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Dynamic behavior of water molecules at metal oxide-liquid interface by quantum chemical molecular dynamics

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Introduction

The surface properties and sorption behavior of metal oxides in aqueous media have been the subject of many investigations recently, because they play an important role in understanding the interaction mechanisms of ions or molecules with the surface. Atoms, molecules and ions exert forces upon each other at the interface; hence, adsorption reactions at the interface are affected directly in terms of intermolecular interactions between the liquid and the solid phase. Dealing with interaction phenomena at solid-liquid interfaces, the presence of structured water layers must also be considered as under those conditions, because water molecules always cover the adsorbent. Oxides, which are important materials in catalytic processes, are also covered with surface hydroxyl groups in the presence of water. In this study, the structure and dynamics of water molecules at the interface of MgO(100) surface are investigated by means of computational chemistry methods.

Method

The periodic density functional theory (DFT) calculations were applied to optimize the geometries of the structures and to calculate the energies. Hybrid quantum chemical molecular dynamics (QCMD) calculations were carried out with the Hybrid-Colors program, which combines an integrated classical molecular dynamics (New-Ryudo) and quantum chemical molecular dynamics (Colors) programs developed in our laboratory. The calculations were performed for 2000 steps with a time interval of 0.1 fs and temperature was set to 300 K during the simulation. The adsorption energy (E_{ads}) has been calculated according to the expression;

$$E_{ads} = E_{(adsorbate + substrate)} - (E_{adsorbate} + E_{substrate})$$

Results and Discussion

The results show that molecular adsorption of H₂O takes place at the perfect MgO(100) surface. The water oxygen adsorbs on the nearest Mg atom and the hydrogens interacting with two of surface oxygens, with a distance of 2.3 Å, and 1.9 Å, respectively. The adsorption energy was calculated as 13.2 kcal/mol, which was in agreement with the experimental studies.

The structure of water molecules at the MgO-water interface is shown in Figure 1. The dynamics simulation of 34 water molecules, considered as liquid phase, resulted that the nearest water molecules to the MgO surface exhibit a well-ordered water monolayer at the interface, while the others are less ordered, so-called water diffuse layer that connect to the water monolayer by hydrogen bonding. The orientations of the water molecules in the monolayer are nearly parallel to the surface and O atoms pointing toward the surface Mg atoms, as almost one water molecule for each Mg atom at the surface. The water monolayer is aligned nearly 2.5 Å from the MgO surface plane. The present study has revealed that our hybrid QCMD method is useful to investigate the solid-liquid interface.

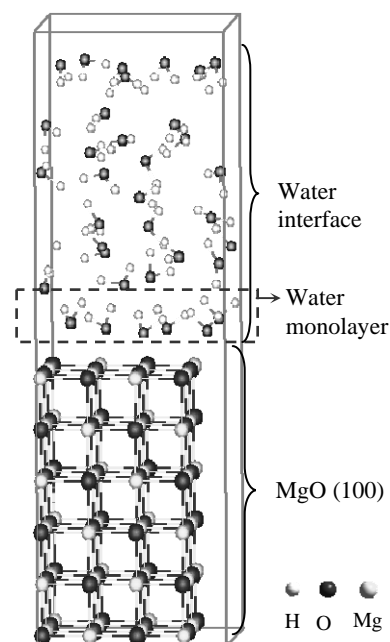


Figure 1. Structure of water molecules at the MgO-water interface