Ab initio molecular dynamics studies of CO_2 and CH_4 adsorption at $CaCO_3$ (10-14) surface

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Capture and storage of carbon dioxide and methane is a perspective approach in order to reduce its atmospheric concentrations by sequestration. Carbonaceous systems are an abundant material in nature and are a main component of sedimental rocks, and in many cases these minerals constitute hydrocarbon reservoirs. The accurate description of CO_2 and CH_4 adsorption to calcite rock is an important step to understand the mechanisms and improve the technologies of sequestration and the Enhanced Oil recovery in calcite rocks.

We have studied interaction and adsorption of carbon dioxide and methane with the most stable $CaCO_3$ (10-14) surface (this surface contains the same number of metal atoms and carbonate groups, what keeps total charge neutral) in the wide range of temperatures, from 0K to 1500K, by means of the *ab initio* Car-Parrinello molecular dynamics [1] in the framework of density functional theory (DFT) with energy functional containing the van der Waals (vdW) correction. Our calculations have been performed using the BLYP [2] approximation for the exchange-correlation energy term and Troullier-Martins pseudopotentials [3]. Plane waves with energy cutoff of 680 eV have been included into calculations, which guarantees well-converged results. We use supercell geometry for slabs with surface regions represented by four $CaCO_3$ layers and bottom layers with atoms fixed to simulate bulk part. At the beginning of the simulation gas molecule has been placed 0.2 nm close to the surface and included into the Nose thermostat.

The performed calculations reveal the following picture. When we perform static calculation (i.e., at T = 0K), it turns out that the CO_2 molecule does not bind to the calcite surface. The geometry optimization leads to a state with the molecule separated from the surface. But at elevated temperatures, when molecular dynamics is involved, it turns out that the carbon atom of CO_2 is attracted to calcium atoms of (10-14) calcite surface. Molecular dynamics calculations show that CH_4 molecule can be accumulated at the surface in parallel to CO_3 groups at low temperatures (Fig.1), and even take part in reconfiguration of the surface by dehydrogenation process with the increase of temperature.

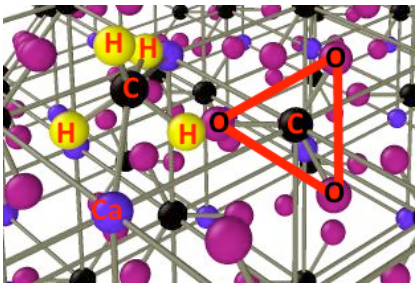

Figure 1. Adsorbed CH_4 molecule at (10-14) calcite surface

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[1] www.cpmd.org
[2] A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
[3] N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).

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