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ABSTRACT

Theoretical Studies of Adsorption on Reactive Ionic Surfaces

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Metal oxide surfaces are generally recognized as active substrates for many catalytic reactions. Density Functional Theory (DFT) has been found as a useful computational tool to investigate the geometry, energy, and electronic structure of reactive oxide surfaces and their interaction with small molecules and fragments. In this thesis, primary efforts have been made on studying adsorptions of some adsorbates, such as $CH_3\cdot$, H_2O and Vanadium, on Hematite, α-Fe_2O_3, (0001) surfaces.

Methyl radical, $CH_3\cdot$, is a critical molecular fragment among the intermediates often encountered in hydrocarbon reactions. Knowledge of the detailed mechanism of methyl radical interaction with metal oxides will be very helpful in understanding the initial stages of similar reactions of hydrocarbon compounds with metal oxide catalysts. In this study, first principles band structure and embedded-cluster methods are applied to analyze the relevant geometries, energetics, adsorption sites and electronic structure on various Hematite (0001) terminations, finding that the partially oxidized "ferryl structure" has largest adsorption energy, and that regular surface sites can also adsorb methyl radicals. The results obtained from theoretical work then will be discussed in comparison with the experimental results. Although these two approaches produce large discrepancies, the systematic errors in DFT methodology and drawbacks in experimental techniques keep the window open for future improvements.

The adsorption of H_2O on a Fe-terminated Hematite (0001) surface is the second hematite

research topic presented here. Molecular adsorption and dissociative adsorption in monolayer H_2O coverage are considered as the initial stages of interaction. Molecular adsorption is found to have small effects on the underlying surface structure, while dissociative adsorption, especially, heterolytic dissociation, which produces two types of surface hydroxyls, shows a relatively stronger effect. Although the ferryl site has a remarkable affinity to free radicals, it is found to be fairly weak toward H_2O adsorption, and shows little local reactivity enhancement.

The adsorptions of sub-monolayer/monolayer Vanadium on idealized Hematite (0001) surfaces and subsequent oxidation are also studied by DFT. It is found that in most cases, Vanadium forms three-fold bonds with surface O atoms, inducing a large geometry change at the hematite surface and near surface region. The adsorption geometry and energy are mainly decided by interplay between adsorbed metal atom and subsurface metal interaction. V generally functions as an electron donor, causing nearby Fe to be partially reduced; the Fe and V oxidization state depends very much on the coverage and detailed adsorption configuration.

Hydroxyapatite (HAP) is the second reactive ionic surface studied here. The initial stages of the hydration process are simulated on a single-Ca(I) terminated HAP (0001) surface using DFT. Water adsorption configuration and energetic properties are detected at different H_2O coverage. At low H_2O coverage, surface Ca-O_{ad} bonds are found to form, but as coverage increases, H_2O tends to loosely float on the already-formed water layer. The hydration process does not cause the decomposition of surface phosphate groups and hydroxyl channel, but does affect the energetics of subsequent Zn substitution and occupation on two metal sites. The Ca(II) vacancy site is found to be energetically more favorable for occupation due to less spatial constraint. This suggested mechanism of preferential occupation is different from previous attempts to explain the site preference in bulk by ionic radius and electronegativity differences.

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