Abstract

Carbon dioxide emission in the atmosphere is a major cause of climate change. Borate-based compounds as homogeneous catalysts have been observed to be CO_2 capture agents in natural and synthetic setups [Guo et al., 2011]. Carbon capture in such systems has been proposed to take place via hydration of CO_2 ($CO_2 + H_2O \rightleftharpoons$ HCO_3^- + $\mathrm{H^+})$ resulting in bicarbonate ion formation. Several experimental studies have reported borate-based catalysts for CO₂ hydration reaction and the mechanism of the reaction has been proposed to follow the enzymatic carbonic anhydrase action. In view of the absence of detailed physical insights into the mechanistic aspects of borate-catalyzed CO_2 hydration, computational investigations were carried out in this study under the density functional theory (DFT) framework to explain the mechanism of the reaction over borate-based systems. Three borate-based catalysts viz., borate ions, triborate ions and tetraborate ions were tested as for the aqueous phase carbon capture reaction. Free energy landscapes provided the details of the elementary steps of the reaction concluding the mechanism of the reaction to be indeed biomimetic consisting of parallel and bent CO_2 complexation, intramolecular proton transfer, bicarbonate ion complex formation and displacement of bicarbonate ion by water molecule to form (poly)borate-water complexes. All three ions were found to be active for catalyzing the reaction. NMR and FTIR spectra of all the intermediates proposed during the biomimetic mechanism were computed and compared against the experimentally reported spectra. The comparative analyses proved the identities of the intermediates thus further confirming the mechanism of the reaction.

In the series of development of biomimetic for CO_2 capture catalysts, DFT calculations were carried out with five transition metals (Co, Ni, Pd, Rh, Ru) testing their activities towards biomimetic carbon dioxide hydration. Periodic plane wave calculations demonstrated the formation of surface species which were in accordance with the mechanism of reaction known for α -carbonic anhydrase action. To determine activation barriers for different elementary steps involved during the reaction, DFT calculations using a cluster model of transition metals with Gaussian-type orbitals were carried out. Feasibility of CO_2 capture with varied activities by transition metals was established by DFT calculations.

Carbon dioxide, carbonate ion and bicarbonate ion adsorption were observed previously on titania surfaces by experimentally and computationally. A titania nanocluster of 15 molecules was used to develop the mechanistic insight into CO_2 hydration by DFT calculations. Titania nanoclusters followed the mechanistic cycle of CO_2 hydration catalyzed by α -carbonic anhydrase enzyme with five elementary steps of H₂O dissociation, parallel CO_2 adsorption, CO_2 bending, proton transfer, HCO_3^- ion by second H₂O molecule adsorption. Proton transfer was observed as the rate limiting step with highest activation energy. NMR and FTIR spectral analyses were done to validate the formation of intermediates existing in CO_2 hydration reaction and further confirm the mechanism on titania nanocluster.

Biomimetic CO₂ hydration activities of Ru/Rh-doped fullerenes, hydrogen terminated metal doped carbon nanotube/graphene (M-CNT/Gr, MN₃-CNT/Gr,

M=Ru/Rh) and Ru cluster decorated carbon nanotube/graphene (Ru₄-CNT/Gr) were revealed by DFT calculations. The carbonic anhydrase action was followed for the reaction of CO₂ with H₂O resulting in a bicarbonate ion and a proton. All the catalysts were found to be active for CO₂ hydration and the mechanism proved them to be biomimetic. Free energy landscapes over the catalysts were developed for CO₂ hydration. Activation energies of H₂O dissociation and CO₂ bending were observed to be substantially smaller over Ru₄-CNT when compared to those over the other catalysts. Thus, Ru₄-CNT was concluded to be the best catalyst for CO₂ hydration amongst the tested carbonaceous supports with rate limiting step as the HCO₃⁻ ion formation.