*Supporting Information*

# Operando DRIFTS and DFT study of propane dehydrogenation over solid and liquid supported $Ga_xPt_y$ catalysts

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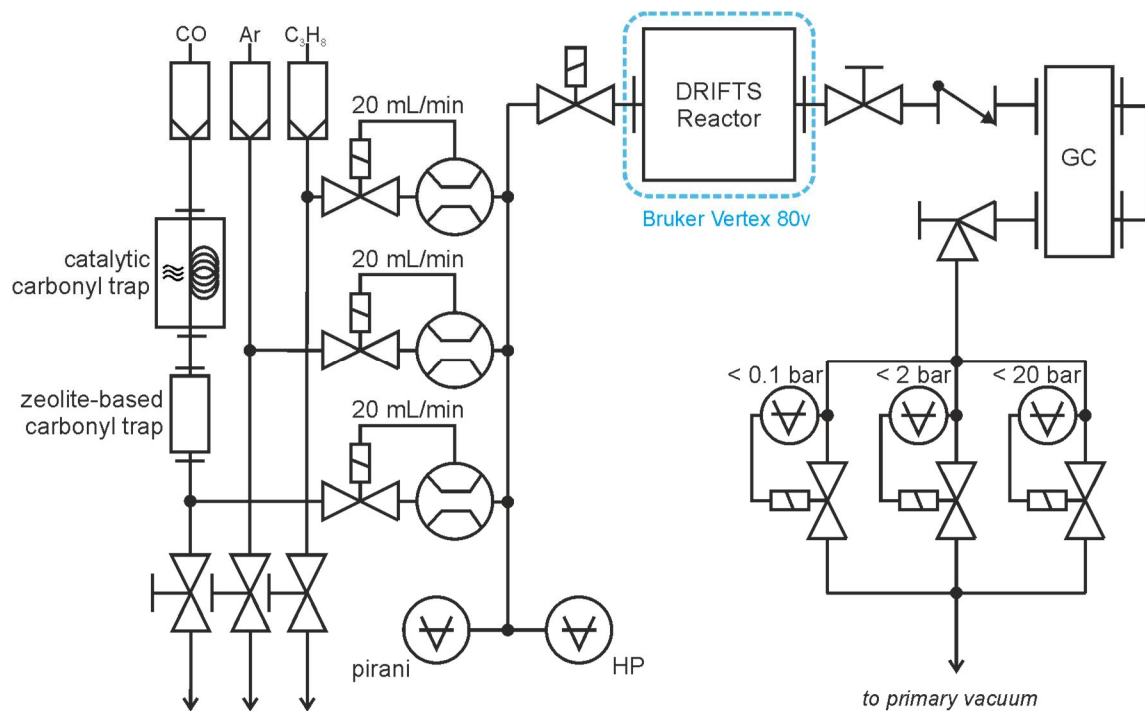
**Reactor setup**



**Figure S1:** Schematic representation of the experimental setup used in this study.

**Subtraction of gas phase signals**

To improve the quality of the spectra, residual CO gas phase rotational-vibrational peaks were removed in two steps. The procedure was previously applied by Kaftan et al.[1] At first, the high frequency part of the CO gas phase was removed by Fourier Transformation (FT), application of a low-pass filter and reverse FT back to the frequency domain. This procedure was performed with the averaged spectra obtained in the operando experiment ($n_{exp}$) and a selected reference spectrum showing exclusively the CO gas phase without any adsorbates ($ref$). The resulting spectra show no gas phase features in the region of the P- and R- branches of the CO gas phase spectrum. Secondly, the remaining signals were subtracted from $n_{exp}$ with the help of $ref$ and a scaling factor:

$$n_{subtracted} = n_{exp} - x * ref$$

The scaling factor was selected for spectrum $n_{exp}$ such, that the signal intensity of the CO gas phase peaks was minimized. Figure S2 illustrates the procedure for two selected spectra.
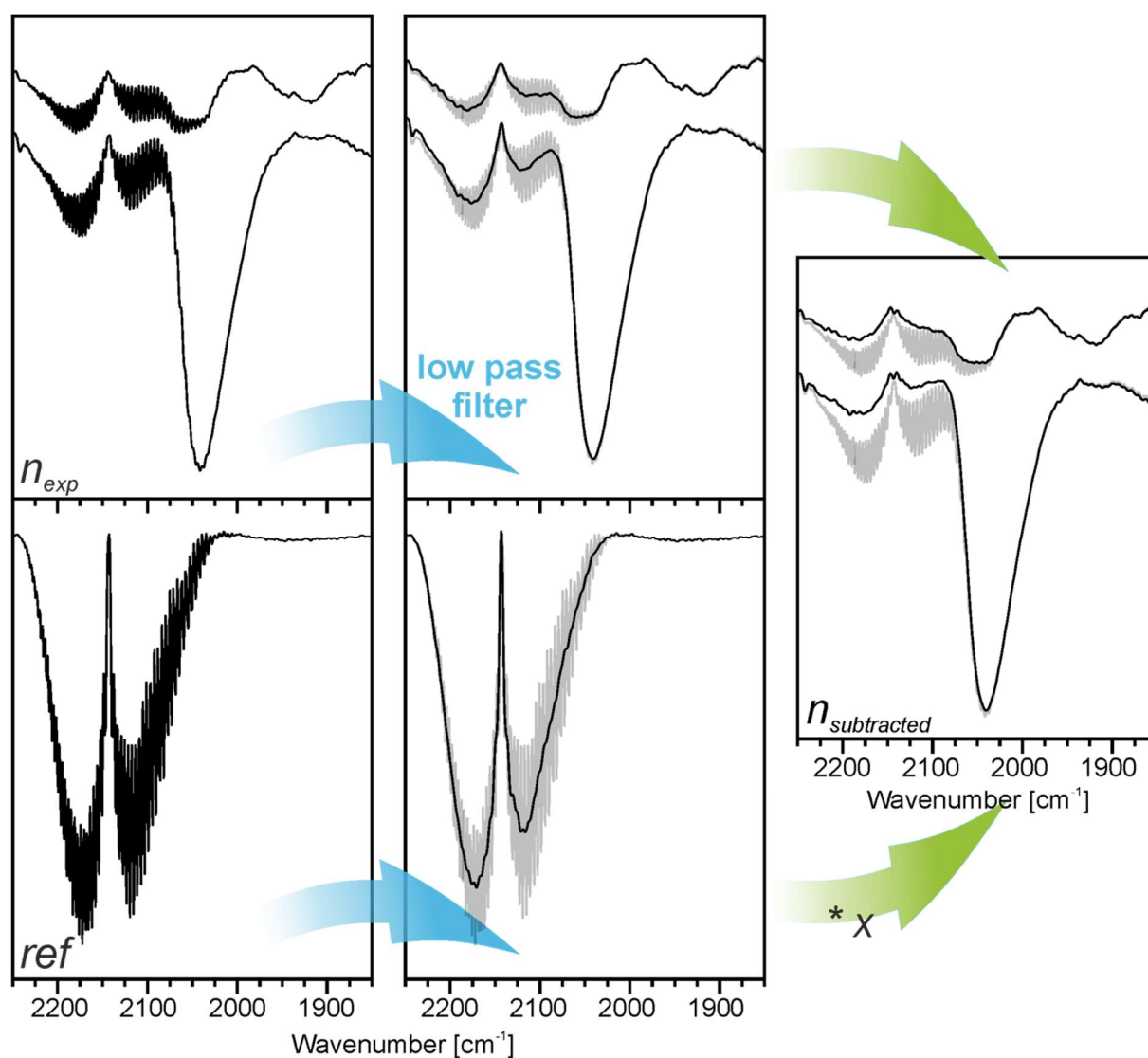


**Figure S2:** Steps during removal of residual CO gas phase signals from spectra obtained during the operando experiment.
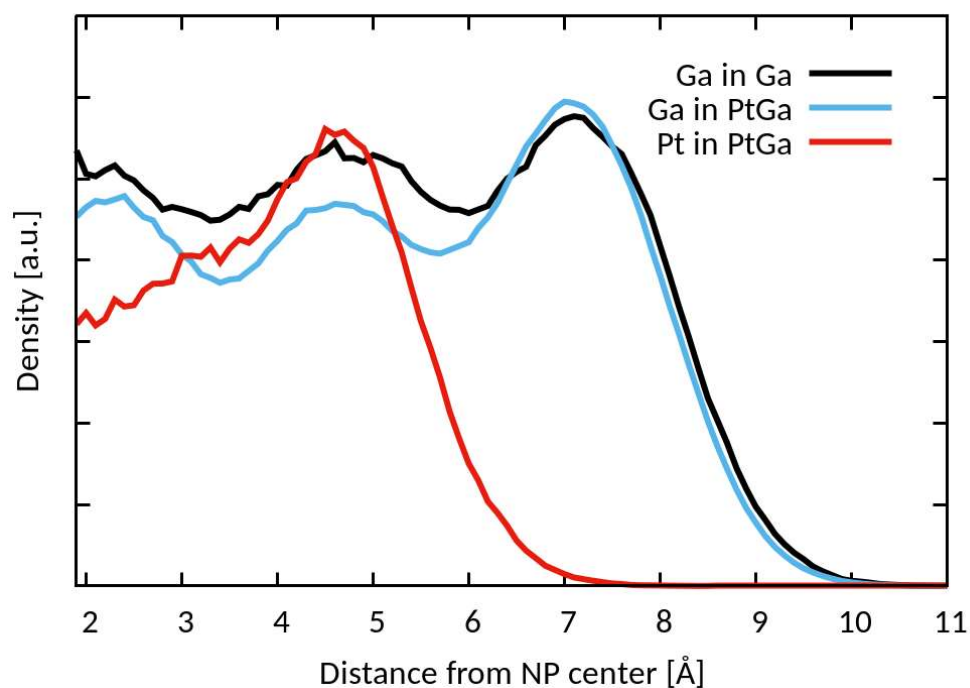
**DFT calculations**



