

## Supporting Information

### **GaPt Supported Catalytically Active Liquid Metal Solution catalysis for propane dehydrogenation – support influence and coking studies**

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## Continuous gas-phase reactor setup

A detailed flow scheme of the reactor is shown in Figure S1.

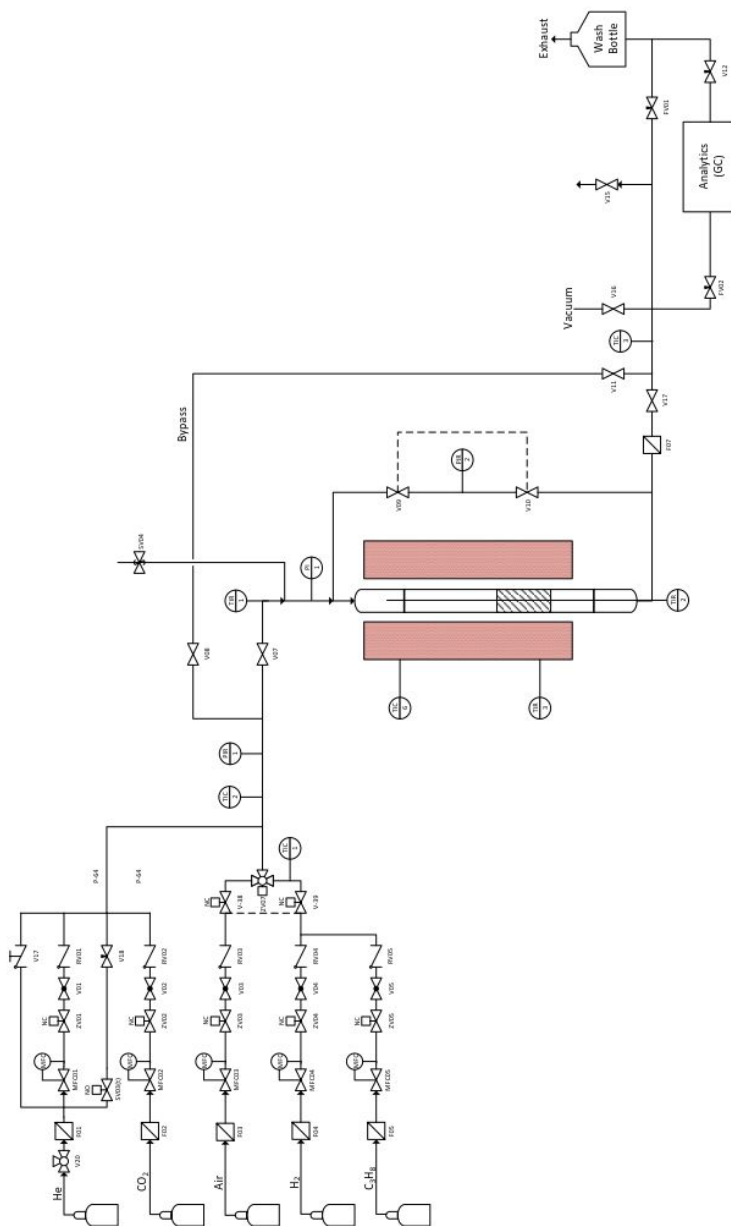


Figure S 1. Flow scheme of the continuous gas-phase reactor used for propane dehydrogenation studies.

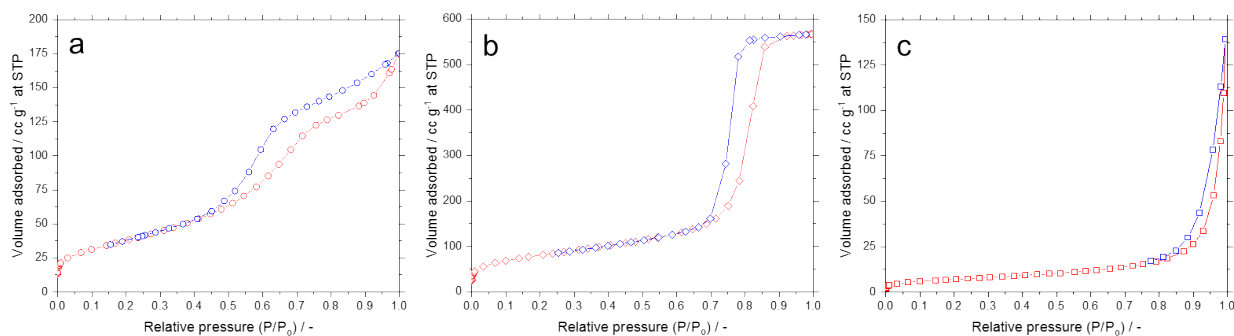


Figure S 2. Adsorption (red) and desorption (blue) isotherms obtained during N<sub>2</sub>-sorption measurements at 77 K for bare supports, Al<sub>2</sub>O<sub>3</sub> (a), SiO<sub>2</sub> (b) and SiC (c).

## Propane dehydrogenation

The initial activity  $a(t_0)$  of the catalyst was taken as  $X_0$ , the conversion value at the beginning of the reaction. With declining conversion, the relative activity  $a(t)$  was calculated based on Equation (S1).

$$a(t) = \frac{X(t)}{X_0} \quad (\text{S1})$$

Plotting these relative activities at 500 °C for all three support materials yields Figure S 3.

