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Review Article

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Catalytic Functions for Hydrogen Production and Storage

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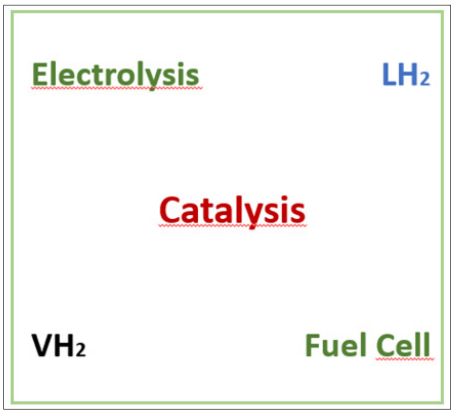
ABSTRACT

Unlike current hydrogen storage methods aiming for permanent storage, the method presented is a transient process that transforms liquid hydrogen into gas during a period of time that can be adjusted to suit the desired end-up application. The porous materials used in the suggested storage are similar to those acting as catalysts in industrial liquefiers, but they combine a larger variety of functions: transient adsorption, flow regulation, heat exchange, catalytic conversion of hydrogen. The material compound of the microporous plugs introduced in the vessels will be related to necessary temporal functions. Three material parameters of the catalysts: surface electronic structure, porosity, thermal conductivity ensure these main functions. Among the porous adsorbents under consideration, metal–organic frameworks present a configuration of metal ions connected via organic linkers promising materials for H2 storage due to their high surface area and their high chemical and structural tunability. Their ability to bind hydrogen at open metal coordination sites, characterized also by sharp electromagnetic gradients, allows also fast catalytic rates. While the hydrogen conversion energy emitted is a harmful inconvenience in the cooling process, it is advantageous in storage because it absorbs the environmental heat. Similarly, the inconvenience of the pressure drops produced by the catalyst porosity in the liquefiers are advantageous in the storage by producing necessary expansions that regulate the hydrogen capillary flow. Along the hydrogen current, each of successive microporous plugs retains some molecules and opens the door to a cascade, producing a JT expansion that reduces the pressure of the following compartment. The presented transient hydrogen storage using the complementary, although inverse, liquefaction and storage processes promotes a rational way in the delivery of future storage tanks and thus in the use of the hydrogen energy by integrating the production, storage and dispensing processes.

Keywords: Hydrogen, Catalysis, Hydrogen Liquefaction, Hydrogen Storage



Presentation

My purpose is to develop hydrogen storage devices as intermediates between the different hydrogen production, transmission and distribution networks, enabling new linkages between energy supply and demand in connection with the electric grid. I promote a new system of Transient hydrogen Storage where the inserted catalysts regulate the storage time.

I present First, the necessity of a catalytic device in the industrial production of liquid hydrogen, then show how such catalytic systems could be inserted with extended functions in the Storage devices.

Large quantities of hydrogen could be continuously stored, and released, facilitating the integration of variable renewable energy into the Electric Grid.

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Hydrogen Production

For hydrogen production there is a need for significant improvement in plant efficiencies, reduced capital costs and operating flexibility. Water Electrolysis and Natural gas Reforming with Carbon capture are the technologies of choice in the current term.

Hydrogen is a quantum gas mixing two Molecular Varieties, that are difficultly interchanged without a catalyst. Its rotational spectrum is divided in two parts: the even states are associated to non-magnetic nuclear spin states whereas the odd ones carry a parallel configuration of the two proton spins.

Any sample is a compound of two nuclear spin varieties: the ortho and para ones and in general behaves as a mixture of two different gases.

Hydrogen behaves as a single gas only when the sample is in thermal equilibrium with a thermostat. The energy released in the op conversion is important, about 500 kJ /g at low temperature.

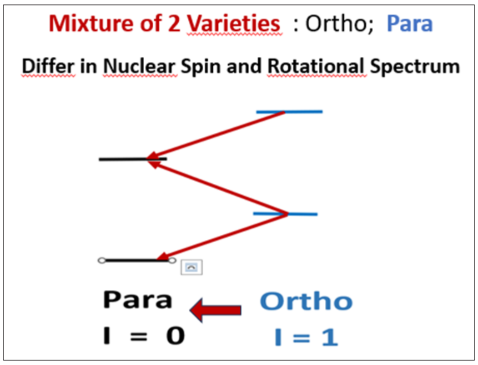


Figure 1: Hydrogen as a quantum gas

Catalysis in industrial liquefiers

Main advantage of liquid hydrogen over other possible vectors is its high volumetric density. In the liquefaction process, catalysis is fundamental because the conversion heat in cooling H gas to liquid at 20 K is larger than the vaporization heat.