**Figure S3:** Density (a.u., arbitrary units) of Ga in $Ga_{135}$ (black) and Ga (blue) as well as Pt (red) in $Ga_{125}Pt_{10}$ NPs as function of the distance from the NP center as obtained in *ab initio* molecular dynamics (AIMD) simulations. The Pt density is scaled such that it is comparable to the Ga density.
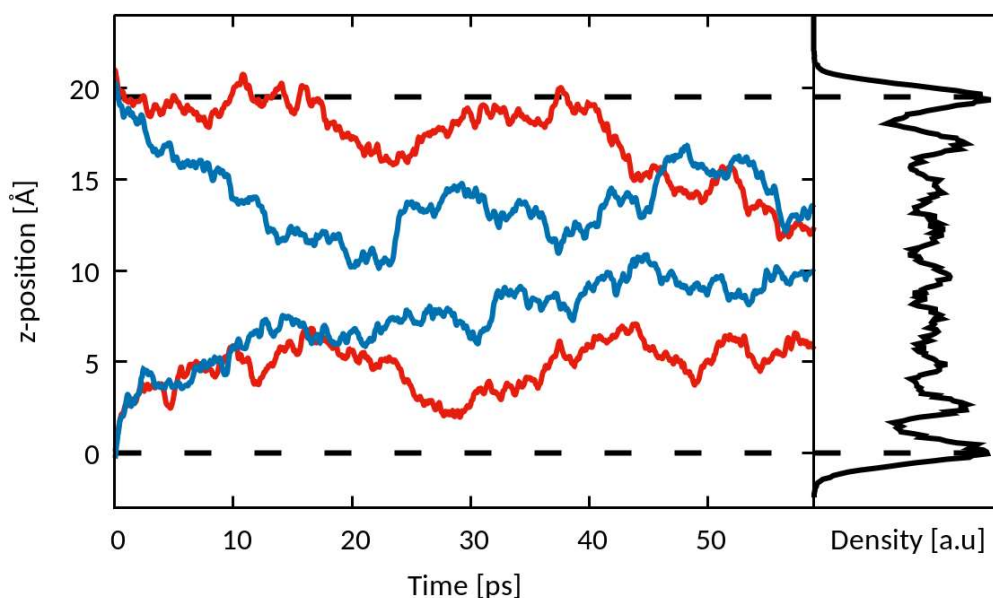


**Figure S4:** Time evolution of z-position of selected Pt atoms as obtained in AIMD simulations. Two trajectories are shown (red and blue) each with one Pt initially located at the top surface of the slab, one at the bottom surface. The Ga density is shown for orientation. Dashed lines mark the first maximum in the Ga density.
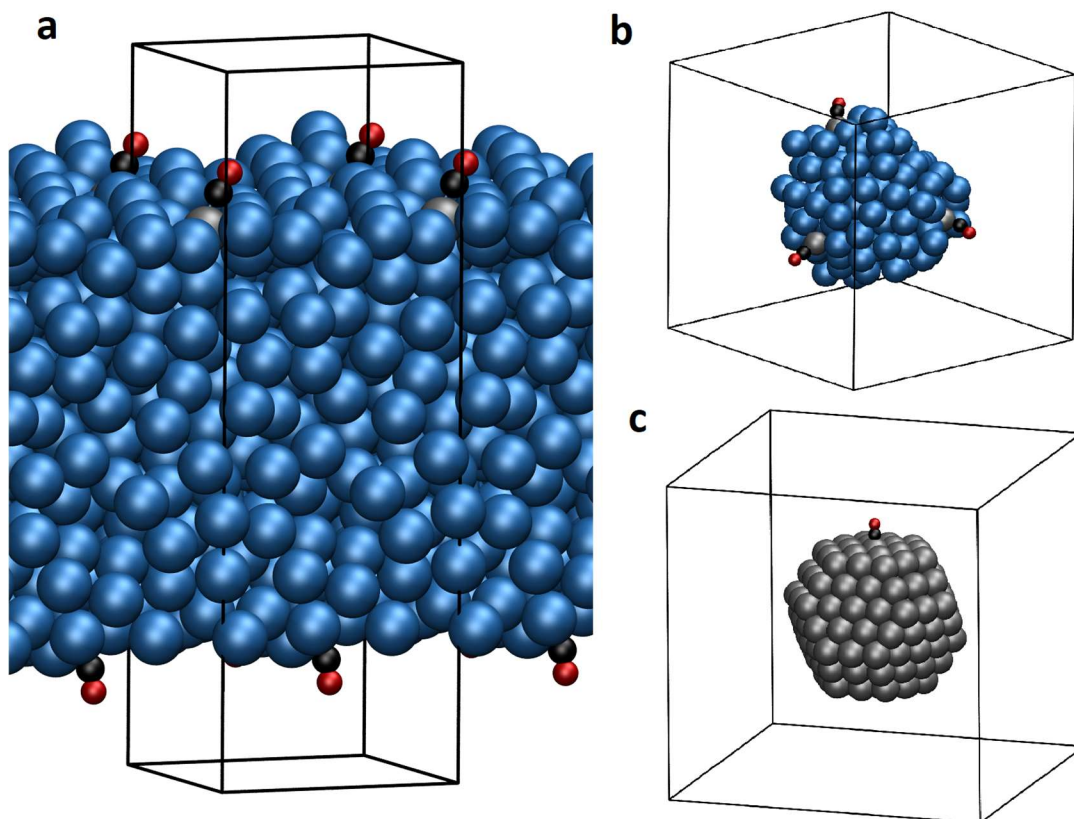
**Figure S5:** Liquid slab (a) and nanoparticle (b,c) models used in DFT calculations. Ga, Pt, C and O are depicted in blue, silver, black and red, respectively.
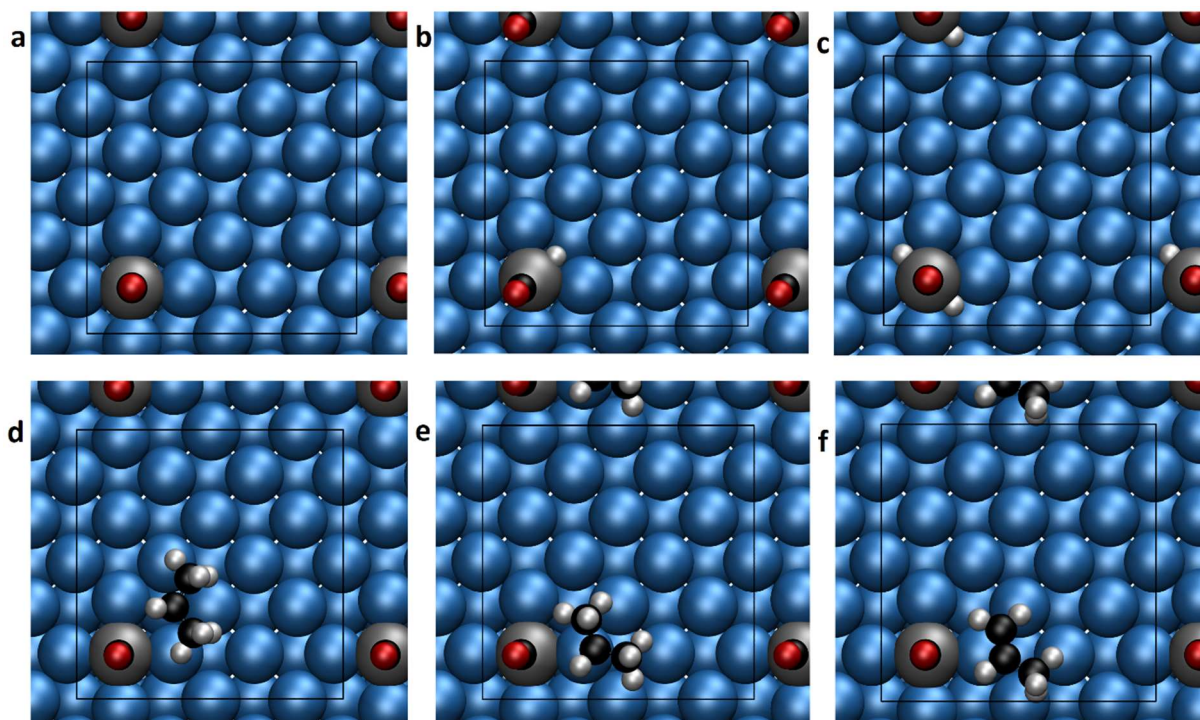