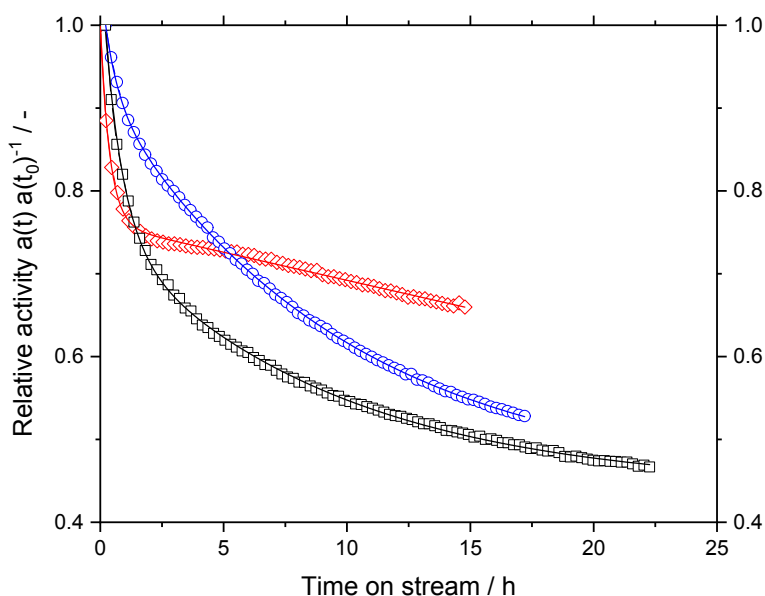


Figure S 3. Relative activity decline in propane dehydrogenation at 500 °C using SCALMS catalysts with three different supports SiO<sub>2</sub> (red), Al<sub>2</sub>O<sub>3</sub> (blue) and SiC (black). Second order exponential decay function was used for data fitting. Reaction conditions: 1.2 g catalyst (Ga<sub>49</sub>Pt/Al<sub>2</sub>O<sub>3</sub>: 2.11 wt-% Ga, 0.12 wt-% Pt; Ga<sub>48</sub>Pt/SiO<sub>2</sub>: 3.63 wt-% Ga, 0.21 wt-% Pt; Ga<sub>41</sub>Pt/SiC: 2.2 wt-% Ga, 0.15 wt-% Pt) He flow 89 mL<sub>N</sub> min<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub> flow 8.9 mL<sub>N</sub> min<sup>-1</sup>, GHSV 4900 h<sup>-1</sup>.

A second order exponential decay function allowed the best fit of all three data sets.

$$y = y_0 + A_1 \cdot \exp(-x/t_1) + A_2 \cdot \exp(-x/t_2) \quad (\text{S2})$$

The same procedure was applied to the data for 550 °C and 600 °C as shown in Figure S 4 and Figure S 5.

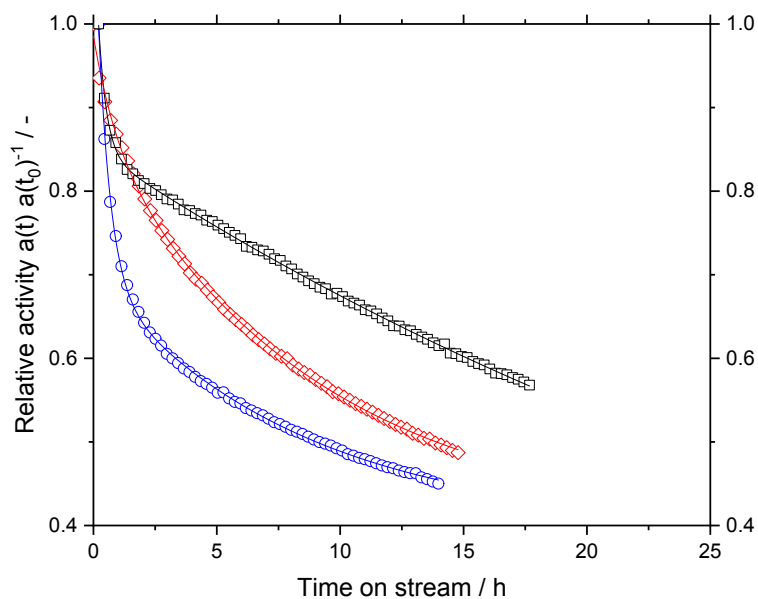


Figure S 4. Relative activity decline in propane dehydrogenation at 550 °C using SCALMS catalysts with three different supports SiO<sub>2</sub> (red), Al<sub>2</sub>O<sub>3</sub> (blue) and SiC (black). Second order exponential decay function was used for data fitting. Reaction conditions: 1.2 g catalyst (Ga<sub>49</sub>Pt/Al<sub>2</sub>O<sub>3</sub>: 2.11 wt-% Ga, 0.12 wt-% Pt; Ga<sub>48</sub>Pt/SiO<sub>2</sub>: 3.63 wt-% Ga, 0.21 wt-% Pt; Ga<sub>41</sub>Pt/SiC: 2.2 wt-% Ga, 0.15 wt-% Pt) He flow 89 mL<sub>N</sub> min<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub> flow 8.9 mL<sub>N</sub> min<sup>-1</sup>, GHSV 4900 h<sup>-1</sup>.

