

1 Structural Principles to Steer the Selectivity of the Electrocatalytic Reduction

2 of Aliphatic Ketones on Platinum

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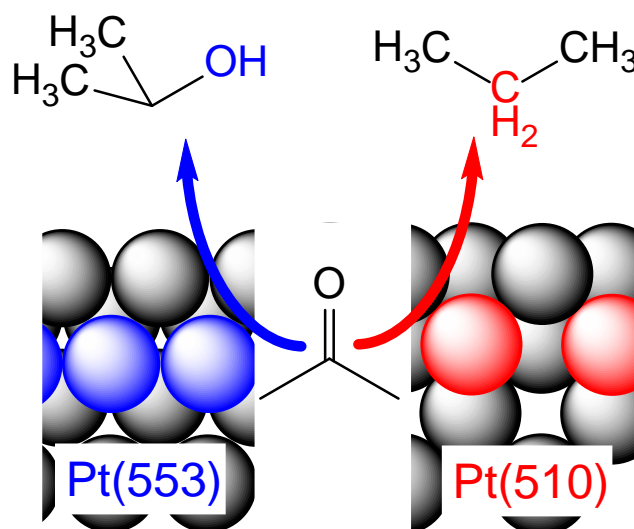
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9 TOC entry



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1 **ABSTRACT**

2 Due to a general shift of the resource basis, chemical industry is charged with the task of finding ways
3 to transform ketones to value-added products. A viable route to do so is the electrochemical
4 hydrogenation of the carbonyl functional group. Here we report a study on acetone reduction at
5 platinum single-crystal electrodes using online electrochemical mass spectroscopy, in situ FTIR
6 spectroscopy and DFT calculations. Acetone reduction at platinum displays a remarkable structural
7 sensitivity: not only the activity but also the product distribution depends on the surface
8 crystallographic orientation. At Pt(111) neither adsorption nor hydrogenation occur. A
9 decomposition reaction deactivating the electrode happens at Pt(100). Acetone reduction proceeds
10 at (110) steps: while Pt[(n-1)(111)x(110)] electrodes produce 2-propanol, Pt[(n+1)(100)x(110)]
11 electrodes produce propane. Using DFT calculations, we build a selectivity map to explain the
12 intricacies of the acetone reduction on platinum. Finally, we extend our conclusions to the reduction
13 of higher aliphatic ketones.

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1 Pyrolysis of lignin-rich waste materials and biomass to bio-oils has the potential to become a
2 new, valuable source of aromatic platform chemicals¹. However, bio-oils consist of carboxylic acids,
3 ketones and aldehydes that need further refinement²⁻⁴. Therefore, studies on the electrochemical
4 hydrogenation of carbonyl compounds such as acetophenone⁵, benzaldehyde^{6,7}, 5-
5 hydroxymethylfurfural⁸⁻¹⁰, or ethyl pyruvate^{11,12} have received renewed attention, as they might
6 give valuable insight into the electrorefinement of biomass. The electrochemistry of the ethyl
7 pyruvate is also interesting because it is the standard substrate of the Orito reaction by which α -keto
8 esters can be enantioselectively hydrogenated using heterogeneous catalysis¹³. However, each of
9 these carbonyl compounds features a second functional group that is also susceptible to
10 hydrogenation. For instance, the phenyl ring of acetophenone behaves similarly to benzene, which
11 has a rich and rather complex electrochemistry of its own¹⁴.

12 To provide fundamental knowledge on the electrochemistry of carbonyl functional groups,
13 here we study the electrochemical reduction of acetone as a model system for the electroreduction
14 of carbonyl compounds. As acetone is the simplest ketone, its reduction is not convoluted by the
15 presence of additional functional groups or by the formation of acetals. It was shown previously that
16 acetone can be reduced electrochemically at polycrystalline platinum electrodes¹⁵⁻¹⁹ to both propane
17 and 2-propanol^{16,17}. To the best of our knowledge, single crystal studies on the electrochemical
18 hydrogenation of acetone have never been reported. However, Hazzazi *et al.* showed that ethyl
19 pyruvate adsorbs preferentially at (110) steps at Pt electrodes and, via CO formation, at Pt(100)
20 terraces¹¹. This suggests a strong influence of the surface structure on the electrochemistry of
21 ketones.

22 In this study, we employ single crystal platinum electrochemistry in combination with in situ
23 and online techniques (infrared spectroscopy FTIR and online electrochemical mass spectroscopy,
24 OLEMS) to show that activity, selectivity and the extent of catalytic poisoning of acetone
25 electroreduction are highly sensitive to the platinum surface structure. Using DFT calculations, we

1 propose detailed pathways for the electrocatalytic reduction of acetone to 2-propanol and propane,
2 and show that the product selectivity is driven by the coordination of the active sites.

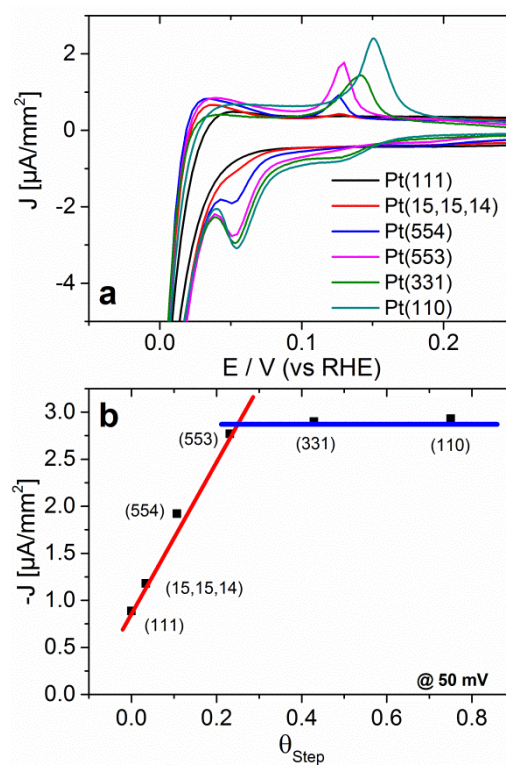
3 **RESULTS**

4 ***Acetone Reduction at Single Crystal Platinum Electrodes***

5 Figure 1A shows the CVs at stepped Pt(111)-type single crystal electrodes in an electrolyte of 0.1 M
6 H₂SO₄ containing 0.1 M acetone. At all stepped electrodes a peak due to hydrogen desorption from
7 (110) step sites is observed in the positive going sweep at approximately 0.12 V. In the blank
8 electrolyte the corresponding reduction peak appears in the negative going scan at the same
9 potential. Such a peak is missing in the presence of acetone (c.f. Supplementary Figures 1 to 6) and
10 indicates strong adsorption of acetone at (110) step sites (the interaction between (110)-step sites
11 and acetone is rather strong as further explained by Supplementary Figure 7 and Supplementary
12 Note 2). Hydrogen adsorption is only possible once acetone is fully removed from the surface. No
13 acetone adsorption is observed at Pt(111) terraces as the presence of acetone does not suppress the
14 sulfate spike or the H-upd peak at Pt(111) (c.f. Supplementary Figure 1 and Supplementary Note 1).

