*Review Article***Hydrogen Energy in India: Storage to Application**

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It is well-known that the evolution of society is guided by several environmental strains. One of the important strains existing at this point of time is climate change due to pollution. Other issue of paramount importance is “energy”. One of the comparatively new energy vectors which is typically suited for India is “hydrogen”. Hydrogen is an indigeneous fuel since it can be produced by dissociating water with a variety of input energies, out of which solar energy is of particular importance. India has both of these in plenty. Hydrogen produced from water burns back to water after use. It is thus climate-friendly, inexhaustible, clean and indigenous fuel. Hydrogen must first be produced, afterwards stored, and then used, particularly in vehicular transport. Hydrogen storage is the crucial issue of hydrogen economy, cutting across production, distribution and applications. Finding efficient materials capable of storing hydrogen with high gravimetric and volumetric efficiencies is the central issue for harnessing hydrogen to replace fossil fuel oil (petroleum). We have brought out the relevance of hydrogen, particularly its storage aspect. The study then focuses on various aspects of hydrogen storage materials. The article describes some hydrogen-fuelled devices with particular emphasis on vehicular transport (three-wheelers and small cars).

Keywords: Hydrogen Energy; Hydrogen Storage; Hydrides; Hydrogen-Fuelled Vehicle

Introduction

Energy is an important component of our life. It needs paramount attention with regard to its availability, in ever increasing amounts. As we attempt to improve the quality of our lives and enhance our efficiency for doing work, more and more energy is going to be needed. For India, increase in population is another reason for increasing required quantity of energy. Solar energy can safely be considered as the source of most forms of energy that we use. The commercial forms of energy, the fossil fuels, i.e. coal and oil are indirect manifestation of stored solar energy, which was formed several millions of years ago. Solar cells, both dry (producing electricity) and wet, producing hydrogen are manmade devices and directly convert solar energy to fuel.

With regard to oil, India is an energy-starved country. We have only 0.9% of total oil deposits, the Middle East has about ~60%, China ~5% and USA 15% (bp.com/statistical review, 2012). Owing to emergence of new oil resources and also highest oil sales, it is predicted that USA may surpass Saudi Arabia's oil production. Several other countries such as Russia, Norway, and Libya also have large amount of oil deposit. It is estimated that the indigenous oil supply will last only about 23 years in India. The instability which oil imports create for our economy is well-known. Owing to increasing population and increase in vehicular transport for better comfort and efficiency, we need more and more oil. However, the depletion of oil is fast. We ought to remember that our main source of oil supply “Bombay High” peaked in 1998 and it is rapidly decreasing. We are thus in a paradoxical position.

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Another aspect which is at present comparatively more important is the issue of global warming/climate change. The Stern Report (2006) for the first time quantified the effect of global warming in economic terms. The temperature must not rise more than 2°C by 2050. Many countries are required to reduce their CO₂ remission to achieve the 2°C rise in temperature cap. For developing countries, there are no binding targets; but for developed countries, there are binding targets to reduce CO₂ emissions ([p://unfccc.int/files/kyoto_protocol/status_of_ratification/application/pdf/kp_ratification.pdf](http://unfccc.int/files/kyoto_protocol/status_of_ratification/application/pdf/kp_ratification.pdf)).

One aspect which is often forgotten is the fact that global warming climate change affects different countries differently. For example, global warming/climate change arising out of few degrees change in temperature will initially help cold countries such as USA. On the other hand, rise in temperature by few degrees will produce calamitous difficulty for warm countries such as India. Global warming/climate change produces detrimental effect on agriculture. For USA, the contribution of agriculture to GDP is only 0.9%; whereas for India, it is 22% (The World Fact Book, 2012). Thus, it is obvious that climate change will affect Indian economy drastically, in fact, it has already started affecting.

There are various ways in which global warming/climate change effects are quite different for India as compared to USA.

All the detrimental effects typically affecting India suggest that unlike USA, our country has to take the global warming/climate change much more seriously. Since oil (petroleum) is one of the most dominant sources of CO₂ emission, we have to switch over even if slowly to a renewable fuel for vehicular transport which does not produce CO₂. The urban air pollution resulting from use of petroleum deserves to be mentioned here. This is a serious problem emanating from the use of petroleum for vehicular transport. The air quality of not only Delhi, but many other cities, particularly metropolitan cities is quite bad. This aspect again demands, the gradual replacement of petroleum by a clean fuel. The above facts and figures suggest that for India, we not only need a clean and renewable fuel but also a fuel which is

source regenerating and indigenous. The following lists the motivations which should induce India to switch over to renewable fuel.

- Deficit between oil demand and supply
 - Huge imports ~170 MT (Ariga *et al.*, 2013)
- Economic burden (depletion of indigenous resources)
 - Irreversible climate changes (It could be the first priority.)
 - Air pollution

Decades of researches clearly led to the conclusion that out of the various renewable fuels, hydrogen is the best option for India. Hydrogen can be produced from water and hydrocarbons in a variety of ways. However, the most plausible and long-term sustainable mode is “solar hydrogen”, which is the hydrogen produced from dissociation of water by employing solar energy. India has solar irradiation next only to Africa (India ~800 watts/m², Africa ~1000 watts/m²). India has huge water resources such as the Indian Ocean, Arabian Sea and Bay of Bengal. Hydrogen produced from water burns back to water after use (cold combustion in fuel cells and hot combustion in IC engines). Thus, hydrogen is inexhaustible, indigenous, clean and climate-friendly. It thus solves the triple problems of gap in production consumption, supply, climate change effects and air pollution (Hudson *et al.*, 2009).

We will proceed to deal with hydrogen energy with particular emphasis on its use in vehicular transport. For harnessing hydrogen, its production, storage (including related effect of safety) and applications should be taken care of. It should be pointed out that as far as hydrogen production is concerned, it is already being produced to the tune of 57 MT per annum, which is equivalent to ~170 MT of oil (bp.com/statistical review, 2012). The methods of hydrogen production most commonly used are steam reformation of naphtha or methane. These processes even though practised widely produce CO₂ and hence result in global warming/climate change. Sustainable methods of production are those which employ solar energy to dissociate water or water-containing

species. These are photo-catalytic, photo-electrochemical and photo-biological routes of hydrogen production (Hudson *et al.*, 2009).

It may be pointed out that the search for viable hydrogen production routes takes into account the cost of hydrogen. In fact, the cost of hydrogen is possibly the top consideration in testing the viability of hydrogen as a fuel. However, it should be realized that the real cost of hydrogen takes into the account the costs involved in damages caused by use of fossil fuel. This is presented in Table 1 and Fig. 1.

Table 1: Enviromental and health damages by fossil fuels (after Prof. T.N. Veziroglu, private communication) (\$/GJ)

Type of damage	Coal	Petroleum	N. Gas
On Humans	5.84	4.51	3.33
On Animals	0.82	0.67	0.48
On Plants and Forests	2.15	1.74	1.29
On Aquatic Systems	0.29	1.68	0.18
On Man-Made Structure	1.78	1.43	1.07
Other Pollutant Costs	1.56	1.26	0.94
By Strip Mining	0.79	-	-
By Climatic Change	2.22	1.80	1.34
By Sea-Level Rise	0.51	0.41	0.31
Total Enviromental Damage	15.66	13.50	8.94

Fig. 1: Comparison of economics of hydrogen and fossil fuel systems (after T.N. Veziroglu private communication)

Hydrogen Storage

Hydrogen storage is considered to be the crucial issue for hydrogen economy, cutting across production,

distribution and applications. It is generally believed that storage in the form of hydrides is an efficient and safe storage mode with high hydrogen density (Hudson *et al.* 2009). Earlier, the emphasis was on hydrogen fill-in and take-out type hydrides typified by intermetallics, for e.g. FeTi, LaNi₅ (Züttel *et al.*, 2003), etc. The emphasis has recently shifted to take-out and regenerate type of built-in hydrides such as MgH₂, NaAlH₄, LiNH₂, etc. Out of these, MgH₂ appears to be a promising material because of its high storage capacity (7.6 wt.% H₂), better reversibility and plentiful availability of Mg in the earth's crust. It satisfies most of the requisites for a viable hydrogen storage system for mobile as well as stationary hydrogen devices. Slow hydriding and dehydriding are the major drawbacks of magnesium hydride as hydrogen storage material. Different studies also reveal that carbon-based nano-structures may also be used as effective hydrogen storage materials (Rao *et al.*, 2009).