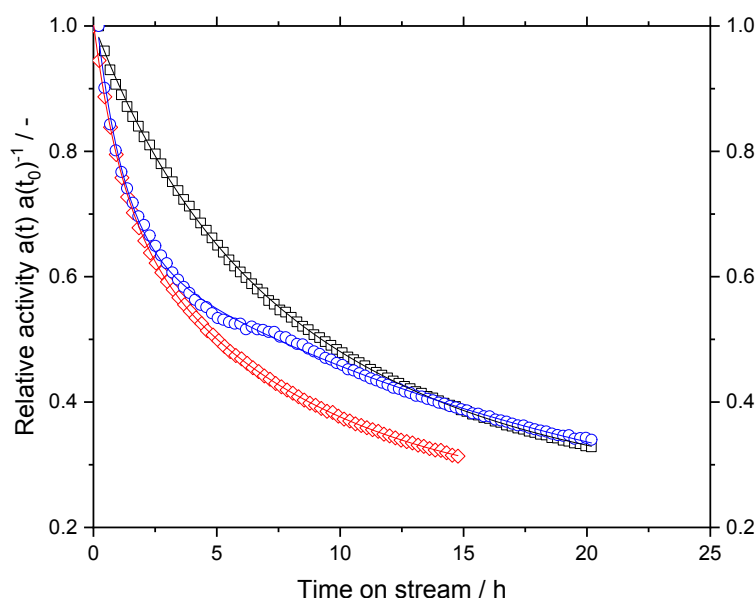


Figure S 5. Relative activity decline in propane dehydrogenation at 600 °C using SCALMS catalysts with three different supports SiO<sub>2</sub> (red), Al<sub>2</sub>O<sub>3</sub> (blue) and SiC (black). Second order exponential decay function was used for data fitting. Reaction conditions: 1.2 g catalyst (Ga<sub>49</sub>Pt/Al<sub>2</sub>O<sub>3</sub>: 2.11 wt-% Ga, 0.12 wt-% Pt; Ga<sub>48</sub>Pt/SiO<sub>2</sub>: 3.63 wt-% Ga, 0.21 wt-% Pt; Ga<sub>41</sub>Pt/SiC: 2.2 wt-% Ga, 0.15 wt-% Pt) He flow 89 mL<sub>N</sub> min<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub> flow 8.9 mL<sub>N</sub> min<sup>-1</sup>, GHSV 4900 h<sup>-1</sup>.

The results of the fitting parameters are shown in Table S 1.

Table S 1. Fitting parameters of the relative activity curve obtained for GaPt catalyst on different supports for propane dehydrogenation at different temperatures

	500°C			550°C			600°C		
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiC	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiC	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiC
$y_0$	1.27E+04	4.61E-01	4.71E-01	4.00E-01	3.98E-01	4.88E-02	2.41E-01	1.45E-01	2.41E-01
$A_1$	2.23E-01	1.23E-01	2.96E-01	1.12E-01	4.69E-01	2.95E-01	2.79E-01	4.00E-01	1.80E-01
$t_1$	3.87E-01	5.21E-01	7.68E-01	9.14E-01	4.93E-01	3.20E-01	1.14E+00	1.12E+00	3.66E+00
$A_2$	1.27E+04	4.69E-01	3.05E-01	4.73E-01	3.00E-01	8.02E-01	4.85E-01	5.10E-01	5.82E-01
$t_2$	1.94E+06	9.96E+00	9.74E+00	8.92E+00	8.39E+00	4.05E+01	7.85E+00	2.04E+01	1.06E+01

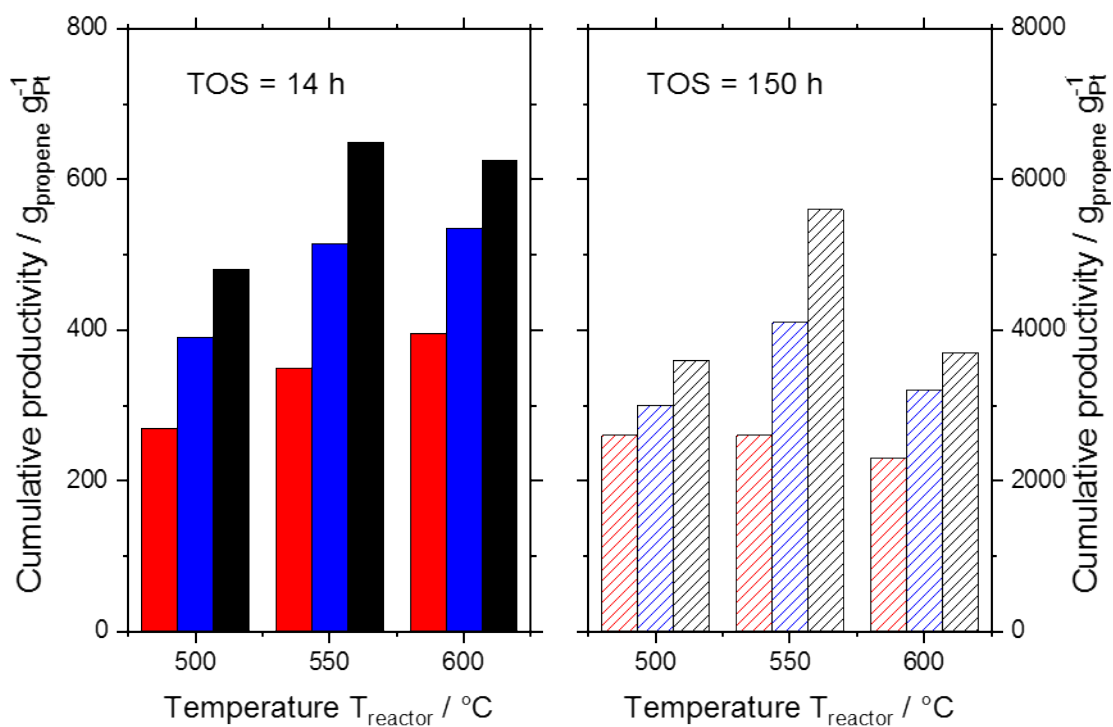


Figure S 6. Cumulative productivity after 14 h on stream (left) and cumulative productivity extrapolated to 150 h on stream obtained at different temperatures using SCALMS catalyst using different supports SiO<sub>2</sub> (red), Al<sub>2</sub>O<sub>3</sub> (blue) and SiC (black).

