Synopsis

Fuel cells offer the best solution to the imminent energy and environmental crisis staring at our face, urging the scientific community to overcome all the challenges faced by its effective commercialization. These harness the power of hydrogen, which requires efficient methods to store hydrogen reversibly. Fuel cells have been known to function the best while employing Pt as the catalyst. An acute setback to the coherent working of a fuel cell is the degradation of expensive and scarce Pt catalyst by CO. Converting this CO to CO_2 through fast reaction kinetics promises an answer to this vital issue. However, CO_2 production will further increase its concentration in the atmosphere undesirably adding to the steady emissions from consumption of fast depleting fossil fuels. Consequently, global warming will accelerate, which threatens the sustainability and prosperity of the society. Converting CO_2 to value-added products should solve both fossil-fuel shortage and anomalous climate change. Storing energy in chemical bonds, as fuels such as CH_4, and finding an electrochemical catalyst to reduce CO_2 to such hydrocarbon fuels would provide an ideal solution for discontinuous renewable energy sources. This thesis effectively addresses these major issues faced by a successful global implementation of fuel cells and sustainable energy. The reported results and findings provide a better understanding of materials properties, which can be generalized to other systems as well. The thesis has been organized as follows:

Chapter 1 introduces fuel cells and heterogeneous catalysis, challenges associated with their large-scale commercialization, and pathways to achieve optimized catalytic and hydrogen storage performance. An overview of importance of nanoparticles in heterogeneous catalysis is given along with traditional methods followed to parametrize and evaluate hydrogen storage and catalytic efficiencies. The motivation of the research work has been highlighted in this chapter.

Chapter 2 describes the theoretical methodology employed for the work. It gives an understanding of first principles-based Density Functional Theory (DFT) and various exchange and correlation energy functional used to obtain electronic and structural information. Theory underlying the methods employed for computationally calculating reaction energy pathways, barriers, rates, and turnover frequency are also described briefly.

Chapter 3 proposes a strategy to enhance the hydrogen storage properties of transition metal clusters. Doping of small Ti clusters by B, enhances their reversible hydrogen storage capacity. Among all $Ti_n{-}1B$ (n = 3, 4, 5, 6, and 7) clusters, Ti_3B stores the maximum number of 12 H_2 molecules (three dissociated and nine Kubas type). The best capacity of Ti_3B originates from the combined effect of a large charge transfer from Ti to B and a high localization of Ti empty d states at a large distance above the Fermi-level. For Ti_3 anchored to B of BC_3, the number of Kubas-bound hydrogen remains the same as that of the free-standing Ti_3B, while the unusable chemisorbed hydrogen are absent. Gibbs energy of adsorption as a function of H_2 partial pressure shows that $Ti_3@BC_3$ adsorbs and desorbs nine Kubas-bound hydrogen at ambient pressures and room temperature.

Chapter 4 investigates the problem of O_2 interference in hydrogen storage on metal decorated carbonaceous systems, which remains one of the major stumbling blocks in the successful realization of the theoretically promised high storage of Kubas bound H_2. The interference is a consequence of preferred O_2 binding at the metal site, thereby blocking it for H_2 adsorption. Arene capping of a Sc-metallocarbene (MCB) efficiently reverses the preferential adsorption

of O2 over H2. The capped Sc-MCB completely repels O2 off the Sc-site allowing solely Kubas binding of H2, consequent of the down-shift of the d-band center of Sc from 1.29 eV in the uncapped to 5.67 eV in the capped MCB, below the Fermi-level, respectively. This optimized d-band center position enables the empty Sc antibonding states to only be available for hydrogen adsorption via Kubas interaction, thereby, to completely avoid oxygen binding.

Chapter 5 shows for the first time that on supported Pt3Co/MgO(100), the preferred CO adsorption site inverts to Co from Pt. This inversion results from the better availability of empty anti-bonding d-states of Co atom in Pt3Co than those of the Pt atoms. The d-band center has a one-to-one correlation with CO adsorption energy and its relative position determines the adsorption site. Furthermore, for Mars van Krevelan (MvK) mechanism of CO oxidation on Pt3Co /Li-doped MgO(100), low reaction barrier of 0.11 eV predicts excellent reaction kinetics. A novel design strategy of d-band center inversion for CO oxidation catalysts with no Pt poisoning and excellent reaction kinetics is proposed.

