

Title: **CO Stability on *hcp* Metals**

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Carbon monoxide (CO) has been used as a probe molecule to study, typically, the chemical activity of Transition Metals (TMs) surfaces, but its study has been normally focused on those TMs with a face-centered cubic (*fcc*) crystalline structure, which are close in the Periodic Table, and so, perhaps, does not allow capturing reliable trends along the *d* series. Here we analyze such trends on hexagonal closed-pack (*hcp*) TMs by means of theoretical simulations, here relying on the accuracy of Density Functional Theory (DFT) using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional using suitable slab models.

The detailed analysis of the obtained results allows disentangling different trends, alongside with particular surface reconstructions and CO adsorption modes not previously reported in the literature. Those TMs with low number of valence *d* electrons adsorb the CO stronger, specially connecting its two atoms. While the number of *d* electrons increase, the CO changes to be adsorbed only through the C atom, up to being not adsorbed. This trend goes along quantitatively with the *d*-band centre descriptor model, but qualitatively with the surface energy or the C-metal distance ones. The bonding analysis reveals a donation/back-donation mechanism, which eventually weakens the CO bond order, and so, makes its bonds longer. This has a direct effect, e.g. on the simulated infrared (IR) spectra, implying lower frequencies for the CO bond stretching vibration, which can become invisible when the CO molecule adsorbs parallel to surface due to the surface dipole selection rule. Furthermore, the results on the CO dissociation energy reveals that such a metal surface catalysed process is thermodynamically favourable for earlier TMs, but grows endothermic when going along the *d* series.