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Ab Initio Study of CH_4, CH_3, and CO_2 Affinity to the (001) MgO Surface

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The dynamics of the methane, methyl, and carbon dioxide adsorption to the (001) surface of cubic magnesium oxide (periclase) has been studied within the *ab initio* molecular dynamics in the temperature range between 0 and 1000 K. For methane, neither chemisorption nor physisorption has been observed in the considered temperature range, whereas methyl group and carbon dioxide build chemical bond to the MgO surface at temperatures 350 K and 450 K, with adhesive energies of 0.218 and 0.935 eV, respectively.

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1. Introduction

Wide-gap semiconducting materials are gaining growing interest for applications in electronics and optoelectronics with the continued advancement of blue to ultraviolet LEDs and lasers [1]. Magnesium oxide is getting importance as a constituent of various heterostructures consisting of wide-gap systems fabricated for devices. It is, therefore, interesting to investigate also the adhesion of various gases to MgO. The gained knowledge of the adhesion processes can then be of importance for the wide range of applications such as gas sensors and nanomechanics [2], and very recently to perspective approach of MgO for the carbon dioxide sequestration in order to reduce its atmospheric concentrations [3]. Computer modeling of adhesion of “simple” gases onto MgO surfaces should also provide useful information for the development of CVD growth processes, not only for MgO [4], but also for other metal oxides with the similar geometrical structures. Here, we demonstrate results of the *ab initio* molecular dynamics studies of adsorption mechanisms of methane (CH_4), methyl (CH_3), and carbon dioxide (CO_2) to the (001) surface of rock salt MgO.

2. Methods

We have studied carbon dioxide and methane interaction with the rock salt MgO (001) surface in the range of temperatures from 0 K to 1000 K by means of first-principles calculations based on density functional theory (DFT) with van der Waals (vdW) correction employing the Carr–Parrinello molecular dynamics (CPMD) as implemented in the “official” CPMD code [5]. Our calculations have been performed with the BLYP [6, 7] approximation for the exchange-correlation energy and the Troullier-Martins pseudopotentials [8] to account for interactions of valence electron with ions. For the plane-wave expansion of the pseudovalence wave functions, the kinetic energy cutoff of 680 eV has been employed in the performed calculations, which has yielded fairly well converged results.

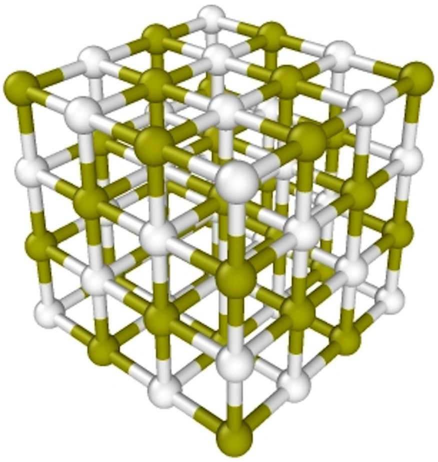

Fig. 1. Stick-and-ball model of bulk MgO in the rock-salt crystallographic structure. Brown and white balls refer to the magnesia and oxygen atoms, respectively.

Crystal structure of rock salt phase of the MgO is presented in Fig. 1. As it is easily seen, the studied (001) MgO surface contains the same number of anions and cations, which makes the surface neutral. This fact considerably simplifies the calculations in comparison to the calculations with the charged surfaces (such as e.g., (001) surfaces in zinc-blende phases), and the “bulk” side of the MgO slab does not need to be saturated with hydrogen atoms. The calculated lattice parameter of MgO is equal to 4.212 Å and is very closed to the experimental value. To study the energetics of the adsorbed molecules, we employ the supercell geometry. The typical supercell employed in these studies contains three layers of MgO, each layer containing the 16 atoms (4×4 lateral unit cell), one molecule of adsorbate, and suitable width of vacuum. Atoms of the bottom layer are fixed to simulate bulk layer of MgO. Altogether, the supercell cell contains 24 Mg and 24 O atoms, plus atoms of the adsorbate. We have carried out very detailed convergence tests for the size of the supercells to eliminate the spurious interaction between adsorbates. Our test revealed also that the width of the used MgO slab is large enough for unique determination of the atomic relaxation at the surface caused by the adsorbate molecule (and also guarantees reasonable simulation times). At the beginning of the simulation, the considered adsorbate gas molecule has been placed at some distance from the surface. The Nose thermostat has been used to stabilize the temperature of the simulations. We have performed simulations for temperatures in the range starting from zero up to 1000 K with the step of 50 K. However, in some cases it has been assumed that the molecule approaching the MgO surface has velocity that exceeds the velocity corresponding to thermal equilibrium. We have observed trajectories of the system for time reaching 5000 fs, with the time step of 3 fs. In the following, we present the results of performed molecular dynamics simulations.

