

Supporting Information

Electrochemical oxidation of isopropanol on platinum-ruthenium nanoparticles studied with real-time product and dissolution analytics

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1. Acetone detection with EC-RTMS

DART ionization mechanism in positive mode is mainly based on proton transfer reaction.¹⁻² This ion source has a moderately soft mechanism of ionization, which means that the extent of the fragmentation is fairly low. However, when the concentration of species in the ionization region is high, even mild fragmentation can lead to fragment signals of significant intensity. For instance, in the case of 2-propanol (IPA) oxidation, IPA gets ionized in the ionization region and it produces fragments which may overlap with acetone (ACE) fragments. According to the NIST database,³ which may be relevant for high ionization energy (70 eV) but is still qualitatively valid under our conditions, one of the fragments of IPA appears at the mass range 59.0-59.1 which increases the background of the protonated acetone at the same mass range. On the other hand, the high proton affinity of acetone (812 kJ mol⁻¹) versus water (691±3 kJ mol⁻¹) and the large equilibrium constant of the protonation reaction make the instrument very sensitive towards acetone. These lead to an overload of the microchannel plate (MCP) detector of the DART-TOF-MS instrument at the mass range 59.0-59.1, when excessive amounts of acetone are formed from IPA oxidation on high surface area PtRu/C catalysts and there is additionally high background signal from IPA fragmentation. Therefore, the protonated acetone-¹³C at the m/z= 60.0-60.1, with corresponding structure of [¹³C¹²C₂H₆O+H]⁺, was instead selected as the representative detection mass for acetone, with an excellent linearity range.

2. Electrochemical removal of adsorbates before the measurements

All Pt-based catalysts deactivate during the oxidation of 2-propanol, because of the adsorption of intermediates (likely adsorbed acetone) at room temperature. To obtain reproducible data, a procedure was introduced prior to each measurement (e.g. linear sweep voltammetry) to remove surface species that were already adsorbed. We intentionally did not apply potential scans to high potentials (cleaning/activation cycles) to prevent excessive ruthenium dissolution which would result in compositional changes of the nanoparticles. Instead, we applied a potential of 0 V_{RHE} for a certain time before starting each electrochemical experiment, which leads to the reduction of surface adsorbates.⁴ Even though this may not lead to an ideally adsorbate-free surface, it was still an effective procedure to obtain reproducible results by reaching a low equilibrium coverage of adsorbates. As it is exemplified for polycrystalline platinum in Figure S1, a potential step to +0.6 V_{RHE} leads to a rapid increase of the intensity for acetone, but the signal gradually decreases with time due to the accumulation of surface adsorbates during the reaction. When a potential of 0 V is applied for 2 min and the same step to +0.6 V_{RHE} is repeated, the signal intensity for acetone can be reproduced.