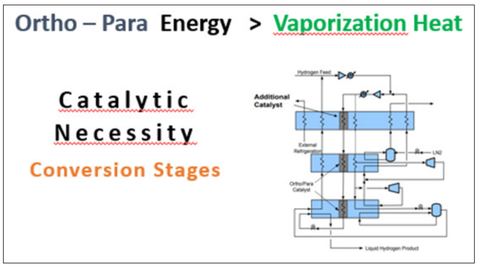


Figure 2: Catalysis in Liquefiers

In between 20 and 50 % of the required work input is used to extract the low-temperature entropy and the conversion heat and reject them at ambient temperature. 3d oxides mainly in gel forms were elaborated more than 60 years ago.

Main liquefiers proceed with successive staged catalyst beds. But recent plants have introduced catalyst filled plate-fin exchangers in the feed stream to approach a continuous catalytic conversion, with simultaneous heat evacuation.

Liquefaction vs Storage

Storage and Liquefaction are Inverse and Opposite Processes involving a double Macroscopic Liquid-Vapor Phase transition in Real space together with a Momentum Transition in the Nuclear Spin Space.

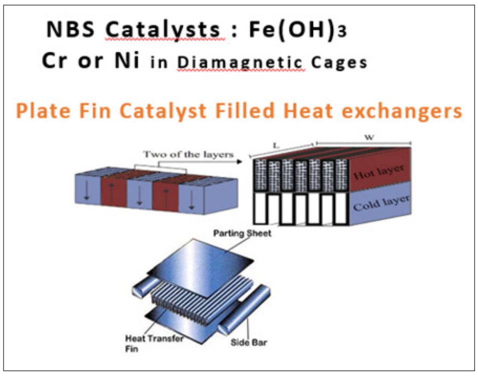


Figure 3: Catalyst filled plate-fin exchangers

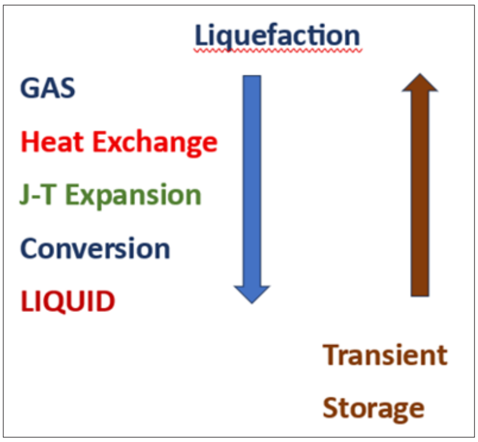


Figure 4: Storage - Liquefaction: Inverse and Opposite Processes

Present Boil-off loss associated with storage, transportation and handling of liquid hydrogen can consume up to 40% of its combustion energy. In the Transient Storage process based on the reverse cycle of liquefaction Pressure Drops and Heat Evacuation that are Inconveniences in Liquefiers become Advantages. Similarly, the reverse o-p catalysis which necessitates extra work in the liquefier absorb the external heat in the storage tanks.

Long Term Hydrogen Storages

The Long-Term hydrogen storage for chemical and electro-mechanical applications presents important Issues. A possible progress would be to extract more natural hydrogen from underground. Another solution would be the dilution in Hydrides. Its inconveniences are its Weight and high desorption temperature [1,2].

In Pure Form the Cryogenic and Compressed Storages are now operational for transport applications. The cryo-pressure vessels have now reached the weight and volume targets of a volumetric capacity of 40 g /Liter of H and a gravimetric capacity of 7 %. These vessels comprise a high-pressure inner vessel with envelopes of carbon-fiber - coated metal, a multilayer vacuum insulation, and a metallic outer jacket. The vacuum space contains numerous sheets of highly reflective metalized plastic.

Unfortunately, these cryo-pressure vessels imply excessive mechanical containment and intensive thermal insulation. Moreover, carbon fibers are complex and expensive.

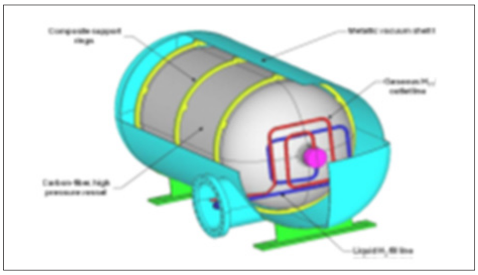


Figure 5: Cryo-pressure vessel

Transient Storages and Continuous Deliveries

Long and Transient Storage, LS and TS enable new linkages between energy supply and demand enhancing overall energy system flexibility.

