

SUPPLEMENTARY MATERIALS

S1. Investigation of the adsorption mode of Butadiene on Pd(100) ($\theta_H = 0$ ML)

Table S1. Adsorption mode investigated and corresponding adsorption energy $\Delta_{\text{ads}}U'$ of butadiene on Pd(100), for $\theta_H = 0$ ML.

Adsorption mode	$\Delta_{\text{ads}}U'$ (kJ.mol ⁻¹)	Figure / Comment
cis di- π	-157	Figure S1-a
cis tetra- σ	-168	Figure S1-b
cis 1,2- π -3,4-di σ	-157	moves to di- π
trans π	-174	moves to trans 1,2- π -3,4-di σ , Figure S1-c
trans di- π	-167	Figure S1-d
trans di- σ	-186	moves to trans 2,3- π -1,4-di σ , Figure S1-e
trans tetra- σ	-174	moves to trans 1,2- π -3,4-di σ , Figure S1-c
trans 2,3- π -1,4-di σ	-186	Figure S1-e

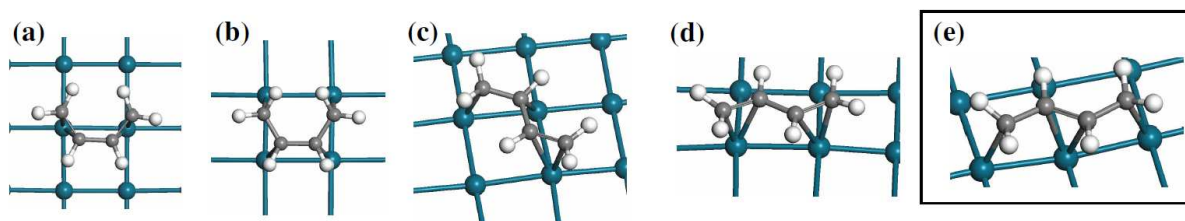


Figure S1. Optimized geometries for the various adsorption modes investigated of butadiene on Pd(100) for $\theta_H = 0$ ML. (a) cis di- π mode; (b) cis tetra- σ mode; (c) trans 1,2- π -3,4-di σ mode; (d) trans di- π mode; (e) trans 2,3- π -1,4-di σ mode (the most stable one).

S2. Electronic analysis of the Butadiene / Pd(100) interaction ($\theta_H = \theta_{H_{surf}} = 1$ ML)

Figure S2 reports the DOS analysis and the density of charge in the $[\epsilon_f - 0.9 \text{ eV} ; \epsilon_f]$ range, for the Pd(100) surface covered by a monolayer of surface hydrogen atoms, and with one butadiene adsorbed per unit cell (trans $d\pi$ mode).