Studies at Hydrogen Energy Center (HEC), Banaras Hindu University (BHU) are focused on hydrogen production, hydrogen storage and demonstration of hydrogen-fuelled vehicles. In this article, we will focus on storage and applications of hydrogen. For storage, the studies focus on Mg, Li-Mg-N-H and NaAlH₄ systems, with respect to the lowering of desorption temperature and enhancement of desorption kinetics by synthesizing these materials with alternative routes and deployment of various new effective catalysts. Here, we describe some important results on hydrogen storage materials which were studied recently at our centre.

Intermetallic Metal Hydrides

Intermetallic metal hydrides are often obtained by combining an element forming a stable hydride with an element forming an unstable hydride. The general formula for the intermetallic hydride is AB_xH_n. The A element is usually a rare earth or an alkaline earth metal and tends to form a stable hydride. The B element is often a transition metal and forms only unstable hydrides. Some well-defined ratios of B to A in the intermetallic compounds are $x = 0.5, 1, 2, 5$ have been found to form hydrides with a hydrogen to metal ratio of up to two. The maximum amount of

hydrogen in the hydride phase is given by the number of interstitial sites in the intermetallic compound for which the following two criteria apply. The distance between two hydrogen atoms on interstitial sites should not be less than 2.1 Å (Switendick, 1979) and the radius of the largest sphere on an interstitial site touching all the neighbouring metallic atoms is at least 0.37 Å (Westlake, 1983). Usually, upon hydrogenation, binary alloys will experience lattice expansion and distortion, but the crystal structure will stay the same. On the other hand, for some hydrides, the crystal structure changes with hydrogen content.

Research on intermetallic compounds for hydrogen storage has already been attempted more than 20 years ago. Sakintuna *et al.* (2007) summarizes the results of different studies/investigations on hydrogen storage characteristics of different intermetallic compounds. The different families of intermetallic compounds are classified on the basis of their crystal structures. AB₂-type (Laves phase), AB₅-type phases and Ti-based body centered cubic (BCC) and quasicrystalline alloys are well-known intermetallic hydrogen-storage system. These are reviewed as follows.

AB₅-Type Hydrogen Storage Materials

LaNi₅ is the most studied compound belonging to this series. Several investigations have already been devoted to the crystal structure, thermodynamic and electrochemical properties. The hydriding properties of this material were first reported by Vuchet *et al.* (1970). LaNi₅ crystallizes in the hexagonal structure of a CaCu₅ type (space group P6/mmm with La in 1a (0 0 0) and Ni in 2c (1/3 2/3 0) and 3g (1/2 0 1/2)). The crystal structure of the metal host-lattice is generally preserved upon hydrogenation. Several types of tetrahedral interstices can be identified within the structure with different metal co-ordination: A₂B₂, AB₃ (2 types) or B₄ (Latroche *et al.*, 1998). Upon hydrogenation, the A₂B₂ sites are filled first, followed by the AB₃ sites. Occupation of the B₄ sites remains low, even for a fully loaded hydride. LaNi₅ absorbs about 1.0 H/LaNi₅ (1.5 wt%) and is easy to activate (5 bar at *T* = 100 °C after a few cycles, to achieve the maximum hydrogen capacity). It has small absorption/desorption pressure hysteresis and the plateaus are

rather flat. The enthalpy of formation of LaNi₅H₆ is -30.9 kJ/mol-H₂ and desorption plateau pressure at 25 °C is 1.6 atm. So far, the multi-component La_{1-x}RE_xNi_{5-x}M_x system has also been extensively studied (M = Mn, Cr, Fe, Co, Cu, Al, Sn, Ge, Si and RE = Mischmetal, Ce, Nd). LaNi₅ has very useful properties, but is rather expensive due to the presence of expensive elemental La.

AB-Type Hydrogen Storage Materials

FeTi is a well-known hydrogen-storage compound. This belongs to the class of intermetallic compounds with a total hydrogen capacity of around 1.90 wt% with inexpensive elements. However, the activation process of FeTi is troublesome due to the formation of Ti oxide layer. Both high-pressure and high temperature is required to achieve a reproducible absorption/desorption of the maximum amount of hydrogen in the compound (Bououdina *et al.*, 2013). Hydrogen capacity of FeTi can be accomplished to 1.90 wt% by the catalytic effect of 1 wt% Pd addition (Zaluski *et al.*, 1995 a, b). The application of mechanical alloying under different atmospheres with the use of catalytic elements, for e.g., Pd, dramatically enhances the activation process and the hydriding/dehydriding kinetics of FeTi (Zaluski *et al.*, 1996). Ball milling under pure argon atmosphere (20-0 h) of FeTi with small amount of Ni can readily absorb H₂ without activation (Bououdina *et al.*, 1999). Drastic improvement of the kinetics is due to the formation of a fine powder of FeTi covered by nanocrystalline Ni particles, which act as catalytic centres for the decomposition of H₂ molecules into H atoms.

AB₂ Laves Phases

AB₂ Laves phases have attracted great attention as potential hydrogen-absorbing materials. The potential AB₂ types are obtained with Ti and Zr on the A site. The B elements are represented mainly by different combinations of 3d atoms, V, Cr, Mn and Fe. AB₂ exists in three types of crystal structure: cubic C15 (MgZn₂, such as ZrV₂, low-temperature TiCr₂ and high-temperature ZrCr₂), hexagonal C14 (MgCu₂, such as ZrCr₂ low temperature, TiCr₂ high temperature and ZrMn₂) and double hexagonal C36 (MgNi₂). Laves phases show relatively high storage

capacities ($\text{ZrV}_2\text{H}_{5.3}$, $\text{ZrMn}_2\text{H}_{3.6}$, $\text{ZrCr}_2\text{H}_{3.4}$), faster kinetics, longer life and a relatively low cost. However, their hydrides are too stable at room temperature. In general, the AB_2 -type compounds seem to be more sensitive to gaseous impurities than the AB_5 -type compounds.

BCC Solid Solution

It has been reported that Ti-based Laves phase alloys of AB_2 type are multiphase alloys consisting of BCC and Laves phases. Both these phases are responsible for hydrogenation (Yang *et al.*, 2011). In fact, the BCC and Laves phase showed the same equilibrium pressure. For this reason, these new classes of alloys are called as Laves phase-related BCC solid solutions. Earlier studies on $\text{Zr}_{0.5}\text{Ti}_{0.5}\text{VMn}$ have shown that this alloy is composed of three phases. In subsequent studies on the Ti-V-Mn system, microstructure analysis by TEM revealed that the BCC phase consisted of two nanoscale phases with a fine lamellar structure of 10nm thickness (Cote *et al.*, 2005). Hydrogen storage capacity was found to be higher than 2 wt% for the system Ti-Cr-V. Furthermore, this system has a smaller hysteresis than Ti-V-Mn and needs only one activation cycle. Usually, BCC solid solution alloys form two types of hydrides: the first (approximately a monohydride) is very stable and usually cannot be desorbed under practical conditions; and the second (dihydride) is mainly responsible for the reversible capacity. Therefore, the challenge is to destabilize the first hydride or increase the intrinsic reversible capacity of the dihydride. Recently, many groups have reported BCC alloys of various compositions which could store hydrogen with a maximum capacity close to 4 wt% and with reversible capacities of more than 2 wt% (Murray *et al.*, 2009).

We proceed further to discuss the other types of hydrides. Here, these hydrides will be elucidated by describing and discussing the research done in our laboratory.

