

Supporting Information

to

Dissociative Adsorption of Acetone on Platinum Single-crystal Electrodes

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Acetone Adsorption at Pt(911) (i.e. Pt[5(100)x(111)])

In order to investigate whether the dissociative adsorption of acetone is limited to Pt(100) terraces, we also investigated different step geometries. The same experiments conducted for Pt(331) (i.e. Pt[2(111)x(110)]) and Pt(100) electrodes were therefore conducted at platinum electrodes with [911], [510] and [533] (i.e. Pt[5(100)x(111)], Pt[5(100)x(110)] and Pt[4(111)x(100)], respectively) orientation.

The black curve in Figure S1 is the CV of the Pt(911) (i.e. Pt[5(100)x(111)]) electrode obtained in the blank electrolyte of 0.1M H₂SO₄ without any prior exposure to acetone. It features two reversible peaks at 0.28 V and at 0.4 V (vs RHE), corresponding to the adsorption-desorption of hydrogen/hydroxyl at the (110)-step sites and the (100)-terrace sites, respectively. The red CV in Figure S1 was obtained after acetone adsorption at 0.3 V (vs RHE) and subsequent electrolyte exchange to 0.1 M H₂SO₄ under potential control. Starting from 0.3 V, the potential is scanned to 0.6 V (vs RHE) and then back to 0.0 V (vs RHE). Both in the positive- and the negative-going scan, hydrogen adsorption at terraces and step sites is suppressed, suggesting the presence of adsorbed acetone or acetone derived adsorbates, respectively. Prior to hydrogen evolution a shoulder appears in the red curve that is not present anymore in the subsequent cycles. As in the experiment conducted at the Pt(331) (i.e. Pt[2(111)x(110)])-electrode, the shoulder suggests the reductive stripping of acetone from the electrode surface. Indeed, in the second CV obtained after electrolyte exchange (blue curve in Figure S1) hydrogen adsorption becomes possible again at the (110)-step sites, while hydrogen adsorption at the (100) terraces sites is still inhibited. That is, while exposure to reductive potentials removes the adsorbate from the step sites, the adsorbate formed at the (100) terrace sites, previously identified as CO, is not removed.

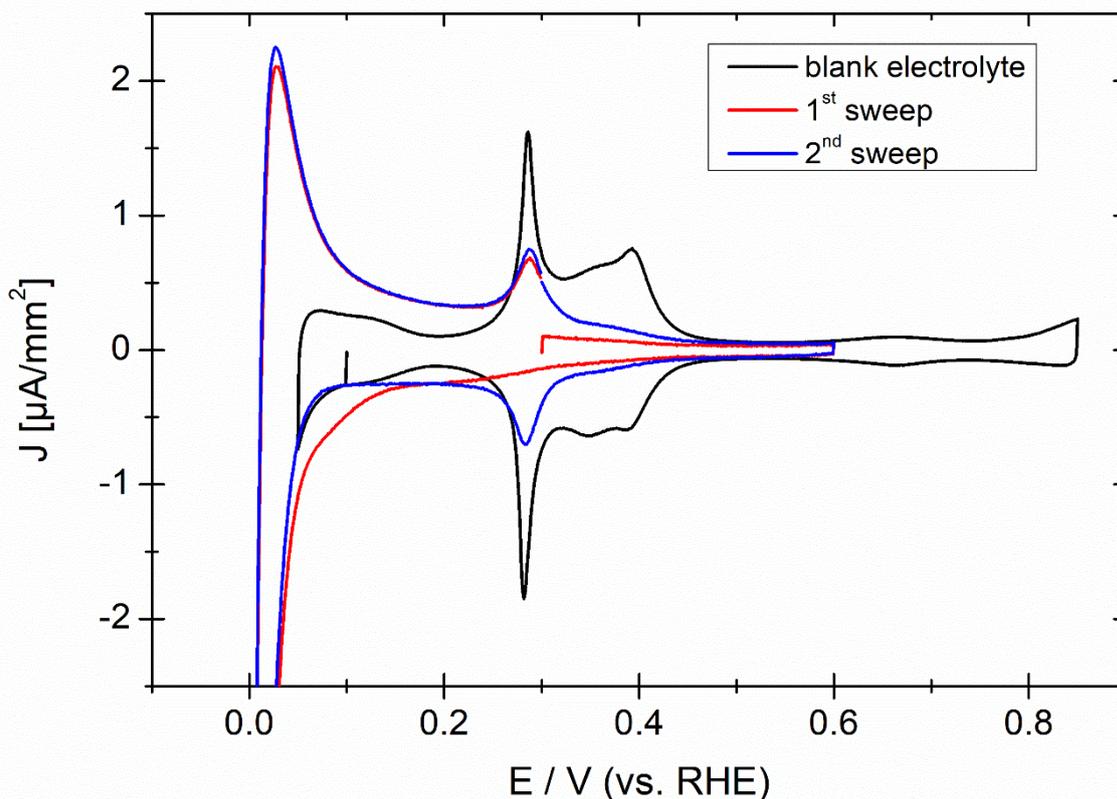


Figure S1: CV of Pt(911) (i.e. Pt[5(100)x(111)]) in 0.1 M H₂SO₄. Black: immediately after preparation; Red: first cycle after acetone adsorption at 0.3 V (vs RHE) and electrolyte exchange under potential control; blue second cycle. Sweep rate: 50 mV/s. Blue and red curves: the lower potential limit is 0.0 V (vs RHE).

