

Stephane Kenmoe

Title: Impact of solvation on the structure and reactivity of the Co_3O_4 (001)/ H_2O interface: Insights from molecular dynamics Simulations

Abstract

The spinel Co_3O_4 has many beneficial properties for potential use in catalysis. In operando, water is always present and alters the properties of the catalyst. We have used ab initio molecular dynamics to understand the effect of water and solvation on the structure and reactivity of the Co_3O_4 (001) A-type and B-type surface terminations. Water adsorbs on both terminations via a partial dissociative mode, and the A-termination is seen to be more reactive. On this surface, a higher degree of dissociation is observed in the topmost layers of the crystal in contact with water. Water dissociates more frequently on the Co^{2+} sites (about 75%) than on the adjacent Co^{3+} sites, where the degree of dissociation is about 50%. Increasing water coverage does not change the degree of water dissociation significantly. OH^- adsorption on the Co^{2+} sites leads to a reduction of the amount of reconstruction and relaxation of the surface relative to the clean surface at room temperature. Proton transfer within the water films and between water molecules and surface has a localized character. The B-terminated interface is less dynamic, and water forms epitactic layers on top of the Co^{3+} sites, with a dissociation degree of about 25% in the contact layer.