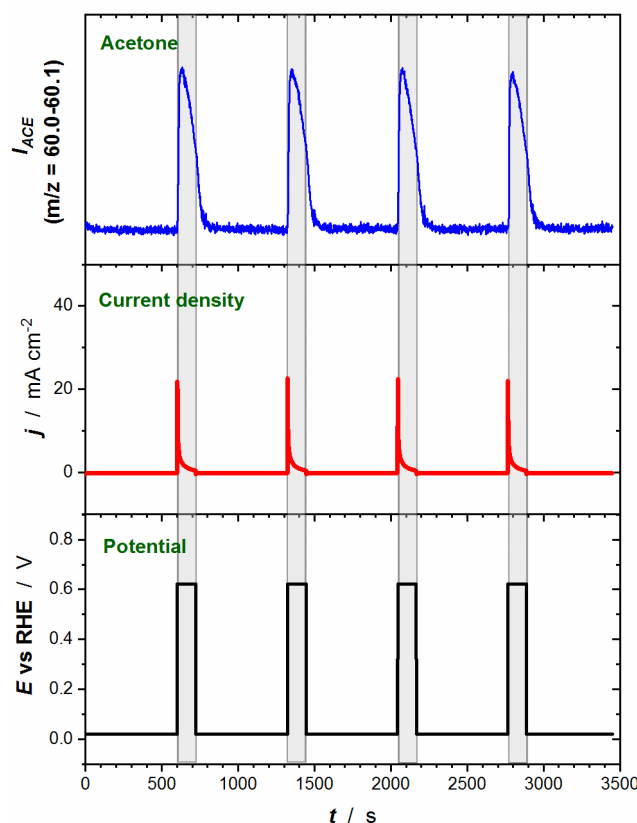


Figure S1. An exemplary representation of the electrochemical protocol for removal of adsorbates from the electrode. Potential step measurements were done on a Pt polycrystalline disk in 0.2 M IPA+ 0.1 M HClO₄. Signal of ACE (blue), current density (red) and potential (black) were plotted versus time. The potential was alternately switched from +0.02 V_{RHE} for 600 s to +0.62 V_{RHE} for 120 s.

3. Carbon corrosion

To understand whether the detected CO₂ during the IPA oxidation reaction on Pt_(1-x)Ru_x/C catalysts originates indeed from IPA oxidation or from the corrosion of the carbon support of nanocatalysts, the LSV experiment as in Figure 1 was repeated with the same catalyst loading in the supporting electrolyte only, i.e. in the absence of IPA, and the I_{CO_2} was recorded at the same time. Figure S2 indicates that the amount of produced CO₂ on either Pt/C or Pt_{0.5}Ru_{0.5}/C is higher when the electrolyte contains IPA compared to the electrolyte free of IPA, where CO₂ is attributed exclusively to carbon corrosion. Assuming that the presence of IPA does not induce the corrosion of the catalyst support, this comparison reveals that the major part of the detected CO₂ arises from the oxidation of IPA.

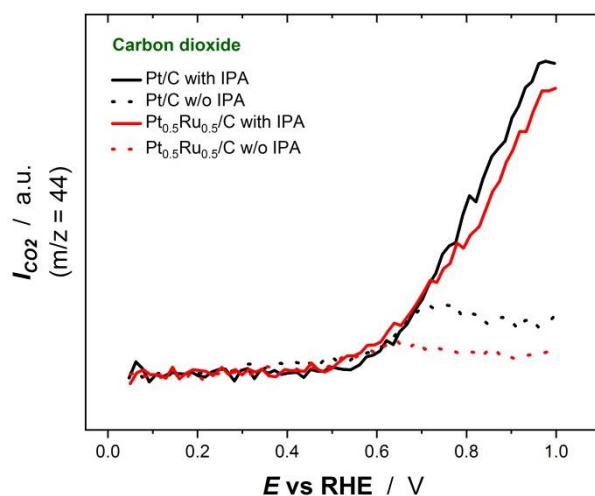


Figure S2. Simultaneously recorded ion current of CO₂ during the linear sweep voltammetry experiments on Pt/C (black) and Pt_{0.5}Ru_{0.5}/C (red). Ion currents were obtained in the presence (solid curves) and absence (dotted curves) of 0.2 M of IPA, in 0.1 M HClO₄ supporting electrolyte at the scan rate of 5 mV s⁻¹.

4. Ruthenium activity for the oxidation of 2-propanol

Figure S3 shows voltammograms obtained under hydrodynamic conditions with platinum or ruthenium as the working electrode, in the presence or absence of 2-propanol. When polycrystalline platinum is used as the working electrode (black curves), the IPA oxidation starts at ca. +0.35 V_{RHE} and the current is maximized at ca. +0.75 V_{RHE}. For a concentration of IPA of 0.2 M, the peak current is ca. 14 mA cm⁻², significantly different from the background current in the IPA-free 0.1 M HClO₄ electrolyte. On the contrary, when a polished ruthenium electrode is used, the current is practically the same independent of the presence or absence of IPA from the solution. This indicates that pure ruthenium is inactive for the oxidation of IPA.