15 In the presence of acetone, a peak at 0.05 V appears in the negative going sweep at Pt(554),
16 Pt(553), Pt(331) and Pt(110), indicating the reduction of the ketone. At an electrode with long
17 terraces such as Pt(15,15,14) only a faint shoulder is observed, while any indication for acetone
18 reduction is missing at Pt(111). Considering that acetone does not adsorb on (111) terraces, the
19 inactivity of Pt(111) is not surprising. Figure 1B illustrates that the activity for acetone reduction only
20 stems from the (110) step sites: the current density at 0.05 V increases linearly as the theoretical
21 step density increases from 0 (i.e. Pt(111)) to 0.23 (i.e. Pt(553)). However, for step densities larger
22 than 0.23 the current density plateaus (the same behavior is observed in Supplementary Figure 8
23 where the current density is plotted versus the experimentally determined surface step density as
24 determined in Supplementary Note 3). In principle, this means that the activity of the individual (110)

- 1 steps decreases for high densities. In other words, the nominal turnover frequency per step site is
- 2 lower at Pt(110) compared to Pt(553).



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5 **Figure 1. Influence of the theoretical step density of Pt[(n-1)(111)x(110)] electrodes on acetone reduction.** A) CVs at various stepped Pt(111) electrodes (Pt[(n-1)(111)x(110)]) in 0.1 M H₂SO₄ containing 0.1 M acetone. B) Current density at 0.05 V plotted as a function the theoretical of step density (no (1x2)-reconstruction is considered). Full potential sweeps for each electrode both in the blank electrolyte and in acetone containing electrolyte appear in Supplementary Figures 1-6 in. A plot of the current density versus the charge of the hydrogen desorption peak (as a measure for the real step density) can be found in Figure S8 in the SI.

11 As long as the number of adsorption sites is the only limiting factor, the current density

12 follows the step density linearly. However, steric hindrance or any other step-step interaction

13 between adsorbed species may limit the maximal achievable surface concentration. This situation

14 appears to be achieved at Pt(553). Increasing the step density further does not result in a higher

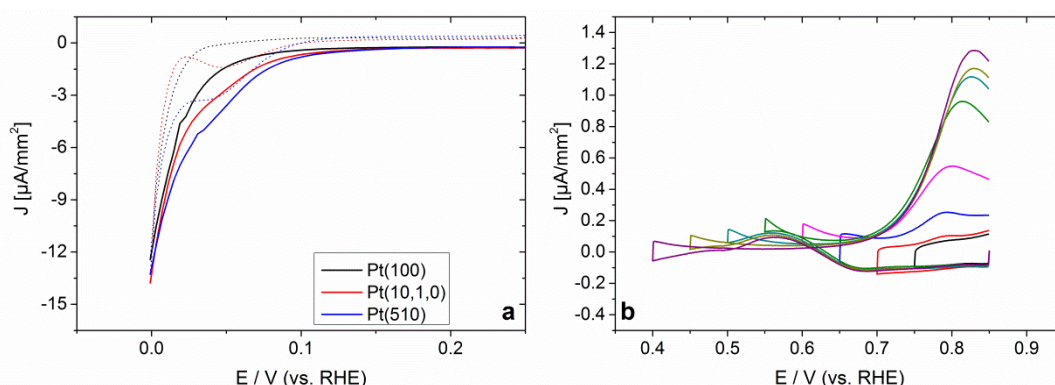
15 surface concentration. As will be shown later in Figures 6-7, individual step sites on Pt(110) are

1 predicted to be more active than those of Pt(553) because their generalized coordination number (
2 \overline{CN} ²⁰, see page S6 in the SI) is close to optimal, but experiments suggest that they participate less
3 frequently in acetone hydrogenation. There appears to be a compensation effect between the
4 density of active sites and their intrinsic activity. A similar effect has been invoked for the
5 hydrogenation of benzene at stepped Pt(111) terraces²¹ and for oxygen reduction on stepped
6 Pt(111)²².

7 Hydrogen evolution and acetone reduction are the only reactions occurring at stepped
8 Pt(n(111)x(110)) electrodes. That is, there is no side reaction that leads to the poisoning of the
9 electrode. As discussed in Supplementary Note 4 this can be derived from Supplementary
10 Figure 9A in which a Pt(553) electrode has been cycled for a prolonged period of time without any
11 effect on the shape of the CV. This is in contrast to other aldehydes (i.e. acetaldehyde) which interact
12 with platinum surfaces by cleavage of the C-C bond, resulting in the accumulation of CH_x-species and
13 carbon monoxide on the electrode²³.

14 Let us now analyze the effect of changing the terrace symmetry from (111) to (100) while
15 keeping the same type of steps. Figure 2A shows the CVs obtained in an electrolyte of 0.1 M H₂SO₄
16 containing 0.1 M acetone at stepped Pt(100) electrodes. A shoulder prior to hydrogen evolution
17 appears in the CV of Pt(10,1,0) and, more prominently, of Pt(510) in the presence of acetone. The
18 shoulder indicates ketone reduction, and is missing in the CV of pristine Pt(100). Similar to stepped
19 Pt(111) electrodes, the activity of stepped Pt(100) electrodes increases with step density. The most
20 likely interpretation for this observation is that the electrochemical hydrogenation takes place at
21 (110) step sites. Computational studies suggest that the activity for acetone reduction at stepped
22 Pt(100) electrodes stems from step sites (see below), while the terraces are inactive for acetone
23 reduction. In addition, the discussion of Supplementary Figures 10 to 12 in Supplementary Note 5
24 provides further arguments why also the CV data suggest that the active surface sites for acetone
25 reduction are the step sites.

1 Aside from acetone reduction, a reaction occurs at stepped Pt(100) electrodes that leads
 2 ultimately to poisoning: Supplementary Figure 9B shows that Pt(510) loses all its activity for acetone
 3 reduction after the third cycle. In order to identify the active surface site for the poisoning reaction
 4 we have conducted the potential opening experiment in Figure 2B. Each cycle in Figure 2B is the first
 5 potential scan recorded at a freshly prepared Pt(100) electrode in an electrolyte of 0.1 M H₂SO₄
 6 containing 0.1 M acetone. As long as the lower potential window remains above 0.7 V, only
 7 capacitive currents are observed in the CV. However, when the lower potential limit goes below 0.7 V
 8 an oxidation current appears in the negative-going scan, with a corresponding oxidation current in
 9 the potential region between 0.7 V and 0.85 V in the following positive-going scan. These results
 10 suggest that acetone is oxidized at (100) terraces at potentials below 0.7 V. This oxidation is
 11 incomplete, since further oxidation takes place in the potential region between 0.7 V and 0.85 V.



12
 13 **Figure 2. Processes at Pt[(n+1)(100)x(110)] electrodes.** A) CVs at stepped Pt(100) electrodes
 14 (Pt[(n+1)(100)x(110)]) in 0.1 M H₂SO₄ containing 0.1 M acetone. Solid lines: negative going sweep; dotted lines:
 15 positive going sweep. B) Potential opening experiment at a Pt(100) electrode. A full potential sweep for each
 16 electrode can be found in Figures S10 to S12 in the SI. Sweep rate: 0.05 V/s; Potential limits: 0 V to 0.85 V.

17 When we accumulate products of incomplete acetone oxidation by exposing a Pt(510)
 18 electrode for 2 minutes to an acetone containing electrolyte at 0.45 V, the electrode loses its ability
 19 to reduce acetone (c.f. Supplementary Figure 13 and Supplementary Note 6). However, exposing the
 20 electrode for 2 minutes to the same solution at 0.85 V, where acetone does not undergo a reaction,
 21 does not impair acetone reduction in the following negative going sweep. This suggests that the

1 oxidation process observed at Pt(100) in the potential range between 0.7 V and 0.45 V causes the
2 poisoning of stepped Pt(100) electrode. That is, it suggests that the Pt(100) terraces are the active
3 surfaces sites for electrode poisoning. Although we do not study the nature of the poisoning reaction
4 in detail, it is interesting to note its sensitivity to the crystallographic orientation of the electrode.