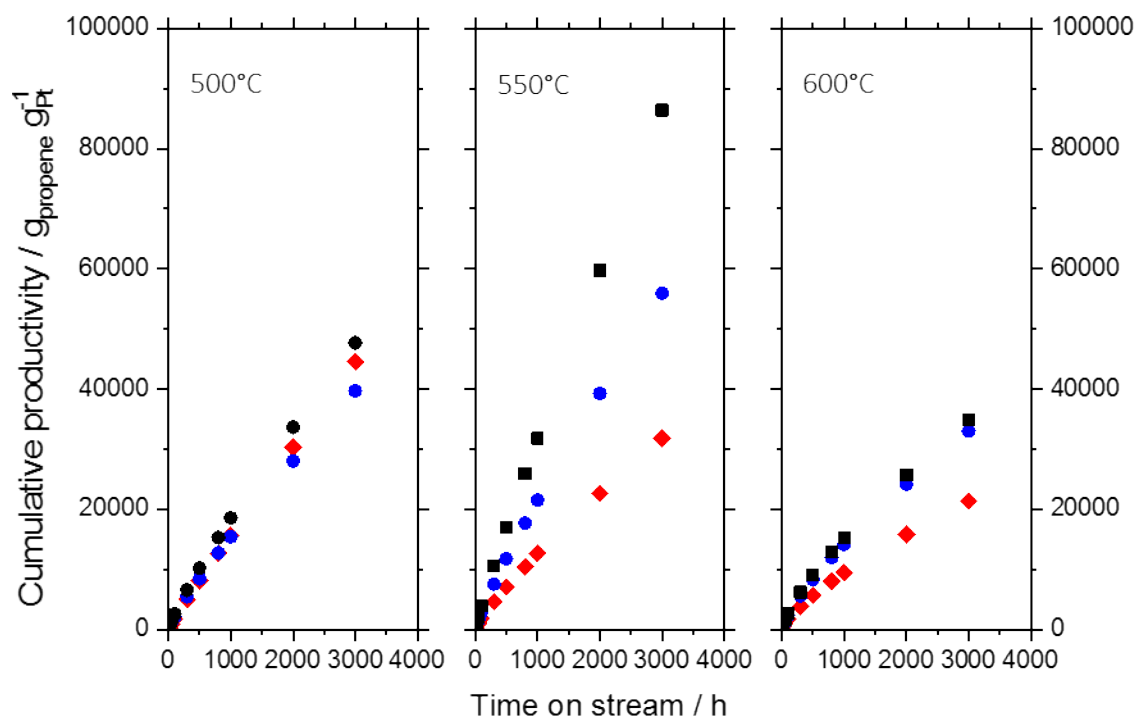


Figure S 7. Cumulative productivity extrapolated to 3000 h based on fitted curve obtained at 500 °C, 550 °C and 600 °C using GaPt SCALMS catalyst on different supports SiO<sub>2</sub> (red), Al<sub>2</sub>O<sub>3</sub> (blue) and SiC (black).

### Post run SEM-EDS

Figure S 8 Shows the SEM-EDS of the spent GaPt/SiO<sub>2</sub> SCALMS catalyst after propane dehydrogenation for 15 h at 600 °C. The catalyst clearly still shows co-location of Ga and Pt and no segregation of the two metals.



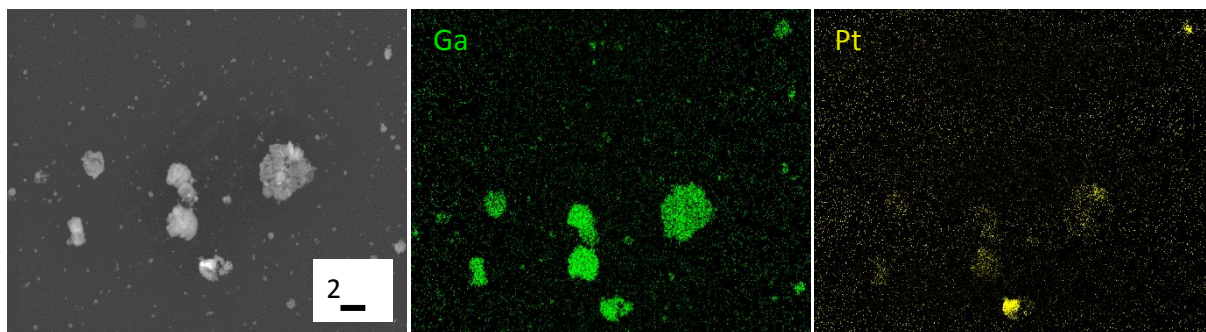


Figure S 8. SEM-EDS of GaPt SCALMS catalyst supported on SiO<sub>2</sub> after propane dehydrogenation at 600 °C for 15 h on stream.

### Post run high-resolution thermogravimetric analysis coupled with mass spectrometry (HRTGA-MS)

The CO<sub>2</sub> signal from the mass spectrometer during temperature programmed oxidation of the spent catalyst could be deconvoluted into two overlapping peaks based on the temperature of oxidation. The ratio of the signal areas of the low temperature and the high temperature peaks is a measure of the graphitic nature of the coke formed on the catalyst. The ratios as calculated for the spent catalyst on different supports and different reaction temperatures is shown in Figure S 9.