**Figure S6:** Adsorption geometries for CO adsorption (a) with different co-adsorbates (b-f) on solid fcc-Ga with additional Pt adsorbed in hollow positions. The co-adsorbates are one H (b), two H (c), propane (d), propyl (e) and propene (f).

**GC – Analysis of experimental errors**

The uncertainty of the selectivity values ($\sigma_{sel}$) depends on the conversion at the respective temperature. At small conversions the amount of products formed is very low which naturally results in large values of $\sigma_{sel}$. In this study, we assume that $\sigma_{sel}$ is inversely proportional to the conversion.

We include this dependency by introducing a conversion dependent factor $\frac{1}{f}$ with f being the normalized conversion: $f = \frac{conversion}{\min(conversion)}$ . Thus, $\frac{1}{f}$ takes into account the dependence on conversion and is multiplied with the maximum standard deviation of the selectivity found in the experiment $\max(dev_{sel})$ and a scaling factor of 100 to yield $\sigma_{sel}$ in %:

$$\sigma_{sel}[\%] = \max(dev_{sel}) * \frac{1}{f} * 100$$

**GC – correction of peak areas by reference experiment**

As mentioned in the manuscript, the GC peak areas were corrected to remove effects of gas feed impurities and conversion of propane at the reactor walls. An example of the procedure is shown in Figure S3. The peak areas obtained from the experiment with pristine $Al_2O_3$ $A(ref)$ were used as a "baseline". In case of all products (like propene), $A(ref)$ was subtracted from the integrated peak areas obtained during investigation of a metal-containing sample $A(metal)$:

$$A_{product}(corrected) = A_{product}(metal) - A(ref)$$

As shown in Figure S3, a slightly modified procedure must be used to correct the area of the propane peak, as the above formula would lead to small, negative peak areas. Here, the peak area obtained at 200 °C at the beginning of the experiment $A_{C3H8,200}(metal)$ reflect best the initial state of the catalyst, as no deactivation has occurred yet. Therefore, the first data point is used as a reference point:

