UNITÉ DE CATALYSE ET CHIMIE DU SOLIDE

ASPROM
LES BIOTECHNOLOGIES ENERGIES NOUVELLES ET RENOUVELABLES

UIMM, 56 avenue de Wagram, 75017 PARIS
Mercredi 10 et jeudi 11 Octobre 2018

H_2 issu de bio-ressources

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- H_2 : Energy of the future
- What is hydrogen ?
- Hydrogen storage
- Today H_2 production
- H_2 production from bio-resources

Hydrogen vision for 2050

A sustainable pathway for global energy transition

Hydrogen can offer economically viable, financially attractive, and socially beneficial solutions

18% of final energy demand

6 Gt annual CO_2 abatement

$2.5 tr/y annual sales (hydrogen and equipment)

30 m jobs created

Hydrogen scaling up

Published in marge of COP23

Hydrogen Council. November 2017. McKinsey study. www.hydrogencouncil.com

A recent report authored by the study task force of the Hydrogen Council, consisting of senior executives of 18 companies: Air Liquide S.A., Alstom, Anglo American plc, Audi AG, BMW Group, Daimler AG, Engie S.A., GM, Honda Motor Co. Ltd, Hyundai Motor Company, Iwatani Corporation, Kawasaki Heavy Industries Ltd, Plastic Omnium, Royal Dutch Shell, Statoil ASA, The Linde Group, Total S.A., and Toyota Motor Corporation.

Hydrogen scaling up

Hydrogen vision

- H_2 could represent 1/5 of the consumed energy in 2050.
- H_2 “economy” would achieve almost one-quarter of the required CO_2 abatement in 2050.
- In 2030, 1 in 12 cars sold in California, Germany, Japan, and South Korea could be powered by hydrogen.
- 10 to 15 million tons of chemicals could be produced using hydrogen and carbon.

November 2017. McKinsey study. www.hydrogencouncil.com

EU countries agree to explore hydrogen as energy source

- Calls for governments to increase cooperation on research into the potential for hydrogen use in energy storage, transport, power and heating.

- "The acceleration of early implementation and wider application of sustainable hydrogen technology is able to contribute to the economic competitiveness of the Energy Union".

Endorsed by 25 EU nations. https://www.cnbc.com - 18 Sept 2018

UCCS

H_2 : Energy of the future

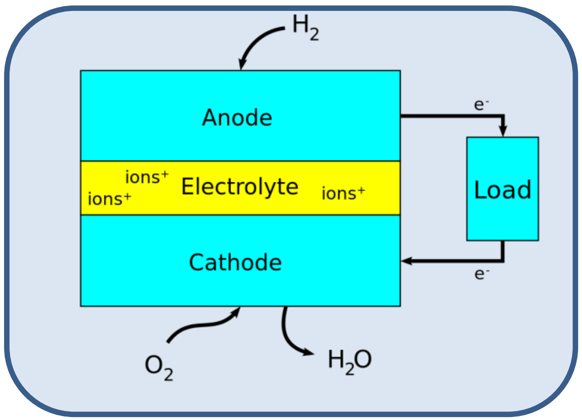
Nowadays H_2 is the most promising energy source of the future

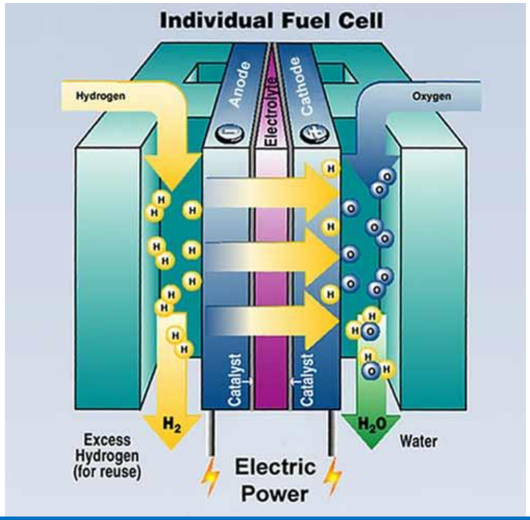
Association française pour l'hydrogène et les piles à combustible. http://www.afhypac.org

H_2 is the most promising energy source

H_2 + Fuel cell → Energy

High conversion efficiency of hydrogen energy to electricity





H_2 + Fuel cell → Electricity

UCCS

Hydrogen scaling up

Pragma Industries
Cherbourg,
France

Sylfen,
Grenoble, France

http://www.afhypac.org

H_2 : Energy of the future

Hydrogen scaling up

Toyota MIRAI, Japan

Hyundai, Korea

Audi AG, Germany

H_2 : Energy of the future

Hydrogen scaling up

Toyota Mirai

Hyundai Motor

HYPE, the world's first taxi company.
Paris, France

H_2 : Energy of the future

Hydrogen scaling up

Toyota Truck

Hydrogen fuel-cell technology for heavy-duty applications at the Port of Los Angeles.

Hyundai Truck
for Europe in 2019

Hydrogen scaling up

H_2 bus, Occitanie, France

Hydrogen fuel cell bus
Ohio State University, USA

Camping car, Mercedes-Benz Vans
Salon 2018, Düsseldorf, Germany

Hydrogen scaling up

Tramway
Qingdao Sifang, China

H_2 : Energy of the future

Hydrogen scaling up

H_2 Alstom train
September 2018, Bremervörde, Germany

Project: Space train (720 km/h)
Loiret, France

H_2 : Energy of the future

Hydrogen scaling up

Avril 2018, NavibusH2, Nantes, France

Avril 2017, Energy Observer
Saint-Malo, France

H_2 water bus, "Alternatives Energies"
La Rochelle, France

Shipping & cruise activity?