Elemental hydride

Magnesium Hydride; Co-catalysed with Ti, Fe and Ni

MgH_2 is one of the promising materials for reversible

hydrogen storage application due to its light mass, high hydrogen storage capacity (both volumetric and gravimetric) and abundance in nature. However, there are some key issues which need to be addressed for using MgH_2 as a practical onboard candidate. The issues associated with MgH_2 are high dehydrogenation temperature, slow kinetics of de/rehydrogenation and thermodynamics limitation. Details of these studies are also discussed and described elsewhere (Shahi *et al.*, 2013). The starting materials: pure MgH_2 (500-1000 μm), Ti (150 μm), Fe (120 μm) and Ni (100 μm), were taken in various compositions. These powders (5 wt% each of MgH_2) were mechanically milled to obtain the desired compositions: $\text{MgH}_2\text{-Ti}_5$, $\text{MgH}_2\text{-Fe}_5$, $\text{MgH}_2\text{-Ni}_5$ and $\text{MgH}_2\text{-Ti}_5\text{-Fe}_5\text{-Ni}_5$. The container with samples was flushed through hydrogen to avoid the effect of residual oxygen. In order to investigate the structural modification of mechanically milled MgH_2 separately and together with Ti, Fe and Ni, XRD is performed for different samples. It is found that the grain size of milled MgH_2 is ~ 15 nm, whereas the grain size for as-received MgH_2 is found to be ~ 199 nm. It is also worth noticing that the XRD patterns of MgH_2 mechanically milled separately with Ti, Fe and Ni give the XRD peaks which correspond to TiH_2 , Mg_2FeH_6 and Mg_2NiH_4 hydride phases shown in Fig. 2A, respectively. On the other hand, when Ti, Fe and Ni are used together with MgH_2 , the alloys Mg_2NiH_4 and Mg_2FeH_6 do not get formed. This is likely since Ti has very little solid solubility. Hence, the presence of Ti may cover the surface of Mg particle due to which there is very less possibility for the diffusion of Fe and Ni in Mg particles for the formation of alloys. This may hinder the formation of Mg_2NiH_4 and Mg_2FeH_6 when Ti, Fe and Ni are used together as catalysts. Fig. 2G represents the decomposition temperature (peak at maximum decomposition temperature) of different samples. From Fig. 2G, it is clear that the maximum decomposition temperature of the received MgH_2 is 410°C and this is reduced to 370°C for nano MgH_2 . However, the decomposition temperatures for nano $\text{MgH}_2\text{-Ni}_5$, $\text{MgH}_2\text{-Ti}_5$, $\text{MgH}_2\text{-Fe}_5$ and $\text{MgH}_2\text{-Ti}_5\text{-Fe}_5\text{-Ni}_5$ are found to be 340, 320, 310, and 280°C , respectively. The effects of transition metals are higher when all these catalysts are used

Fig. 2: X-ray diffraction pattern of (A) received MgH_2 , mechanically milled (B) MgH_2 , (C) MgH_2 +5wt% Ti, (D) MgH_2 +5wt%Fe, (E) MgH_2 + 5wt% Ni and (F) MgH_2 + 5wt% (Ti+Fe+ Ni) (G) TPD profile of different samples and (H) absorption kinetics plot of different samples (Figures 1, 2a, 4b; Shahi *et al.*, 2012)

together. This may occur due to the co-catalysed effect of Ti, Fe and Ni (370 $^{\circ}\text{C}$ to 280 $^{\circ}\text{C}$ for nano MgH_2 to $\text{MgH}_2\text{-Ti}_5\text{-Fe}_5\text{-Ni}_5$).

In order to investigate re-hydrogenation characteristics of different samples, the absorption experiments were performed at 270 $^{\circ}\text{C}$ and 15 atm of hydrogen pressure for 1 h. It is found that nano MgH_2 reabsorbs only 4.2 wt%; whereas, nano $\text{MgH}_2\text{-Ti}_5$, $\text{MgH}_2\text{-Fe}_5$ and $\text{MgH}_2\text{-Ni}_5$ absorb 4.3, 4.98 and 5.0 wt%, respectively. However, the absorption capacity for co-catalysed nano $\text{MgH}_2\text{-Ti}_5\text{-Fe}_5\text{-Ni}_5$ is found to be 5.3 wt% within 15 min. The difference in re-absorption capacity of the samples occurs due to the formation of stable hydrides TiH_2 , Mg_2FeH_6 and Mg_2NiH_4 when Ti, Fe and Ni are mechanically milled separately with MgH_2 . (Liang *et al.*, 1999) have also reported that these hydrides are highly stable and did not decompose under mild desorption condition. The presence of these Ti, Fe and Ni in Mg matrix causes co-catalysed effect of these transition metals and hence the de/re-hydrogenation characteristics of MgH_2 increase appreciably.

Effect of Carbon-based Nanostructures on Hydrogen Sorption in MgH_2

In addition to transition metals, another type of catalysts which has recently caught attention as effective catalyst for de/re-hydrogenation of MgH_2 are the carbon nanostructures. We have synthesized different morphologies of CNSs and investigated their catalytic effect on the hydrogenation behaviour of nano MgH_2 at HEC BHU. The details of these studies are also discussed and described elsewhere (Shahi *et al.*, 2012).

Different CNSs were synthesized through the chemical vapour deposition (CVD) technique. Nanocrystalline MgH_2 (nano MgH_2) was synthesized through the method described previously by the ball milling of as-received MgH_2 (particle size is 50-100 μm) using Retsh PM-400 ball miller. Admixing of CNSs were performed inside the glove box by using locally fabricated mixer (at 4000 rpm) having three chromium nickel stainless steel balls.

In order to explore the effectiveness of CNS as catalyst for improving the de/rehydrogenation

behaviour of MgH_2 , temperature programmed desorption (TPD) (at heating rate $5^\circ\text{C}/\text{min}$) were performed for nano MgH_2 with and without CNS. Fig. 3A shows representative TPD profile for different samples. As seen in figure, desorption temperature is reduced to 346°C from 367°C with admixing of MWCNT (multi-wall carbon nanotube). Desorption temperature for SWCNT (single-wall carbon nanotube) admixed nano MgH_2 is found to be 357°C . Further, it is also found that desorption temperature is $\sim 334^\circ\text{C}$ and $\sim 300^\circ\text{C}$ for the PCNF and HCNF admixed nano MgH_2 . The desorption temperature of nano MgH_2 is reduced to $\sim 300^\circ\text{C}$ from $\sim 367^\circ\text{C}$ with admixing of HCNF (decrease of $\sim 67^\circ\text{C}$). Effectiveness of the catalyst is found to be highest for HCNFs followed by PCNFs, MWCNTs and SWCNTs. The absorption kinetics plots of nano MgH_2 with and without CNS at 300°C and 2 MPa of hydrogen pressure are shown in Fig. 3B. The hydrogen uptake capacity of nano MgH_2 is found to be 4.8 wt%. This gets improved with admixing of MWCNTs, SWCNTs, PCNFs and HCNFs. It is found that the nano MgH_2 admixed with MWCNTs, SWCNTs, PCNFs and HCNFs absorb 5.2, 5, 5.7 and 5.8 wt% of hydrogen within 1 h, respectively. It is also found that HCNF admixed nano MgH_2 absorbs ~ 5.25 wt% within 10 min as compared to pristine nano MgH_2 , which absorbs only ~ 4.2 wt% within the same time and same condition of temperature and pressure. Thus, absorption kinetics of the pristine nano MgH_2 improves significantly with admixing of HCNF.