Chapter 6 extends the search for bimetallic Pt clusters, which possess the CO adsorption site inversion properties inherently. Among all 3d transition metals (M) in Pt3M, only V d-band center is closer to the Fermi level than that of Pt. This leads to a larger affinity of V towards CO, making it more reactive than Pt. The relative position of d-band center from Fermi-level describes the favorable adsorption site in a system. The d- band center position of only the V atom (among all M = Sc, Ti, V, Mn, Fe, Co, Ni, Cu, and Zn) is closer to the Fermi level than that of the Pt atoms, increasing its preference towards CO. Furthermore, anchoring Pt3V on Li-doped MgO(100) activates a spontaneous oxygen vacancy, oxidizing CO via small reaction barrier of 0.13 eV, exhibiting better reaction kinetics than the free-standing cluster.

Chapter 7 elucidates the prospect of tuning catalytic processes as a function of cluster size, which has been a long-sought goal in heterogeneous catalysis. Ptn(V/Co)m, for (n m = 4, 2; 9, 3; 15, 5; 41, 14; and 59, 20) are studied as CO oxidation catalysts. The site inversion is preserved for the CO adsorption on V for all PtnVm. This inversion to Co from Pt is introduced beyond 12-atom cluster for PtnCom. A subsequent peroxo-like O2 adsorption after CO, on the adjacent Pt sites leads to the efficient oxidation of CO to CO2 with low Langmuir-Hinshelwood (L-H) mechanism barriers. The maximized catalytic activity is observed for the 55-atom cluster of Pt41(V/Co)14 pertaining to the optimal CO binding and best reaction kinetics. Finally, MvK mechanism of CO oxidation on Pt41V14/Li-doped MgO(100) proceeds via low reaction barrier of 0.14 eV, promising efficient CO oxidation catalytic activity.

Chapter 8 exhibits insights into low and ambient temperature CO oxidation catalytic activities of Pt plates supported on reconstructed Si 7×7 (111) surface. The catalytic activity of CO oxidation over Pt/Si 7 × 7 (111) reconstructed surface with restricted platinum loading is analysed. We report, tuning of CO oxidation catalytic activity with size of single-layered platinum clusters Ptn/Si-RS (n = 10, 20, 30, and 45). The catalytic performance varies for Ptn plates, which is a consequence of the different interactions between Pt and Si-RS with changing n. The distance of d-band centers of Ptn/Si-RS from π orbitals of CO and O2 correlates with the strength of adsorption energy as n changes. The reaction kinetics analysis reveals that more than 10 CO2 molecules can be produced via CO oxidation on Ptn/Si-RS. This turn over frequency of CO2 exceeds that of the conventional CO oxidation catalysts. The results of this work will lead to the effective use of platinum and Si 7×7 (111) components at ambient atmospheres to design CO tolerant catalysts and ensure its fast oxidation.

Chapter 9 presents a facile solution to the enormous problem of efficient CO_2 mitigation, utilizing the knowledge of increasing catalytic efficiency by employing trimetallic nanoparticles. DFT calculations in combination with the computational hydrogen electrode (CHE) model develop a detailed description of the free-energy landscape and limiting potential for NiTM@Cu (TM = 3d transition metals) alloy core shell nanoparticles. An overview of the thermodynamics of CO_2 conversion to CH_4 as a function of limiting potential establishes that these alloy core shell catalysts promise excellent CO_2 reduction at overpotentials as low as 0.17 V with respect to the equilibrium potential or standard potential value (SPV). This efficiency stems from the fact that the rate limiting step of CO protonation to CHO has small exothermicity, especially for the early transition metals (Sc, Ti, and V). Furthermore, the better stabilization of CHO than CO on the NiTM@Cu core-shell catalysts makes the vastly reported rate limiting step of CO protonation exergonic at very small overpotentials. The chapter also establishes that the limiting potential can be tuned by varying the core composition in $Ni_{13-x}M_x@Cu$, in turn affecting the catalytic activity. The complete reaction profile of CO_2 electro-reduction in the presence of water affects the binding energies. Moreover, the intrinsic solvation effect does not relatively change the reaction pathways and overpotential values.

Chapter 10 summarizes and concludes the work presented in this thesis in addition to a brief description of future projects.