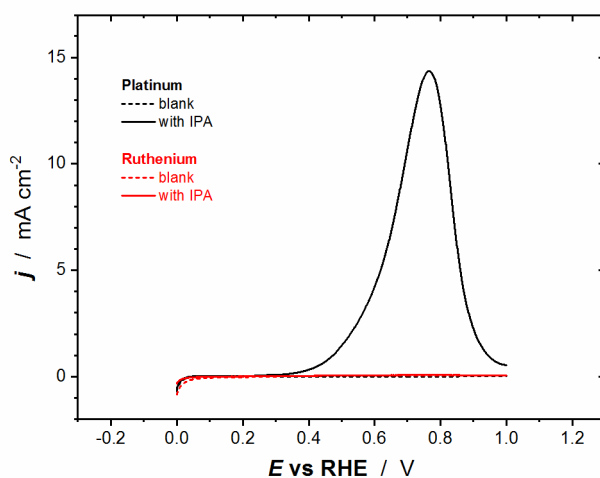


Figure S3. Linear sweep voltammograms on Pt (black) and Ru (red) polycrystalline disks in the presence (solid) or absence (dashed) of 0.2 M IPA. The supporting electrolyte was 0.1 M HClO₄. The voltammograms were recorded starting at 0 VRHE and scanning to the positive direction of the potential with 5 mV s⁻¹. The electrode was always rotated with 900 rpm.

5. Impact of the upper potential limit on the dissolution of platinum and ruthenium

Figure S4 shows the total amount of dissolved ruthenium or platinum that was detected during a potential sweep with 10 mV s^{-1} to different upper potential limits (UPLs), in the presence of IPA. The amount was calculated by integrating the profile of the dissolution rate over time. For all catalysts tested, the amount of dissolved metal increases exponentially with the increase of the UPL. For the higher UPLs used, the amount of dissolved ruthenium increases in catalysts with higher ruthenium content. This is related to the fact that the platinum loading was always constant for all catalysts, so the total mass of ruthenium used in the catalyst film was higher e.g. for $\text{Pt}_{0.33}\text{Ru}_{0.67}/\text{C}$ compared to $\text{Pt}_{0.5}\text{Ru}_{0.5}/\text{C}$.

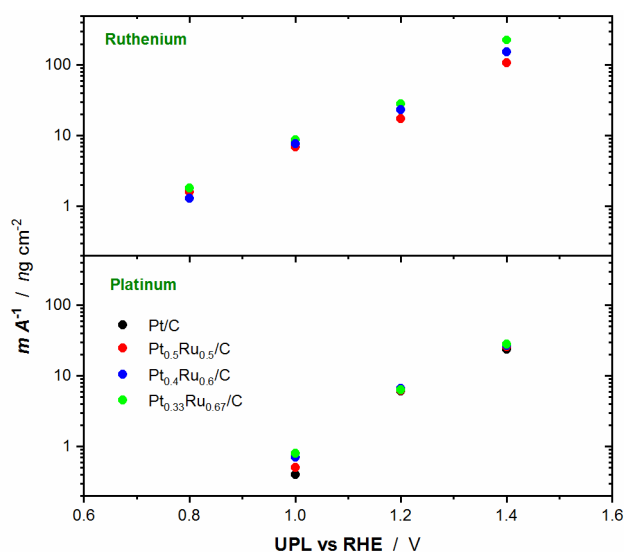


Figure S4. Total amount of ruthenium or platinum dissolved during one cyclic voltammogram from $0.0 \text{ V}_{\text{RHE}}$ to a different upper potential limit, with 10 mV s^{-1} , in a $0.1 \text{ M HClO}_4 + 0.05 \text{ M IPA}$ electrolyte.

