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Contributed Talk

Combined Surface Science and Density Functional Theory Approach towards Water Ordered Structures Formation on Magnetite

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Abstract:

The interaction of water with iron oxide surfaces is relevant for several processes of practical interests, such as, the catalytic dehydrogenation of ethylbenzene to styrene over iron oxide based catalysts in the presence of steam, and the photocatalytic splitting of water over iron oxide electrodes. Three different adsorbed water species were distinguished on Fe-terminated Fe_3O_4 multilayer films using thermal desorption spectroscopy (TDS), and ultraviolet photoelectron spectroscopy (UPS) measured under adsorption-desorption equilibrium conditions [1]. By means of density functional theory (DFT) calculations, the first species (γ -water) were confirmed to correspond to dissociative water adsorption with the resulting hydroxyl (OH) groups of water on the surface iron (Fe) sites and the H-atoms adsorbed onto surface oxygen (O) sites. The DFT result for the γ -water structure is consistent with the two OH-stretch lines observed by infrared-reflection-adsorption-spectroscopy (IRAS) [2], and the UPS study [1]. The DFT calculations confirm the subsequent formation of dimeric water structures (β -water) formed by H-bonded molecular water to the surface OH-groups on surface-Fe, and the H on the surface-O sites, respectively, as suggested by the IRAS [2] and low energy electron diffraction (LEED) experiments [3]. The DFT results reveal that formation of the γ -water overlayer structure results from the diffusion of the mobile H-atoms from the initially molecular adsorbed water on iron sites followed by formation of a transition structure with the H-atom adsorbed the nearest-neighbor oxygen sites, diffusing over the surface to adsorb on-top onto the next O-sites. This result is consistent with the proposed second-order kinetics of the recombinative adsorption process. and with scanning tunneling microscopy (STM) measurements of water adsorption on epitaxial Fe_3O_4 films.

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