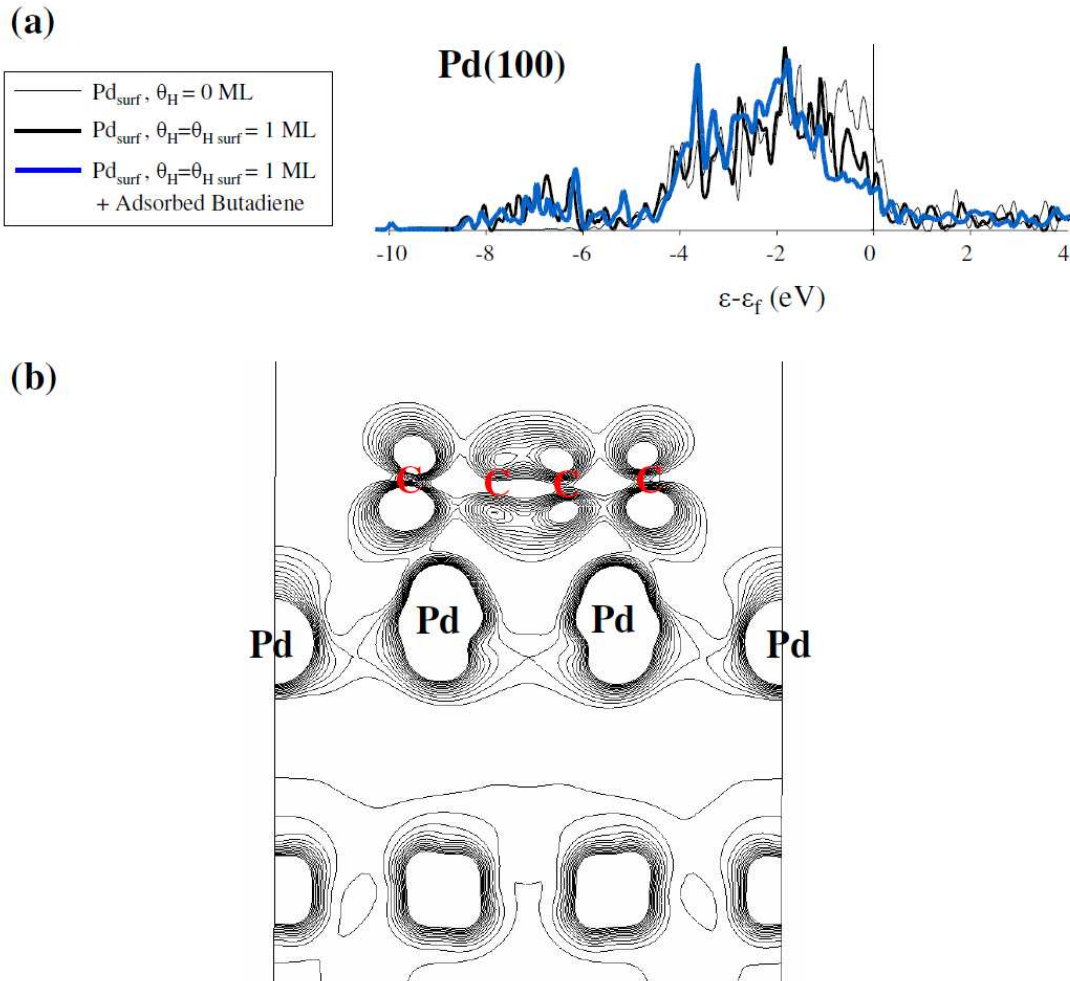


Figure S2. (a), Density of states projected on a palladium surface atom of Pd(100) for $\theta_H = 0$ ML and $\theta_{HC} = 0$ ML, $\theta_H = \theta_{H_{surf}} = 1$ ML and $\theta_{HC} = 0$ ML, $\theta_H = \theta_{H_{surf}} = 1$ ML and $\theta_{HC} = 0.11$ ML (one butadiene molecule). The Pd surface atom is directly bonded to the butadiene molecules in the last case. (c) Contour plot of the charge density, relative to the electronic states with energies in the $[\epsilon_f - 0.9 \text{ eV} ; \epsilon_f]$ range, for $\theta_H = \theta_{H_{surf}} = 1$ ML and $\theta_{HC} = 0.11$ ML (one butadiene molecule). The minimum and maximum charge density values are 0.001 and 0.005 $\text{eV} \cdot \text{\AA}^{-3}$ respectively, the interval between two consecutive lines represents 0.0003 $\text{eV} \cdot \text{\AA}^{-3}$. The (010) plane of the cell, passing through the Pd atoms bonded to the C atoms, is depicted (different orientation as compared to figure 3).

As compared to the same surface with 1 ML of hydrogen only, without the butadiene molecule, the d electrons of the palladium atoms are depleted in the $[\varepsilon_f - 1 \text{ eV} ; \varepsilon_f]$ range in particular. The same trend was already observed between the Pd(100) at 0 and 1 ML (**figure 3** in the manuscript). This shows that these electrons are necessary for the formation of Pd-C bonds. This is also illustrated by the spatial extension of the corresponding charge density (**figure S2-b**): the d_{z^2} type electrons, pointing out of the surface plane, and still partially available after saturation by hydrogen on Pd(100), are strongly perturbed upon adsorption of butadiene. They partially hybridize with π orbitals of butadiene, leading to the formation of Pd-C bonds. On the same plot, the difference with surface Pd atoms which are not bonded to C atoms can be appreciated.

On the Pd(111) surface, such states are quenched upon adsorption of one monolayer of hydrogen (**figure 3**), so that the formation of Pd-C bonds on a pre-covered Pd(111) surface is impossible. This rationalizes the respective behaviours of Pd(111) and Pd(100) under H_2 pressure, towards butadiene, explaining why hydrogen exchange is necessary for the formation of Pd-C bond on Pd(111), contrary to Pd(100).