The continuous presence of CO at the Pt(911) (i.e. Pt[5(100)x(111)]) electrode after exposure to reductive conditions is further confirmed by the experiment of Figure S2A. In Figure S2A the red curve shows the first scan to 1.5 V (vs RHE) after the experiment of Figure S1 was conducted. Compared with the black CV in Figure S2A, which was obtained at the Pt(911)-electrode (i.e. Pt[5(100)x(111)]) in the blank electrolyte without prior exposure to acetone, an additional charge is passed in the potential region between 0.6 V and 1.0 V (vs RHE). As in the case of the Pt(100)-electrode this indicates the oxidative stripping of CO formed during the decarbonylation of acetone at Pt(100)-terrace.

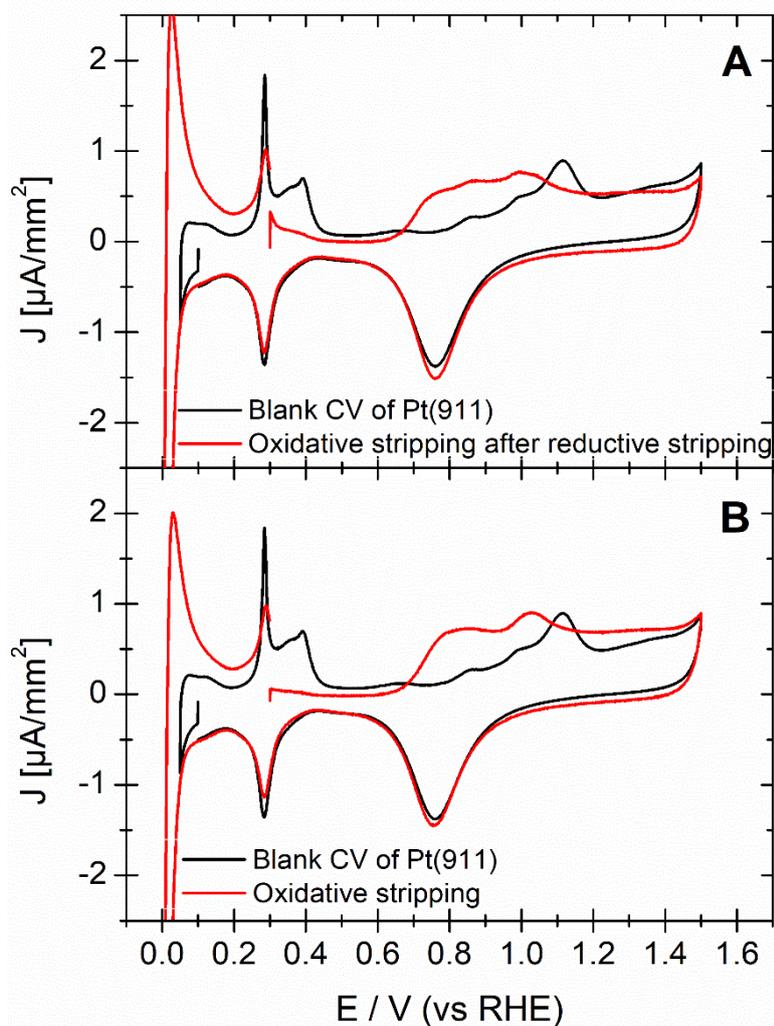


Figure S2: CV of Pt(911) (i.e. Pt[5(100)x(111)]) in in 0.1 M H₂SO₄. Black: immediately after preparation; Red: Oxidative stripping experiment. A: Stripping experiment conducted immediately after the reductive stripping experiment of Figure 2. B: Stripping experiment conducted after preadsorption of acetone and electrolyte exchange. Sweep rate: 50 mV/s. Red curves: the lower potential limit is 0.0 V (vs RHE).

When the adsorbate formed during exposure to an acetone containing electrolyte is oxidatively stripped from the (911)-electrode (i.e. Pt[5(100)x(111)]) directly after the electrolyte exchange was conducted, a similar behavior as in Figure S2A is observed. The red CV in Figure S2B corresponds to such an experiment. Compared to the black CV obtained in the blank electrolyte without prior

exposure to acetone, again an oxidation process in the potential range between 0.6 V and 1.0 V (vs RHE) is observed, which corresponds to the stripping of CO. However, in the red curve of Figure S2B an additional charge is also observed in the potential range of platinum oxide formation. It is difficult to assign this unambiguously to the stripping of an adsorbate as the charge difference could be due to a difference in the exposed electrode surface area, which cannot be reproduced exactly when the electrode is brought into the hanging meniscus configuration. However, since the charge transferred during the reduction of platinum oxide differs barely between the red and the black curve of Figure S2B, also the charge transferred to form the oxide should be the same. Hence, the additional charge transferred in the potential region of platinum oxide formation corresponds to the oxidative stripping of acetone adsorbed to the Pt(110) step sites. Since no reductive stripping as in the experiment of Figure S1 was conducted, it is still present at the electrode surface.