6. Accelerated stress tests

The $\text{Pt}_{0.5}\text{Ru}_{0.5}/\text{C}$ catalyst was subjected to accelerated stress tests (ASTs), which consisted of 1000 cycles with 0.5 V s^{-1} from $0.0 \text{ V}_{\text{RHE}}$ to an upper potential limit of 0.6 or 0.8 or $1.0 \text{ V}_{\text{RHE}}$, using every time a new catalyst film. The dissolution rate of ruthenium and platinum was monitored in parallel with ICP/MS, even though it is not possible to resolve the mass signal between the individual scans due to the very high scan rate (Figure S5). Both ruthenium and platinum were stable during potential cycling in the range 0.0 - $0.6 \text{ V}_{\text{RHE}}$, however, ruthenium dissolution was detected when the UPL was $0.8 \text{ V}_{\text{RHE}}$. The ruthenium dissolution rate was decreasing with the number of cycles likely due to the depletion of ruthenium atoms from the surface of the particles. The integration of the dissolution rate versus time curve yields the total amount of ruthenium dissolved during the AST (2.3 ng), if the area of the electrode is additionally taken into account. The ruthenium dissolution rate is strongly enhanced, and platinum dissolution is also detected, both decreasing with time, if a UPL of $1.0 \text{ V}_{\text{RHE}}$ is used, yielding eventually 21.0 ng and 0.2 ng of dissolved ruthenium and platinum, respectively, after the completion of 1000 cycles. The amount of dissolved ruthenium during this degradation protocol corresponds to 5% of the total ruthenium present initially in the catalyst film, whereas the amount of platinum dissolved is negligible. If the latter treatment (AST in the potential region 0.0 to $+1.0 \text{ V}_{\text{RHE}}$) is complemented with product analysis, a gradual increase in the formation rate of carbon dioxide and acetone is observed (Figure S6).

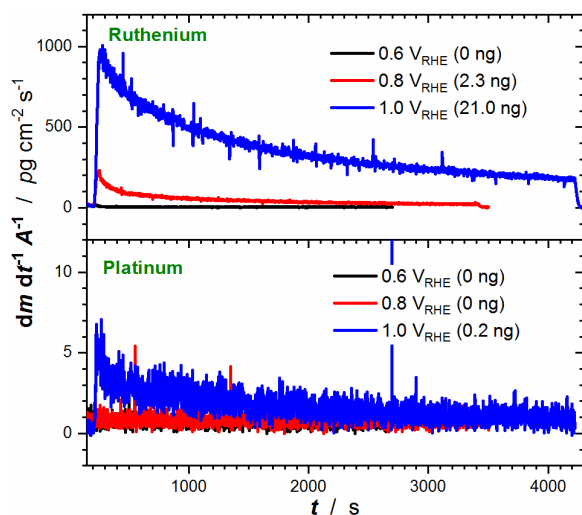


Figure S5. Dissolution profiles for platinum and ruthenium, during ASTs from $0.0 \text{ V}_{\text{RHE}}$ to different UPLs with 0.5 V s^{-1} , with $\text{Pt}_{0.5}\text{Ru}_{0.5}/\text{C}$, in a $0.1 \text{ M HClO}_4 + 0.05 \text{ M IPA}$. The number in brackets indicate the total amount of metal dissolved throughout the entire AST (calculated from integration of the dissolution rate-time curve).

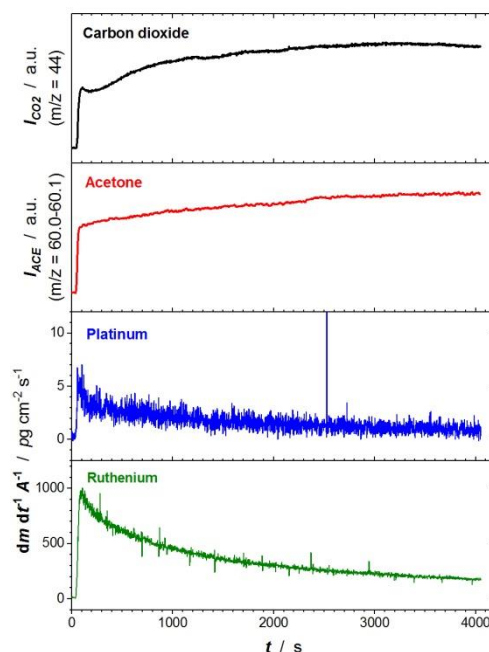


Figure S6. Same as in Figure S5 for the UPL = $+1.0 \text{ V}_{\text{RHE}}$, with additionally the simultaneous detection of acetone and carbon dioxide.