$$A_{C3H8}(corrected) = A_{C3H8}(metal) - A(ref) + A_{C3H8,200}(metal)$$

By using $A(corrected)$ for calculations, the obtained conversion is slightly lower as compared to the non-corrected values. The corrected conversion now exclusively reflects the performance of the catalyst. In particular, conversion at low temperatures is close to zero.
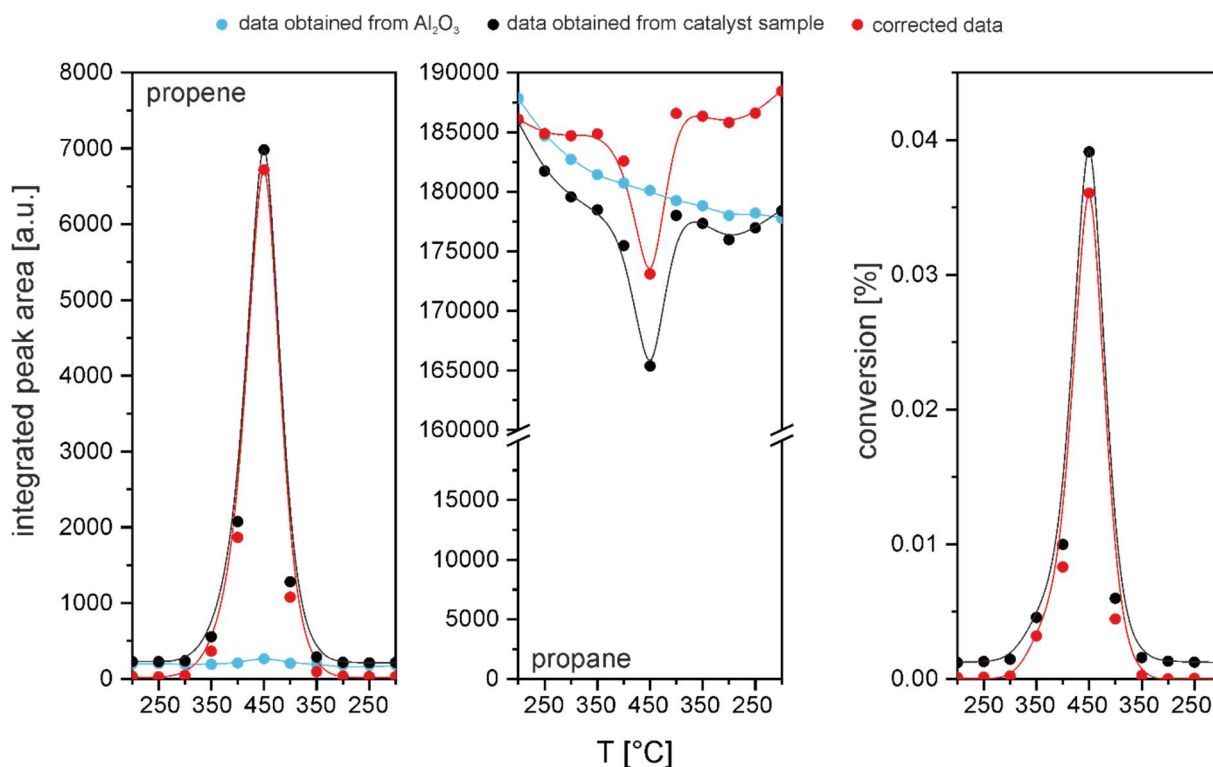
**Figure S7:** Example for the correction of the GC peaks with the help of the reference experiment.
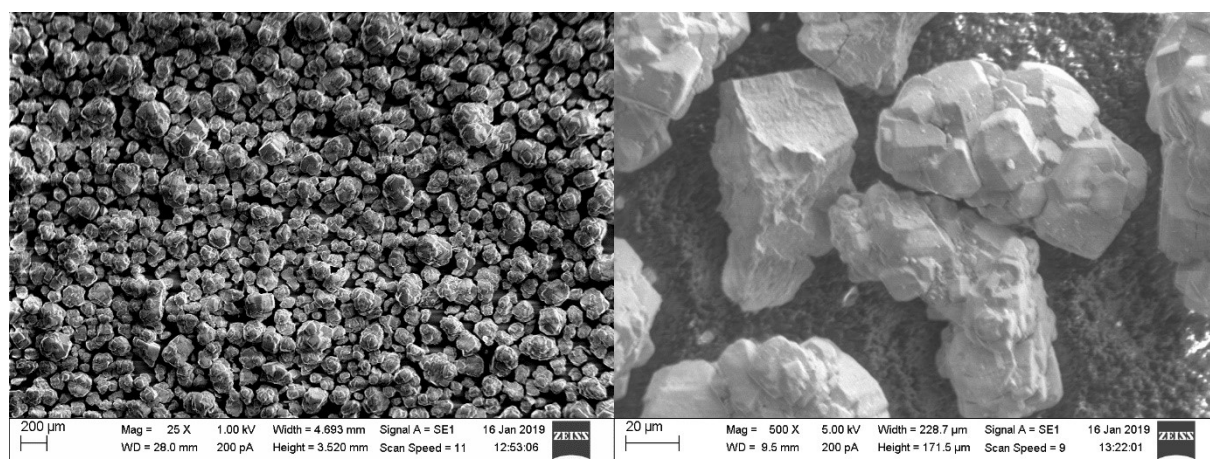
## Characterization of Ga₃₇Pt SCALMS – SEM



**Figure S8:** SEM pictures recorded from the Ga₃₇Pt/Al₂O₃ sample.

All SEM pictures of the Ga₃₇Pt/Al₂O₃ sample were recorded using a Zeiss EVO 40 instrument. The catalyst particles in Figure S8 are <200 μm in diameter and show, at higher magnification, droplet-like deposits on the terraces. The elemental composition of both, the terraces and the droplets, is further analysed in the next chapters by EDX spot analysis and EDX mapping.