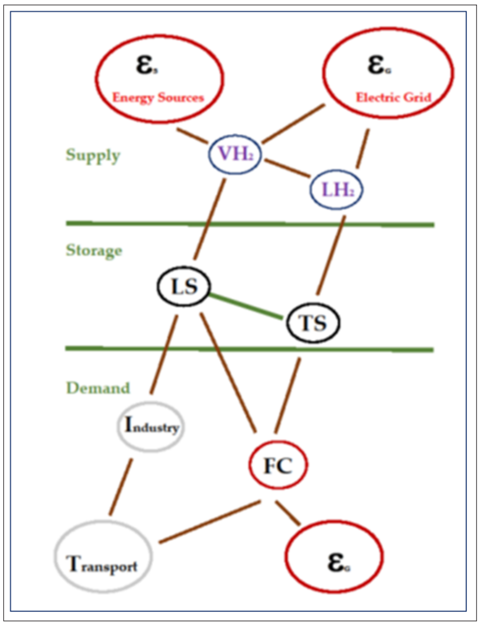


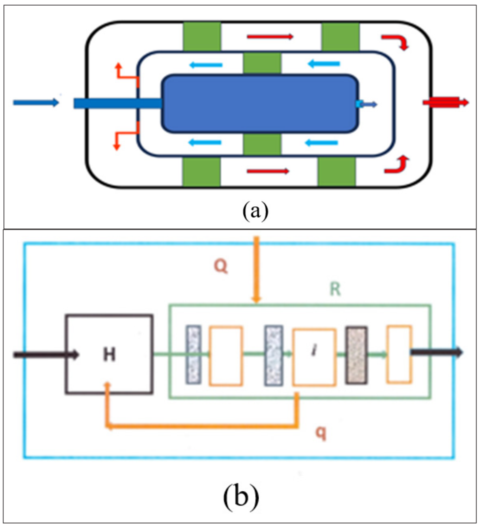
Figure 6: Storage as a link between Supply and Demand

They deliver part of the electrolytic and liquefaction expended labors. Composite storage tank filled with catalysts would connect electrolytic production facilities and liquefaction plants to supply various energy transport and distribution networks.

They would facilitate the integration of variable energy sources of low carbon energy, transformed into hydrogen to provide either Chemical industries or the electric grid through fuel cell devices, or the mobility service of electric vehicles, Trains, Trucks, Planes or Cars. Transient storage tanks with catalytic frames adjusted to each end-use application appear thus as essential intermediates between Supply and Demand structures.

Storage and Catalytic Devices

I'm promoting new Storage systems for Vessels equipped with barrages, consisting in a regulating system of multiple porous catalysts. The figure 7a illustrates a simple couple of opposite flows and counterflows with catalysts insertion enveloping a cold reservoir. The figure 7b represents a simple model of Heat and Matter feedbacks.


(a)

(b)

Figure 7: Transient Storage Schemes

Modern catalysts must accomplish 3 Essential Functions:

- Regulate the diffusion through the porous structures,
- Facilitate the Thermal exchanges between the H flow and the solid support,
- Promote strong Electro Magnetic Interactions that operate as cooling heat pumps.

By inducing a molecular ortho spinning the catalytic surfaces convert the external heat in rotational energy. The catalysts adsorption strength and the granulometry of the whole samples are adjusted to the desired flow diffusion and pressure expansions.

Catalytic Surfaces

Presently the best catalyst used in industrial liquefiers is a ferric oxide gel. However, current developments place emphasis on innovative materials, such as nano-catalysts, bimetallic alloys, or molecular sieves.

Nowadays many cage-like porous structures have sorbent densities larger than 200 g/L such as the Amorphous metal–organic framework. It has the required qualities of a modern catalyst to be strong, of high adsorptive power and large surface area.

Advances in molecular surgery open ligands in the MOF structures by impregnation with reactive species that remove the terminal ligand without detriment to the framework, thereby exposing open metal sites to impinging molecules. In addition, their flexibility allows an accommodation of magnetic ions particularly efficient in stimulating the conversion rates and in transferring the molecular rotational energy to the solid structure.