7. Quantification of products of IPA oxidation during “steady-state” electrolysis

To quantitatively determine the selectivity of the IPA oxidation to ACE, “steady-state” electrolysis experiments were performed. The analysis of products during classical constant potential electrolysis is challenging because the activity at a constant potential decays with time (see Figure 2 of the manuscript) so the amounts of formed products in solution are relatively low, whereas the detection of gaseous CO₂ with GC depends on the time of sampling. To circumvent the problems introduced by the catalyst deactivation, the constant electrolysis potential was interrupted after 10 minutes by a short potential step at 0 V_{RHE} of 30 seconds to remove surface adsorbates and reactivate the catalyst; then the electrolysis step was repeated again for another 10 minutes. In the long term, this protocol ensures sufficient amount of products formed, so quantification of dissolved acetone is possible. The “steady-state” electrolysis experiments were performed on Pt_{0.5}Ru_{0.5}/C in triplicate for each potential (0.6 or 0.9 V_{RHE}). The electrolysis experiments were performed (in triplicate for each potential, 0.6 V_{RHE} or 0.9 V_{RHE}) on Pt_{0.5}Ru_{0.5}/C and the faradaic efficiencies for the two products, namely ACE and CO₂ were calculated by determining the amount of formed product with the analytical techniques described in the experimental section.

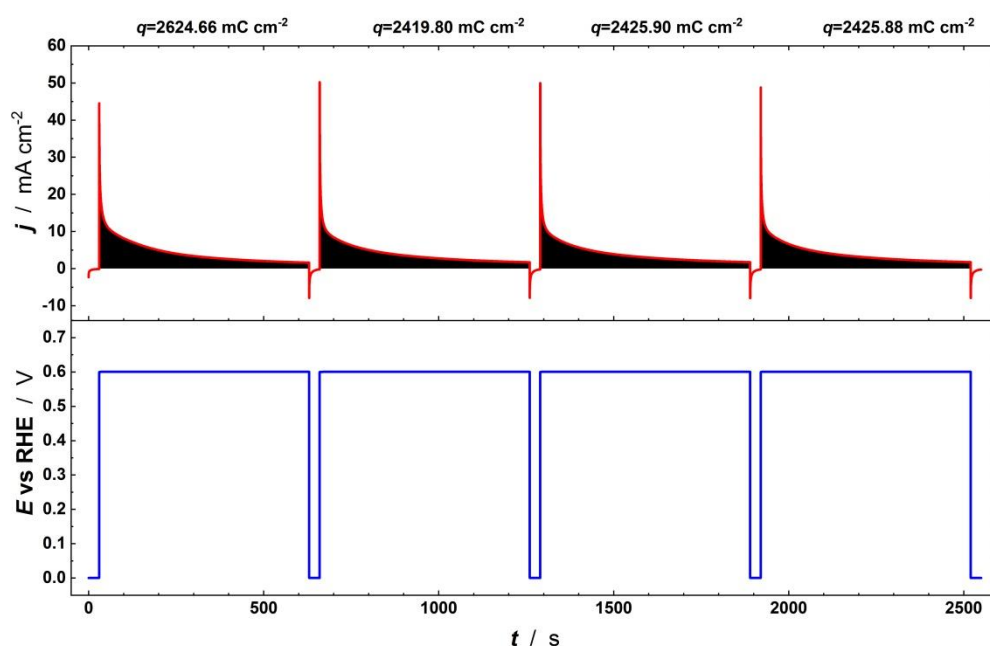


Figure S7. Electrochemical protocol during “steady-state” electrolysis for the quantification of the products of the IPA oxidation reaction. The protocol consists of 600 s potential steps (here shown for +0.6 V_{RHE}) interrupted by step potentials at 0 V_{RHE} for 30 s to remove adsorbed species and regenerate the surface. Electrolyte: 0.1 M HClO₄ + 0.2 M IPA. The integrated area of the current-time transient is highlighted in black.

