## **Electronic Supplementary Information**

## Hydrogenation of ethylene over palladium: Evolution of the catalyst structure by operando synchrotron-based techniques

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Figure S1. Schematic representation of the gas line for operando experiment.



Figure S2. A summary of the all experimental conditions black and red squares correspond to regions II and III in the Figure 1 of the main text. Blue squares correspond to the data presented in Figure 2 of the main text. Green and purple circles correspond to the data measured for a fresh sample to reproduce the results and were followed by XRPD only.



Figure S3. Results of LCF analysis of two series of XRPD data collected in the variable total flow (region I in the Figure 1 of the main text) and in the constant total flow (simultaneous increasing  $H_2$  and decreasing He).



Figure S4. The full set of normalized XANES spectra (LCF analysis is shown in the Figure 1c of the main text).



Figure S5. Malinowski indicator function (IND) for the XANES data presented in Figure S4.



Figure S6. The components obtained by SIMPLISMA approach from the XANES data presented in Figure S4, identified as metallic palladium (black), palladium hydride (blue) and palladium carbide (red).