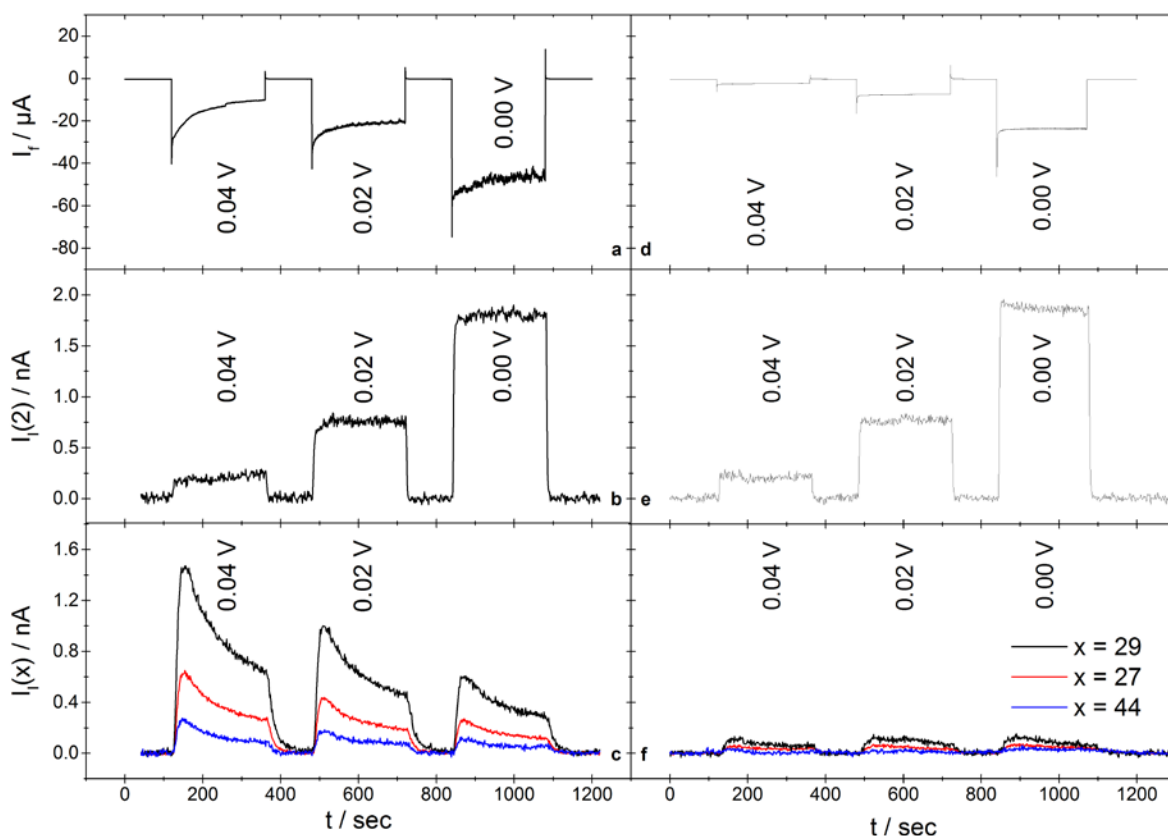
5 ***Product Distribution of Acetone Reduction***

6 To demonstrate the influence of surface orientation on product distribution, Figure 3 shows OLEMS
7 results obtained at Pt(553) and Pt(510) during potential steps into the potential window of acetone
8 reduction. After each step, an intense signal in the ionic current for mass 2 is observed (Figure 3B and
9 3E) corresponding to hydrogen evolution. Since the signal intensity at both crystals is roughly the
10 same, we can infer that the sensitivity for the two experimental setups is comparable. Parallel to
11 hydrogen evolution signals in the ionic currents for masses 27, 29 and 44 with an intensity ratio of
12 $I_{29} : I_{27} : I_{44}$ is 100 : 43 : 24 are observed in the experiments conducted at Pt(510) (Figure 3C). Only
13 faint signals for the same masses are observed for Pt(553) (Figure 3F).

14 The observed masses and intensity ratio correspond to the fragmentation pattern of
15 propane, and indicates significant acetone reduction to propane on Pt(510). Since only a faint signal
16 for propane formation is observed during acetone reduction at Pt(553), we derive that the
17 hydrocarbon is only a minor product of acetone reduction. Hence, the dominant product of acetone
18 reduction at Pt(553) electrodes should be 2-propanol. Note that alcohols are difficult to detect by
19 means of OLEMS, because they do not pass readily from the aqueous phase into the vacuum of the
20 mass spectrometer.

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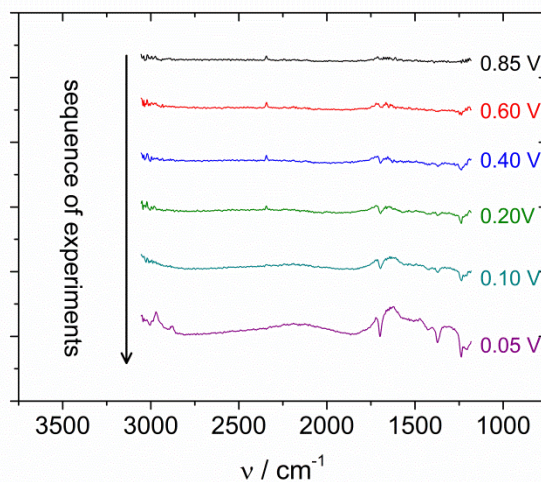


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2 **Figure 3. Structure sensitivity of propane formation upon acetone reduction.** OLEMS results obtained at
 3 Pt(510) (left) and Pt(553) (right). The step potential program was 0.85 V, 0.04 V, 0.85 V, 0.02 V, 0.85 V, 0 V and
 4 0.85 V. A and D: faradaic current; B and E: Ionic current for mass 2; C and F: ionic current for mass 29 (black), 27
 5 (red) and 44 (blue). Electrolyte: 0.1 M H₂SO₄ containing 0.1 M acetone.

6 The FTIR spectra in Figure 4 confirm the assertion that acetone is reduced to 2-propanol at
 7 Pt[(n-1)(111)x(110)] electrodes. After a potential step to 0.05 V at Pt(110), two bands at 2971 cm⁻¹
 8 and 2877 cm⁻¹ appear. These bands correspond to the asymmetric and symmetric stretching
 9 vibrations of the methyl groups of 2-propanol at $\nu(\text{CH}_3)_{\text{as}} = 2971 \text{ cm}^{-1}$ and at $\nu(\text{CH}_3)_{\text{s}} = 2888 \text{ cm}^{-1}$ ²⁴. On
 10 the other hand, propane has only a single band at 2940 cm⁻¹ due to both $\nu(\text{CH}_3)_{\text{as}}$ and $\nu(\text{CH}_3)_{\text{s}}$ ²⁵. The
 11 appearance of two bands therefore strongly indicates that acetone is reduced only to 2-propanol at
 12 Pt(110). If propane was formed, a third band would be expected in Figure 4. Although perfect

1 selectivity cannot be proven with the employed techniques, it can be asserted that acetone is
2 reduced to 2-propanol with good selectivity at Pt[(n-1)(111)x(110)] electrodes.