Figure S7 shows an example of the described protocol for electrolysis at 0.6 V_{RHE} (where 2-propanol is oxidized to acetone) and surface “cleaning” at 0 V_{RHE} where the adsorbed acetone is reductively

removed.. This oxidation-reduction cycle was repeated 12 times (shown only 4 times in figure S7 for simplicity), resulting in a total length of 120 minutes of oxidation of IPA. The recorded current versus time curve was integrated for each 10-minute potential step, to determine the associated oxidation charge (see Figure S7) as the sum of the individual charges at each step, which was necessary for the calculation of the faradaic efficiency.

8. Characterization of catalysts with EDX and XPS

X-ray photoelectron spectroscopy (XPS) was used to measure survey spectra (0-1100 eV) on a PHI quantera II x-ray scanning microprobe system, at a pass energy of 280 eV and a resolution of 1 eV. An area with 200 μm diameter was probed by an Al K α x-ray beam generated with 50 W and 15 kV accelerating voltage, while the dwell time per data point was 1 s. Using CasaXPS (V. 2.3.22), the survey spectra were then calibrated to the C peak at 284.8 eV and peaks were integrated using instrument-specific relative sensitivity factors and Shirley-type backgrounds. Compositions were also measured by energy-dispersive x-ray spectroscopy (EDX) mapping of a 100 x 100 μm area with a 64x64 pixel resolution. Each pixel was measured for 50 ms and the entire area was passed twice. The Phenom-World, Phenom XL scanning electron microscope (SEM) was operated at 15 kV accelerating voltage backscattering detector at a pressure of 1 Pa.

All bimetallic nanoparticles were characterized by XPS and EDX. The gray line indicates the nominal catalyst composition, according to the information from the catalyst manufacturer. The ruthenium composition determined by XPS is lower than that obtained from EDX, indicating that the surface of the particles is enriched with platinum. In detail, the ruthenium composition from XPS was 35.1%, 43.5%, and 49.0%, while from EDX it was 54.8%, 64.6%, and 71.5%, for Pt_{0.5}Ru_{0.5}/C, Pt_{0.4}Ru_{0.6}/C and Pt_{0.33}Ru_{0.67}/C, respectively.

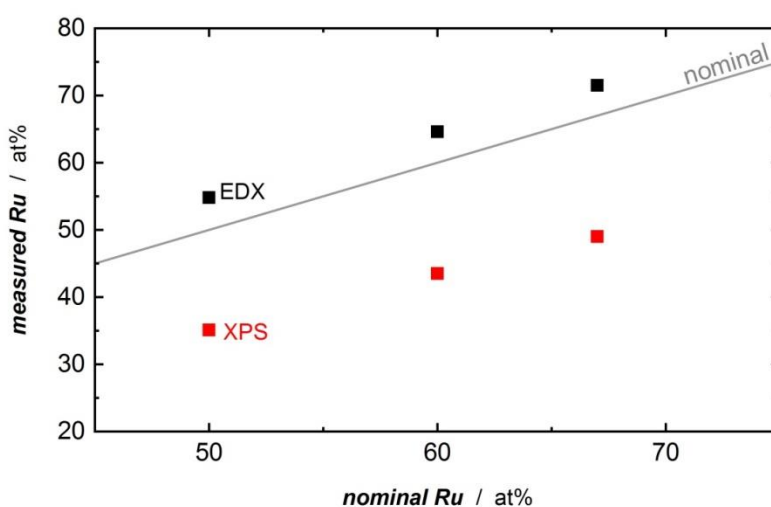


Figure S8. The atomic Ru concentrations for the three Pt_(1-x)Ru_x/C ($x=0.5, 0.6$, and 0.67) catalysts used in this study. The gray line refers to the expected concentration of Ru based on the supplier information and the black and red squares represent the measured ruthenium concentration with EDX and XPS respectively in the bimetallic catalyst.

References

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