3. Results and discussion

3.1. Methane affinity to MgO

Let us start the presentation of results with the case of CH_4 adsorption to the MgO surface. Methane consists of one carbon and four hydrogen atoms, exhibiting tetrahedral molecular geometry. It is commonly used as a precursor in the production of many organic compounds. In general, methane reactions are difficult to control and to large extent not very well known. However, our theoretical studies provide physical insight into energetics and dynamics of methane adsorption process, as illustrated in Fig. 2.

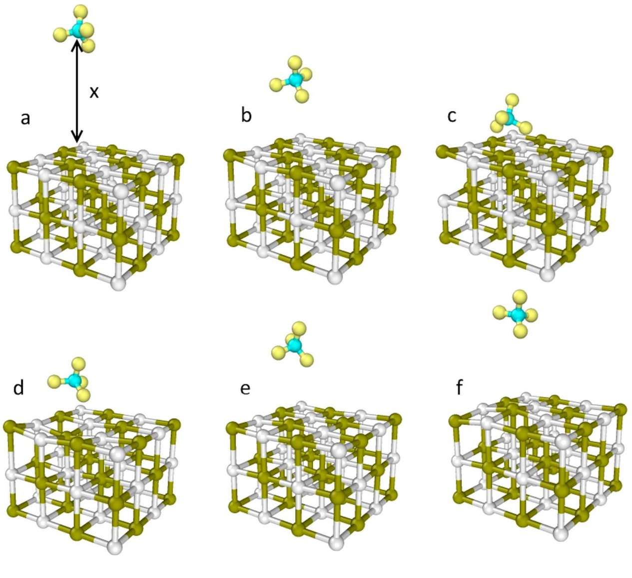

Fig. 2. Interaction of CH_4 molecule with MgO surface at temperature of 500 K. (a) Initial configuration of atoms at time step $t = 0$. CH_4 molecule is placed at distance of 5 Å from the surface with excess initial velocity. Positions of CH_4 molecule at later simulation times: (b) $t = 1800$ fs; (c) $t = 2700$ fs; (d) $t = 3400$ fs; (e) $t = 3900$ fs; and (f) $t = 4800$ fs. Atoms are depicted by balls of following colors: greenish-brown — Mg, white — O, blue — C, and light yellow — H.

At first, we performed the dynamic simulation placing the CH_4 molecule at the distance 2 Å (without excess velocity) from the MgO surface and performed simulations for the series of temperatures from 0 up to 1000 K with the step of 50 K. The required temperature has been guaranteed by the Nose thermostat. For such conditions, methane molecule exhibited no reactivity with the surface and simply “flew away” from the surface, so we did not observe physisorption of methane to the MgO surface. We changed the strategy then and set the initial excess velocity to the CH_4 molecule in the direction of the surface. Theoretically, this approach is closer to the real physics of the adsorption processes, where the molecule is used as a precursor in chemical vapor deposition type of growth. The higher initial velocity of the molecule should result in the higher adsorption probability. Typical time-evolution of the system is depicted in Fig. 2. With excess velocity, the molecule is able to reach the surface (Fig. 2a and b). The interaction of the molecule with the surface results in changing the orientation of the molecule and the curvature of its trajectory. In the same time, the surface atoms exhibit large shifts from their equilibrium positions as a result of the interaction with the molecule, demonstrating that an elastic collision between molecule and the surface occurs. The situation depicted in Fig. 2c and d corresponds to the stages before and after the collision, when the surface finally “pushes” methane away (Fig. 2d) and retains back its more-or-less flat shape exhibiting some kind of residual vibrations. The described collision scenario happens for the whole range of temperatures (0–1000 K).

Our molecular dynamics studies reveal that neither physisorption nor chemisorption of methane to the MgO (001) surface takes place in fairly large range of studied temperatures.