3
4 **Figure 4. FTIR spectra obtained at Pt(110) and at the indicated potentials in an electrolyte of 0.1 M H₂SO₄**
5 **containing 0.1 M acetone.**

6 Aside from the positive bands at 2971 cm⁻¹ and 2877 cm⁻¹, there are three negative bands at
7 1697 cm⁻¹, 1370 cm⁻¹ and 1237 cm⁻¹ in Figure 4. These bands correspond to the symmetric stretching
8 vibration of the C-O bond ($\nu(\text{C-O})_s = 1710 \text{ cm}^{-1}$), the symmetric deformation vibration of the methyl
9 groups ($\delta(\text{Me})_{as} = 1361 \text{ cm}^{-1}$) and the asymmetric stretching vibration of the carbon skeleton ($\nu(\text{Me-}$
10 $\text{C-Me})_{as} = 1220 \text{ cm}^{-1}$) of free acetone^{26 27}. These bands suggest the depletion of acetone from the thin
11 layer between electrode and prism. This happens already at potentials more positive than 0.05 V and
12 before the formation of 2-propanol indicates the electrochemical consumption of acetone. Given our
13 conclusion that acetone starts to adsorb at Pt(553) in the potential range between 0.4 V and 0.6 V
14 (c.f. Figure S7), it is likely that the negative bands are due to the adsorption of acetone.

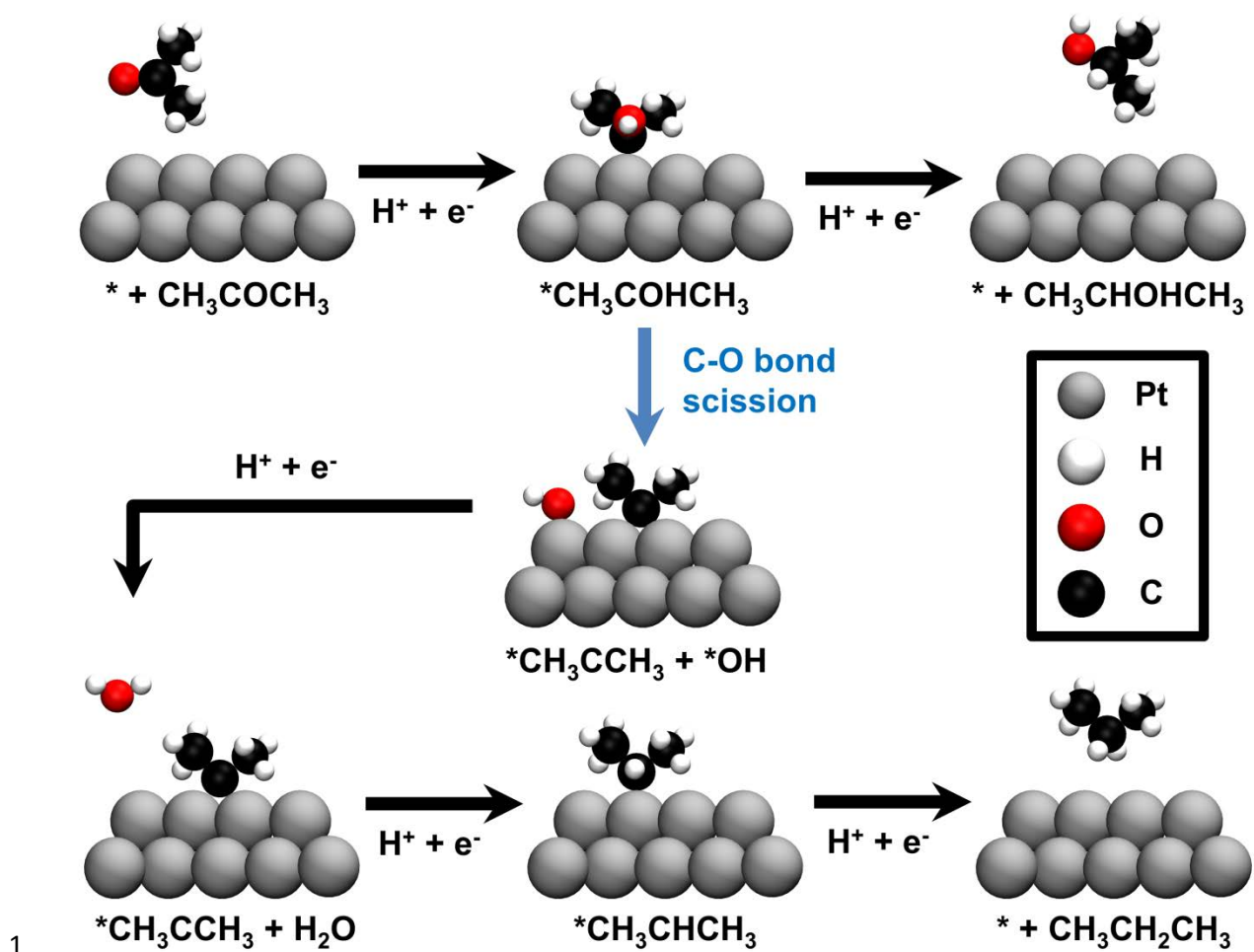
15 The FTIR-Spectra in Figure 4 do not feature any positive bands that could be assigned to
16 adsorbed acetone. However, the large background due to water and acetone in the gap between
17 prism and electrode makes it difficult to observe weak bands in FTIR spectra. In the SI, we provide

1 Raman spectra that show that acetone adsorbed in a Raman active mode experience a weakening
2 of the C-O binding strength (Supplementary Figure 14 in Supplementary Note 7).

3

4 ***Computational Modelling of Acetone Reduction***

5 To gain insight into the intriguing structure-sensitive selectivity of acetone reduction, we now resort
6 to DFT calculations. We have modelled acetone reduction on six sites at Pt surfaces (see the
7 structures and active sites in Supplementary Figure 16; Supplementary Note 8) through the reaction
8 networks shown in Supplementary Figure 15. After modelling all the possible pathways in
9 Supplementary Figure 15 (including those starting with propenol, the enol tautomer of acetone), we
10 conclude that the most favorable pathways for acetone reduction to 2-propanol and propane,
11 namely those with the lowest overpotential, are those in Figure 5. Both pathways proceed via
12 acetone molecular adsorption and subsequent hydrogenation to *CH_3COHCH_3 . If the carbon atom
13 bound to the surface of this intermediate is hydrogenated, 2-propanol is formed. Conversely, if the C-
14 O bond is cleaved, propane and water are produced. Thus, there are two key factors for acetone
15 reduction: first, whether acetone adsorbs or not determines the activity of the catalyst. Second, the
16 relative ease of protonation or C-O bond scission of *CH_3COHCH_3 determines the selectivity of the
17 reaction.

