^*_{s}	Ni	2.36	55.9, 72.5, 79.5	593
C^*_{s}	Co	2.32	55.9, 72.5, 79.5	443
C^*_{s}	Ru	1.42	55.9, 72.5, 79.5	453
C^*_{s}	Re	1.35	55.9, 72.5, 79.5	559
C^*_{s}	Cu	3.92	55.9, 72.5, 79.5	549
C^*_{s}	Au	4.67	55.9, 72.5, 79.5	564
C^*_{s}	Ag	5.32	55.9, 72.5, 79.5	452
$C-C^*_{s}$	Pd	6.37		2798
$C-C^*_{s}$	Rh	5.56		3116
$C-C^*_{s}$	Ir	5.36		2767
$C-C^*_{s}$	Ni	5.86		2774
$CC-H^*_{s}$	Pt	5.29		3273
$CC-H^*_{s}$	Pd	5.46		2713
$CC-H^*_{s}$	Rh	4.54		2764
$CC-H^*_{s}$	Ir	4.63		2722
$CH-CH^*_{s}$	Pt	3.9		832
$CH-CH^*_{s}$	Pd	4.45		831
$CH-CH^*_{s}$	Rh	3.49		837
$CH-CH^*_{s}$	Ir	3.31		909
$CH-C^*_{s}$	Pt	4.85		1635
$CH-C^*_{s}$	Pd	5.38		1639
$CH-C^*_{s}$	Rh	4.27		1739
$CH-C^*_{s}$	Ir	4.45		1590
$CH-C^*_{s}$	Ni	4.69		1645
$CH-C^*_{s}$	Co	4.69		1665
$CH-C^*_{s}$	Ru	4.0		1718
$CH_2-CH_2^*_{s}$	Pt	3.58		19
$CH_2-CH_2^*_{s}$	Pd	3.74		3094
$CH_2-CH_2^*_{s}$	Rh	3.14		948
$CH_2-CH_2^*_{s}$	Ir	3.15		1528
$CH_2-CH_2^*_{s}$	Ni	3.17		3025
$CH_2-CH^*_{s}$	Pt	3.55		928
$CH_2-CH^*_{s}$	Pd	3.97		910
$CH_2-C^*_{s}$	Pt	4.58		2609
$CH_2-C^*_{s}$	Rh	4.21		2386
$CH_2-C^*_{s}$	Ir	4.12		2032
$CH_2-C^*_{s}$	Co	4.5		2384
$CH_2-C^*_{s}$	Ru	3.53		2004
$CH_2-HCH^*_{s}$	Pt	3.56		3611
$CH_2-HCH^*_{s}$	Rh	3.65		3605
$CH_2-HCH^*_{s}$	Ni	3.83		3442
$CH_2-HCH^*_{s}$	Co	3.88		3636
$CH_2C-H^*_{s}$	Pt	3.64		401
$CH_2CH-H^*_{s}$	Pt	2.62		1300
$CH_2CH-H^*_{s}$	Pd	2.98		1352
$CH_2CH-H^*_{s}$	Rh	2.33		1476
$CH_2CH-H^*_{s}$	Ir	1.99		1471