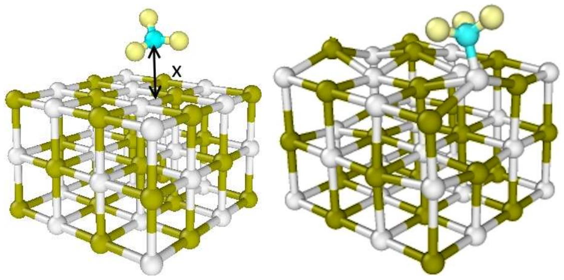

Fig. 3. Methyl adhesion to the MgO surface. Left part: Initial configuration of atoms at the distance between methyl molecule and the surface equal to 2 Å. Right part: Equilibrium configuration of the surface with the adsorbed CH_3 molecule obtained after heating the system up to 350 K for 300 fs. Greenish-brown balls refer to the magnesia atoms, white — to the oxygen atoms, and blue — to the carbon atoms.

3.2. Methyl group affinity to MgO

Methyl is a functional group derived from methane containing one carbon atom bonded to three hydrogen atoms, and is very often produced *in situ* as a precursor to other hydrocarbons. The molecular geometry of the methyl radical is quasi-trigonal planar, although the energy cost of distortion to a pyramidal geometry is small. As shown on Fig. 3, we have placed CH_3 molecule 2 Å apart from the MgO surface and started molecular dynamic simulations for the series of temperatures, starting with 0 K and systematically increasing temperature in the next run by 50 K. We observe that methyl molecule adsorbs to the MgO surface, creating chemical bond, at temperature equal to 350 K. It is in agreement with the general description of chemisorption process, where these exists a barrier for adsorption. We observe the appearance of the chemical bond between carbon atom of the methyl and oxygen from the MgO surface. The bond length is equal to 2.13 Å. The computed adsorption energy is equal to 0.218 eV.

3.3. Carbon dioxide affinity to MgO

The simulation of carbon dioxide adsorption to the MgO surface has similar character to the adsorption of methyl. CO_2 is composed of one carbon atom covalently doubly bonded to two oxygen atoms placed along a straight line.

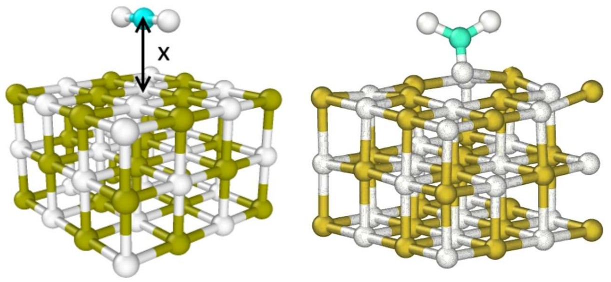

Fig. 4. Adsorption process of carbon dioxide onto the MgO surface. Left part: Initial configuration of atoms with CO_2 molecule at the distance of 2 Å from the surface. Right part: Equilibrium configuration obtained after heating the system up to 450 K for 300 fs. Adhesive energy is equal to $E_{\mathrm{adh}} = 0.935$ eV. Greenish-brown balls refer to the magnesia atoms, white — to the oxygen atoms, and blue — to the carbon atoms.

We have applied the Nose thermostat for different temperatures, starting from 0 K and increasing the temperature in the next run by 50 K. At 450 K we observe that carbon atom of CO_2 creates chemical bond to oxygen atom from the surface (with bond length equal to 1.29 Å), the initial geometry of CO_2 is strongly modified (see Fig. 4), and surface atoms around adsorption site exhibit considerable relaxation. Therefore, at this temperature apparently we observe the well-known chemical reaction: $MgO + CO_2 \rightarrow MgCO_3$ [3, 9]. This reaction could be reversible. In fact, majority of magnesium oxide produced today is obtained from the calcination of naturally occurring mineral magnesite, $MgCO_3$, by the reverse reaction. Magnesium carbonate, most often referred to as "chalk", is commonly used as a drying agent.

Thus, carbon dioxide molecule is chemisorbed by the MgO surface at the temperatures higher than 450 K. The computed adsorption energy is equal to 0.935 eV.

4. Conclusions

We have studied adsorption processes of methane, methyl, and carbon dioxide to the (001) surface of rocksalt magnesium oxide by means of *ab initio* molecular dynamics. Our studies reveal that CH_4 is not adsorbed to the surface in the temperature range up to 1000 K and at ambient pressure, whereas CH_3 and CO_2 are chemisorbed to the surface at critical temperatures of 350 K and 450 K, respectively. The very important outcome of the study is that we determine a substance (i.e., MgO) with adsorption rate for CO_2 much higher than for CH_4; the issue of essential relevance for the future sequestration processes of CO_2.

Acknowledgments

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