Acetone Adsorption at Pt(510) (i.e. Pt[5(100)x(110)])

The (510) (i.e. [5(100)x(110)]) surfaces features (100) terraces and kinked steps, where one atom long rows with (100) and (110) step geometry alternate. Therefore, it is not surprising that the stripping experiments conducted with the Pt(510) (i.e. Pt[5(100)x(110)]) electrode yield qualitatively the same results as those conducted with the Pt(911) electrode (i.e. Pt[5(100)x(111)]). Compared to the black CV in Figure S3, hydrogen/hydroxyl adsorption at 0.28 V (steps) and at 0.4 V (vs RHE) (terraces) is inhibited in the red curve by the presence of an adsorbate formed during exposure of the electrode to an acetone containing electrolyte. Reductive stripping at 0.1 V (vs RHE) removes the adsorbate from the step sites, allowing the latter to adsorb hydrogen in the subsequent sweep (blue curve in Figure S3). However, reductive stripping does not remove the adsorbate from the (100) terraces as they remain blocked for hydrogen adsorption in the blue curve of Figure S3. Instead, this adsorbate is oxidized in the positive going scan between 0.7 V and 0.9 V (vs RHE) (c.f. Figure S4A) suggesting again the formation of CO at the Pt(100) terraces. When immediately after acetone adsorption an oxidative stripping experiment is conducted, the formed adsorbates are oxidized in the potential range from 0.6 V to 1.5 V (vs RHE) (c.f. Figure S4B). At the Pt(510) (i.e. Pt[5(100)x(110)]) electrode the oxidation of CO formed at the Pt(100) terraces sites and the oxidation of acetone adsorbed to the steps sites are not resolved.

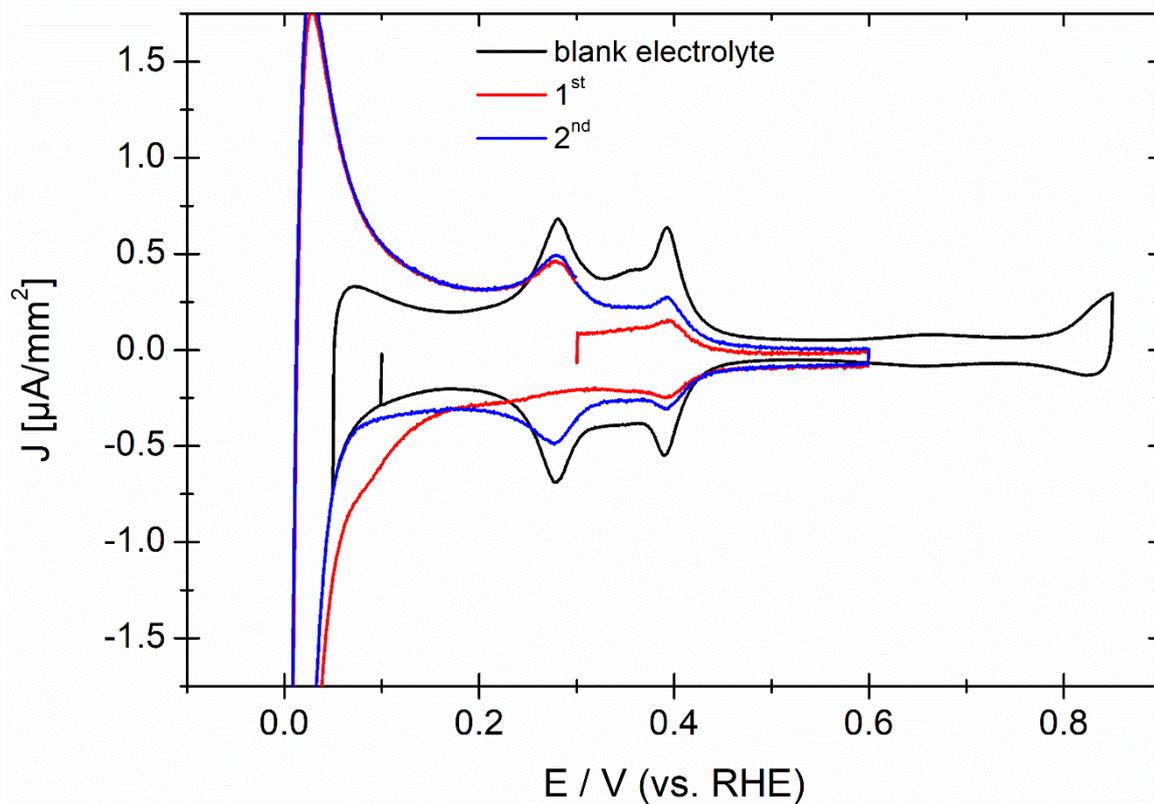


Figure S3: CV of Pt(510) (i.e. Pt[5(100)x(110)]) in 0.1 M H₂SO₄. Black: immediately after preparation; Red: first cycle after acetone adsorption at 0.3 V (vs RHE) and electrolyte exchange under potential control; blue second cycle. Sweep rate: 50 mV/s. Blue and red curves: the lower potential limit is 0.0 V (vs RHE). (CVs of Pt(510) (i.e. Pt[5(100)x(110)]) to 0 mV in the blank electrolyte can be found in the Supporting Information of Reference 10)