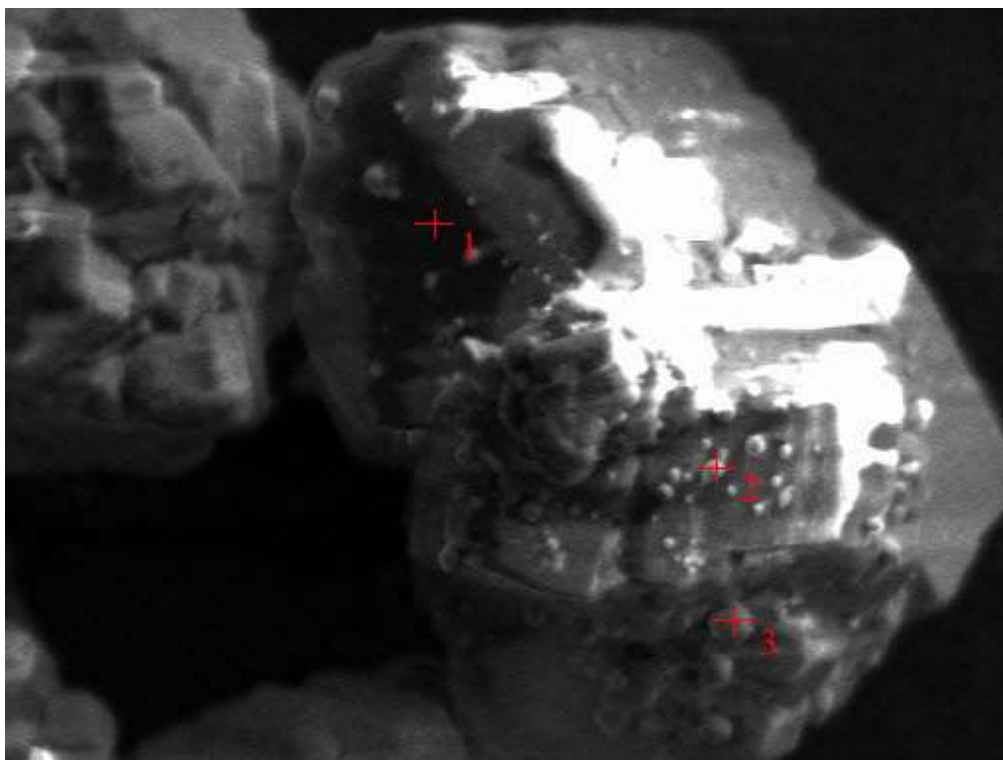**Characterization of Ga₃₇Pt SCALMS – EDX spot analysis**



**Figure S9:** SEM picture recorded from the $Ga_{37}Pt/Al_2O_3$ sample, the crosses indicate position selected for the EDX spot analysis.

Figure S9 shows a SEM picture of a selected catalyst particle. The marked positions *1*, *2* and *3* were analyzed by EDX spot analysis. Spot *1* was recorded on an extended particle terrace, spots *2* and *3* on drop-like deposits.
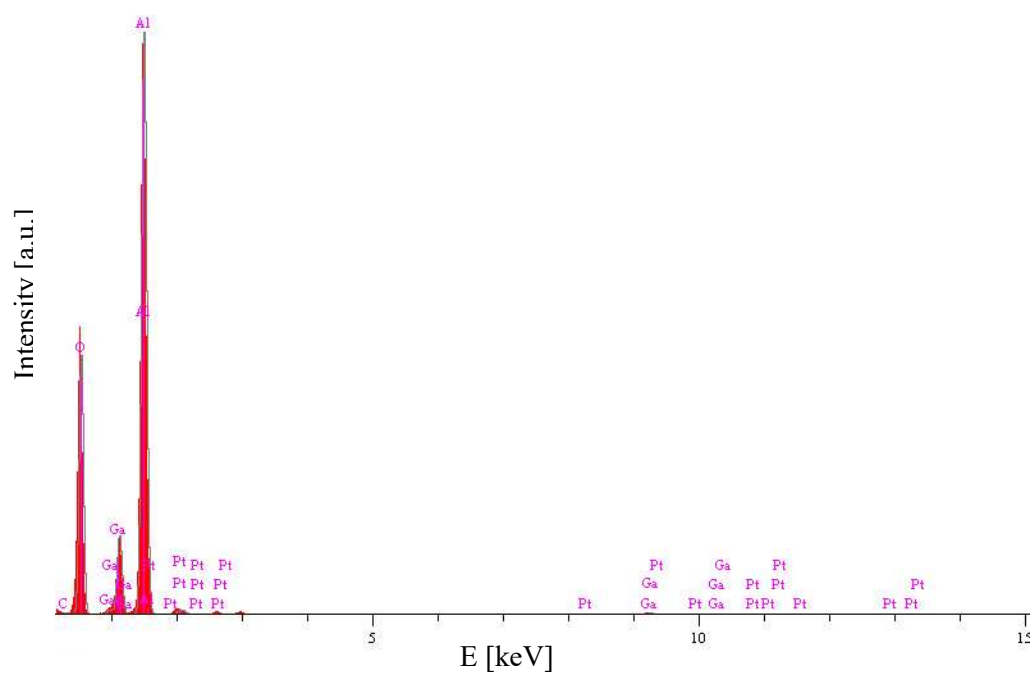
**EDX spot analyis *1***



**Figure S10:** EDX spectrum recorded at spot *1* (particle terrace).

The quantitative analysis of the EDX spectrum (15.0 kV, Takeoff Anlge 35.0°, Elapsed Livetime 100.0) taken from spot *1* is given in the table below:

| Element | Intensity (c/s) | Error (2σ) | Concentration (wt%) |
|---------|-----------------|------------|---------------------|
| C       | 13.44           | 0.733      | 2.021               |
| O       | 1668.02         | 8.168      | 53.322              |
| Al      | 4332.82         | 13.149     | 41.463              |
| Ga      | 19.47           | 0.882      | 2.836               |
| Pt      | 0.40            | 0.126      | 0.358               |
|         |                 |            | 100.000 (Total)     |