There are two possible reasons for lowering of desorption temperature and improvement in rehydrogenation kinetics of CNS-catalysed nano MgH_2 . These are (a) type and morphology of carbon nanostructures and (b) presence of synthesis-acquired metallic particles. In order to confirm the catalytic effect of metallic particles, we have also conducted TPD experiments with acid-treated (purified) CNS under previously performed condition and compared the desorption results with that of pristine nano MgH_2 . From these investigations, we can say that the catalytic activity of purified CNS becomes less significant as compared to as-synthesized CNS. The purified MWCNT shows the marginal effect on desorption behaviour of pristine nano MgH_2 ($\sim 16^\circ\text{C}$),

Fig. 3: A: TPD profile and B: absorption kinetics plot of different samples (Shahi *et al.*, 2012)

whereas purified HCNF admixed sample exhibits the significant effect ($\sim 37^\circ\text{C}$). Hence for the present case, we can say that the fibrous morphology shows better catalytic activity than the tubular morphology of carbon nanomaterials. Furthermore, the presence of synthesis-acquired metallic particles enhances the

catalytic activity of CNF. Hence, we can say that the morphology of carbon nanostructures is not the only factor for lowering of the desorption temperature. It is the combined effect of both, morphology and the presence of metallic particles in carbon nanostructures which play a vital role in lowering the desorption temperature of MgH_2 .

Effect of TiO_2 Nanoparticles of Different Sizes on Hydrogen Sorption Behaviour in MgH_2

The effect of variation in concentration of the catalyst on improving the sorption characteristics of MgH_2 has been widely investigated by various researchers (Shahi *et al.*, 2012; Vegge *et al.*, 2005; Magusin *et al.*, 2008; Fernández *et al.*, 2012; Charbonnier *et al.*, 2004; Pandey *et al.*, 2013). However, the effect of variation in size of the catalyst particles on the sorption behaviour of MgH_2 has been studied only sparsely. An important aspect of catalytic activity relates to the size of the catalyst which may lead to uniform distribution over and/or within MgH_2 . This will lead to selection of optimum size of catalyst particle for efficient hydrogen sorption in the case of MgH_2 . Here, we describe the effect of the size variation of TiO_2 nanoparticles (np) and determination of optimum size for improving the hydrogen sorption behaviour of MgH_2 . Details of these studies are also discussed and described elsewhere (Shahi *et al.*, 2012).

Fig. 4A brings out a representative dark field TEM image taken with (211) rutile reflection of TiO_2 nanoparticles. As seen in the figure, the TiO_2 nanoparticles (with bright contrast) are almost uniformly distributed into MgH_2 large particles with the TiO_2 nanoparticles of size 50 nm. The corresponding selected area diffraction pattern is shown in the inset of Fig. 4A. The diffraction pattern (inset) shows spots corresponding to large MgH_2 particles and ring pattern for TiO_2 nanoparticles. In Fig. 4B, the microstructural features of MgH_2 - TiO_2 (50 nm) have also been analysed from secondary electron image employing SEM. At the resolution level of SEM, TiO_2 nanoparticles cannot be visualized. However, the contrast in the SEM picture suggests the presence of large particles together with very small particles on and around the large particles.

Presumably, the large particles are MgH_2 and the smaller ones are TiO_2 nanoparticles. Fig. 4C brings out the representative TPD curves of MgH_2 catalysed with different sizes of TiO_2 nanoparticles as a function of temperature. TPD was carried out at the heating rate of $2^\circ\text{C}/\text{min}$ from room temperature to 450°C . It can be clearly observed from the TPD curves that the dehydrogenation temperature of MgH_2 catalysed with various sizes of TiO_2 (np) has shifted to a lower onset desorption temperature than that of the ball-milled MgH_2 and as-received MgH_2 . The TPD curves can be divided into two broad categories. It is noted that the onset desorption temperatures for the first category is found to be $\sim 335^\circ\text{C}$ for the ball-milled MgH_2 as well as for MgH_2 catalysed with TiO_2 nanoparticles having particle sizes of 250 nm and 100 nm. This temperature is $\sim 55^\circ\text{C}$ lower than as-received MgH_2 , for which the onset temperature is at $\sim 390^\circ\text{C}$; whereas, the onset desorption temperature for the second category is up to 310°C and lower. Thus, for MgH_2 catalysed with TiO_2 (np) of sizes 7, 25 and 50 nm, the onset desorption temperatures are 300, 305 and 310°C , respectively. Fig. 4D exhibits representative re-hydrogenation kinetic curves of Mg and TiO_2 (np) catalysed Mg. The better reabsorption kinetic is achieved for Mg catalysed with 50 nm of TiO_2 . The Mg- TiO_2 (50 nm) reabsorbed 5.1 wt% of hydrogen within 6 min. During the same period, the sample catalysed with TiO_2 (25 nm) could reabsorb only 4.2 wt% of H_2 and the sample catalyzed with (7, 100 and 250 nm) TiO_2 could reabsorb merely 3 wt% of H_2 . In the present sorption studies, MgH_2 catalysed with TiO_2 (50 nm) is annealed up to a temperature of $\sim 340^\circ\text{C}$, the TiO_2 is expected to undergo reduction leading to formation of non-stoichiometric TiO_x . In order to check the reduction of TiO_2 , we have studied temperature-programmed reduction (TPR) under hydrogen atmosphere at the heating rate of 5°C min^{-1} . It is found that reduction of TiO_2 in MgH_2 -50nm TiO_2 system by hydrogen takes place at $\sim 340^\circ\text{C}$. It may be pointed out that even at temperatures lower than 340°C , partial reduction may take place. Considering the observed results in the present investigations, it can be said that TiO_2 can undergo reduction. TiO_{2-x} being more electronegative (Pauling scale electronegativity of TiO_2 is 1.9 and for MgH_2 , it

Fig. 4: A: Dark field TEM micrograph and inset represent corresponding SADP, B: SEM micrograph C: TPD profile at 5°C/min and D: re-hydrogenation kinetics at 250°C under 30 atm hydrogen of MgH₂ catalysed with different sizes of TiO₂ nanoparticles (Pandey *et al.*, 2013)

is 1.4) (Vegge *et al.*, 2005) will therefore weaken the Mg-H bond by attracting the electrons from MgH₂. As a result, decomposition of MgH₂ will occur at a lower temperature leading to fast desorption kinetics. During absorption, reverse reaction will take place, which leads to lowering of the absorption activation energy.

Li-Mg-N-H System

Chen *et al.* have discovered a Li-N-H system for hydrogen storage in 2002. This discovery added a new material to the class of complex hydrides. In spite of high reversible storage capacity, this system possesses unfavourable thermodynamics (Song *et al.*, 2009; Janot *et al.*, 2007). Numerous other studies reveal that the substitution of Li by Mg provides a system having beneficial hydrogen sorption properties. It has already been described by different research groups that the Mg(NH₂)₂/LiH mixture is much better than those of LiNH₂/LiH (Song *et al.*, 2009; Janot *et*

al., 2007) with respect to thermodynamics and hydrogen uptake and release capacity. This is because Mg(NH₂)₂ is less stable and easily transforms into corresponding imide (MgNH) than LiNH₂ (Chen *et al.*, 2002). Further studies on this system revealed that Li-Mg-N-H system has slow desorption kinetics and the hydrogen uptake and release kinetics of the system is further improved by deployment of suitable catalysts. Some improvement has occurred in the kinetics with tuning, ball-milling of the Li-Mg-N-H system (Chen *et al.*, 2003; Ichikawa *et al.*, 2004; Weifang, 2004; Lohstroh *et al.*, 2007). Till date, no catalyst has been found for improvement in desorption kinetics and/or lowering of desorption temperature of Li-Mg-N-H system.