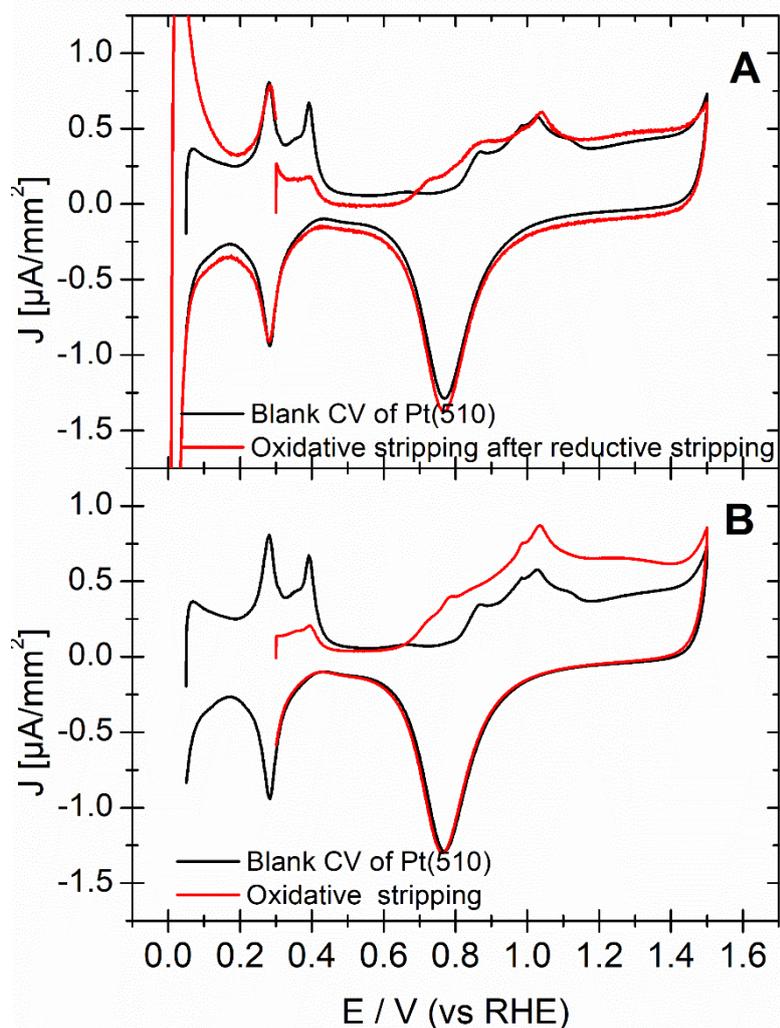


Figure S4: CV of Pt(510) (i.e. Pt[5(100)x(110)]) in 0.1 M H₂SO₄. Black: immediately after preparation; Red: Oxidative stripping experiment. A: Stripping experiment conducted immediately after the reductive stripping experiment of Figure S3. B: Stripping experiment conducted after preadsorption of acetone and electrolyte exchange. Sweep rate: 50 mV/s. Red curve in A: the lower potential limit is 0.0 V (vs RHE).

Acetone Adsorption at Pt(533) (i.e. Pt[4(111)x(100)])

The (533) (i.e. Pt[4(111)x(100)]) surfaces features (111) terraces and (100) step sites. Interestingly, stripping experiments conducted at the Pt(533) (i.e. Pt[4(111)x(100)]) electrode yield the same results as the Pt(331) (i.e. Pt[2(111)x(110)]) electrode. After exposure to an acetone containing electrolyte, acetone adsorbs to the (100) step sites. This is evident from the inhibited hydrogen adsorption at 0.28 V (vs RHE) (c.f. black and red curve in Figure S5). However, reductive stripping indicated by a peak at 0.1 V (vs RHE) removes the acetone adsorbate from the step sites. This is evident from the blue curve in Figure S5, where hydrogen adsorption is possible again. In the red curve of Figure S6A the potential is scanned for the first time after the reductive stripping experiment beyond 0.6 V (vs RHE). Compared to the black curve of Figure S6A no additional charge is passed in the potential region between 0.6 V and 0.9 V (vs RHE), suggesting that the adsorbates formed at the Pt(533) (i.e. Pt[4(111)x(100)]) electrode were stripped reductively in the previous experiment. That is, no decarbonylation of acetone that would result in the formation of CO is observed at the Pt(100) step sites. In the stripping experiment of Figure S6B the adsorbate formed at the Pt(533) (i.e. Pt[4(111)x(100)]) electrode is stripped in the potential region of platinum oxide formation, suggesting again that no decarbonylation of acetone proceeds at the Pt(100) step sites.

