

Correlation of FTIR of CO/(Pt Alloys) with DFT and XANES Experiments and Simulations

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Two mechanisms applicable to CO adsorption on Pt are the Blyholder mechanism and the wall effect. The former involves 5s donation - 2p* back donation between the CO and the metal surface and the latter emphasizes electrostatic repulsion between the metal surface and the core electrons of CO. A Self-Consistent Field (SCF) simulation study applied to a series of spin-optimized Pt clusters examining the 5s/2p* molecular orbital shifts and broadening due to renormalization with the crystal orbitals, confirms the importance of both mechanisms on Pt and Pt alloys. The CO stretching frequencies shift to lower energies when Pt is alloyed with oxophilic metals such as Ru and/or Os. This suggests that alloying with oxophilic components increases back donation between the metal d-band and the CO 2p* molecular orbital. However XANES spectra of PtRu alloy catalysts show an increase in d-band vacancies relative to pure Pt. The question of how increased back donation to the 2p* is concomitant with an average decrease in the metal d-band occupancy is resolved by simulated XANES spectra coupled with Mulliken population analysis, of model clusters with adsorbed CO. Although the average number of d-electrons is lowered upon alloying, the Pt atom to which CO is adsorbed serves as a central Pt atom to which neighboring ligand metal atoms donate electron density, facilitating increased 2p* back donation. Thus the XANES evidence of increased d-band vacancies in Pt alloys is reconciled with the Blyholder mechanism by invoking a local "ligand" effect. Also, the increased electron density on the CO ligated Pt contributes to core electron repulsion, which explains the insensitivity of Pt-C bond lengths to the extent of back donation to the 2p* back donation. The calculations confirm that the wall effect decouples elongation of the C-O bond resulting back donation to the 2p* CO orbital, from the expected increase in the Pt-C stretching frequency for electrostatic reasons. Thus the Blyholder mechanism explains the reduction in

CO stretching frequencies upon alloying while the wall effect counters the effect of the Blyholder mechanism making the Pt-C stretching frequencies and bond lengths insensitive to extent of back donation.