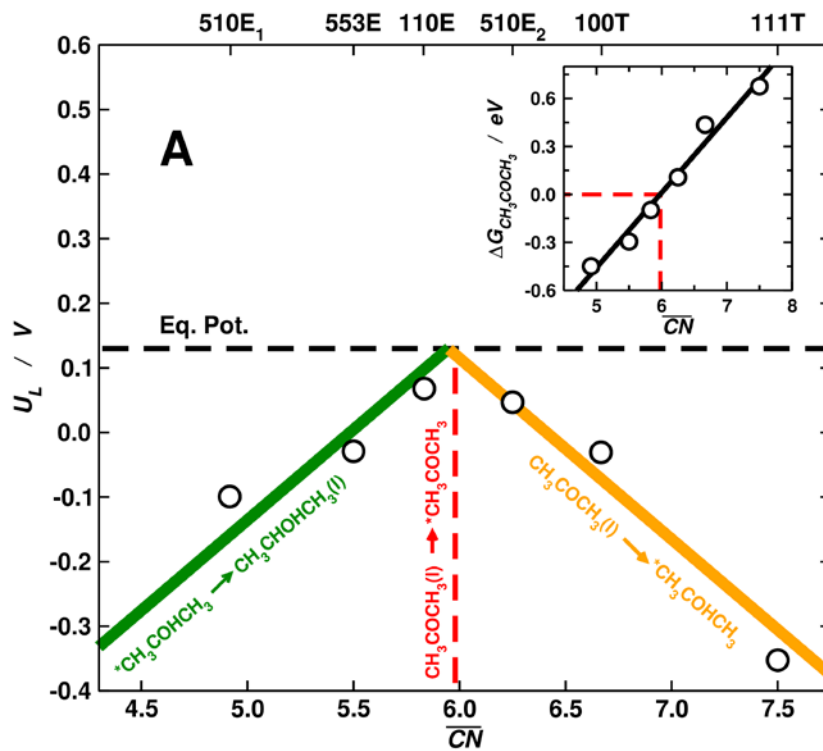


1
2 **Figure 5. Most favorable reaction pathways for acetone reduction to 2-propanol and propane at Pt**
3 **electrodes.** The entire reaction networks from which they were derived appear in Supplementary Figure 15.

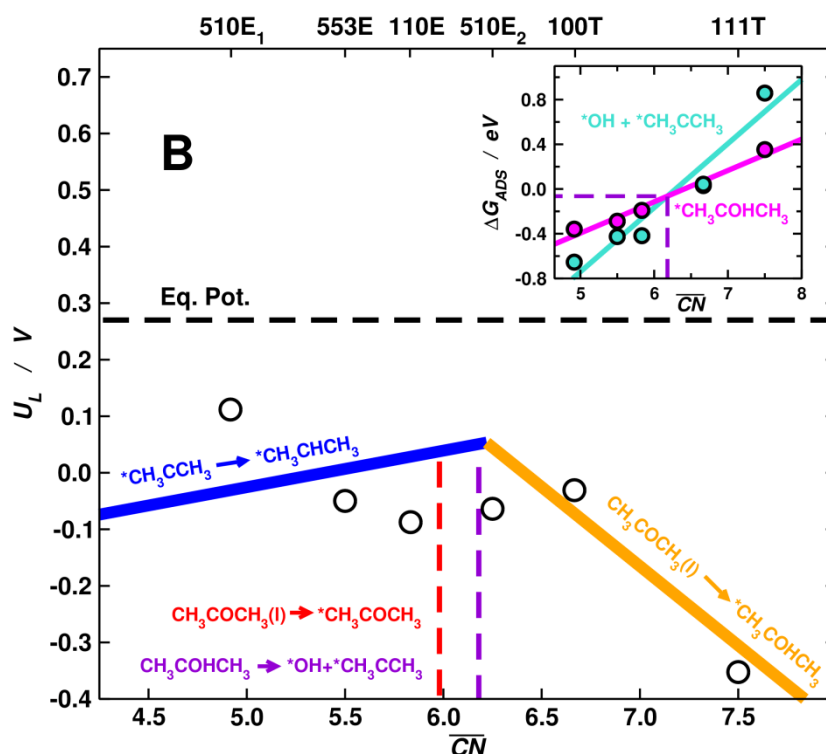
4
5 First, let us focus on the activity trends among Pt sites. In Figure 6 we provide separate
6 coordination-activity plots for 2-propanol and propane production modelled following the pathways
7 in Figure 5. For 2-propanol production the most active surface is Pt(110). Since only two electrons are
8 transferred in this reaction, the top of the volcano and the equilibrium potential coincide in
9 Figure 6A²⁸. The orange line in the plot (weak binding sites) corresponds to acetone hydrogenation to
10 $*\text{CH}_3\text{COHCH}_3$ being the potential-determining step. The green line (strong binding sites) corresponds
11 to the hydrogenation of $*\text{CH}_3\text{COHCH}_3$ to produce 2-propanol being the potential-determining step.
12 The inset shows the correlation between \overline{CN} and the adsorption energies of acetone. The red
13 dashed line at $\overline{CN} \approx 6.0$ corresponds to the limit of exothermic acetone adsorption on Pt facets

1 (Supplementary Figure 18B in Supplementary Note 8 shows that for $\overline{CN} \leq 5.8$ acetone adsorption
 2 energies are more favorable than those of *H).

3 Figure 6B shows that Pt(510) is predicted to be the most active surface under study for
 4 propane production. The orange line (weak binding) in the plot corresponds again to acetone
 5 hydrogenation. The blue line (strong binding) represents the hydrogenation of *CH₃CCH₃ to
 6 *CH₃CHCH₃. The inset shows that for $\overline{CN} < 6.2$ (purple line in the main panel),
 7 *CH₃COHCH₃ + * → *CH₃CCH₃ + *OH is thermodynamically favorable, which is necessary to shift
 8 the selectivity toward propane production.



9



1
 2 **Figure 6. Coordination-activity plots for acetone reduction.** reduction to (A) 2-propanol, and (B) propane. Six
 3 different Pt surface sites are studied, see the top x-axis and Supplementary Figure 16. The most favorable onset
 4 potentials (U_L) are reported for each site. The dots are calculated data points from the DFT simulations. The
 5 orange, green and blue lines come from Supplementary Figure 18A and result from the correlations between
 6 generalized coordination numbers and adsorption energies. The mean absolute errors between the fits and the
 7 calculated data points are in all cases smaller than 0.10 eV. The black dashed lines correspond to the
 8 equilibrium potentials. The red line comes from the inset in (A) and separates sites with/without (left/right)
 9 exothermic acetone adsorption. The purple line comes from the inset in (B) and separates sites for which
 10 $*CH_3COHCH_3 + * \rightarrow *CH_3CCH_3 + *OH$ is exothermic/endothermic (left/right).

11
 12 Furthermore, Figure 5 shows that the pathway of acetone reduction bifurcates before 2-
 13 propanol is formed. This suggests that once the alcohol is formed no further reduction is possible.
 14 Indeed, we arrive at the same conclusions experimentally: Supplementary Figure 19 and the related
 15 discussion in Supplementary Note 9 shows that 2-propanol cannot be reduced at the Pt(510)
 16 electrode under the same conditions under which acetone is reduced to propane.