We have also explored this new class of complex hydrides as a storage material at our laboratory. We have synthesized Mg(NH₂)₂/LiH mixture and investigated the sorption kinetics with and without different catalysts such as vanadium and

vanadium-based compounds and carbon-based nanostructures. Vanadium is one of the typical transition metals which has better affinity towards electrons due to the presence of unoccupied d-orbital. It has been found that desorption kinetics and temperature of $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture gets improved with admixing of V, V_2O_5 and VCl_3 . The VCl_3 has been found to be the most effective followed by V and V_2O_5 (Chen, 2006; Shahi *et al.*, 2010). Here, we will describe the summary of the results obtained with the addition of carbon nanofibres to $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture. The details of these studies are also discussed and described elsewhere (Shahi *et al.*, 2010). The used carbon nano fibres (CNFs) are synthesized by the catalytic thermal decomposition of acetylene (C_2H_2) gas over LaNi_5 alloy (Shahi *et al.*, 2013). The samples for hydrogenation characteristics were prepared by the admixing of 4 wt% different types of a CNFs (planer (P) and helical (H)) in the parent material for 5min, inside the glove box through the high energy (4000 rpm) mixer (Shahi *et al.*, 2013). The decomposition behaviour of mixture with and without CNFs were examined by TPD experiment at heating rate of $2^\circ\text{C}/\text{min}$. The initial desorption temperature of $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture is 90°C and lowered to $\sim 70^\circ\text{C}$ and 50°C for PCNF and HCNF admixed $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture, respectively (Shahi *et al.*, 2013). The maximum decomposition temperature for without catalyst is found to be 250°C , which is lowered to 150°C and 140°C for PCNF and HCNF admixed samples, respectively. TPD experiments indicate that the admixing of CNF reduce the decomposition temperature of 1:2 $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture. The mixture without CNF desorbs ~ 3.5 wt% within 60 min; whereas, desorption of ~ 5 wt. occurs within 50 and 40 min for PCNF and HCNF admixed $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture respectively (Shahi *et al.*, 2013). The hydrogen uptake capacity of pristine and 4 wt% of each PCNF and HCNF admixed $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ mixture after 5h was found to be ~ 1.8 , 3.4 and 3.7 wt%, respectively (Shahi *et al.*, 2013). This may occur due to the presence of carbon fragments having various hybridized orbitals and these hybridized orbitals which can interact with the hydrogen molecule and provide transit site for the hydrogenation. The different catalytic effect of these CNFs is attributed to the fact

that these CNFs (PCNF and HCNF) have the same synthesis-acquired metallic particles. Hence, these different levels of improvement arise due to the morphological differences in CNFs.

Complex Hydride

Complex hydrides consist of hydrogen atoms which are covalently bonded to a central atom in an anion complex (e.g. $[\text{AlH}_4]^-$, $[\text{AlH}_6]^{3-}$, $[\text{AlH}_4]$, $[\text{BH}_4]^-$, $[\text{NH}_2]^-$) and stabilized by the cation, particularly alkali metal complex hydrides (e.g. NaAlH_4 , NaBH_4 , NaNH_2) or alkaline earth metal complex hydrides (e.g. $\text{Mg}(\text{AlH}_4)_2$, $\text{Mg}(\text{BH}_4)_2$) (Li, 2013). All these materials are known as “complex hydrides”, although only the alanates contain anionic metal complexes. In case of amides and borohydrides (saline materials), the hydrogen atom is covalently bonded to central atoms in “complex” anions (in contrast to interstitial hydrides). These materials offer high hydrogen gravimetric densities. After the pioneering research of Bogdanovic’ and Schwickardi (1997), the complex hydride (particularly, NaAlH_4) was considered as viable candidate for application as practical, onboard hydrogen storage material. Bogdanovic and Schwickardi show that, upon doping with selected titanium compounds, reversibility can be achieved in NaAlH_4 under moderate conditions (Bogdanovic *et al.*, 1997).

Complex Hydrides: Sodium Aluminium Hydrides

Hydrogen desorption in complex aluminium hydride (Alanates) containing alkali atoms takes place in three sub-steps as follows (Bhatnagar *et al.*, 2013).

(X denotes alkali element)

The decomposition of hydride in step 3 takes place at high temperature. Therefore, step 3 is generally omitted, while considering complex aluminum hydride for hydrogen storage. Many experiments have been carried out on alanate, with an objective to improve the thermodynamics of steps 1 and 2. Among

complex aluminium hydrides, NaAlH_4 , the prototype alanate is a widely studied hydrogen storage material (Jensen *et al.*, 2001; Sandrock *et al.*, 2002; Bogdanovic *et al.*, 2000,2007; Hassel *et al.*, 2012; Wang *et al.*, 2004).

Sodium aluminum hydride (NaAlH_4), would seem to be a possible candidate for application as a practical on-board hydrogen-storage material due to the theoretically reversible hydrogen-storage capacity of 5.6 wt%, low cost and its availability in bulk. The group of complex hydrides that have received the most attention over the last decade are the alanates (Bogdanovic *et al.*, 2007; Hassel *et al.*, 2012; Wang *et al.*, 2004).

Alanates are remarkable due to their high storage capacities; however, they decompose in two steps upon dehydriding.

Theoretically, NaAlH_4 and Na_3AlH_6 contain large amounts of hydrogen, 7.4 and 5.9 wt%, respectively. Reversibility of the above two reactions is a critical factor for practical applications. Although they have good hydrogen-storage capacity, complex aluminum hydrides are not considered as rechargeable hydrogen carriers due to irreversibility and poor kinetics, until Bogdanovic and Schwickardi (1997) showed that titanium-doped NaAlH_4 can reversibly be dehydrogenated and rehydrogenated. The addition of Ti-based compounds (such as TiCl_3 or $\text{Ti}[\text{O}i\text{Bu}]_4$ to NaAlH_4) was found to lower the first decomposition temperature of the hydride. A quantity of 3.7 wt% is released at 353 K, but at the expense of lowering the hydrogen content from 5.5 wt% in the hydride without a catalyst (Jensen *et al.*, 2001; Bogdanovic *et al.*, 2000). Furthermore, the reaction is reversible; a complete conversion to product was achieved at 270°C under 175 bar hydrogen pressure in 2-3 h (Bogdanovic *et al.*, 2000).

The operating temperatures are between 185°C and 230°C for the first and the second reaction, respectively. Finally, the decomposition of NaH occurs at a much higher temperature, with the total hydrogen

release of 7.40 wt%. For hydrogen storage, only the first two reactions need to be considered, because the decomposition of NaH occurs at too high temperature of 425°C for practical storage systems (Bogdanovic *et al.*, 2007). With 2 mol% TiN as doping agent, cyclic storage capacity of 5 wt% H_2 is achieved after 17 cycles (Hassel *et al.*, 2012; Bogdanovic *et al.*, 2003). However, decrease in hydrogenation rate with number of cycles is observed (Srinivasan *et al.*, 2004). This clearly indicates that the addition of titanium species enhances not only the dehydrogenation kinetics, but also the rehydrogenation reaction of NaAlH_4 (Bogdanovic *et al.*, 2003; Sun *et al.*, 2002; Balema *et al.*, 2000), which demonstrates reversible hydrogen cycling in Ti-catalysed sodium alanate over 100 cycles with a measured capacity of nearly 4 wt% H_2 at 160°C.

The van't Hoff plot of Ti-doped NaAlH_4 revealed that the enthalpy of the dehydrogenation of NaAlH_4 to Na_3AlH_6 and Al has been determined to be 37 kJ/(mol of H_2). This value is in line with the predictions of the studies discussed earlier. In accordance with this value, the temperature required for an equilibrium hydrogen pressure of 0.1 MPa has been determined as 33°C and highly practical hydrogen plateau pressures of 0.2 and 0.7 MPa have been found at 60°C and 80°C, respectively (Sun *et al.*, 2003). Unfortunately, the equilibrium hydrogen plateau pressures of the $\text{Na}_3\text{AlH}_6/\text{NaH} + \text{Al} + \text{H}_2$ equilibrium in the 70-100°C temperature range are insufficient for utilization in a PEM fuel cell system in which the heat of the steam exhaust would be used to drive hydrogen release for the storage material.