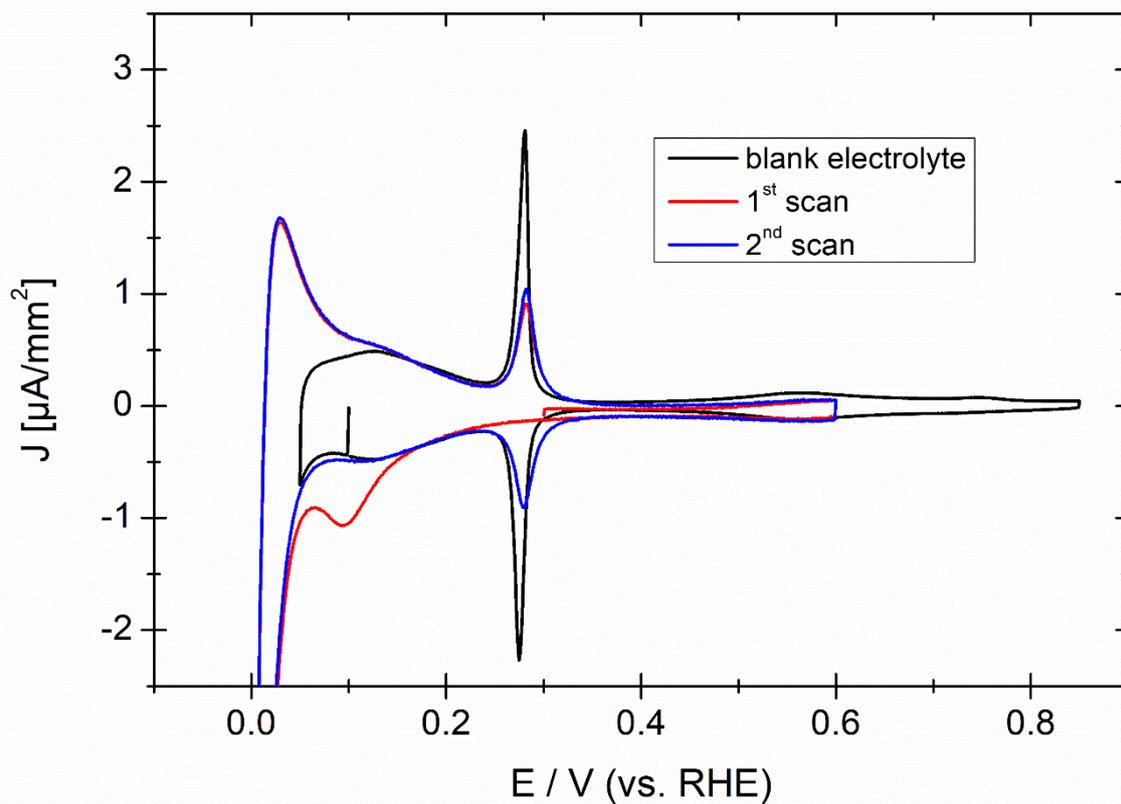


Figure S5: CV of Pt(533) (i.e. Pt[4(111)x(100)]) in 0.1 M H₂SO₄. Black: immediately after preparation; Red: first cycle after acetone adsorption at 0.3 V (vs RHE) and electrolyte exchange under potential control; blue second cycle. Sweep rate: 50 mV/s. Blue and red curves: the lower potential limit is 0.0 V (vs RHE).