1 It is useful to determine whether and how coordination influences the pathway bifurcation.
2 In Figure 7 we have overlapped Figures 6A and B together with the H₂ evolution trends from ref.²⁹ to
3 provide a selectivity map that predicts the most favorable product of acetone reduction and its onset
4 potential based on the geometry of the Pt active sites. Essentially, we detect three regions:

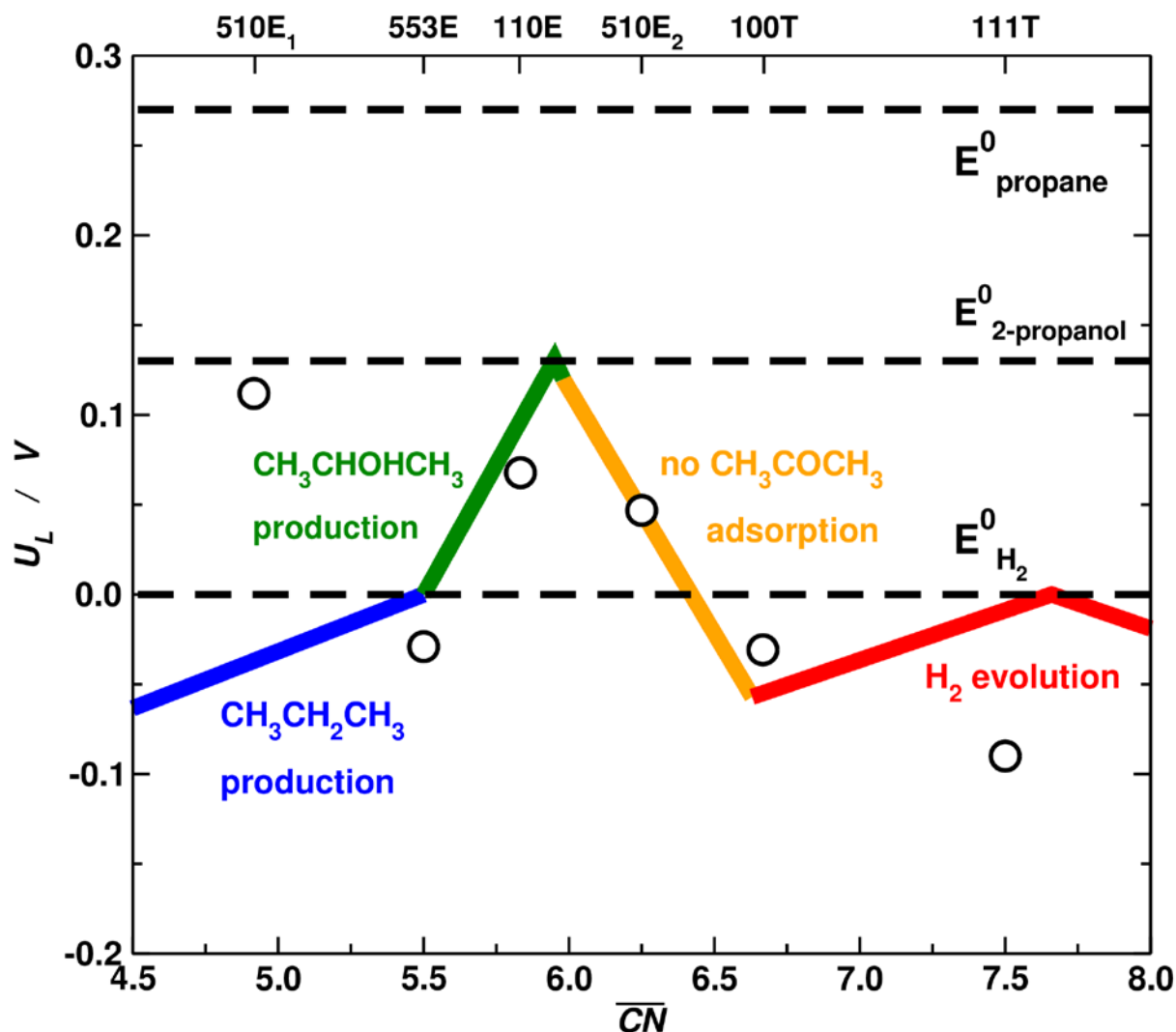
5 1) For large coordination number ($\overline{CN} > 6.6$, red lines in Figure 7), *H adsorption and H₂ evolution
6 are most favorable (see also Supplementary Figure 18 B), so the sites are inactive for acetone
7 reduction. This is the case for the terrace sites at Pt(111) and Pt(100).

8 2) For intermediate coordination number, the orange line in Figure 7 ($6.0 < \overline{CN} < 6.6$) marks the
9 region in which 2-propanol formation is more favorable than H₂ evolution, but acetone molecular
10 adsorption is endothermic. On sites with coordination in the range $5.5 < \overline{CN} < 6.0$ (green line in
11 Figure 7), acetone adsorption becomes exothermic and more favorable than that of *H
12 (Supplementary Figure 18B), and *CH₃COHCH₃ hydrogenation is more favorable than the scission of
13 the C-O bond, so that 2-propanol predominates in the product distribution. This is the case of for
14 Pt(110) and for the step sites in Pt(553).

15 3) For low coordination number ($\overline{CN} < 5.5$, blue line), the cleavage of the C-O bond in *CH₃COHCH₃ is
16 rather favorable, so that propane is the preferred product. This is the case for the undercoordinated
17 step sites on Pt(510) (510E₁ sites in Figure 7).

18 The slopes of the lines in Figure 7 come from Figure 6 and give an account of the structural
19 dependence of the potential-determining steps of each reaction pathway. The orange and green
20 lines are steeper than the blue one because in the former two the reaction energy involves only a
21 single adsorbed intermediate. Conversely, the blue line involves two adsorbed species (one as a
22 reactant, another as a product), which leads to a small slope because of the similarity between the
23 adsorbed species. This is illustrated in Supplementary Figure 18, where it is also shown that the mean
24 absolute errors between the calculated data points and the fits are below 0.10 eV in all cases. The

- 1 red lines for H₂ evolution have a small slope because the variations in hydrogen adsorption energy as
- 2 a function of the coordination of the active sites are typically small (although systematic)²⁹.



3
 4 **Figure 7. Structure-sensitive selectivity map for acetone reduction to 2-propanol and propane.** The top x-axis
 5 locates the six different Pt sites under study, see also Supplementary Figure 16. The most favorable onset
 6 potentials (U_l) are reported in each case. The most active sites are the steps on Pt(110) for 2-propanol
 7 production, and (110) steps at Pt(510) for propane production. Black dashed lines represent equilibrium
 8 potentials. White dots are calculated data points from the DFT simulations. The data for H₂ evolution (red line)
 9 come from ref.²⁹, the orange, green and blue lines come from Figure 6 and are linear regressions built from 6
 10 data points in each case. See Supplementary Note 8 and Supplementary Figure 18 for further details.

11

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1 ***Extension of the Results to Other Aliphatic Ketones***

2 The results obtained for the electrocatalytic hydrogenation of acetone at platinum single crystals has
3 been extended to butanone and 3-pentanone. In Supporting Note 10 Supplementary Figures 20 to 28
4 compare the CVs in an acetone containing electrolyte with those recorded in butanone and
5 pentanone containing electrolytes. Essentially, the same trends as for acetone are observed: with
6 increasing step density of Pt(111)-type electrodes, the activity increases (c.f. also Supplementary
7 Figure 29). However, as the carbon chain becomes longer, ketone reduction is shifted to more
8 negative potentials. While acetone reduction takes place in a well-defined peak, butanone reduction
9 takes place in a shoulder, and 3-pentanone reduction is barely distinguishable from hydrogen
10 evolution. This might reflect a better stabilization of the C-O bond by hyperconjugation with the σ -
11 orbital of a C-C bond in butanone and 3-pentanone compared to by hyperconjugation with the σ -
12 orbital of a C-H bond in acetone.

