

Abstract

With the increasing concern on several global issues like's shortage in fossil fuel, climate change, environmental pollution, and sustainability has become one of the essential principles to meet the objectives of human being's development. To ensure sustainable development, we have to rely on clean, green, and renewable energy resources such as solar, wind, tidal, geothermal, hydrogen, etc. Among these resources, hydrogen is the most abundant element in the universe and a potent energy carrier due to its clean, renewable, indigenous, and higher energy density (33.33 kWh/kg) nature. However, despite all such merits, a flawless economic system based upon H₂ fuel (hydrogen economy) could not be readily framed due to technical challenges in hydrogen production, hydrogen storage, and its onboard applications. Out of these challenges, hydrogen storage presents a significant challenge due to its very low density (0.08988 g/L). To increase hydrogen density, work must either be applied to compress the gas, the temperature decreased below the critical temperature or the repulsion reduced by the interaction of hydrogen with another material. All these processes are cost-intensive and risky; thus, the main concern regarding the onboard application of hydrogen energy is the development of safe and efficient solid-state hydrogen storage materials. In order to have safe and efficient solid-state hydrogen storage materials, the United States Department of Energy (US-DOE) has set some targets for onboard hydrogen storage particular for vehicular purpose. These targets include the system gravimetric density needs to be 5.5 wt% (1.8 kWh/kg), system volumetric density 1.3 kWh/L (0.04 kg/ L), system fill time (5 kg) 3.3 min, operational cycle life more than 1500 cycles, and the operating ambient temperature below 60 °C. Unfortunately, we could not develop such materials that meet these requirements so far.

MgH₂ is one of the most attractive options as a solid-state hydrogen storage material owing to its high hydrogen storage capacity ~ 7.60 wt% (volumetric capacity of 110 g/L). Other factors which make MgH₂ as one of the promising materials for hydrogen storage are high abundance of Mg in earth crust (6th abundant), light weight

etc.,. However, the pristine MgH_2 has a high operating temperature ≥ 400 °C and slow hydrogen ab/de-sorption kinetics (< 1 wt%/min). Besides MgH_2 , the complex hydride NaAlH_4 is also one of the solid-state hydrogen storage materials with high hydrogen density and manageable thermodynamics and fulfills the proposed US-DOE target for an onboard hydrogen storage system. However, the reversibility (hydrogen ab/de-sorption during cycling) and dehydrogenation kinetics of NaAlH_4 is quite sluggish below its melting point *i.e.*, 183 °C. In this thesis, the main emphasis is given on solving the various issues related with MgH_2 and NaAlH_4 as hydrogen storage materials *i.e.*, improving thermodynamics and kinetics of MgH_2 and NaAlH_4 . Finally, the studies on hydrogen storage has been extended to the system which can be a viable hydrogen storage option especially for space vehicle application *i.e.* Metal-organic frameworks (MOF) *i.e.*, $\text{M}_2(\text{m-dobdc})$ MOFs (M= Fe and Mn) ($\text{m-dobdc}^{4-} = 4,6\text{-dioxido-1,3-benzene-di-carboxylate}$). We have also studied these MOF materials as electrode materials for supercapacitor application. The thesis embodies six chapters which are briefly described and discussed in the following:

The **first chapter** discusses the background of hydrogen energy and the principle of hydrogen storage in various storage modes with special emphasis on metal hydrides. The principle and mechanism of hydrogen storage in metal hydrides has been discussed. The limitations of conventional alloys/intermetallics for reversible hydrogen storage are pointed out. It also discusses the hydrogen storage behavior of light weight hydrides, especially, MgH_2 , NaAlH_4 , porous nanomaterials like MOF and some new materials with improved hydrogen storage capacity.

The **second chapter** describes the experimental and theoretical techniques/methods employed in the thesis. These techniques include ball-milling, glove box *etc.*, X-ray diffraction (XRD) technique has been employed for gross structural characterization. In addition, Scanning electron microscopy (SEM) using secondary electron imaging mode, Transmission electron microscopy (TEM), high resolution electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS) and EDAX have been used for microstructural and compositional characterization. The temperature based Raman, Fourier transforms infrared spectroscopy (FT-IR), and Nuclear magnetic resonance (NMR) spectroscopy has been used for spectroscopic

analysis. Hydrogen storage measurements were carried out using an automated one and two channel Gas Reaction Controller (GRC) operated by a Lab-View based program.

The **third chapter** investigated the comparative study of graphene, Vanadium disulfide (VS_2), Tungsten disulfide (WS_2), and Molybdenum disulfide (MoS_2) as a catalyst for improving the hydrogen sorption properties of MgH_2 . Based on the de/re-hydrogenation study; it is found that VS_2 works as an optimum catalyst over graphene, MoS_2 , and WS_2 for MgH_2 . The MgH_2 - VS_2 has the onset dehydrogenation temperature of $\sim 242^\circ\text{C}$, which is $\sim 134^\circ\text{C}$ than the desorption temperature of pristine MgH_2 and $\sim 88^\circ\text{C}$, $\sim 58^\circ\text{C}$, $\sim 35^\circ\text{C}$ than MgH_2 - MoS_2 , MgH_2 -Gr, MgH_2 - WS_2 , respectively. There is a slight degradation in the hydrogen storage capacity (0.2 wt%) even after 25th cycles. However, the catalysts VS_2 graphene, MoS_2 , and WS_2 do not play a significant role to lower the thermodynamics of the MgH_2 . The hydrogen desorption activation energy barrier to converting MgH_2 into Mg in the presence of VS_2 catalyst was found to be 98.09 kJ/mol, which is 36.86 kJ/mol, 19 kJ/mol, 5.91 kJ/mol and ~ 42 kJ/mol less than from activation energies of MgH_2 -Gr, MgH_2 - MoS_2 , MgH_2 - WS_2 and pristine MgH_2 respectively. The studies in the present investigation indicate that VS_2 is a better catalyst that replaces graphene and possibly other 2D materials (like MoS_2 , WS_2 , *etc.*) as a catalyst for MgH_2 .

