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Chapter 8

Adsorption of Hydrogen on Metal Clusters

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8.1 Introduction:

In the modern age that we live in, energy has become the most important aspect for living and comfort. We need energy for everything in the home or in the office to perform almost every daily task. The demand for energy in our society is very crucial for the quality our current living style and is increasing due to new emerging economies. On the other hand, the energy sources the world is now dependent on are not so prominent that can be used for a long period of time. The current primary sources of energy are:

1. Fossil energy (oil, coal, natural gas etc.)
2. Nuclear energy, and
3. Other renewable sources (solar, wind, geothermal and hydropower)

At present the world economy is mostly dependent on fossil fuels which take millions of years to form and besides, they release highly toxic elements into the atmosphere. In 2012, 80% of the total energy used in Europe came from the fossil fuels [2]. This increasing rate of our dependence on energy and the simultaneous high decreasing rate of our traditional energy resources is appearing to be a huge problem to worry about. The fossil fuels such as oil, coal and natural gas are mainly compositing of hydrocarbon and release carbon dioxide to the atmosphere when they are burned. Since its discovery the fossil fuels have been the major energy source till now, due to which the carbon dioxide level in the atmosphere has been increased more than 25% over the past 150 years [2]. The high levels of carbon dioxide in our atmosphere are one of the primary factors of global climate change. Today, global warming is one of the major destructive consequences of fossil fuels. Other major environmental problems such as acid rain, air pollution is also mainly because of our dependence on fossil fuels. Below are some of the harmful products formed due to the incomplete combustion of the fossil fuels-

1. Carbon Monoxide (CO)
2. Carbon Dioxide (CO_2)
3. Sulphur Dioxide (SO_2)
4. Nitrogen Oxides (N_mO_n)
5. Lead (Pb)
6. Particulate Matter (PM)

Most importantly, the fossil fuels are non-renewable and the rate at which we are burning these means that they will cease to exist very soon. These deficiencies of our traditional fuels can cause huge socio-economic problems in future.

To get rid of such troubles, we need a clean, renewable and safe source of energy that doesn't produce as much carbon dioxide and methane, to replace the harmful fossil fuels.

8.2 Hydrogen as the Future Energy Source:

Hydrogen is a clean and safe energy source with the largest abundance in the universe, and is the only energy source which our mother nature uses. Moreover, it is also used in many other chemical reactions such as synthesis of ammonia, hydrogenation of organic compound, petroleum refining etc. This high efficient pollution free fuel can therefore be a perfect alternate of the traditional energy sources. On mass basis, hydrogen contents 120MJ of energy per kg, this is nearly three times the energy content of gasoline (44MJ/kg). On the other hand liquid hydrogen has energy density of 8 MJ/L whereas gasoline has energy density of 32 MJ/L. This means that we need such a storage which can store hydrogen up to a sufficient wt. %. According to the U.S. Department of Energy (DOE) the fuel-cell-powered vehicles require hydrogen storage in the range of approximately 5–13 kg to provide a driving range of more than 300 miles.

The current on-board hydrogen storage approaches are:

1. As compressed hydrogen gas which requires high pressure tanks typically of (300-700) bar.
2. As liquid hydrogen, this requires cryogenic temperature due to the low boiling point of hydrogen, which is -252.8°C at one atmosphere pressure.
3. As solid fuel stored on the surfaces of solids (adsorption), or within solids (absorption).

Among these three types of storages the liquid and gaseous storages have very low hydrogen storage density and also cause major safety problems for on-board transportation. While, on the other side, the solid state storage under moderate temperature and pressure has higher hydrogen storage density and also has the important safety advantage over the gas and liquid storage methods. For MgH_2 the hydrogen density is 6.5 H atoms/cm^3 which is higher than that of hydrogen gas (0.99 H atoms/cm^3) and liquid hydrogen (4.2 H atoms/cm^3) [3].

Therefore the metal hydride storage seems to be a safe and volume-efficient method for hydrogen storage. Considering the economic and environmental parameter the U.S. Department of Energy (DOE) predicted minimum hydrogen-storage capacity should be 6.5 wt. % and 65g/L hydrogen, at decomposition temperature between (60-120) °C for commercial feasibility. Moreover the cost of the storage medium and its toxicity properties should be carefully considered.

8.3 Hydrogen Storing Materials:

Depending upon the binding energies the hydrogen storage materials are divided into three categories [4]:

1. **Sorbent Materials:** Materials such as carbon nano-tubes, fullerenes, graphene, mesoporous silica, metal-organic frameworks (MOFs), isoreticular metal-organic frameworks(IRMOFs), covalent-organic frameworks (COFs), and clathrates belong to this category [4, 5-10]. In these materials hydrogen is physisorbed and weakly bound to the material.

