The Energetic and Electronic Properties of Atomic Hydrogen on MgO(001) Surface: Tight-Binding and Ab Initio Calculations

Soong-Hyuck Suh1, Woong-Ki Min, Woo-Chul Kim, Seung-Bak Rho, Won-Sool Ahn, Ki-Ryong Ha, Costinel Lepadatu* and Viorel Chihaia

Department of Chemical Engineering, Keimyung University, Taegu 704-701, Korea
*Institute of Physical Chemistry "I.G. Murgulescu", Romanian Academy, Bucharest 77208, Romania
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Abstract—We report the computational results of hydrogen adsorption atop Mg and O atoms on the MgO(001) surface, followed by its absorption under the target atoms, using two approaches: tight-binding and ab initio methods. We present the energetic and electronic aspects of these interactions and discuss the qualities of the non-self-consistent field tight-binding results compared with the ab initio results. There is the qualitative reproduction of ab initio results in the hydrogen adsorption phase on both types of ions. The tight-binding results are found to be more accurate in the hydrogen absorption phase than in the adsorption phase. In the adsorption calculations the introduction of the surface dipole term in the tight-binding total energy would be required to compensate for the absence of electronic relaxation in the MgO(001) surface.

Key words: Energetic and Electronic Properties, Hydrogen Atom, MgO(001) Surface, Tight Binding Method, Ab Initio Method

INTRODUCTION

The applications of MgO, clean or doped with alkaline metals, have made it a very studied material in the areas of science and industrial engineering [Maksimov et al., 1998; Kim and Kwon, 1999]. Its usage as catalyst (H2-D2 exchange, methanol hydrogenation, support for metallic catalyst, etc.) and its simplicity (large separation between anion and cation bands, and large band gap) have recommended it as an ideal candidate for molecular simulation studies.

On the ionic surfaces, H2 [Dercole and Pisani, 1999] and H2O [Dai et al., 1995; Chacon-Taylor McCarthy, 1996] can also be dissociated on surface defects as hydrogens [Kobayashi et al., 1994] or as H* and OH* fragments [Ahlswede et al., 2000]. The free hydrogen tends to be bound onto the surface oxygen ions, forming new OH* groups that cannot be easily distinguished from OH* hydroxyl groups in water dissociation. This is the reason why, from the experimental point of view, we cannot directly interpret the hydrogen diffusion on or inside the ionic surface. In such cases we must choose the detailed description for the hydrogen-MgO interactions for the studies of hydrogen surface diffusion in the MgO(001) surface.

Computational approaches, such as equilibrium geometry searching methods, and molecular dynamics or Monte Carlo simulations employing ab initio calculations based on density functional or Hartree-Fock theories, have become an excellent tool in material science. However, in order to analyze phenomena on a large scale of time and space, we must be able to describe the potential energy surface in a great number of points for the nuclear configuration space. It is required to solve the electronic motion over 10^1-10^4 points or even more to obtain reliable statistics in a given system. As these methods employ self-consistent or non-self-consistent field techniques, we are often limited in computational time and power for solving the electronic motion. For low degrees of freedom less than six, the potential energy surface from ab initio calculations can be analytically fitted for molecular-based computer simulations.

The tight-binding (TB) method can be one of the good candidates in this area. In this work, we have tested the applicability of the TB computational method, namely, the extended Hückel method based on the atomic superposition and electron delocalization form [Anderson and Hoffman, 1974; Calzaferri et al., 1989; Calzaferri and Brandle, 1992], for the atomic hydrogen reactivity with the MgO(001) surface. To the best of our knowledge, such comparative studies using the TB method have not been reported yet for the hydrogen adsorption and diffusion phenomena on MgO surface. The resulting calculations are compared with the ab initio (AI) results. The capacity to reduce the effort of electronic structure calculations in hydrogen interaction with the MgO(001) surface allows us to characterize the hydrogen motion on and into the surface. We also discuss the energetic and electronic analysis obtained from both TB and AI calculations for the hydrogen adsorption and absorption atop Mg and O ions.

COMPUTATION METHOD

The extended Hückel method [Hoffman, 1963], which is known as a particular type of the tight-binding (TB) method, is one of the simplest approaches in quantum simulations. Their applications, based on the atomic superposition and electron delocalization form [Anderson and Hoffman, 1974; Calzaferri et al., 1989; Calzaferri and Brandle, 1992], have turned out to be useful even in the quantitative characterization of the equilibrium geometries [Calzaferi...
TB and AI Calculations for H/MgO(001) System

and Hoffman, 1991; Brandle and Calzafferi, 1994]. Such approaches have been used successfully to investigate the extended systems [Hoffmann, 1988] and adsorption systems [Schott et al., 1990]. Another example is the simulation work of the metallic oxides with the electrostatic potential corrections [Hafit and Hoffman, 1989].