Flow Control by Porous Catalysts

Each microporous plug retains molecules at the cryogenic temperatures and release them at higher ones which keeps the flow going on when it starts to slow down. The diffusion through each porous plug opens the door to a cascade, which together with the catalytic process reduce the pressure and the temperature of each following compartment.

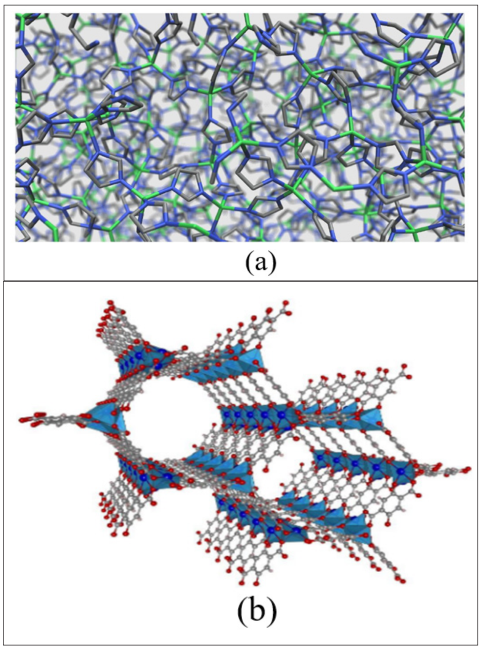


Figure 8: (a) Amorphous metal–organic framework (b) Nanocage

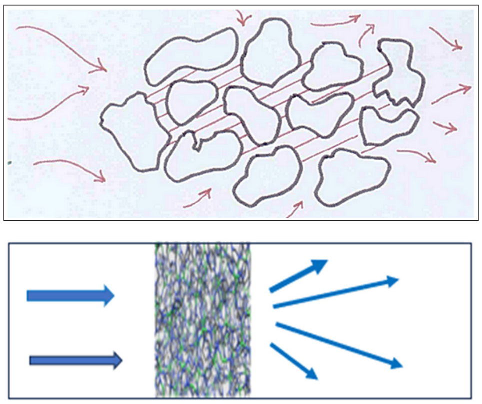


Figure 9: (a) Diffusion through a Porous Catalyst (b) Adsorption and Expansion

Finally in such vessels the counterflow absorbs part of the incoming thermal heat, transformed into a directional and continuous hydrogen flow. The relative number and size of the pores, is correlated to the volumetric optimization required by the desired stored energy and period. At the lowest temperature, diffusion is governed by the wider pores because of their lower energy barrier. The temperature increases lead to an increasing contribution of the narrow pores.

Electro-Magnetic Catalytic Channels

Since the last 30 years, I have discovered a variety of efficient conversion channels where Coulomb repulsion induces electron exchanges and transfers between the catalyst and the adsorbed molecules.

The hydrogen antibonding sigma orbital acts as a transient or virtual intermediate state that stimulates the exchange of antibonding and bonding electrons. While the surface electrons penetrate the molecular clouds, they induce a double spin flip-flop of the electrons and the protons that complete the catalytic reaction.

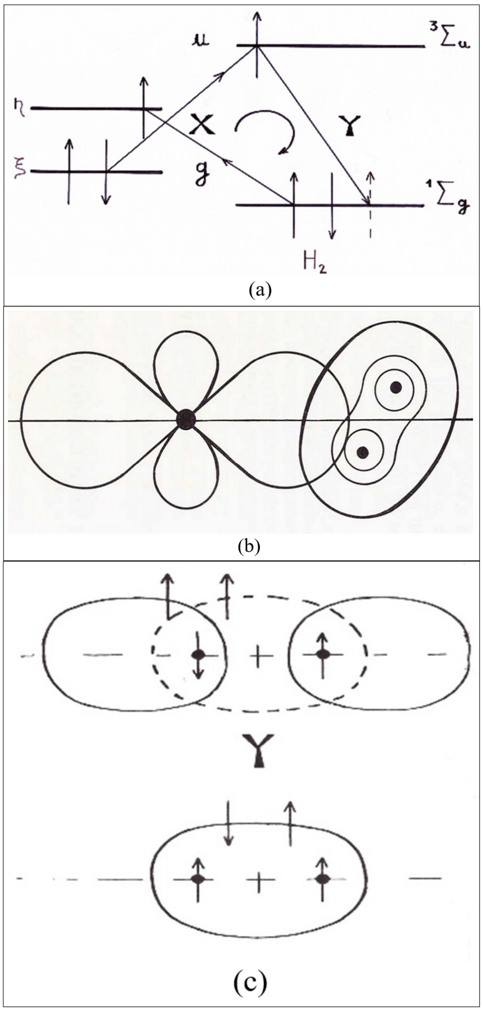


Figure 10: (a) Electron Exchange (b) Molecule -3d ion electron overlap (c) Double electron and protons spin flip-flop

Depending on the magnetic structure, on the electron spin pair correlations at the catalyst surface, the reaction energy can be transferred to the solid or through desorption to the molecular kinetic flow.