   Although these materials displays promising hydrogen storage capacities at 77 K, but only less than 1 wt % of hydrogen can be stored at 298 K and 100 atm of pressure [4]. Recently Wang and Yang reviewed the Hydrogen spill over by different techniques (e.g., physical mixing, chemical doping, ultrasonication etc.) and spillover-assisted storage on carbon nanostructures, MOFs, IRMOFs, COFs, zeolites, and mesoporous silica. There are much significant work still to be done for upgrading the hydrogen uptake by sorbent materials using the hydrogen spill over mechanism under ambient thermodynamic conditions [4].
2. **Complex Hydrides:** These consist of metal hydrides and chemical hydrides [4] form strong covalent bonds with hydrogen. Due to the strong binding of hydrogen, these materials show poor thermodynamics and kinetics. MgH_2 and salts of $[AlH_4]_{-}$ (alanates), $[NH_2]$- (amides), and $[BH_4]$- (borohydrides) like $NaAlH_4$, $LiNH_2$, Li_2NH, and $Mg(BH_4)_2$ are in the former category,[11] while $NaBH_4$, $C_{10}H_{18}$, and NH_3BH_3 are categorized as chemical hydrides.[12,13]. The chemical hydrides are mainly produced through chemical reactions and are not reversible on board applications. Even though these materials contain a great density of hydrogen, because of their poor thermodynamics, kinetics,

and reversibility they were initially not considered as suitable hydrogen storage materials [4].

3. **Nanostructured Materials:** The nano-scale structures of any light metal cluster have a great capability of absorbing hydrogen [2, 4]. These are composed of functionalized sorbent materials as well as complex hydride nanoparticles. The hydrogen binding energy of these materials can be manipulatedto a desired intermediate between physisorption and chemisorptions. In the nanoscale the kinetics of uptake and release of hydrogen increases and the sorption properties can also be fine-tuned by controlling the particle sizes. The high surface to volume ratio of the nano clusters has many applications in catalysis and energy storage [2]. The high surface area in nanostructures offers additional binding, which enhances its storage capacity.

8.4 Hydrogen Storage on Metal Clusters:

Materials at this scale size exhibits enhanced properties including reactivity, greater sensing capability and increased mechanical strength. Nanotechnology offers simple, fast, efficient, and economic facilities for the synthesis of a variety of organic molecules. The primary reasons why nanomaterials different and exhibits so different properties from those of bulk are:

a. **Surface Effects:** atoms at the surface have less neighbour atoms than the inner atoms. Due to this lower coordination and unsatisfied bonds, the surface atoms remain unstable and hence more reactive. Since, the surface to volume ratio scales with inverse size, therefore the number of atoms at the surface increases with decreasing size of a cluster. The smaller the size of a cluster the larger the size of atoms at the surface.

b. **Quantum Size Effects:** reducing the size of materials to the nanometer range leads to the discrete energy levels. Hence, at this scale electrons can be treated as “particle in a box” where the state and energies of the particles depend crucially on the size of the box. The density of states scales smoothly with size but with a different scaling law from that of surface effect.

For ideal hydrogen storage we need a light material of low cost which is abundant and can store a reasonable amount of hydrogen with favourable kinetics. There are many light metals, which can absorb hydrogen to reasonably high wt%. But, on metal surfaces, hydrogen undergoes dissociative chemisorptions, which results in the strong metal-hydrogen bonds and therefore slow kinetics. Hence, the big challenge is to design such a hydrogen storage which fulfills the basic requirements of high gravimetric and volumetric density along with fast kinetics and favorable thermodynamics. This can be achieved by doping/substituting suitable atoms on the metal clusters so that the binding falls within a realistic limit. Which is according to DOE falls within (0.2-0.6) eV/H_2. The nano scale structures of the light metal cluster have a great capability of absorbing hydrogen [2]. In the nanoscale the kinetics of uptake and release increases and the sorption properties can also be fine-tuned by controlling the particle sizes. The high surface to volume ratio of the nano clusters has many applications in catalysis and energy storage [2]. The high surface area in nanostructures offers additional binding which enhances its storage capacity. The light materials such as Li, Al, Mg and their alloys can store 4-6 MJ/kg gravimetric energy density or 2-3 MJ/L volumetric energy density [14]. Studies have also shown that the binding energy of hydrogen with clusters can be improved with doping of several other metals [4], which has attracted the attention to find cheaper hydrogen-activation ways based on metal clusters for hydrogen-storage materials [15-17]. However, there are still many directions for investigations on hydrogen storage for household applications and it holds a tremendous possibility that developing metal clusters the target is achievable.

8.5 References:

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