For the TB calculations employed in this work, we used the ICON&INPUTC package of Calzaferri and Brandle [Calzaferri and Brandle, 1992]. They have corrected the total energy by introducing the electrostatic core-core repulsion terms and electronic-core attraction terms. The Hamiltonian terms can be calculated through the formula

\[ H_{ov} = \frac{K}{2} [(1 + \Delta) H_{ov} + (1 - \Delta) H_{vo}] \] (1)

where

\[ \Delta = \frac{H_{ov} - H_{vo}}{H_{ov} + H_{vo}} \] (2)

\[ H_{ov} \] terms are estimated as the ionization potentials of atomic orbitals \((\sigma = \mu, \nu)\) of free atoms, and \(S_{ov}\) is the overlap matrix between \(\mu\) and \(\nu\) atomic orbitals. For the parameter \(K\), we choose the standard value of 1.75 although the program allows its calculation as a function of the internuclear distance. We do not take the charge interactions into consideration for two reasons: the total CPU time proportionally increases with the number of SCF iterations, and, for nuclear configurations far from equilibrium geometries, the SCF convergence is scarce especially in ionic systems.

The parameters employed in this work are listed in Table 1. The values in parentheses indicate the implicit values in the ICON&INPUTC program. The parameters for oxygen and hydrogen atoms were taken from the ionic solid systems [Alemany et al., 1993]. In this case the charge of ions for the cluster structure has been improved from 1.2 electrons to 1.5 electrons, which is more reliable compared to the Al band structure calculations. The CRYSTAL 95 program [Dovesi et al., 1996] for ab initio (AI) calculations is based on the description for the linear combination of atomic orbitals using the Hartree-Fock and density functional formalisms. In our AI calculations we have used only the Hartree-Fock formalism because it reproduces the excellent result for equilibrium geometry [Chihaya, 1999]. We have employed the tolerance parameters of integral calculations (TOLINTEG parameters, 6 6 7 14), and, for summations in the reciprocal space (IS, ISHF and ISP parameters, 8 6 8). For magnesium and oxygen, we have used the 8-61G basis set and 8-51G basis set [Causa et al., 1986], respectively, and, for hydrogen, a 3-1*G basis set [Ojamae et al., 1994].

![Fig. 1. The 5x5x5 cluster used in the simulation of atomic hydrogen atom interacting with the MgO(001) surface. The hydrogen atom moves along the normal z-direction to the target atoms, magnesium (A=Mg, B=O) or oxygen (A=O, B=Mg) in the MgO(001) surface.](image)

We have simulated the MgO(001) surface in two ways since each program is based on a different formalism (i.e., the molecular orbital formalism in the ICON&INPUTC program, and the crystal orbital formalism in the CRYSTAL 95 program). In our TB calculations, the MgO(001) surface was modeled as a 5 x 5 x 5 cluster. As shown in Fig. 1, the cluster structure is constructed by five atomic layers and each layer contains 25 atoms of A type or B type (A=Mg or O and B=O or Mg) in the 5 x 5 rectangular lattice. We have built two such structures depending on the type of adsorption site, which is the central Mg or O ion in the first layer in this structure (numbered as 1 in Fig. 1). Such a model cluster cannot reproduce the detailed electrostatic field of the crystal, but, near the adsorption site, it has a reliable description for the electrostatic field. In our AI calculations the MgO(001) surface was modeled through a slab-supercell structure: the slab contains five layers and the surface supercell is \((2\sqrt{2} \times 2\sqrt{2}) \times 4\)\(^5\). The unit of the supercell structure for AI computations is the same as in the 5 x 5 x 5 cluster employed in the TB method. The supercell in our computations is large enough so that we can eliminate the direct interactions (less than 10\(^7\) hartree) and the indirect interactions mediated by the surface (less than 10\(^7\) hartree) between two hydrogen atoms from two neighboring supercells. In the cluster and supercell structure, the distance between two neighboring ions was fixed as the experimental value of 2.106 Å [Wyckoff, 1931]. The two preferred adsorption-states are located atop and under Mg and O ions. In both TB and AI methods, we treated the adsorption/absorption processes for hydrogen atom on Mg and O.