The **fourth chapter** reports the results of investigations of de/re-hydrogenation in the Mg/ MgH_2 -graphene templated Ti-based catalysts (Ti, TiO_2 , and TiH_2) system. Based on de/re-hydrogenation study graphene templated TiH_2 (TiH_2 @Gr) was found to be the optimum catalyst as TiH_2 @Gr catalyzed MgH_2 has the onset dehydrogenation temperature of $\sim 204^\circ\text{C}$ which is 31°C , 36°C , and 66°C lower than the dehydrogenation temperature of MgH_2 -Ti@Gr, MgH_2 - TiO_2 @Gr, and BM MgH_2 . Most importantly, the effect on the thermodynamics of MgH_2 which has not been observed in case of VS_2 catalyst has been seen for MgH_2 - TiH_2 @Gr, the change in enthalpy of MgH_2 - TiH_2 @Gr is ~ 6.12 kJ/mol lower than ball-BM MgH_2 . There is slight decrease (0.1 wt%) in hydrogen storage capacity of MgH_2 - TiH_2 @Gr up to 5 cycles and then capacity remains unchanged up to 25 cycles. The improved

hydrogen sorption in $\text{MgH}_2\text{-TiH}_2\text{@Gr}$ can be attributed to three effects namely catalytic effect of TiH_2 , $\text{TiH}_{1.924}$ which forms due to interaction of TiH_2 and graphene, co-catalytic effect of graphene and absence of agglomeration of TiH_2 and $\text{TiH}_{1.924}$ due to their anchoring on graphene. Graphene besides ceasing the agglomeration of TiH_2 also helps in electron transfer to and fro from TiH_x to MgH_2 . The studies carried out in the present investigation indicate that further research on graphene and possibly other two-dimensional (2D) material as a template for the existing catalyst may open a new avenue for catalyzing MgH_2 , so as to make it a viable hydrogen storage system for practical applications.

The **fifth chapter** investigates the effect of quasicrystal (QC) (neither amorphous nor crystalline) as catalyst on yet another highly efficient solid-state hydrogen storage material *i.e.*, the complex metal hydride NaAlH_4 system. The present study found leached ball-milled $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ QC as a better catalyst for the NaAlH_4 . The leached ball-milled $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ (LBMACF) catalyzed NaAlH_4 sample has the lowest hydrogen desorption temperature of $140\text{ }^\circ\text{C}$ as compared to NaAlH_4 catalyzed by other versions of QC as well as with uncatalyzed NaAlH_4 . $\text{NaAlH}_4\text{-LBMACF}$ shows faster rehydrogenation kinetics by absorbing $\sim 4.68\text{ wt\%}$ in 10 minutes at $130\text{ }^\circ\text{C}$ under 100 atm hydrogen pressure and promising cyclic stability up to 25 cycles. Based on XRD, electron microscopy, temperature based Raman spectroscopy, temperature based NMR spectroscopy, and XPS analysis, it has been established that the weakening of Al-H in NaAlH_4 is one of the main reasons for destabilizing NaAlH_4 . The destabilization of the Al-H bond is found greater in LBMACF due to a more multi-electronic state environment around NaAlH_4 than other catalysts. Therefore, synthesizing multivalent QC-based catalysts seems to be a promising approach for destabilizing NaAlH_4 and promotes the use of complex hydrides for onboard applications.

In chapters 3-5, we have discussed about the catalyzed and uncatalyzed version of metal hydrides like MgH_2 , NaAlH_4 for hydrogen storage applications keeping the US-DOE target for hydrogen fuel cell vehicle in view. In **chapter six** we

have investigated porous nanomaterial Metal-organic frameworks (MOF) for hydrogen storage application in space vehicle. Here the hydrogen uptake and release temperatures and pressures are drastically different from the need of US-DOE target. The hydrogen storage properties are usually evaluated at $-196\text{ }^{\circ}\text{C}$ (liquid (LQ) N_2 temperature) for space vehicle application. The hydrogen storage capacity of $\text{Mn}_2(\text{m-dobdc})$ MOF is determined to be the highest of 7.72 wt% at $-196\text{ }^{\circ}\text{C}$ (LQ N_2 temperature) under 5-100 atm H_2 pressure, which is 3.81 wt% higher than $\text{Fe}_2(\text{m-dobdc})$ MOF under identical temperature and pressure conditions. As a result, $\text{Mn}_2(\text{m-dobdc})$ out performs $\text{Fe}_2(\text{m-dobdc})$ when it comes to gravimetric hydrogen storage capacity. The isosteric heats of adsorption and desorption for $\text{Mn}_2(\text{m-dobdc})$ were also computed and found to be -4.83 kJ/mol and -4.68 kJ/mol , respectively. The isosteric heats of adsorption and desorption for $\text{Fe}_2(\text{m-dobdc})$ are -15.89 kJ/mol and -16.74 kJ/mol , respectively. On the other hand, the supercapacitance application for the $\text{Mn}_2(\text{m-dobdc})$ and $\text{Fe}_2(\text{m-dobdc})$ based electrode materials were evaluated. In the comparative study present in the current work indicates that $\text{Mn}_2(\text{m-dobdc})$ based supercapacitor exhibited higher capacity ($\sim 25\text{ F/g}$ at 0.41 A/g current density) as compared to $\text{Fe}_2(\text{m-dobdc})$ based supercapacitor.

In conclusion, the thesis work has been summarized, and their potential outcomes with future aspects have been discussed.

