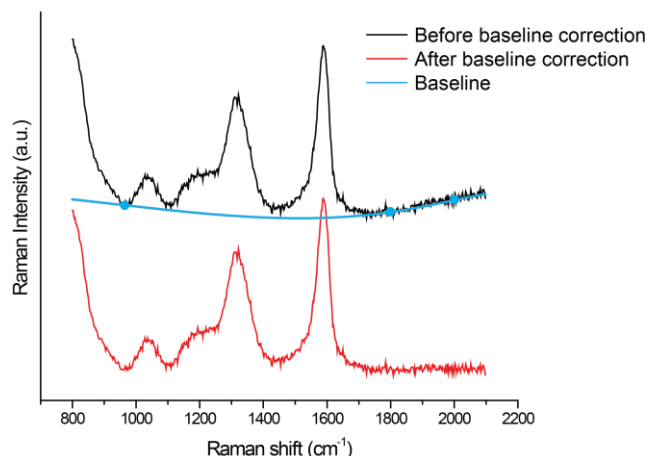


## Electronic Supplementary Information

### Deconvolution of the Raman spectra

The first step of the deconvolution procedure used was the subtraction of the fluorescence background signal. A detailed description of this process is shown in Fig. S1.

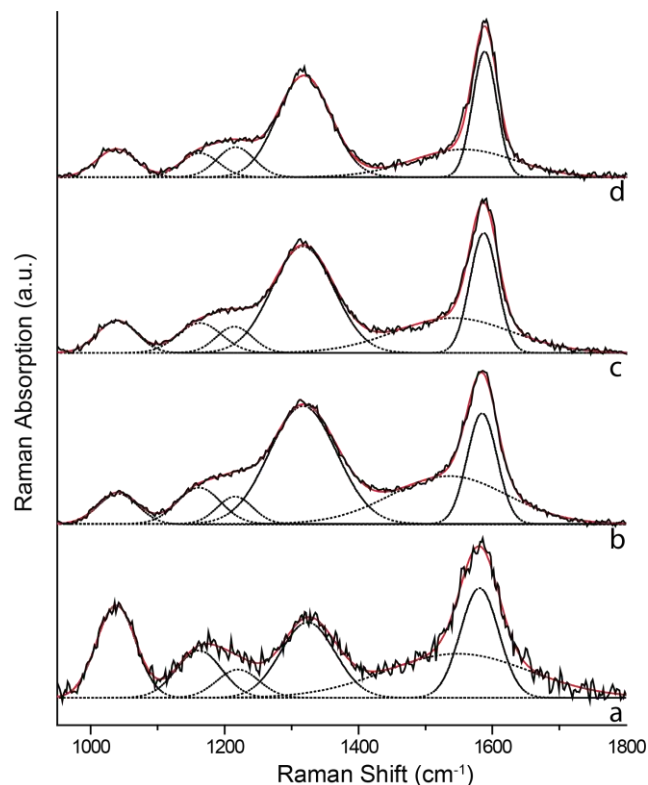


**Fig. S1.** Explanation of the baseline subtraction procedure. The original spectrum, shown as the black line has a background, whose shape and intensity may be different for each spectrum. To correct for this, a baseline subtraction is performed. Three fixed points on the Raman spectrum, at 950, 1800 and 2000  $\text{cm}^{-1}$ , in the Figure indicated as blue dots, are chosen on the original spectrum. The program fityk draws a smooth line between these points, indicated as the blue line in the Figure. This line is then subtracted to yield the red spectrum. This procedure is easily reproducible and does not alter the shape or intensity of the spectra.

The second step after the baseline subtraction is the actual fitting of a set of bands. An approximation of a set of bands is manually fitted, after which the program improves the fit by using a Levenberg-Marquardt algorithm.

Different combinations of line shapes for fitting these spectra were investigated. First of all, it was not possible to fit the spectrum using only Lorentzian line shape functions. The bands corresponding with the quartz signals at 1040 and 1162  $\text{cm}^{-1}$ , and the  $D_3$  and  $D_4$  band at 1220 and 1500  $\text{cm}^{-1}$  could only be fitted by using Gaussian line shapes. By using Lorentzian shapes for the  $D_1$  and G bands, an optimal fit was obtained, as is shown in Fig. 5 and Table 1 of the manuscript.

An alternative was to use only Gaussian line shapes to fit the spectrum. This is shown in Fig. S2. The combination of these bands does not correspond as well with the spectra as the set of bands from Table 1. First of all, when the Raman bands become more narrow, the Gaussian functions do not describe the shape of the D and G bands very well any more, specifically at the top and bottom of these bands. Also the part of the spectrum between 1400 and 1500  $\text{cm}^{-1}$  does not correspond as well when using only Gaussian line shapes. Another direct consequence of using this fitting method, is that the  $D_3$  band becomes very broad and has the largest surface area of all the bands in the spectrum. The band