13 A further difference between acetone, butanone and 3-pentanone becomes evident from
14 Supplementary Figure 20. From the reversibility of the sulfate spike at Pt(111) we inferred that
15 acetone does not adsorb at this electrode. While the spike in the first negative going scan appears in
16 the presence of butanone and 3-pentanone, it is lost in the subsequent positive going scan. In the
17 presence of 3-pentanone the spike is shifted to more positive potentials and hydrogen adsorption is
18 shifted to more negative potentials both in the presence of butanone and pentanone. The altered
19 adsorption energy for hydrogen and the change in the peak potential for sulfate adsorption indicate
20 the adsorption of butanone and 3-pentanone, respectively. Since H-upd is not severely suppressed,
21 the adsorption of butanone and 3-pentanone is weak and might be the result of enhanced van der
22 Waals interactions due to the longer carbon chains.

23 From the CVs in Supplementary Figures 26 to 28 (c.f. also Supplementary Figure 30) it is less
24 obvious that the reduction of butanone and 3-pentanone takes place at the steps of Pt(100)-type
25 electrodes. However, this is evident from the OLEMS results in displayed in Supplementary Figure 31

1 and discussed in Supplementary Note 11. As in Figure 3, steps from 0.85 V into the potential region
2 of butanone reduction have been conducted and in parallel the mass spectrometric response has
3 been measured. The ionic current measured for mass 43 indicates the formation of butane, which is
4 most prominent at Pt(510). Comparatively small amounts of butane are formed at pristine Pt(100).
5 Hence, the reduction of higher aliphatic ketones proceeds at the steps of Pt(100)-type surfaces as
6 well. In addition, no formation of butane is observed at Pt(553). Therefore, it can be concluded that
7 higher ketones are also reduced to the corresponding alcohol at stepped Pt(111)-type electrodes.

8 **DISCUSSION**

9 Figures 1 and 2 show that acetone reduction does not proceed at the (111) and (100) basal planes of
10 platinum. The activity of the platinum electrodes, thus, depends on the presence of steps. The DFT
11 calculations (Figures 6 and 7) show that the interaction of acetone with Pt(111) and Pt(100) is
12 energetically unfavorable due to the high coordination number of its surface atoms. Based on our
13 experimental results, it was difficult to assess whether acetone reduction at stepped Pt(100)
14 electrodes proceeds at (100) terraces and/or step sites. Figure 7 shows that the inactivity for acetone
15 reduction is inherent to the (100) terraces and not caused by the poisoning reaction that occurs at it.
16 Hence, acetone reduction takes place at the step sites of both Pt[(n-1)(111)x(110)] and
17 Pt[(n+1)(100)x(110)] electrodes. However, experiments suggest that the poisoning of the electrode
18 occurs due to a reaction taking place at (100) terraces. This poisoning reaction was not subjected to
19 detailed investigation in this work as our emphasis was on the selectivity of the hydrogenation
20 reaction, but it is observed that this reaction leads to the accumulation of incomplete oxidation
21 products at Pt(100)-type electrodes, which ultimately results in the full deactivation of the catalyst
22 (c.f. Supplementary Figure 9B). Furthermore, the poison can be removed oxidatively.

23 OLEMS (Figure 3) and FTIR (Figure 4) results show that the nature of the steps has a
24 significant influence on product distribution. Acetone is reduced predominantly to 2-propanol at the
25 steps of Pt[(n-1)(111)x(110)], while propane is formed at the step sites of Pt[(n+1)(100)x(110)]. The

1 selectivity map in Figure 7 explains that the different products are due to the dissimilar stabilization
2 of reaction intermediates, which is a function of the coordination number of the active sites. The
3 selectivity-determining intermediate is *CH_3COHCH_3 and the competing reactions are its
4 hydrogenation and the cleavage of its C-O bond. Note in passing that once 2-propanol is desorbed
5 from the surface, it neither adsorbs again nor undergoes further reduction according to both
6 experiments and calculations. In other words, 2-propanol is not an intermediate of propane
7 evolution from acetone, according to our observations.

8 In a previous paper, we suggested that the *CH_3COHCH_3 intermediate does not form from
9 the keto tautomer³⁰. Instead, acetone adsorbs either as propenol (its enol tautomer) or as
10 protonated acetone from the solution. We have assessed the effect of propenol as prime reactant on
11 our conclusions for Pt(510) and Pt(553) and the results are shown in Supplementary Figure 17. The
12 onset potentials are nearly the same and so are the most favorable reaction pathways, which
13 bifurcate on *CH_3COHCH_3 and differ only in the reactant. This gives confidence in the robustness of
14 the computational results and substantiates the findings in Figures 5-7. In conclusion we have
15 investigated the electrochemical hydrogenation of aliphatic ketones at platinum single crystal
16 electrodes, with emphasis on acetone. The selectivity of the reaction displays a remarkable structural
17 sensitivity: while no reaction proceeds at Pt(111) terraces, a reaction that ultimately leads to the
18 electrode poisoning proceeds at Pt(100). In contrast, the actual hydrogenation on stepped surfaces
19 happens at (110) steps, yielding different products: while aliphatic ketones are reduced to the
20 corresponding alcohol at Pt(111)-type electrodes, Pt(100)-type electrodes catalyze hydrogenolysis to
21 produce the respective hydrocarbon.

22 With the help of DFT calculations, we built a structure-sensitive selectivity map which
23 suggests that the inability of (111) and (100) terraces to molecularly bind acetone and the
24 predominance of *H adsorption and H_2 evolution renders them inactive and corroborates the
25 experimental observation that (110) steps are the active sites for acetone reduction. A semi-

1 quantitative rationale for estimating whether the main product of acetone reduction will be 2-
2 propanol or propane, based on the coordination number of the surface active site, was also
3 provided.

4 The combination of detailed experimental and computational work presented here therefore
5 allows us to conclude that surfaces with high generalized coordination number (Pt(111) and Pt(100))
6 do not adsorb acetone and are therefore inactive for the reduction of the ketone. 2-propanol is
7 formed at Pt(553) and Pt(110) electrodes that feature medium generalized coordination numbers,
8 and propane production occurs only at surfaces that feature low generalized coordination numbers
9 such as that of the Pt(510) electrode. Furthermore, computational modeling elucidates the
10 mechanism of acetone reduction in which the pathways to the alcohol and the hydrocarbon separate
11 before 2-propanol is formed. This explains the experimental finding that acetone can be reduced to
12 both propane and 2-propanol, but that the reduction of 2-propanol to the hydrocarbon is not
13 measurable at Pt(510) electrodes.

14 **METHODS**

15 ***Chemicals and Materials***

16 The blank electrolyte was prepared from *MilliQ* water and H₂SO₄ (suprapure, *Merck*). The ketones
17 used were acetone (HPLC-grade, *Sigma-Aldrich*), butanone (>99%, *Sigma-Aldrich*) and 3-pentanone
18 (>99%, *Sigma-Aldrich*). All solutions were freed from oxygen by purging with argon (6.0, *Linde*). All
19 potentials were measured versus a reversible hydrogen electrode (RHE) in contact with the blank
20 electrolyte. A platinum wire was used as a counter electrode. Under acidic conditions, ketones are
21 expected to undergo a condensation reaction³¹. To avoid both the accumulation of condensation
22 products and the depletion of the ketone, the electrolyte was changed every hour. Cyclic
23 voltammograms (CV) were recorded on either a PGSTAT 12 potentiostat (*Autolab*) or an Iviumstat
24 potentiostat (*Ivium Technologies*).