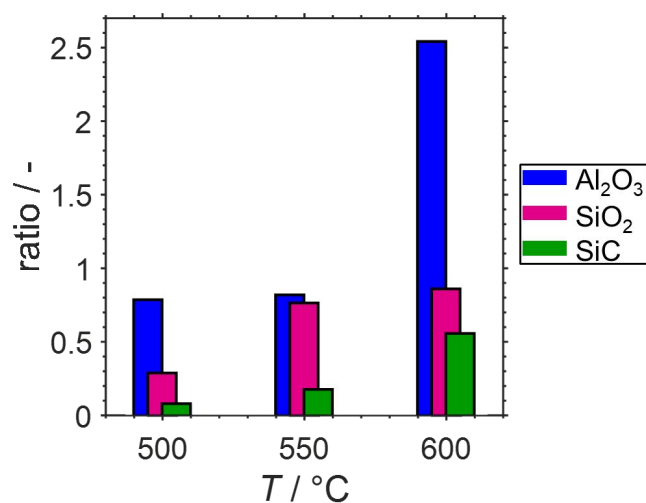


Figure S 9. Ratio of integrals of CO<sub>2</sub> formation of the high temperature over the low temperature peak (graphitic vs. amorphous) after peak deconvolution of the CO<sub>2</sub> profile with two peaks from

temperature programmed oxidation in spent GaPt SCALMS using various support materials after previous application in propane dehydrogenation at 500-600 °C as monitored via high-resolution thermogravimetry coupled with mass spectrometry

## **Post run Raman spectroscopy**

In addition to TPO of the SCALMS after PDH, the spent catalysts were analyzed by Raman spectroscopy for additional qualitative characterization of the carbon deposits. However, the small amounts of coke (<0.5 wt.-%) in most spent catalysts are below the lower detection limit, while fluorescence of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> (green laser) make the analysis of several SCALMS catalysts even more challenging. Nevertheless, a Raman spectrum could be collected for the GaPt/Al<sub>2</sub>O<sub>3</sub> SCALMS after PDH at 600 °C (Figure S 10) due to suppression of fluorescence by the large coke content in this particular sample. SiC is Raman active<sup>1</sup> and features the prominent D and G band of carbon (Figure S 10). Therefore, the deviation of the spectra for GaPt/SiC after PDH at 500, 550 and 600 °C from the spectrum of SiC has to be analyzed for qualitative discussion of coke in these samples. A clear trend is identified for the intensity ratio of the G band over the D band ( $I_G/I_D$ ), which increases with the reaction temperature during PDH. This increase in the degree of graphitization is consistent with the results from TPO showing less reactive coke after PDH at higher temperatures (Figure S 10). This is also indicated by a narrowing of the G band resulting in a decrease of the full-width-half-maximum (FWHM) after PDH at higher temperatures (Figure S 10), which also suggest the formation of more graphitic coke.

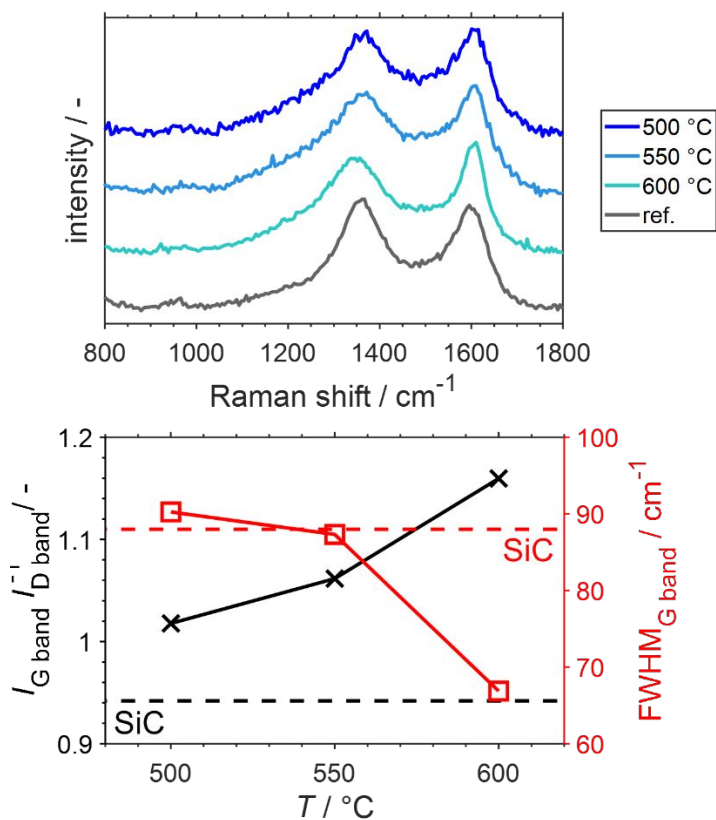


Figure S 10. Raman spectra of spent GaPt/SiC SCALMS (solid lines) after propane dehydrogenation at 500 (dark blue), 550 °C (blue) and 600 °C (light blue) with the reference spectrum of the bare SiC support material (grey) and intensity ratios of the G band over the D band (black crosses), as well as the peak width of the G band (red squares) as a function of reaction temperature with the values of bare SiC (black and red dashed lines).

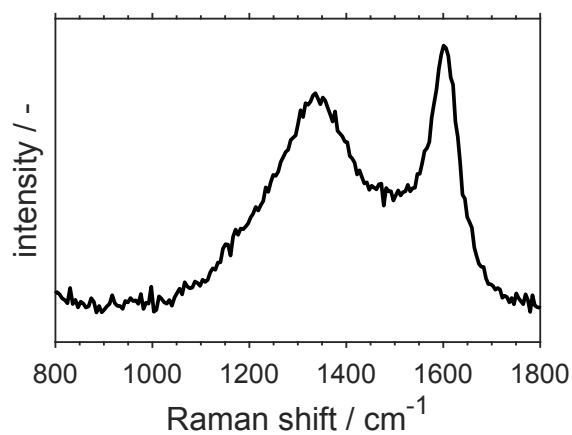


Figure S 11. Raman spectrum of spent GaPt/Al<sub>2</sub>O<sub>3</sub> SCALMS after propane dehydrogenation at 600 °C.