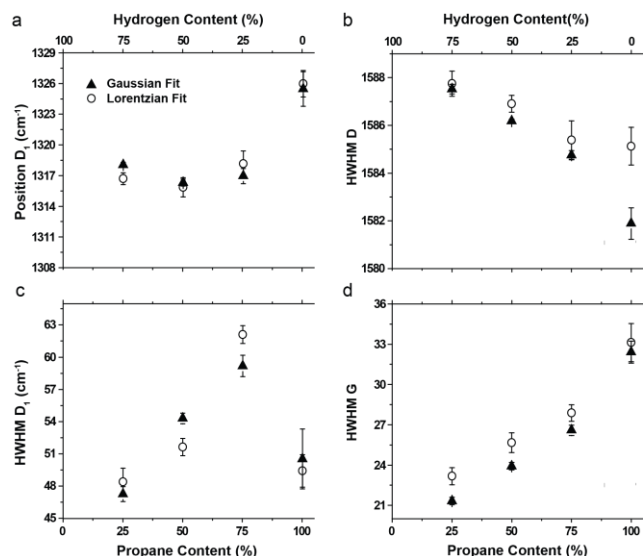


**Fig. S2.** Deconvoluted Operando Raman spectra of the carbon deposits formed on the surface of a  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst material for 25% (a), 50% (b), 75% (c) and 100% (d) propane feed obtained under propane dehydrogenation conditions. A set of 6 Gaussian functions has been used to fit the spectra.

corresponds with amorphous carbon and has not been reported to be so dominant in literature on this type of materials.<sup>15</sup> Furthermore the determination of the  $D_1/\text{G}$  ratio is complicated with this strong  $D_3$  band. Finally, using a different amount of bands to fit the spectrum did not result in a more accurate fit of the experimental data. The use of asymmetric bands to fit the spectra has not been investigated.

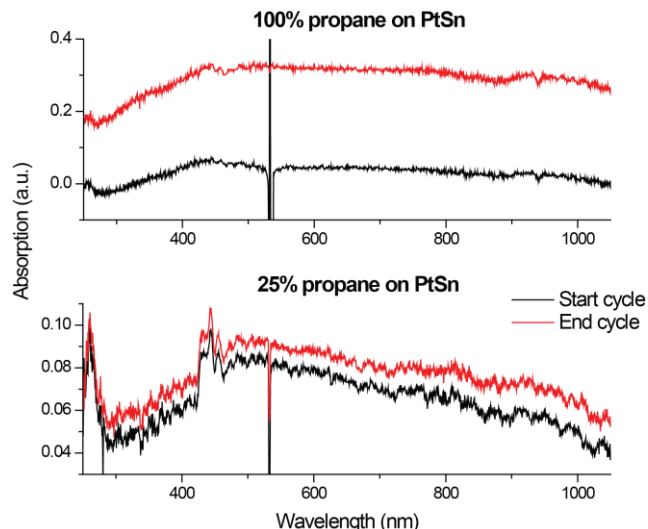
To determine if using solely Gaussian line shapes for fitting the spectra affected the conclusions of the article, the width and position of the  $D_1$  and G bands obtained by this analysis, are compared with the width and position obtained by using the fitting parameters as described in Figure 5 and Table 1. This comparison is made for the different propane/ $\text{H}_2$  ratio's on the  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst, and is shown in Fig. S3. To compare the two fitting methods, the same 10 spectra are used. Finally, error bars corresponding with the standard deviation are shown in the Figure.

Fig. S3 reveals that the values for the width and position of the  $D_1$  and G bands only slightly alter if a different fitting method is used. Most importantly, the trends observed in the spectra remain the same, regardless which fitting technique is used. For both fits, the  $D_1$  and G bands appear to shift as a function of hydrogen concentration. Also both bands appear to become more narrow as the hydrogen concentration increases.



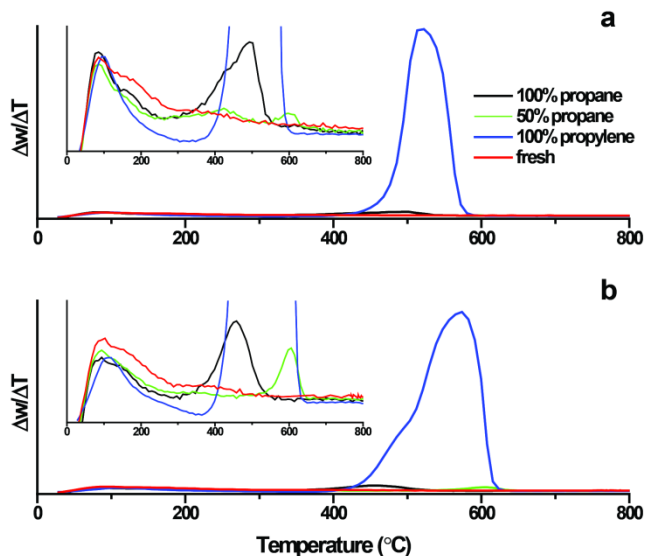
**Fig. S3.** Positions (a, b) and Half Width Half Maximum (HWHM) (c, d) of the D<sub>1</sub> (a, c) and G (b, d) bands of Raman bands obtained by using either Gaussian or Lorentzian line shapes for deconvoluting the bands. The values shown are the average of 10 spectra (including standard deviation shown with error bars) were obtained during the dehydrogenation of propane on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst with a feed of 100% propane.

## Operando UV-Vis spectroscopy



**Fig. S5.** Operando UV-Vis spectra collected at the start and end of the first dehydrogenation cycle on a PtSn catalyst. In the top figure, the spectra obtained using a feed of 100% propane, and in the bottom figure the spectra obtained using a feed of 25% propane and 75% hydrogen are shown. For the experiment where a feed of 100% propane is used, the absorption strongly increases during the cycle. This increase is very small when a feed of 25% propane is used.

## Thermogravimetric analysis



**Fig. S4.** Thermogravimetric analysis on the spent Pt/Al<sub>2</sub>O<sub>3</sub> (a) and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> (b) catalysts, deactivated by feeds consisting of either 100% propane, 50% propane and 50% hydrogen, or 100% propylene. In the figure's inset a zoomed view is shown.