According to the EDX spot analyis the extended particle terraces are composed mostly of Al (~41%) and O (~53%). the Ga content is around 3%, the Pt concentration <1%. The obtained composition is in good agreement with the support material, $Al_2O_3$.
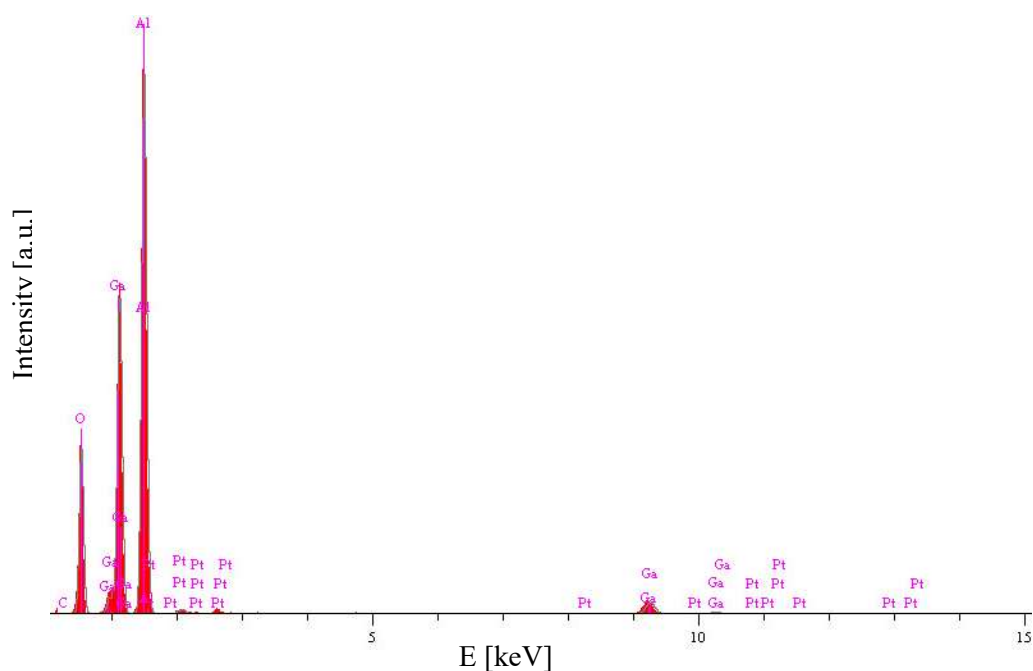
**EDX spot analysis *2***



**Figure S11:** EDX spectrum recorded at spot *2* (small droplet).

The quantitative analysis of the EDX spectrum (15.0 kV, Takeoff Anlge 35.0°, Elapsed Livetime 100.0) taken from spot *2* is given in the table below:

| Element | Intensity (c/s) | Error (2σ) | Concentration (wt%) |
|---|---|---|---|
| C | 0 | 0 | 0 |
| O | 220.85 | 2.972 | 36.032 |
| Al | 835.39 | 5.781 | 43.000 |
| Ga | 32.29 | 1.136 | 20.968 |
| Pt | 0.00 | 0.000 | 0.000 |
| | | | 100.000 (Total) |

According to the quantitative analysis from the peaks in the EDX spectrum, the small droplet shows contributions of Al (~36%), O (~43%) and Ga (~21%). Compared to spot *1*, the Ga content is significantly increased. The spectrum in Figure S11 also shows small Pt peaks, but they were too weak to be integrated during the quantitative analysis.
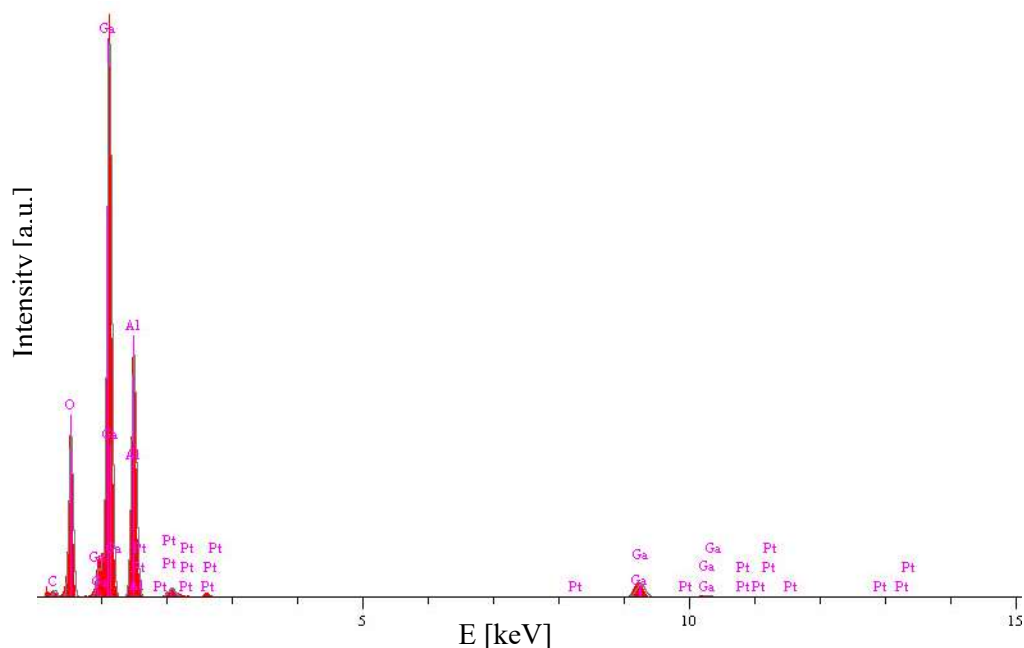
**EDX spot analysis *3***



**Figure S12:** EDX spectrum recorded at spot *3* (larger droplet).

The quantitative analysis of the EDX spectrum (15.0 kV, Takeoff Anlge 35.0°, Elapsed Livetime 100.0) taken from spot *3* is given in the table below:

| Element | Intensity (c/s) | Error (2σ) | Concentration (wt%) |
|---|---|---|---|
| **C** | 23.37 | 0.967 | 7.221 |
| **O** | 498.64 | 4.466 | 41.159 |
| **Al** | 869.36 | 5.897 | 45.255 |
| **Ga** | 85.76 | 1.852 | 27.365 |
| **Pt** | 0.00 | 0.000 | 0.000 |
| | | | 100.000 (Total) |

According to the quantitative analysis from the peaks EDX spectrum, the larger droplet shows contributions of Al (~45%), O (~41%) and Ga (~27%). Again, compared to spot *1* the Ga content is significantly increased. This proves that the droplets consist largely of Ga. The spectrum in Figure S12 also shows small Pt peaks, but they were too weak to be integrated during the quantitative analysis. Further information on the distribution of Pt on the sample can be obtained from EDX mapping presented in the next section.