## Pt on support - reference experiments

Platinum catalysts on each of the supports in this study were also tested to compare their activity with the corresponding GaPt SCALMS catalyst. All platinum catalyst was reduced *in situ* before the reaction at 500 °C under 20% hydrogen flow diluted with helium. The productivity values obtained for each of the supports at 500 °C, 550 °C and 600 °C are shown below (Figure S 12-14). Silica supported Pt showed a maximum productivity of  $\sim 10 \text{ kg}_{\text{propene}} \text{ kg}_{\text{Pt}}^{-1} \text{ h}^{-1}$  (Figure S 12) at 600 °C but much lower than the values observed for the corresponding GaPt SCALMS catalyst under similar conditions. Moreover, with increasing temperature the Pt/SiO<sub>2</sub> was dominated by coking and rapid deactivation.

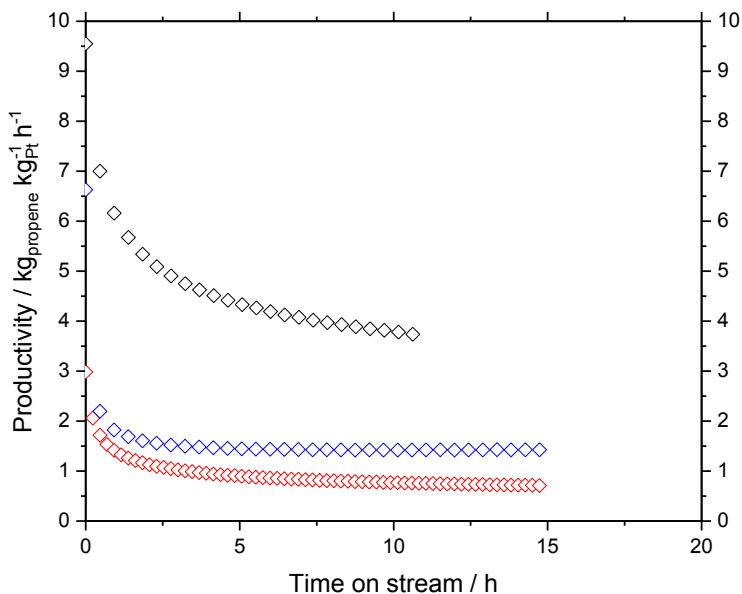


Figure S 12. Productivity during propane dehydrogenation obtained for Pt supported on SiO<sub>2</sub> at 500 °C (red) 550 °C (blue) and 600 °C (black). Reaction conditions: 1.2 g catalyst (Pt/SiO<sub>2</sub>: 0.2 wt-% Pt); He flow 89 mL<sub>N</sub> min<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub> flow 8.9 mL<sub>N</sub> min<sup>-1</sup>, GHSV 4900 h<sup>-1</sup>.

Pt supported on  $\text{Al}_2\text{O}_3$  reached a productivity of  $\sim 30 \text{ kg}_{\text{propene}} \text{ kg}_{\text{Pt}}^{-1} \text{ h}^{-1}$  at  $600 \text{ }^\circ\text{C}$  which was higher compared to Pt/ $\text{SiO}_2$  but still lower than than GaPt-SCALMS on  $\text{Al}_2\text{O}_3$ . The higher productivity could be due to better dispersion of platinum as a results of stron metal-support interaction. Just as with Pt/ $\text{SiO}_2$  catalyst, Pt/ $\text{Al}_2\text{O}_3$  also shows rapid deactivation at higher temperatures.

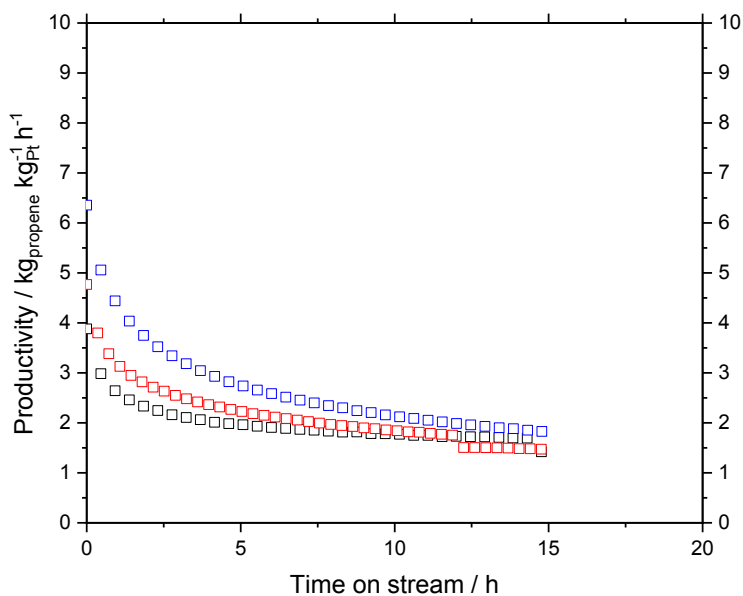


Figure S 13. Productivity during propane dehydrogenation obtained for Pt supported on SiC at  $500 \text{ }^\circ\text{C}$  (red)  $550 \text{ }^\circ\text{C}$  (blue) and  $600 \text{ }^\circ\text{C}$  (black). Reaction conditions: 1.2 g catalyst (Pt/SiC: 0.32 wt-% Pt); He flow  $89 \text{ mL}_N \text{ min}^{-1}$ ,  $\text{C}_3\text{H}_8$  flow  $8.9 \text{ mL}_N \text{ min}^{-1}$ , GHSV  $4900 \text{ h}^{-1}$ .

