Theoretical Insight on CO_2 Hydrogenation over Small SnO_2 Clusters

Ramesh Chandra Deka* and Plaban J. Sarma

Tezpur University, India

Global optimisation of $(SnO_2)n$ clusters in the range of n=1-20 is performed by employing genetic algorithm implemented in Knowledge Led Master Code (KLMC) software suite. For each cluster size, prescreening of each cluster size are done with interatomic potential followed by density functional theory geometry optimisation for a reasonable numbers of conformers. By analyzing different stability criteria, such as binding energy per atom, second difference in energy, the lowest energy structures were determined. From the second order energy differences of the global minima, n =10 is found to be the most stable cluster. The optical properties of the clusters were correlated with the calculated HOMO-LUMO energy gap of the global minima clusters. Furthermore, mechanism of hydrogenation of CO_2 to formic acid over SnO_2 monomeric and dimeric structures as catalysts shows a new route for the formation of formic acid via 'Hydride Pinning Pathway'. This mechanism provides a unique selectivity for HCOOH through hydride transfer step over CO formation and H_2 recombination reaction at lower overpotential. We consider that the enhanced activity of SnO_2 clusters for CO_2 conversion would help in designing efficient catalysts for experimental studies. We also investigated the influence of titanium dopant on Sn_2O_4 cluster for H_2 dissociation on the doped systems and then the subsequent mechanism for the conversion of CO_2 into formic acid (FA) via a hydride pinning pathway. The lowest barrier height for H_2 dissociation is observed across the 'Ti-O' bond of the Ti-doped Sn_2O_4 cluster, with a negatively charged hydride (Ti-H) formed during the heterolytic H_2 dissociation, bringing selectivity towards the desired FA product. The formation of a formate intermediate is identified as the rate determining step (RDS) for the whole pathway, but the barrier height is substantially reduced for the Ti-doped system when compared to the same steps on the undoped Sn_2O_4cluster.

Biography:

Ramesh Chandra Deka completed his Ph. D. from National Chemical Laboratory, 1998, Post-doc at Tokyo University from 1999-2001, AvH post-doc at Technical University of Munich, Germany from 2003-2004. He is a Lecturer in Tezpur University from 2001-2004, Reader in Tezpur University from 2004-2006, Associate Professor in Tezpur University from 2006-2010, Professor in Tezpur University from 2010 to till date. He has Publications of about 200.

Awards: Secretary of Catalysis Society of India 2018; Professor A. S. R. Anjaneyulu Endowment Award, 2017 by the Indian Chemical Society; Fellow of the Royal Society of Chemistry (FRSC) 2017; Bronze Medal, Chemical Research Society of India (CRSI) 2013; Professor H. C. Goswami award by Assam Science Society, 2013.