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$CH_2CH-H^*_{s}$	Ni	2.73		1437
$CH_2CH-H^*_{s}$	Co	2.63		1464
$CH_2CH-H^*_{s}$	Ru	2.02		1458
$CH_2CH-H^*_{s}$	Re	1.89		1453
$CH_2CH-H^*_{s}$	Cu	3.95		1438
$CH_2CH_2-H^*_{s}$	Pt	1.94		664
$CH_2CH_2-H^*_{s}$	Pd	2.12		617
$CH_2CH_2-H^*_{s}$	Rh	2.03		3338
$CH_2CH_2-H^*_{s}$	Ir	1.9		3189
$CH_2CH_2-H^*_{s}$	Ni	2.15		3386
$CH_2CH_2-H^*_{s}$	Co	2.06		3361
$CH_3-CH_3^*_{s}$	Pt	3.77		1591
$CH_3-CH_3^*_{s}$	Pd	3.5		1715
$CH_3-CH_3^*_{s}$	Rh	3.43		3253
$CH_3-CH_3^*_{s}$	Ir	3.63		1771
$CH_3-CH_3^*_{s}$	Ni	3.21		2823
$CH_3-CH^*_{s}$	Pt	3.12		809
$CH_3-CH^*_{s}$	Rh	3.05		1099
$CH_3-CH^*_{s}$	Ir	2.63		1061
$CH_3-C^*_{s}$	Pt	4.15		2887
$CH_3-C^*_{s}$	Rh	3.99		2973
$CH_3-C^*_{s}$	Ir	3.38		2924
$CH_3-C^*_{s}$	Ni	4.12		2976
$CH_3C-H^*_{s}$	Pt	2.22		2191
$CH_3C-H^*_{s}$	Pd	2.4		2237
$CH_3C-H^*_{s}$	Rh	2.05		3462
$CH_3C-H^*_{s}$	Ir	1.64		2217
$CH_3C-H^*_{s}$	Ni	2.21		2157
$CH_3C-H^*_{s}$	Co	2.29		2235
$CH_3C-H^*_{s}$	Ru	1.82		2180
$CH_3C-H^*_{s}$	Re	1.7		2169
$CH_3C-H^*_{s}$	Cu	3.78		2142
$CH_3CH-H^*_{s}$	Pt	2.01		520
$CH_3CH-H^*_{s}$	Pd	2.44		355
$CH_3CH-H^*_{s}$	Rh	1.92		492
$CH_3CH-H^*_{s}$	Ir	1.74		552
$CH_3CH_2-H^*_{s}$	Pt	1.68		3318
$CH_3CH_2-H^*_{s}$	Pd	1.77		159
$CH_3CH_2-H^*_{s}$	Rh	1.65		3178
$CH_3CH_2-H^*_{s}$	Ir	1.67		174
$CH_3CH_2-H^*_{s}$	Co	2.09		209
$CHC-H^*_{s}$	Pt	4.21		2302
$CHC-H^*_{s}$	Pd	4.26		2517
$CHC-H^*_{s}$	Ir	3.79		2518
$CHC-H^*_{s}$	Ni	3.66		2493
$CHC-H^*_{s}$	Co	3.48		2578
$CHCH-H^*_{s}$	Pt	3.13		1254
$CHCH-H^*_{s}$	Pd	3.26		1264
$CHCH-H^*_{s}$	Rh	2.82		1316
$CHCH-H^*_{s}$	Ir	2.84		2863
$H-CH_2CH^*_{s}$	Pt	2.49		1843
$H-CH_2CH^*_{s}$	Pd	2.94		1892
$H-CH_2CH^*_{s}$	Rh	2.41		1902
$H-CH_2CH^*_{s}$	Ir	2.21		2423

Species	Surface	Formation Energy [eV]	Vibrational Frequencies [meV]	Database id
$H-CH_2CH^*_{s}$	Ru	2.05		3226
$H-CH_2C^*_{s}$	Pt	2.9		631
$H-CH_2C^*_{s}$	Pd	3.21		633
$H-CH_2C^*_{s}$	Rh	2.41		718
$H-CH_2C^*_{s}$	Ir	2.24		722
$H-CH_3CH_2^*_{s}$	Pt	3.12		3701
$H-CHC^*_{s}$	Pt	4.19		2522
$H-CHC^*_{s}$	Pd	4.17		2605

(a) Volcano plot for methane production at 873 K, 0.2 bar C_2H_6 (g), $2 \cdot 10^{-4}$ bar C_2H_4 (1% carbon conversion), 0.6 bar H_2 (g), 10^{-9} bar CH_4 and 10^{-12} bar C_2H_2 . The red dashed line shows the scaling between the descriptors, the vertical and horizontal error bars are the ± 1 BEEF standard deviations on the descriptors and the ellipses show the covariances of the BEEF ensemble between the descriptors.

(b) Volcano plot for acetylene production at 873 K, 0.2 bar C_2H_6 (g), $2 \cdot 10^{-4}$ bar C_2H_4 (1% carbon conversion), 0.6 bar H_2 (g), 10^{-9} bar CH_4 and 10^{-12} bar C_2H_2 . The red dashed line shows the scaling between the descriptors, the vertical and horizontal error bars are the ± 1 BEEF standard deviations on the descriptors and the ellipses show the covariances of the BEEF ensemble between the descriptors.

Figure S.9: Production rates calculated at 600°C, 0.2 bar ethane, 0.6 bar hydrogen.