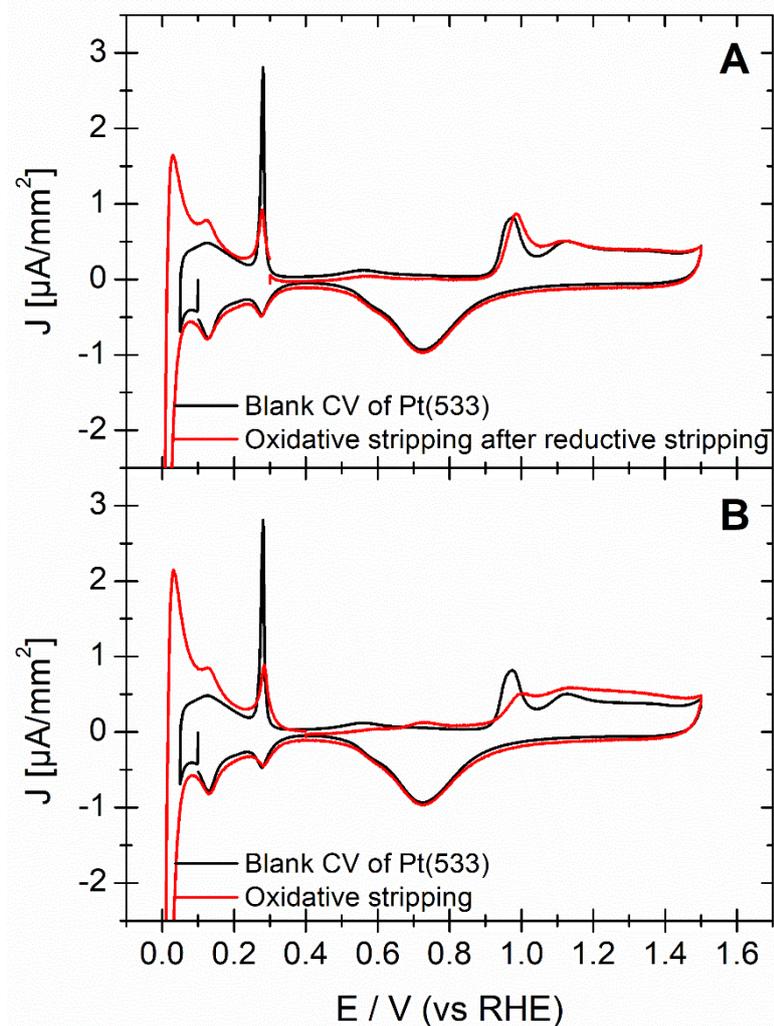


Figure S6: CV of Pt(533) (i.e. Pt[4(111)x(100)]) in in 0.1 M H_2SO_4 . Black: immediately after preparation; Red: Oxidative stripping experiment. A: Stripping experiment conducted immediately after the reductive stripping experiment of Figure S5. B: Stripping experiment conducted after preadsorption of acetone and electrolyte exchange. Sweep rate: 50 mV/s. Red curves: the lower potential limit is 0.0 V (vs RHE).

Additional FTIR-spectra

The spectra presented in Figure S7, S8 and S9 were recorded at Pt(100), Pt(110) and Pt(111) electrodes in an electrolyte of 0.1 M H₂SO₄ containing 10 mM of acetone. Before the electrode was pressed onto the prism to produce a thin layer, the electrodes were held for approximately 1 hour at 0.4 V (vs RHE). As the potential decreases from 0.4 V to 0.05 V (vs RHE) the spectra of Figures S7, S8 and S9 a bimodal band in the range of 2000 cm⁻¹ appears, which indicates the presence of adsorbed CO at all Pt basal planes at a potential of 0.4 V (vs RHE). Since the background spectrum is recorded at 0.4 V (vs RHE) it already features the absorbance due to adsorbed CO. When this background spectrum is subtracted from the spectrum recorded at 0.4 V (vs RHE), which features the CO band at the same wavenumber and with the same intensity, no band appears in the presented spectra. As the potential is altered the band of the adsorbed CO experiences a Stark shift to smaller wavenumbers. Therefore, subtraction of the background spectrum leads to negative band appears at 2020 cm⁻¹, 2025 cm⁻¹ and 2045 cm⁻¹ for Pt(100), Pt(110) and Pt(111), respectively, which is due to the band of CO in the background spectrum. Conversely, a positive band due to the Stark-shifted adsorption band appears on the lower wavenumber side of the spectrum. As the potential is stepped in positive direction again CO is oxidized to CO₂, which is indicated by the appearance of a band 2345 cm⁻¹ and a negative band at 2020 cm⁻¹, 2025 cm⁻¹ and 2045 cm⁻¹ for Pt(100), Pt(110) and Pt(111), respectively. The formation of CO₂ starts at around 0.5 V (vs RHE), which is clear for Pt(110) and Pt(111) (Figures S8 and S9). However, in Figure S7 a band at 2345 cm⁻¹ appears already at 0.3 V in the negative going sweep. These bands are assigned to the presence of CO₂ in the thin layer gap prior to the experiment: due to the drift of the thin layer, the background spectrum does not account for the background CO₂ properly anymore. However, up to a potential of 0.3 to 0.4 V this increase of the band intensity at 2345 cm⁻¹ is rather gradual. At more positive potentials the band intensity increases rapidly. This indicates that the the electrochemical stripping of CO to CO₂ occurs also at Pt(100) electrodes at potentials of approximately 0.4 to 0.5 V.

The spectra in Figure S7, S8 and S9 are insofar different from the spectra presented in Figure 7 in the main article as they indicate the formation of CO at al Pt basal planes. This would suggest that the decarbonylation of acetone is not limited to extended Pt(100) terraces. However, in order to create a thin layer between Pt single crystal and CaF₂ prism the electrode is pressed with considerable force onto the surface of the prism. This results over time in defect-rich single crystals and it is likely that the CO observed in the spectra of Figures S7, S8 and S9 formed on defects sites from which it migrates across the entire surface. This interpretation appears likely as we do not observe the formation of CO in the electrolyte exchange experiments conducted at bead type Pt(331) (i.e. Pt[2(111)x(110)]) and Pt(533) (i.e. Pt[4(111)x(100)]) electrodes, which feature far less defects than the disc shaped single crystals used in for the FTIR spectra.