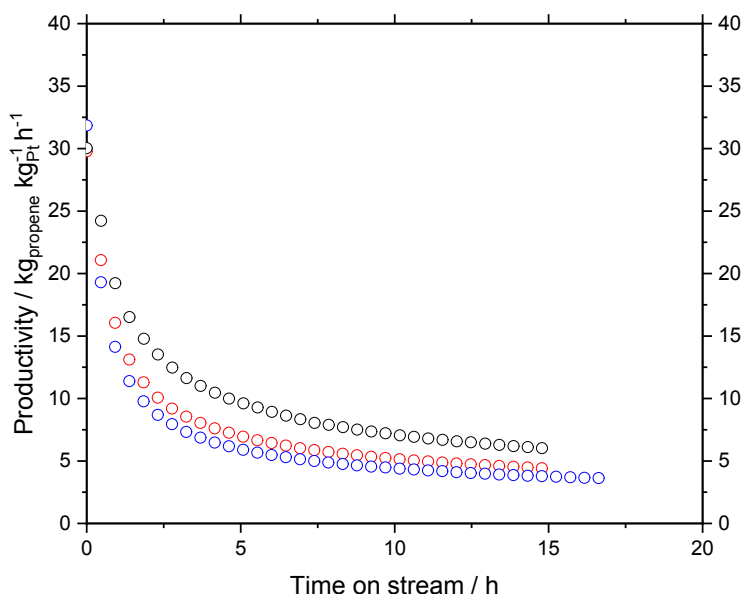


Figure S 14. Productivity during propane dehydrogenation obtained for Pt supported on Al<sub>2</sub>O<sub>3</sub> at 500 °C (red) 550 °C (blue) and 600 °C (black). Reaction conditions: 1.2 g catalyst (Pt/Al<sub>2</sub>O<sub>3</sub>: 0.32 wt-% Pt); He flow 89 mL<sub>N</sub> min<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub> flow 8.9 mL<sub>N</sub> min<sup>-1</sup>, GHSV 4900 h<sup>-1</sup>.

The productivity values obtained with platinum supported on SiC were between 3 to 7 kg<sub>propene</sub> kg<sub>Pt</sub><sup>-1</sup> h<sup>-1</sup> at 500-600 °C and were very similar in value to those of Pt/SiO<sub>2</sub>. GaPt SCALMS catalyst on SiC on the other hand had initial productivity value almost 20 times higher. Here also, the catalyst is prone to rapid deactivation by coking.

### Ga on support - reference experiments

As a reference, gallium deposited on each of the supports was also tested for activity. As reported in our earlier work<sup>2</sup>, the activity observed with pure gallium catalyst is likely due to the small amounts of gallium oxide catalyst passivating the surface of gallium metal. In the absence of a noble metal, it is extremely difficult to reduce gallium oxide.

In case of both SiO<sub>2</sub> and SiC (Figure S15 and Figure S17) the conversion of propane is extremely small upto 550 °C. Gallium supported on Al<sub>2</sub>O<sub>3</sub> (Figure S16) on the other hand has significant activity even above 500 °C. This is most likely due to the formation of gallium-aluminum mixed oxide which are formed at 500 °C.

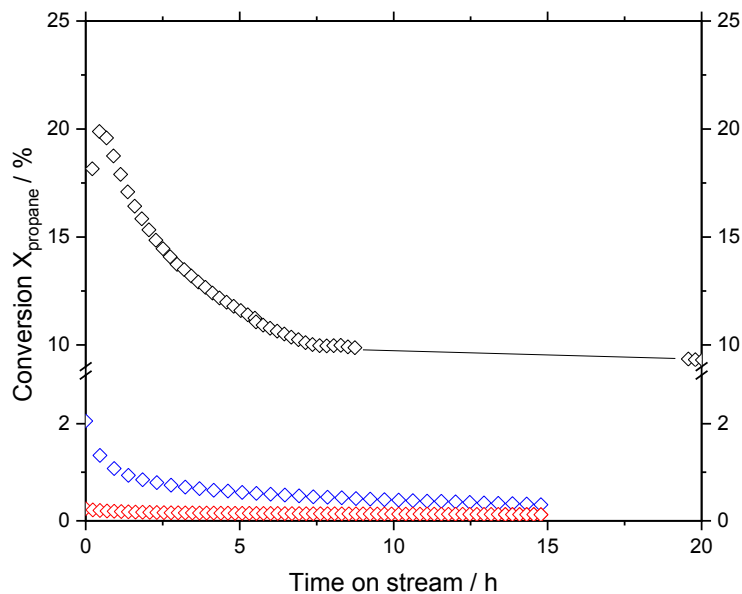


Figure S 15. Conversion during propane dehydrogenation obtained for Ga supported on SiO<sub>2</sub> at 500 °C (red) 55 °C (blue) and 600 °C (black). Reaction conditions: 1.2 g catalyst (Ga/SiO<sub>2</sub>: 4.5 wt-% Ga); He flow 89 mL<sub>N</sub> min<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub> flow 8.9 mL<sub>N</sub> min<sup>-1</sup>, GHSV 4900 h<sup>-1</sup>.

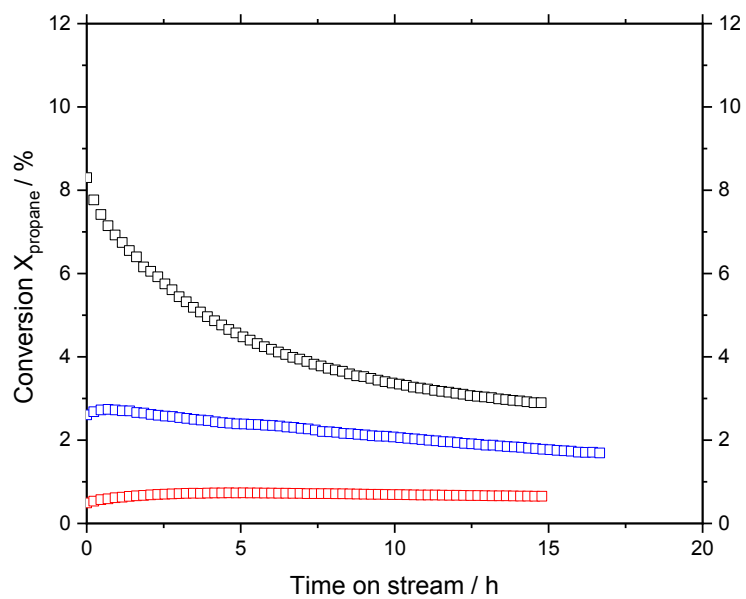


Figure S 16. Conversion during propane dehydrogenation obtained for Ga supported on SiC at 500 °C (red) 550 °C (blue) and 600 °C (black). Reaction conditions: 1.2 g catalyst (Ga/SiC: 4.28 wt-% Ga); He flow 89 mL<sub>N</sub> min<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub> flow 8.9 mL<sub>N</sub> min<sup>-1</sup>, GHSV 4900 h<sup>-1</sup>.



