**Controlling CO adsorption on Pt clusters by dopant induced charge transfer**

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A major drawback of state-of-the-art proton exchange membrane fuel cells (PEMFCs) is that the platinum catalyst is highly susceptible to CO poisoning. CO molecules present as trace components in the fuel preferentially adsorb to Pt nanoparticles, thereby blocking the active sites and degrading the cell's performance. It is known that CO poisoning is reduced if platinum alloys are used, but the underlying mechanism therefore is still under debate [1-3]. We study the CO adsorption on small doped platinum clusters in the gas phase using reactivity measurement in a low pressure collision cell [4] and infrared multiple photon dissociation spectroscopy [5]. Pressure dependent reaction kinetics demonstrates that the CO adsorption energy can be reduced by doping the platinum clusters with Nb or Mo atoms, and measured CO stretching frequencies reveal cluster size dependent charge transfer. Complementary density functional theory calculations show that the significant reduction in the reactivity for Nb and Mo doped clusters is attributed to electron transfer from the dopants, which occupy a high-coordinated position in the clusters, to the Pt atoms and the concomitant reduction of the CO binding energies. On the other hand Sn and Ag dopants have a lower coordination in the Pt clusters and have a limited effect on the CO adsorption. Analysis of the density of states demonstrates a correlation of the cluster's electronic structure with the enhanced tolerance to CO poisoning.

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