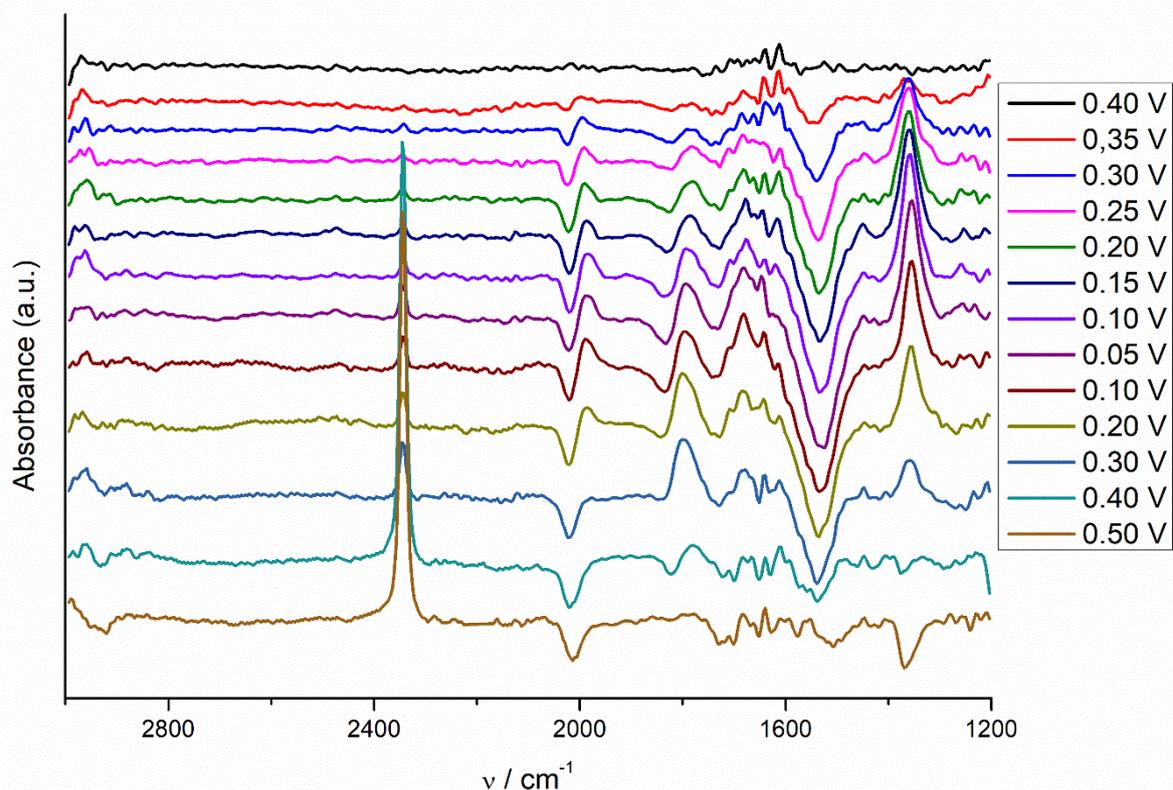


Figure S7: Background and baseline corrected FTIR spectra obtained at a Pt(100) electrode in an electrolyte of 0.1 M H₂SO₄ containing 10 mM acetone. Before the electrode was pressed onto the prism to create the thin layer gap, it was held for 50 min at 0.4 V (vs RHE). The background was

collected at 0.4 V (vs RHE). Spectra were collected in the sequence indicated in the figure (top to bottom).

