Supporting Information for:

Active surfaces for CO oxidation on palladium at the hyperactive state

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Figure S1. CO oxidation on Pd(110) at an oxygen rich condition.[Chen, M. S.; Cai, Y.; Yan, Z.; Gath, K. K.; Axnanda, S.; Goodman, D. W. Surf. Sci. 2007, 601, 5326.]
Figure S2. A schematic diagram of the experimental setup for the new build IRAS.

Figure S3. IRAS spectra for (Left panel): gas phase $^{18}$O$^{16}$O and $^{16}$O$^{16}$O; (Right panel): Pd$^{18}$O/Pd(100) and Pd$^{16}$O/Pd(100). The spectra were taken at room temperature.
Figure S4. *In-situ* IRAS spectra for a Pd(100) surface pre-oxidized in 2 Torr $^{18}$O$_2$ at 700 K for 5 min, then exposed to 27 Torr CO and 18 Torr $^{18}$O$_2$ at 450 K. The spectrum taken at 1620 s was used as a background spectrum to be subtracted for each spectrum above. The insert shows the IR intensity of the band 648 cm$^{-1}$ as a function of CO exposing time.
Figure S5. (A) In-situ IRAS for CO oxidation on Pd(100) surface at 525 K using $^{18}$O$_2$. The spectra were taken continually with each of 40 s. The total pressure is 45 Torr (O$_2$;CO ~ 2:1) at the beginning. Spectra of a Pd$^{18}$O surface and a surface after the hyperactive state (cooled down to RT at UHV) were compared together.
Figure S6. In-situ IRAS for CO oxidation on a polycrystalline Pd in a batch reactor without continuous feeding of CO:O$_2$ mixture. The initial CO:O$_2$ ratio is 1:2. All the spectra in (A) were subtracted by the clean surface one. While, the spectra in (B) before and during the critical point are subtracted by the first spectrum that reach the reaction temperature, and those after the critical points were subtracted by the spectrum just before the critical point.