In addition to NaAlH_4 and Na_3AlH_6 , there are a number of other alanates capable of rehydrogenation under moderate pressures and temperatures including $\text{Na}_2\text{LiAlH}_6$, KAlH_4 , K_3AlH_6 , K_2LiAlH_6 and K_2NaAlH_6 . However, all these compounds have lower gravimetric hydrogen densities and are more stable than sodium alanate. On the other hand, there are a few alanates that are known to be less stable than sodium alanate, which also exhibit high gravimetric hydrogen densities such as LiAlH_4 , Li_3AlH_6 , $\text{Mg}(\text{AlH}_4)_2$, $\text{Ca}(\text{AlH}_4)_2$, $\text{Ti}(\text{AlH}_4)_4$ among others. Despite their promising capacities, these

materials are not known to be irreversible under moderate pressure conditions.

Complex Hydride: Borohydride

Hydrogen atoms in the borohydrides are positioned at the corners of the tetrahedral $[\text{BH}_4]^-$, where boron coordinates the hydrogen atoms located at the centre. The charge transfer from alkali or alkaline earth or by few transition metals helps in additional charge localization for the stabilization of the complex boron-hydrogen tetrahedron (Orimo *et al.* 2007). General dehydrogenation reaction of alkali metal tetrahydroborates can be represented by the following equation.

(C: alkali metals)

However, for alkaline earth metal tetrahydroborates, the dehydrogenation reaction can be written as:

(D: alkaline earth metals)

Recently, the hunt to find a high capacity reversible hydride has shifted to borohydrides. The most well-known borohydrides are lithium borohydride, LiBH_4 , and sodium borohydride, NaBH_4 . They are promising materials owing to their high gravimetric hydrogen contents up to 18 wt%. However, very high temperatures are required for the release of hydrogen from borohydride. Substantial effort has gone into finding ways of thermodynamically destabilizing the materials. LiBH_4 , one of the well-known borohydrides decomposes at temperatures 438°C to LiH and B and releases 13.5 wt% H_2 through the following reaction:

Since, borohydrides are thermodynamically very stable material; research efforts are mainly focused on reducing the decomposition enthalpy by destabilizing the LiBH_4 . Moreover, creating nanoscale powders and incorporating the hydride into nanoporous scaffolds or frameworks which inhibit agglomeration and sintering during cycling are some

efforts which are being made to improve the reaction kinetics of borohydrides. Researchers around the globe show considerable interest in the alkaline earth and transition metal borohydrides ($\text{Mg}(\text{BH}_4)_2$ (Matsunaga *et al.*, 2008 ; Ronnebro *et al.*, 2007; Nakamori *et al.*, 2006), which are much less stable than Group 1 borohydrides. These materials have demonstrated promising capacities at reasonable decomposition temperatures, but similar to less stable alanates, reversibility is the main issue. However, due to their higher hydrogen gravimetric capacity of storing hydrogen than aluminohydrides, they are at present considered appealing candidates for hydrogen storage. Detailed study on borohydride can be found in the review report of Enis *et al.*, 2004.

Quasicrystal: Materials for Hydrogen Storage and Catalytic Application

Quasicrystal

Quasicrystals (QCs) are orientationally ordered structures, which may often possess classically forbidden rotational symmetries (e.g. five-fold, eight-fold, ten-fold and twelve-fold). For the revolutionary discovery of QC, the 2011 Nobel Prize in Chemistry has been awarded to Professor Danny Shechtman. Before Shechtman's 1982 discovery of the first quasicrystal (QC), it was universally accepted, though never proven, that the internal order of crystals was achieved through a periodic filling of space. Crystallography treated order and periodicity synonymously, both serving equally to define the notion of a crystal. With that came the so-called "crystallographic restriction," stating that crystals cannot have certain forbidden symmetries such as 5-fold rotations. Shechtman *et al.* (1984) discovered the first icosahedral quasicrystal (IQC), formed under rapid solidification conditions in binary Al-Mn, quasicrystals have sparked debate over their atomic structure, stability, and other basic scientific issues. Quasicrystals are of great interest due to their potential for creating unusual structural form of matter having extraordinary physical properties. During the last three decades, significant progress has been made in the preparation, characterization and application of quasicrystals. Quasicrystal was discovered initially in

Al-based alloys (Shechtman *et al.*, 1984; Chattopadhyay *et al.*, 1985) and later in other binary Al-TM-based alloys containing Cr (Inoue *et al.*, 1987), V (Inoue *et al.*, 1986), and different ternary alloys (Rabe *et al.*, 1991; Kelton, 1995). Additionally, the icosahedral phase was observed in Ga-, Ti-, Mg-, and Pd-based alloys (Louzguine-Luzgin *et al.*, 2008) as well as in Cd- (Guo *et al.*, 2000), rare-earth (RE)- (Fisher *et al.*, 2000), and Zn-based (Kaneko *et al.*, 2001) alloys.

Similar to many intermetallics, QCs are expected to exhibit properties different from conventional metallic materials, which can be exploited for industrial applications (Somekawa *et al.*, 2011; Dubois, 2011). Quasicrystalline materials are characterized by a combination of such properties, as low friction, high hardness, low surface energy, and thermal expansion comparable to that of the metals (Dubois *et al.*, 2011; Lifshitz *et al.*, 2011; Hu *et al.*, 2011). Moreover, Ti/Zr-based QCs seem to be good candidates for hydrogen storage applications (Viano *et al.*, 1995).

Hydrogen Storage in Quasicrystal

The large free volume associated with quasi-periodicity and the high density of tetrahedral interstitial sites displayed by metallic alloys with quasicrystalline structure makes them materials of potential technological interest in the field of hydrogen storage and such structural features may indeed result in improved hydrogen storage capabilities (Wang *et al.*, 2004). The Ti-3d transition metal-Si icosahedral phases can absorb hydrogen from the gas phase and by electrolytic methods (Bahadur *et al.*, 1989; Viano *et al.*, 1993). The Ti-Zr-Ni icosahedral phase may contain interstitial sites for hydrogen and therefore, it is considered to be a new, promising hydrogen storage material (Taksaki *et al.*, 2006). The substitution of chemical elements in the Ti-based icosahedral phase powders may control hydrogen desorption properties. Both Ti-Hf-Ni and Ti-Zr-Ni alloys were reported to absorb hydrogen without the formation of a detectable crystal hydride phase (Molokanov *et al.*, 1990). The maximum hydrogen concentration of Ti-Zr-Ni phase powders is approximately 60 at %, which can be attained by either gaseous-phase or electrochemical

loading of hydrogen (Gibbons *et al.*, 2004; Tsai *et al.*, 1995; Wehner *et al.*, 1997). The two different absorption methods, one at room temperature and another requiring elevated temperature, successfully introduce hydrogen into Ti-Zr-Ni alloys (Viano *et al.*, 1998). The Ti-Zr-Ni alloys are good candidates for hydrogen storage because they contain two elements, Ti and Zr, which have high affinities for hydrogen and presence of Ni is beneficial in that it often creates a pathway for H diffusion through a surface oxide layer (Sawa *et al.*, 1990; Stroud *et al.*, 1996). The hydrogen storage capability of the quasicrystal compares to or exceeds those of the Ti-Zr-Ni crystal and amorphous phases and a complete determination of the absorption curves with a varying number of days prior to hydrogen exposure has been discussed in Fig. 5.