Figure S.10: Computed coverage maps at 873 K, 0.2 bar C_2H_6 (g), $2 \cdot 10^{-4}$ bar C_2H_4 (1% carbon conversion), 0.6 bar H_2 (g), 10^{-9} bar CH_4 and 10^{-12} bar C_2H_2 . The red dashed line shows the scaling between the descriptors, the vertical and horizontal error bars are the ± 1 BEEF standard deviations on the descriptors and the ellipses show the covariances of the BEEF ensemble between the descriptors.

Figure S.11: Computed coverage maps on a log scale at 873 K, 0.2 bar C_2H_6 (g), $2 \cdot 10^{-4}$ bar C_2H_4 (1% carbon conversion), 0.6 bar H_2 (g), 10^{-9} bar CH_4 and 10^{-12} bar C_2H_2 . The red dashed line shows the scaling between the descriptors, the vertical and horizontal error bars are the ± 1 BEEF standard deviations on the descriptors and the ellipses show the covariances of the BEEF ensemble between the descriptors.

Figure S.12: Computed directional rate maps at 873 K, 0.2 bar C_2H_6 (g), $2 \cdot 10^{-4}$ bar C_2H_4 (1% carbon conversion), 0.6 bar H_2 (g), 10^{-9} bar CH_4 and 10^{-12} bar C_2H_2 . The red dashed line shows the scaling between the descriptors, the vertical and horizontal error bars are the ± 1 BEEF standard deviations on the descriptors and the ellipses show the covariances of the BEEF ensemble between the descriptors. The directional rates are the individual rates of all elementary reactions in the model. There are up to two maps per reaction, one for the forward rate and one for the reverse rate.

Figure S.13: Computed directional rate maps at 873 K, 0.2 bar C_2H_6 (g), $2 \cdot 10^{-4}$ bar C_2H_4 (1% carbon conversion), 0.6 bar H_2 (g), 10^{-9} bar CH_4 and 10^{-12} bar C_2H_2 . The red dashed line shows the scaling between the descriptors, the vertical and horizontal error bars are the ± 1 BEEF standard deviations on the descriptors and the ellipses show the covariances of the BEEF ensemble between the descriptors. The net rate maps are equal to point-wise subtracting the reverse directional rates from the corresponding forward directional rates, thus there is up to one map per reaction. Maps are generally omitted if their values are below a threshold in all points, e.g. if there is nowhere in the map where the net rate is reverse, then the net reverse map is omitted for that reaction.

Figure S.14: Computed directional rate maps at 873 K, 0.2 bar C_2H_6 (g), $2 \cdot 10^{-4}$ bar C_2H_4 (1% carbon conversion), 0.6 bar H_2 (g), 10^{-9} bar CH_4 and 10^{-12} bar C_2H_2 . The red dashed line shows the scaling between the descriptors, the vertical and horizontal error bars are the ± 1 BEEF standard deviations on the descriptors and the ellipses show the covariances of the BEEF ensemble between the descriptors. The net rate maps are equal to point-wise subtracting the reverse directional rates from the corresponding forward directional rates, thus there is up to one map per reaction. Maps are generally omitted if their values are below a threshold in all points, e.g. if there is nowhere in the map where the net rate is reverse, then the net reverse map is omitted for that reaction.

Figure S.15: Computed degree of rate control maps (DRC) for ethylene production. The maps show the DRC with respect to the transition state of dehydrogenating ethyl (**left**) and dehydrogenating ethane (**right**). These are calculated at 873 K, 0.2 bar C_2H_6 (g), $2 \cdot 10^{-4}$ bar C_2H_4 (1% carbon conversion), 0.6 bar H_2 (g), 10^{-9} bar CH_4 and 10^{-12} bar C_2H_2 . The red dashed line shows the scaling between the descriptors, the vertical and horizontal error bars are the ± 1 BEEF standard deviations on the descriptors and the ellipses show the covariances of the BEEF ensemble between the descriptors.

Figure S.16: Computed degree of rate control (DRC) maps for methane production. The maps show the DRC with respect to the four most relevant C-C breaking transition states. The transition state CH-C (Upper left) is the most relevant for the Pt group metals. These are calculated at 873 K, 0.2 bar C_2H_6 (g), $2 \cdot 10^{-4}$ bar C_2H_4 (1% carbon conversion), 0.6 bar H_2 (g), 10^{-9} bar CH_4 and 10^{-12} bar C_2H_2 . The red dashed line shows the scaling between the descriptors, the vertical and horizontal error bars are the ± 1 BEEF standard deviations on the descriptors and the ellipses show the covariances of the BEEF ensemble between the descriptors.

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