63h Density Functional Study of Adsorbates and Cationic Metal/Ceria Surfaces

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M^{x+}/ceria catalysts have recently been found to be active for several reactions[1,2] including CO oxidation, water-gas shift, NO reduction, and hydrocarbon oxidation. In particular the water-gas shift reaction has the potential to remove CO from proton-exchange membrane (PEM) fuel cell streams. The cationic metals experimentally studied include Cu, Au, Rh, Pd, and Pt. The exact structure of the M^{x+}/ceria system is unknown, but one model suggested is the substitution of a lattice Ce^{4+} ions with the dopant M^{x+} ions. Using density functional theory (DFT) we modeled the substitution process of Pt and Rh in order to better understand the cationic arrangement. We also modeled the interactions of CO with M^{x+}/ceria surfaces and found carbonate-like (CO_3) species to arise upon CO adsorption. Carbonate-like species were previously found to form on nondoped ceria surfaces[3]. CO is a common molecule present during many reactions, and thus understanding CO interactions with ceria-based catalysts is essential for many kinetic models. We discuss the formation of the different CO species on the doped surfaces and the relevance to the relevant catalytic processes. We also examined the formation of hydroxyl species on the ceria surface, which becomes important when H_2O is present.

(1) Fu, Q.; Saltsburg, H.; Flytzani-Stephanopoulos, M. Science 2003, 301, 935. (2) Bera, P.; Patil, K. C.; Jayaram, V.; Subbanna, G. N.; Hegde, M. S. Journal of Catalysis 2000, 196, 293. (3) Yang, Z. X.; Woo, T. K.; Hermansson, K. Chemical Physics Letters 2004, 396, 384.