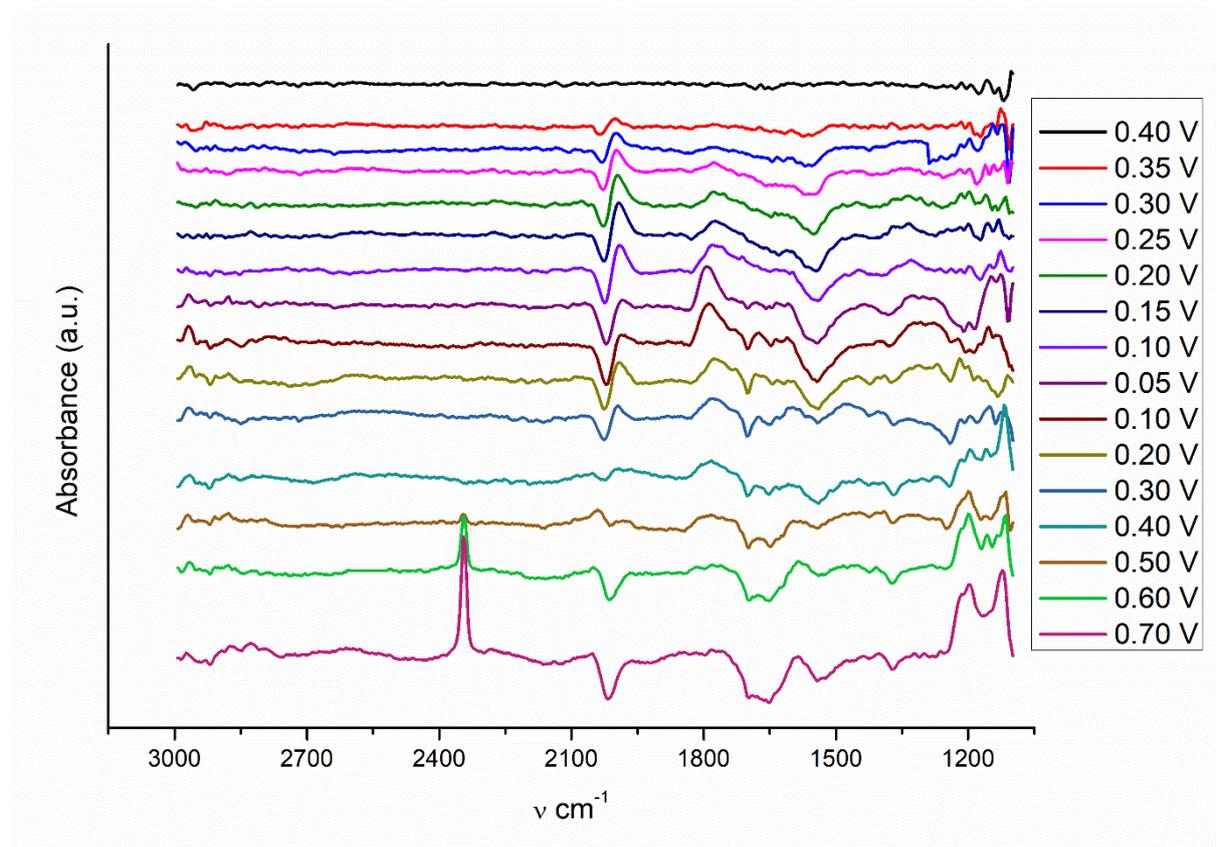


Figure S8: Background and baseline corrected FTIR spectra obtained at a Pt(110) electrode in an electrolyte of 0.1 M H_2SO_4 containing 10 mM acetone. Before the electrode was pressed onto the prism to create the thin layer gap, it was held for 50 min at 0.4 V (vs RHE). The background was collected at 0.4 V (vs RHE). Spectra were collected in the sequence indicated in the figure (top to bottom).

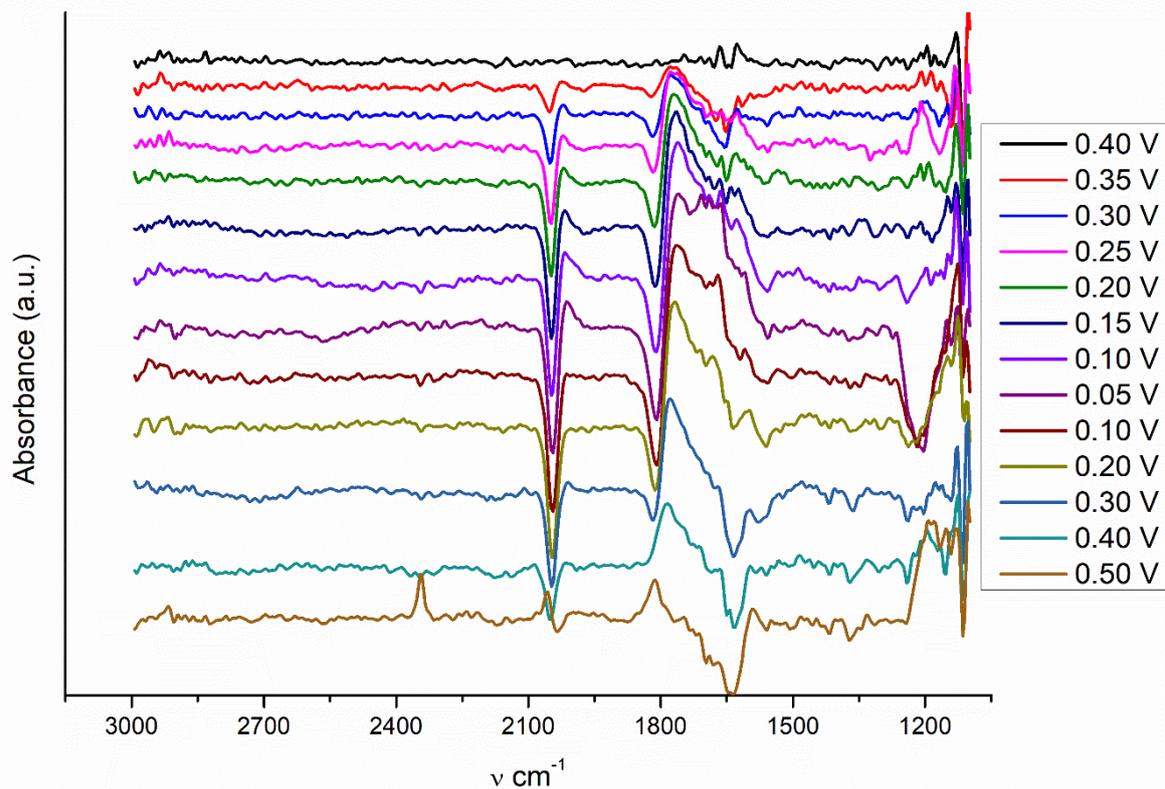


Figure S9: Background and baseline corrected FTIR spectra obtained at a Pt(111) electrode in an electrolyte of 0.1 M H_2SO_4 containing 10 mM acetone. Before the electrode was pressed onto the prism to create the thin layer gap, it was held for 50 min at 0.4 V (vs RHE). The background was collected at 0.4 V (vs RHE). Spectra were collected in the sequence indicated in the figure (top to bottom).