Fig. 5: Absorption curves for samples of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ stored in air for a varying number of days prior to hydrogen exposure. The drop in pressure corresponds to hydrogen absorption. For clarity, the data for days 5 and 20 are clipped to show only the part corresponding to absorption (Viano *et al.*, 1998)

The high-resolution synchrotron-radiation powder diffraction experiments were performed to observe structural changes induced by hydrogen loading in rapidly-quenched Ti-Zr-Ni alloy ribbons with dominant icosahedral character (Nicula *et al.*, 1998). It was suggested that moderate strains generated by hydrogen absorption was accommodated by the icosahedral structure at the cost of increasing phason disorder only, both quasilattice parameter and phonon disorder coefficient being unaffected (Nicula *et al.*,

1998). The formation of quasicrystalline phase in Ti-Zr-Ni system by mechanical alloying (MA) has revealed better hydrogenation than bulk (Takasaki *et al.*, 2002). The maximum amount of hydrogen that could be loaded into the amorphous and the QC phase powders, at a temperature of 573K and an initial hydrogen pressure of 3.8 MPa, were almost the same, about 60 at.% (M/H = 1:5) indicating that there was no dependence of the hydrogen solubility on the atomic structure (Fig. 6). The QC was retained after hydrogenation, with no formation of hydrides. Activation energy for hydrogen desorption was 127 kJ mol⁻¹ for the QC powder and 168 kJ mol⁻¹ for the amorphous powder (Takasaki *et al.*, 2002, 2006). For a rapidly quenched Ti₄₀Hf₄₀Ni₂₀ alloy, there exists a high-order approximant 3/2 phase, whose structure is very similar to the QC phase, absorbing hydrogen up to H/M=1.2 (Kelton *et al.*, 2006). Hydrogen storage behaviours were also compared in rapidly quenched Ti-Zr-Ni and Ti-Hf-Ni alloys in details (Kelton *et al.*, 2006). Although Ti₄₀Hf₄₀Ni₂₀ has nearly identical hydrogenation properties to those of the icosahedral Ti₄₅Zr₃₈Ni₁₇ phase, no evidence of a hydride phase is observed after loading from the gas phase at 250°C, suggesting that Ti-Hf-Ni could have superior cycling properties (Huett *et al.*, 2002). The PCT curves (Fig. 7) measured at 300°C for both samples, i.e. Ti-Zr-Ni and Ti-Hf-Ni show a higher-pressure plateau at higher hydrogen concentrations (Kelton *et al.*, 2006) and both indicate the existence of a pressure plateau beginning at an H/M of about 1.2-1.5 and extending to an H/M of 3.

Hydrogen storage activities were also observed in additional element substituted Ti-based alloys (Baozhong *et al.*, 2006; Liu *et al.*, 2006, 2007, 2008, 2009a, b). Pd-substituted Ti-Zr-Ni alloys were prepared by melt-spinning at different circumferential velocities and a mixed structure of Laves phase, QC phase and a little amorphous phase is formed at $v = 10$ m/s (Liu *et al.*, 2009). Moreover, the hydrogenation characteristics of Ti-Zr-Ni-Pd alloy electrode was better than that of Ti-Zr-Ni-Y and Ti-Zr-Ni-La alloy electrodes, which mainly ascribed to the excellent electrochemical activity of Pd (Liu *et al.*, 2008, 2009). Electrochemical hydrogen storage in Ti-V-Ni alloys comprising icosahedral quasicrystalline phase was also

Fig. 6: Hydrogen concentration as a function of time for the i-phase powder during (A) the first, and (B) the second hydrogenation (Figure 2; Takasaki and Kelton, 2002)

investigated in detail (Hu *et al.*, 2009, 2013; Wen *et al.*, 2013; Liu *et al.*, 2013 a, b). The effect of substitution of Zr for Ti on the discharge performance of electrodes consisted of Ti_{45-x}Zr_{30+x}Ni₂₅ ($x = -4, 0, 4$) powders produced by MA subsequent annealing was investigated by a three-electrode cell at room temperature (Ariga *et al.*, 2013). All the powders after MA were amorphous, but a subsequent annealing caused the formation of the icosahedral quasicrystal phase with a Ti₂Ni type crystal phase as the second phase. The discharge capacities of the amorphous electrodes were lower than those of the QC phase ones if the composition levels were alike (Zhao *et al.*, 2012).

The synthesis parameters were also an influence on hydrogen storage behaviour of Ti-Zr-Ni QC alloys (Huogen *et al.*, 2008 a, b; Kocjan *et al.*, 2011; Shahi

Fig. 7: Equilibrium hydrogen vapour pressure for icosahedral phase ($\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$) and 3/2 rational approximant phase ($\text{Ti}_{40}\text{Hf}_{40}\text{Ni}_{20}$) samples produced by rapid quenching, measured as a function of hydrogen concentration during absorption at 300°C (Kelton *et al.*, 2006)

et al., 2011; Jenk *et al.*, 1998; Takasaki *et al.*, 2013). The effect of solidification rate on phase formation and the microstructure of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ as quenched ribbons are discussed in detail (Figs. 8 and 9). The XRD pattern of the alloy melt spun at 35 m/s (Fig. 8A) reveals the presence of icosahedral quasicrystalline phase and further increased the wheel speed from 40 m/s to 45 and 50 m/s (Fig. 8B-D). The peak broadening occurs due to the formation of finer grains and strain developed at higher wheel speeds. Ribbons of the alloy were synthesized at different quenching rates obtained through different wheel speeds (35, 40, 45 and 50 m/s) and investigated for their hydrogen storage characteristics (Figs. 10 and 11). The lower cooling rate obtained through low wheel speed (35 m/s) produces, i-phase grains whose size ranges from 300–350 nm, whereas higher cooling rates obtained through high wheel speed (45 and 50 m/s) promote the formation of grains with size ranging from 100–150 nm in $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ ribbons. It was found that ribbons synthesized at 35 m/s absorbed ~2.0 wt%, whereas ribbons synthesized at 50 m/s absorbed ~2.84 wt% of hydrogen (Fig. 10). The hydrogen storage capacity of ribbon increases for ribbons produced at higher quenching rate. One of the salient features of the present study is that the improvement of hydrogen storage capacity obtained through higher quenching

Fig. 8: XRD patterns of as-synthesized ribbon at wheel speed of (A) 35 m/s, (B) 40 m/s, (C) 45 m/s and (D) 50 m/s (Shahi *et al.*, 2011)

Fig. 9: TEM micrograph of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ as-synthesized ribbons at 50 m/s (A) bright field microstructure, (B) dark field microstructure and (C) corresponding diffraction pattern (Shahi *et al.*, 2011)

rates (~45 to 50 m/s wheel speed) leads to the formation of lower grain size.

Quasicrystals as a Catalyst in Hydrogen Storage

In the methanol decomposition reaction, the quasicrystalline catalyst achieved the highest amount of hydrogen gas generated and the lowest reaction initiation temperature (Li *et al.*, 2013; Tsai *et al.*, 2001; Yoshimura *et al.*, 2002; Ngoc *et al.*, 2008). The powder of thermally stable icosahedral (i) Al-Cu-Fe quasicrystal leached with NaOH aqueous solutions shows excellent activity for steam reforming of

Fig. 10: Hydrogen absorption kinetics curves of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ ribbons synthesized at wheel speed of 35, 40, 45 and 50 m/s. (Figure 4; Shahi *et al.*, 2011)

Fig. 11: Temperature-programmed desorption curve of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ as-synthesized ribbons at wheel speeds of 35, 40, 45 and 50 m/s (inset shows the TPD difference curves for each consecutive step) (Figure 6; Shahi *et al.*, 2011)

methanol (Kameoka *et al.*, 2004; Tanabea *et al.*, 2006, 2010). The leaching treatments yield Cu and Fe nanoparticles on the quasicrystalline surface. These nanoparticles are believed to be responsible for catalytic reactions (Tanabea *et al.*, 2011). Recently, the leached (i) Al-Cu-Fe quasicrystal and mechanical activated (i) Al-Cu-Fe quasicrystal were used as a catalyst in hydrogen storage of MgH_2 (Mishra *et al.*, 2007). The scanning electron micrograph (SEM) in secondary

electron image mode of the fractured as well as leached surface of $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ alloy was shown (Fig. 12), where existence of a single-crystal (nearly 10-20 μm size) of icosahedral phase, exhibiting the faceted pentagonal dodecahedral morphology and a homogeneous distribution of particle together with very small particles on and around the large particles, were observed on the leached surface.