The conversion mechanism attributed in the past to a physical process, of magnetic inhomogeneities uncoupling the proton spins, is now more related to electronic interactions and thus closer to chemical mechanisms.

Chemical Pre-Treatments and Spectroscopic Measurements

The catalysts are prepared either by Impregnation of a solid support or from a Precursor solution dried and calcinated at high temperature. Materials are provided in various forms, Gels, Supported Oxides, Powders, or compressed Pellets. Surface Area of common industrial catalysts measured by BET methods reach a few hundreds of m2/g, with pore diameter of 20 to 30 A. Their structures observed by Electron Microscopy, and X-ray display quite disordered surfaces.

Pair correlations of the metallic ions in ferric oxides, measured by Neutron Spectroscopy, extend up to 3 nm. Hydrogen Loading measured by Neutron Vibration NVS displays a surface coverage of a monolayer of 400 mmol characterized by important hindered rotations.

Table 1: Chemical Pre-Treatments and Spectroscopic Measurements

Preparation and Pre-Treatments
Precursor solution, Dessication and Calcination
Materials
Gels, Supported Oxides, Powders, Pellets
Ionex and Oxisorb
Surface Measurements
Surface Area BET
Scanning Electron Microscopy SEM
X-ray Adsorption Fine Structure XAFS
Neutron Pair-Distribution Function PDF
Hydrogen Loading and Adsorption
Neutron Vibration NVS
Hydrogen Conversion
In Situ and Time Dependent Infra-Red FTIR
Raman Spectra

Dynamic Conversion investigations consist in diffusing hydrogen through various micro-porous catalytic structures and varying the flow rate. Hydrogen samples prepared at different temperatures diffuse through a catalytic powder maintained at a fixed temperature, with para contents Measured by Raman spectroscopy.

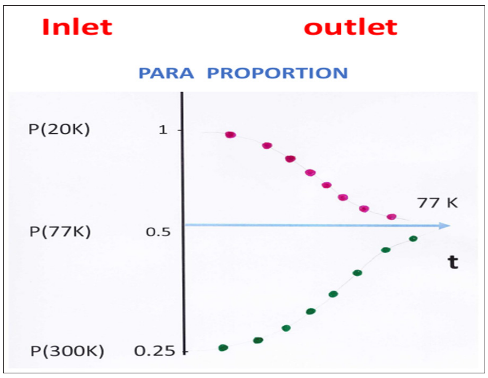


Figure 11: Raman measurements of Para concentrations

Hydrogen sample prepared either at 20K or 300K diffuse trough a catalytic powder maintained at 77K. The para contents p is measured in function of the hydrogen spatial velocity and thus of the time t spent by the sample in the powder.

Hydrogen as Energy Carrier

Hydrogen is considered as a valuable energy carrier because on a weight basis it can liberate an energy 3 times larger than petrol oil without any carbon rejection. In the described chain, hydrogen produced by steam reforming or electrolysis stores energy in chemical form.

For practical use, it is necessary to reduce the volume of gas by compression or liquefaction. Storing this energy recovers the work expended, to produce and compress the hydrogen.

It allows the distribution from a structured system of catalytic barriers according to the storage time required by the intended application. That energy chain makes it possible to adapt the intermittency of renewable energies and respond to the urgent need for electrification of the modern lifes.

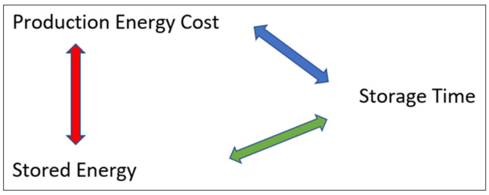


Figure 12: The "Break Even" Triad

References

1. That Invited Perspective was presented at the 7th Edition of Advanced Chemistry World Congress held in Rome, Italy. 2026.
2. The presented PowerPoint summarized part of the publication: Ernest Ilisca, Magneto-chemistry of catalysts for liquid hydrogen production and storage, Physical Chemistry Chemical Physics, where the relevant bibliography can be found. 2025. 27: 17130-17156.