

**CO adsorption on alloys – influence of geometry, charge transfer, magnetism and other puzzles**

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Adsorption of carbon monoxide on metal surfaces is one of the best-studied model systems of adsorbate-surface interaction and of fundamental importance for many fields of catalysis. In spite of the importance of alloy catalysts, adsorption on alloys is still poorly understood. Using scanning tunneling microscopy with chemical contrast [1], we are able to determine the adsorption sites of CO on alloys with respect to the chemical environment provided by the alloy surface (Fig. 1, Ref. [2]). By this technique, we have studied adsorption of CO on the fcc(111) surfaces of PtCo, PtFe, PtCr, and PtV alloys with high Pt surface concentrations (50 – 80% Pt in the first monolayer) as well as on PtMe alloys with a pure Pt surface and the 3d transition metal in the subsurface layers only.

We find molecular CO on all surfaces under investigation; in addition some CO dissociation on the 3d metal atoms of the PtCr and PtV surfaces is found. These observations follow the expected trend of increasing reactivity with decreased filling of the metal d-band, i.e., towards the left in the periodic table.

The adsorption of molecular CO offers several surprises, however. On all alloy surfaces investigated, molecular CO adsorbs on top of Pt atoms only, never on the 3d metal atoms. Adsorption of CO on the noble metal Pt is in clear contradiction to the usual concept of reactivity of metals and does not conform to a simplistic d-band model which predicts that CO adsorption energies should increase as the d-band filling decreases. Furthermore, some PtV and PtCr surfaces studied are very unreactive with respect to CO adsorption; on these surfaces molecular CO is not stable in UHV at room temperature.

Further insight into CO adsorption on alloys comes from the study of the ligand effect, i.e., the influence of the neighbors of a given Pt atom on the binding energy of a CO molecule adsorbed on top of it [2]. We find that subsurface 3d metal neighbors weaken CO bonding on a Pt atom, while the influence of in-plane (surface) 3d metal atoms can vary.

Based on ab-initio calculations, the experimental observations can be understood qualitatively, though not always quantitatively. The well-known influence of the d-band energy [3] is only one of the factors influencing CO bonding. Other effects like the weakening of CO bonding by magnetism [2,4] and the repulsive interaction of delocalized electrons with the CO 5 $\sigma$  orbital [5,6] are comparably strong. The latter effect also explains the preference of CO for adsorption on protruding or undercoordinated metal atoms.

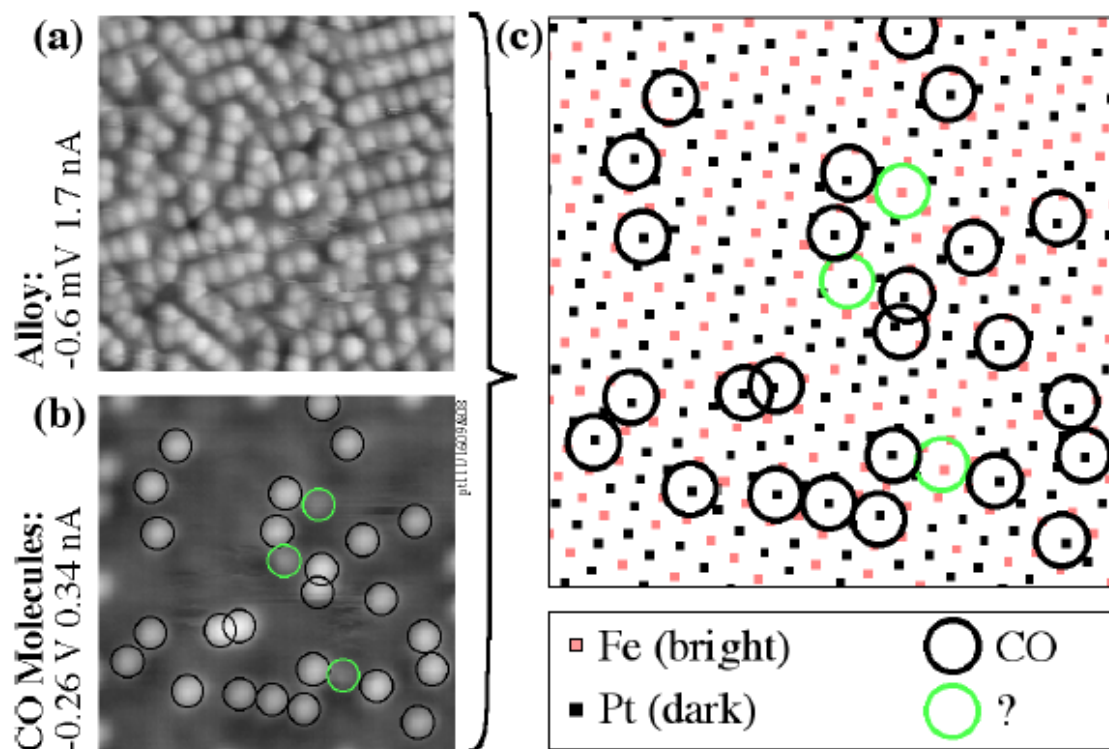


Fig. 1: STM images of a PtFe(111) alloy surface showing (a) chemical contrast (Fe atoms appear bright) and (b) the same area as (a) with adsorbed CO at 77 K. Frame (c) shows the binding sites of the CO molecules determined from (a) and (b). A few impurities of unknown nature are also present.

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