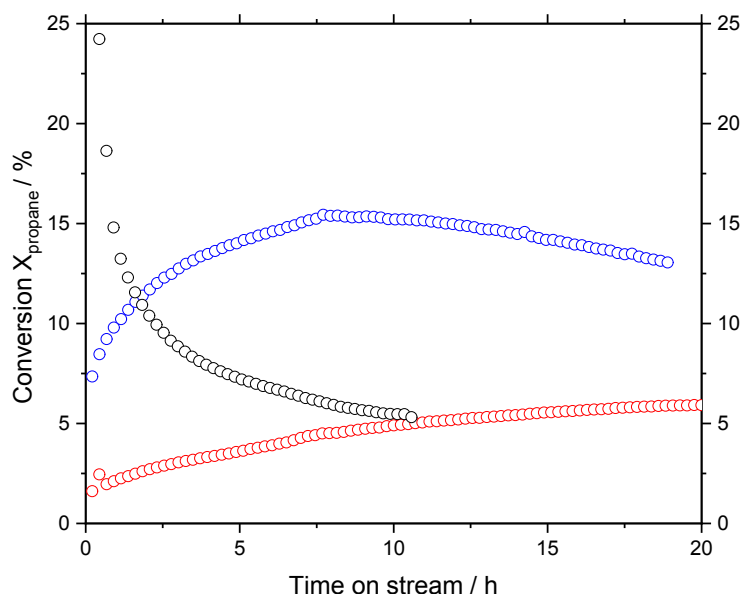


Figure S 17. Conversion during propane dehydrogenation obtained for Ga supported on Al<sub>2</sub>O<sub>3</sub> at 500 °C (red) 550 °C (blue) and 600 °C (black). Reaction conditions: 1.2 g catalyst (Ga/Al<sub>2</sub>O<sub>3</sub>: 4.2 wt-% Ga); He flow 89 mL<sub>N</sub> min<sup>-1</sup>, C<sub>3</sub>H<sub>8</sub> flow 8.9 mL<sub>N</sub> min<sup>-1</sup>, GHSV 4900 h<sup>-1</sup>.

## Particle size distribution

Particle size distribution(PSD) measurements based on the SEM images of GaPt/SiO<sub>2</sub> before and after reaction at 500 °C and 600 °C (Figure 10 of the manuscript) are shown below in Figure S 18. Similar analyses for GaPt/Al<sub>2</sub>O<sub>3</sub> and GaPt/SiC were not possible due to morphology of the support surface. The smooth outer surface of SiO<sub>2</sub> was more conducive to such an analysis. As seen in the figure, the maxima of the PSD in all cases were around 400 nm. Reliable detection of droplets below 100 nm was not possible due to limitation of the instrument and challenges in imaging due to excessive charging of the samples. It must be noted here, that the distribution of the droplets is inhomogeneous over the support particles. Moreover, overlapping clusters of droplets, present in all samples, cannot be correctly evaluated. Therefore, the PSD analysis is only representative of

the total size range of the droplets, which - as seen in Figure S 18 - is as high as 1400 nm in all cases. The PSD, however, cannot be correctly interpreted with respect to any overall change in the distribution itself.

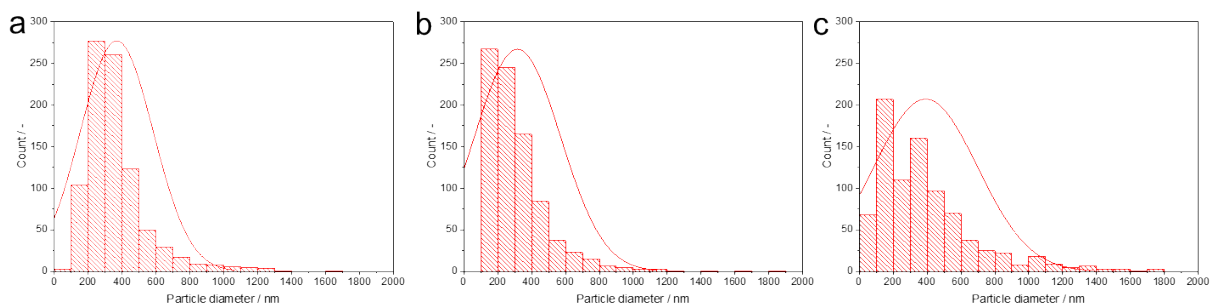


Figure S 18. Particle size distribution of the droplets calculated from the SEM images shown in Figure 10 for GaPt catalyst supported on SiO<sub>2</sub> as prepared (a), after PDH at 500 °C (b) and after PDH at 600 °C (c).

## References

1. P. colomban, *Materials, Processing and Applications in Electronic Devices*, 2011, DOI: 10.5772/24347.
2. N. Raman, S. Maisel, M. Grabau, N. Taccardi, J. Debuschewitz, M. Wolf, H. Wittkamper, T. Bauer, M. Wu, M. Haumann, C. Papp, A. Gorling, E. Spiecker, J. Libuda, H. P. Steinruck and P. Wasserscheid, *ACS Catal*, 2019, **9**, 9499-9507.