Abstract

Alkaline earth oxide clusters today represent a large class of materials of great technological importance. An increasing research effort has been spent on these materials during the last three decades, mainly for understanding their many interesting electronic and chemical properties. The first part of this thesis is devoted to study of structure cluster of some binary alkaline earth metal oxides by means of DFT calculations. In particular the $(MgO)_n$ and $(CaO)_n$ clusters were considered. In an initial study, the convergence of binding energies in $(MgO)_n$ and $(CaO)_n$ clusters were addressed for $1 \leq n \leq 12$. The applicability of the B3LYP functional was validated by means of MP4 calculations. Properties such as bond length and binding energy were investigated. Limiting binding energies for monolayers of MgO and CaO were determine to be 8.3 eV and 9.2 eV as compared to the 10.4 eV and 11.0 eV bulk values respectively. Furthermore, the class of systems addressed was extended to include also the $(SrO)_n$ and $(BaO)_n$ clusters. A comparative structure and stability study was also performed to learn about preferred cluster growth pathways and how cluster structure stability ordering changes among the alkaline earth oxides. An analysis of ionic and atomic radii was employed to explain the different stability ordering of isomers. The calculations reveal that the stacks of hexagonal $(MO)_3$ ring structures are slightly preferred in the case of $(MgO)_n$ and $(BaO)_n$, while for $(CaO)_n$ and $(SrO)_n$ the rock salt structural analogue prevails.

The electronic structure calculations imply the hexagonal ring stack $(MgO)_9$ and slab shaped $(CaO)_9$ clusters to be good representatives of the corresponding oxide clusters, and therefore these were employed to investigate differential properties of $(MgO)_n$ and $(CaO)_n$ toward the adsorption of NO_2, CO_2, and SO_2. The adsorption energy of NO_2 on the $(MgO)_9$ cluster was generally found to be weak, i.e. less than 0.5 eV at various sites, and found to increase with diminishing cluster size. This is in contrast to the1.66 eV obtained of $(CaO)_9$ cluster. For reference the adsorption of CO_2 and SO_2 onto the same oxide clusters were investigated. Adsorption of NO_2 becomes particularly competitive relative to CO_3^{2-} and SO_3^{2-} if