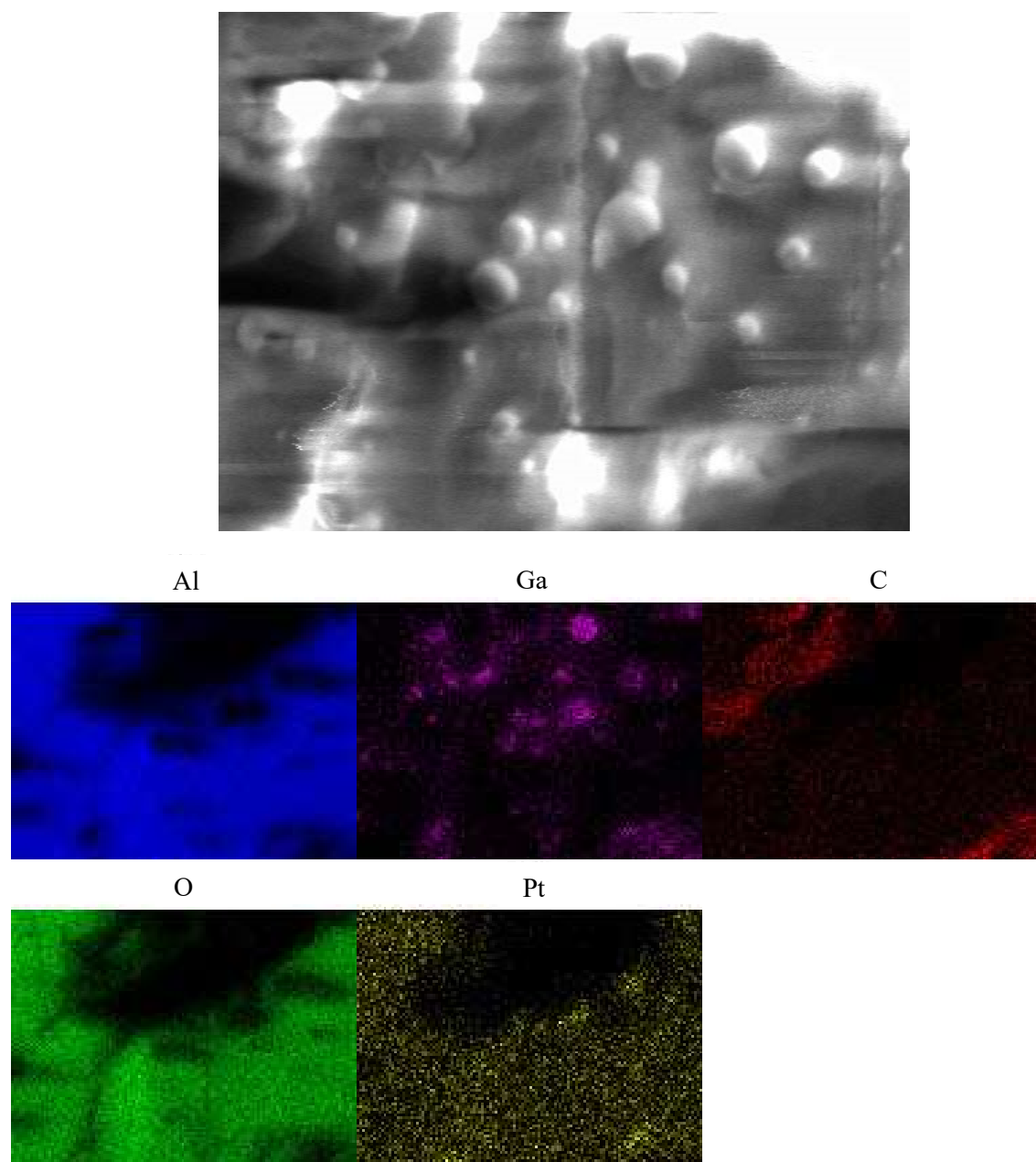**Characterization of Ga₃₇Pt SCALMS – EDX mapping**





**Figure S13:** EDX mapping

The EDX mapping shown in Figure S13 was recorded from a close-up on the Ga-containing droplets. The maps clearly show that the particle terraces are composed of $Al_2O_3$. Furthermore, the Ga-density is clearly higher at the deposited droplets, as was also found during EDX spot analysis. The Pt distribution is more difficult to evaluate, due to the overall low concentration and high noise level. However, the Pt map indicates Pt accumulation in the Ga-rich areas.

**Literature**

(1) Kaftan, A.; Schönweiz, A.; Nikiforidis, I.; Hieringer, W.; Dyballa, K. M.; Franke, R.; Görling, A.; Libuda, J.; Wasserscheid, P.; Laurin, M.; Haumann, M. Supported Homogeneous Catalyst Makes its own Liquid Phase. *J. Catal.* **2015,** *321*, 32-38.