25 ***Single Crystal Electrodes***

1 Electrochemical experiments and OLEMS (OnLine Electrochemical Mass Spectrometry) experiments
2 were conducted with bead-type single crystals purchased from Icryst. Prior to each experiment the
3 surface of the crystal was prepared by flame annealing following the protocol established by
4 Clavilier³². The used glassware was kept for at least 8 hours in acidic permanganate solution. Prior to
5 use, the glassware was rinsed with acidic peroxide solution and boiled several times in *MilliQ* water.

6 In the this paper, we use Pt(111), Pt(15,15,14), Pt((554), Pt(553), Pt(331) and Pt(110) electrodes.
7 These surfaces are derived from the (111) basal plane by introducing (110) steps. While the terrace
8 size of the (111) electrode is in theory infinite, its length is reduced to 30 atoms in Pt(15,15,14), 10
9 atoms in Pt(554), 5 atoms in Pt(553) and 3 atoms in Pt(331). In principle, there are no (111) terraces
10 in the (110) surface. The step density on these surfaces increases accordingly, defined as $\theta_{\text{step}} = 1/(n-$
11 $2/3)$,³³ where n is the width of the terraces (in number of atoms). However, in reality a (1x2)
12 reconstruction of Pt(110) is observed³⁴. In the ideal (1x2) reconstructed Pt(110) surface, every
13 second row of (110)-step sites is missing, which reduces the step density by half and introduces 2
14 atom long (111) terraces.

15 The other set of electrodes was Pt(100), Pt(10,1,0) and Pt(510). These electrodes are derived from
16 the (100) basal plane. In theory, the terrace width of Pt(100) is infinite. By introducing (110) steps the
17 terrace width of the Pt(10,1,0) electrode is reduced to 10 atoms and that of the Pt(510) electrode to
18 5 atoms.

19 ***Online Electrochemical Mass Spectrometry***

20 Online mass spectra were recorded in the multiple-ion detection mode at the indicated potentials on
21 a PrismaPlus mass spectrometer (*Pfeiffer Vacuum*). A vacuum better than 10^{-5} mbar throughout the
22 experiment was achieved by a turbo molecular pump with a suction power of 60 l/s. A Teflon frit
23 inserted into an Kelf-tip, was used as an interface between electrolyte and vacuum of the mass
24 spectrometer³⁵. The surface area of the Teflon frit was 0.8 mm^2 . Volatile compounds can diffuse
25 through the frit and an attached capillary into the vacuum.

1 In this setup the intensity of the mass spectrometric response depends not only on the
2 amount of products, but also on the exact geometry of the setup. That is, the placement of the tip
3 with respect to the electrode will influence the efficiency with which products are collected.
4 Unfortunately, this geometry is difficult to reproduce between two different experiments and the
5 sensitivity of the setup might vary. In order to ensure comparability of OLEMS data obtained in two
6 different setups one can observe the mass spectroscopic response for a product that has the same
7 formation rate in both experiments. If in this case the same signal intensity is observed, the
8 collection efficiency between both setups is the same for any product. Since hydrogen evolution
9 proceeds with very similar formation rates at Pt(553) and Pt(510), we use the signal on the ionic
10 current for mass 2 to ensure that the collection efficiency and, therefore, the sensitivity in both
11 experimental setups is the same.

12 Although our OLEMS results have a qualitative rather than quantitative character, we chose
13 the OLEMS technique to study acetone reduction because of its high sensitivity (quantities
14 corresponding to a single monolayer can be detected³⁶) and because of the possibility to work in
15 online mode during cyclic voltammetry. In theory an offline approach would allow quantification of
16 the results, but is unsuitable for the present case: an offline approach requires the accumulation of
17 reduction products, which is not possible due to the rapid deactivation of the Pt(510).

18 ***In situ Fourier-Transform Infrared Spectroscopy***

19 Fourier-transform infrared spectra (FTIRS) were recorded on a Vertex V80 (*Bruker*). The used FTIR cell
20 was home-built and accommodated a prism made of calcium fluoride³⁷. By pressing the electrode
21 with a diameter of 1 cm on the prism, a thin gap between electrode and prism was achieved. All
22 spectra were recorded with a resolution of 4 cm⁻¹ and are the average over 200 scans. A background
23 spectrum was recorded at 0.85 V vs. RHE. Next, a potential step to the indicated values was
24 performed and another spectrum was recorded, from which the background spectrum was
25 subtracted.

1 **Computational Details**

2 The DFT simulations were made with VASP³⁸ using the PBE functional³⁹ and the projector
3 augmented-wave method⁴⁰. The topmost two layers of the slabs and the adsorbates were relaxed in
4 all directions, whereas the bottommost ones were fixed at the bulk equilibrium distances. We used a
5 plane-wave cut-off of 450 eV, $k_B T = 0.2$ eV (extrapolating the total energies to 0 K), and the
6 conjugate-gradient scheme until the maximal force was <0.05 eV/Å. Monkhorst-Pack meshes⁴¹ of
7 $6 \times 6 \times 1$, $6 \times 6 \times 1$, $6 \times 4 \times 1$, $4 \times 3 \times 1$, and $5 \times 3 \times 1$ for Pt(111), Pt(100), Pt(110), Pt(510), and Pt(553), ensured
8 convergence of the adsorption energies within 0.05 eV. The distance between repeated images in
9 the vertical direction was >14 Å and dipole corrections were used. Isolated molecules were
10 calculated in boxes of $15 \text{ Å} \times 15 \text{ Å} \times 15 \text{ Å}$ using $k_B T = 0.001$ eV and the Γ -point.

11 The reaction energies were approximated as: $\Delta G \approx \Delta E_{\text{DFT}} + \Delta ZPE - T\Delta S + \Delta E_{\text{solvation}}$, where ΔE_{DFT}
12 is the DFT-calculated reaction energy, ΔZPE is the zero-point energy change and $T\Delta S$ is the entropy
13 change at 298.15 K. ΔS includes all contributions for free molecules and only vibrational entropy for
14 adsorbates. Proton-electron pairs were modelled with the computational hydrogen electrode⁴².
15 Solvation was modelled as an external correction depending on the chemical nature of the
16 adsorbates^{43,44}, see the specific values in Supplementary Table 1. The generalized coordination
17 number (\overline{CN}) of a surface site “ i ” is calculated based on the conventional coordination numbers (cn)
18 of its n_j nearest neighbors as^{45 46}:

$$19 \quad \overline{CN}_i = \sum_{j=1}^{n_i} \frac{cn_j}{cn_{\text{max}}} \quad (0)$$

20 where cn_{max} would be the number of nearest neighbors of the site if in the bulk, i.e. 12 for a single
21 atom. The sites under study are shown in Supplementary Figure 17. The construction of
22 coordination-activity plots for various reactions can be found in the SI and elsewhere,^{22,47,48} the data
23 for H_2 evolution come from reference²⁹.

1 The coordinates of the reaction intermediates on Pt(110) and Pt(510) are given in Supplementary
2 Data 1.

3

4 DATA AVAILABILITY

5 All data is available from the authors upon reasonable request.

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15 **Author Contributions**

16 CJB co-conducted the FTIR experiments and conducted the remaining experimental work (i.e. CV
17 studies, OLEMS studies and SERS studies), co-conceived the concept of the presented work and co-
18 wrote the manuscript. FCV conducted the theoretical modeling, co-conceived the concept of the
19 presented work and co-wrote the manuscript. MCF co-conducted the FTIR experiments. MTMK co-
20 conceived the concept of the presented work and co-wrote the manuscript.

21 **Competing interests**

22 The authors declare no competing interest.

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