Fig. 12: Scanning electron microscopy of (A-B) as grown (i)- $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$, (C) leached surface of as-grown (i)- $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$, (D-F) mechanically activated (i)- $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ and (F) leached surface of mechanically activated (i)- $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$

The results of TEM investigation on the microstructure of as-cast (i)- $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ and mechanically activated QC along with leached powder are discussed in detail (Fig. 13). A rosette and coral-like morphology of the as-cast alloy and corresponding selected area diffraction patterns was demonstrated. The two different types of contrast were observed in the leached as-cast (i)- $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ QC alloy, however in the leached mechanically activated alloy, a homogeneous distribution of small

particles was observed (Fig. 13). These particles were identified as Cu and Fe in the leached powder.

Fig. 13: (A) Transmission electron microscopy microstructure of as-cast (i)-Al₆₅Cu₂₀Fe₁₅, (B) corresponding selected area diffraction (SAD), (C) microstructure of mechanically activated powder, (D) corresponding SAD patterns, (E) microstructure of the leached as-cast (i)-Al₆₅Cu₂₀Fe₁₅, (F) corresponding SAD patterns, microstructure leached mechanically activated (i)-Al₆₅Cu₂₀Fe₁₅ powder and (G) corresponding SAD pattern

In order to explore the effectiveness of leached as-cast (i)-Al₆₅Cu₂₀Fe₁₅ and leached mechanically activated (i)-Al₆₅Cu₂₀Fe₁₅ powder as catalysts (which was abbreviated as LACF and LBACF for the sake of simplicity), these QCs were ball-milled separately with MgH₂ to investigate its hydrogen sorption behaviour. The representative TPD profile for MgH₂ catalysed with LACF and LBACF was shown to be 6.3 and 6.5 wt% hydrogen capacity, respectively (Fig.

14). TPD experiments were carried out under continuous heating rate of 5°C/min. The onset desorption temperature of as-received MgH₂ was found to be 422°C (Vegge *et al.*, 2005), but for MgH₂ catalysed with LACF and LBACF, it was ~225°C and ~215°C, respectively. Therefore, the leached QC alloy showed its catalytic activity by reducing the onset desorption temperature ~200°C of MgH₂. The hydrogen absorption curve of MgH₂+LACF and MgH₂+LBACF charged at 250°C under 20 atm of hydrogen pressure was also discussed (Fig. 15). It was observed that MgH₂+LBACF sample exhibits better rehydrogenation kinetic curve than MgH₂+LACF as well. Desorbed MgH₂+LBACF

Fig. 14: TPD profile of leached as-cast and mechanically activated (i)-Al₆₅Cu₂₀Fe₁₅ powder admixed with MgH₂ at heating rate of 5°C/min

Fig. 15: Absorption kinetics plots of as-cast and mechanically activated (i)-Al₆₅Cu₂₀Fe₁₅ powder admixed with MgH₂ samples at 250°C

absorbed 5.5 wt% of hydrogen in less than 1 min; on the other hand desorbed MgH_2 catalysed with LACF absorbed 5.2 wt% of hydrogen in 10 min. It has been demonstrated that leached QC was an effective catalyst for hydrogen desorption/absorption from MgH_2 .

Applications

There is a wide variety of applications of hydrogen. In fact, hydrogen can be used as replacement for both the fossil fuels: the coal and petroleum. Thus, instead of coal, it can be burned to run turbines to produce electricity. It can also be subjected to cold combustion to produce electricity through fuel cells. Fuel cells are also considered for road transport (electrical vehicles). Hydrogen can substitute for petroleum/diesel/kerosene engine sets. Hydrogen can also be used for cooking (replacement of LPG). In India, road transport consisting of two-wheelers and three-wheelers is the largest in number, followed by cars and trucks. Two and three-wheelers are most petroleum consuming and also most polluting vehicles. About 35% of greenhouse gas (CO_2) is produced by road transport in India. Keeping these aspects in view, we have focused our attention regarding hydrogen application on vehicular road transport. We have carried out R&D and developed hydrogen-fuelled three-wheelers and more recently small cars (Tata Nano, Figs. 16 and 17).

In all the applications of hydrogen in vehicular transport, hydrogen has been stored in hydrides ($\text{MmNi}_{4.6}\text{Fe}_{0.4}\text{H}_x$, BHU-HEC is able to produce this storage material in kilogram level) (Mishra *et al.*, 2007). This is because hydrides are the most efficient storage system for hydrogen. In hydrides, unlike high pressure gaseous and liquid hydrogen storage modes, hydrogen atoms rather than molecules are stored. Thus, the storage capacity is very high. Such efficiencies cannot be reached in the usual high pressure gaseous storage mode. For example, volumetric storage density (which is very important for vehicular transport) of hydride is between ~ 60 and $\sim 100 \text{ kg/m}^3$. In gaseous state, even at 400 bar pressure, this is only $\sim 20 \text{ kg/m}^3$. Hydrides are also the safest storage modes. Here, hydrogen is locked in the lattice and is not free to combine with atmospheric

Fig. 16: Hydrogen-fuelled Nano car developed at HEC-BHU

Fig. 17: Hydrogen-fuelled three-wheeler developed at HEC-BHU

oxygen to burn/explode. It is the above said aspects, which have induced us to use the hydrogen storage mode.

Hydride powder is put in the heat exchanger system. This is coupled to IC engine exhaust gas (which is mostly steam and nitrogen in the case of hydrogen). Quantity of hydride employed is $\sim 18 \text{ kg}$. Exhaust gas coming out at a temperature of $\sim 60^\circ\text{C}$ in

two-wheelers is circulated in the hydride heat exchanger bed. Since thermal conductivity of the hydride is very poor (0.5 to 1.0 W/mk), a hydride heat exchanger tank (HHET) has been designed. To heat the hydride effectively by the exhaust heat of the engine, 20 kg of hydride (storage capacity ~1.8 wt%) is distributed in the HHET by 20 aluminum tubes of 1 inch diameter and 12 inch length. Exhaust heat from the 100 cc two-wheeler engine is able to raise the temperature of hydride to ~60°C. For a Nano car, the temperature rise is about 85°C. We have removed the carburetor and the hydrogen is made to enter the engine during suction stroke through a port near the engine inlet valve. The timing of hydrogen entry is controlled through a cam valve. In a two-wheeler system, the hydride tank is mounted below the driver's seat. In the Nano car, the hydride tank is mounted in the rear above the engine. We have chosen vehicular transport based on IC engine rather than fuel cell. This is because India manufactures high quality internal combustion engines. Also fuel cell technologies have not matured in spite of persistent efforts in the last two decades. Fuel cells capable of being used for vehicular transport require platinum as catalyst which is very expensive (~5 times more expensive than gold). Also, there is rather limited stock of platinum.

The Hydrogen Energy Centre has collaborated with the company Indian Cars and Motors Ltd. (ICML, a sister concern of Sonalika Tractors at Jalandhar, Punjab) to develop the first hydrogen-based three-wheeler for ICML which was demonstrated at Auto Expo Delhi in 2007. At present, we are developing eight hydrogen-fuelled three-wheelers which will be run at Varanasi and Delhi to demonstrate the feasibility of hydrogen-fuelled vehicles. More recently, we have developed a hydrogen-fuelled Nano car. It is planned to develop six more hydrogen-fuelled Nano cars.

It is hoped that the above developments will lead

to the public perception that hydrogen is a viable, clean, climate-friendly, inexhaustible fuel and is typically suited for India.

Conclusion

In this article, we have attempted to bring out the relevance of hydrogen, particularly in the Indian context. India is known to be an energy-starved country, particularly with reference to oil/petroleum. Hydrogen which can be produced from water through a variety of energy inputs including solar energy appears to be a first priority option for India with regard to replacement of oil (and later on coal). Since India has significant solar irradiance and large water resources, and after use the water is returned, hydrogen is definitely a potential energy vector. For harnessing hydrogen, three key ingredients are involved, these are production, storage (safety is mostly related to storage) and applications. We have shown that two equally important factors, namely, large gap between demand and supply of oil and climate change effects make hydrogen a fuel of choice for India. We have provided the necessary input for hydrogen production, some detailed discussion on storage which is possibly the most crucial aspect for the use of hydrogen and applications of hydrogen as replacement for oil in vehicular transport.

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