Hydrogen scaling up

HY4, DLR. September 2016, Germany

APU, Liebherr & GM, USA

Boeing, USA

Project: CityHawk Flying Taxi Urban Aeronautics Israel

H_2 : Energy of the future

Hydrogen scaling up

HYCOPTER
Singapore

Drone-helicopter
HCX2 Jupiter, Japan

Hydrogen scaling up

Special vehicles
Mobypost
France

Forklifts
Kansai airport, Japan

Daimler and HPE
data centers

http://www.afhypac.org

Hydrogen scaling up

Hyundai Motor with Air Liquide, Germany

H_{2SYS} Generator, France

Hydrogen fueling station

Aaqius, STOR-H distributor of hydrogen cartridges, Switzerland

http://www.afhypac.org

Mobile hydrogen fueling station, Tokyo, Japan

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- What is hydrogen ?
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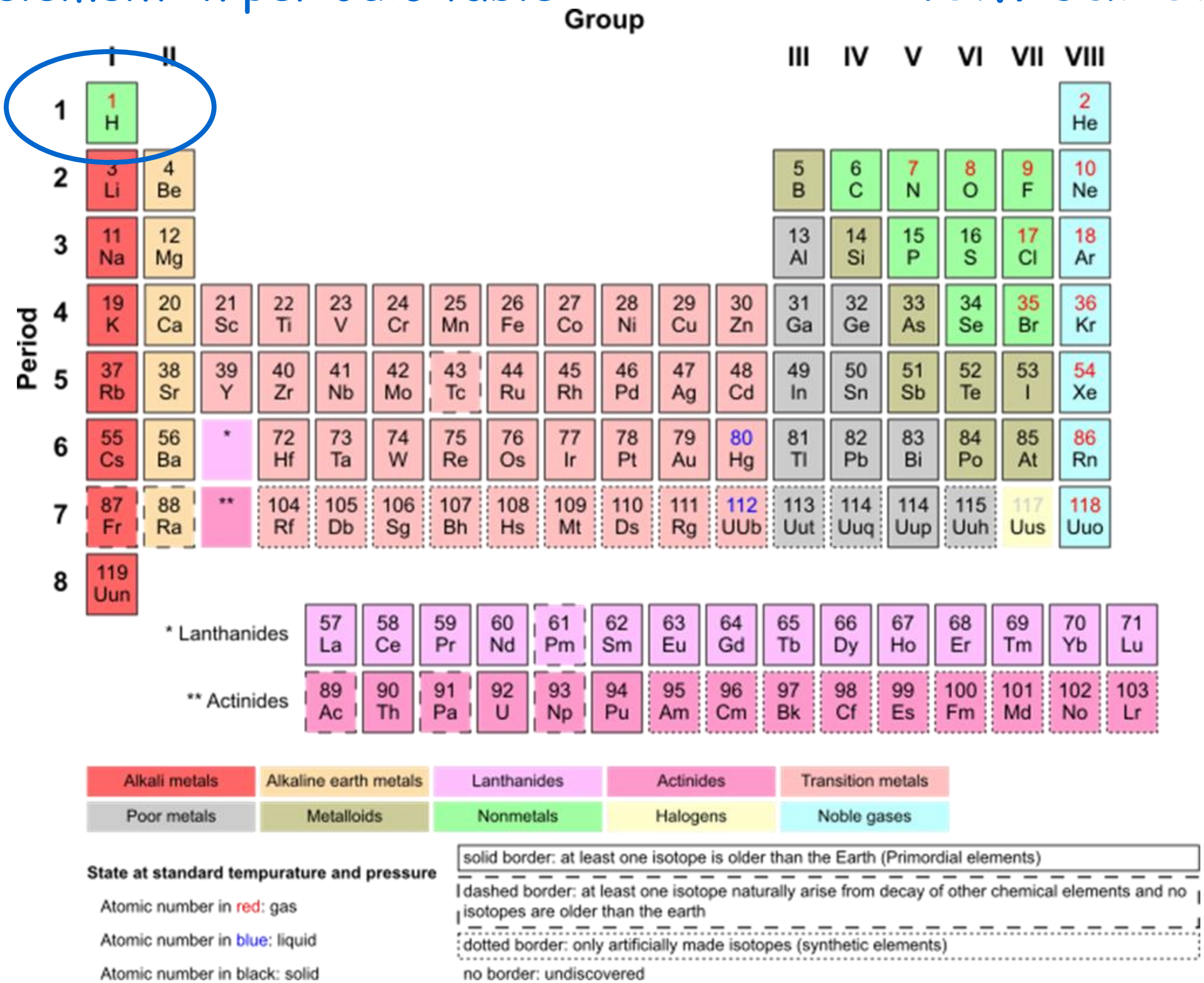
What is hydrogen ?

Chemical element H

The first element in periodic table



What is hydrogen ?

H_2 gas

Under ordinary conditions on Earth, elemental hydrogen exists as the diatomic gas, H_2.

H_2

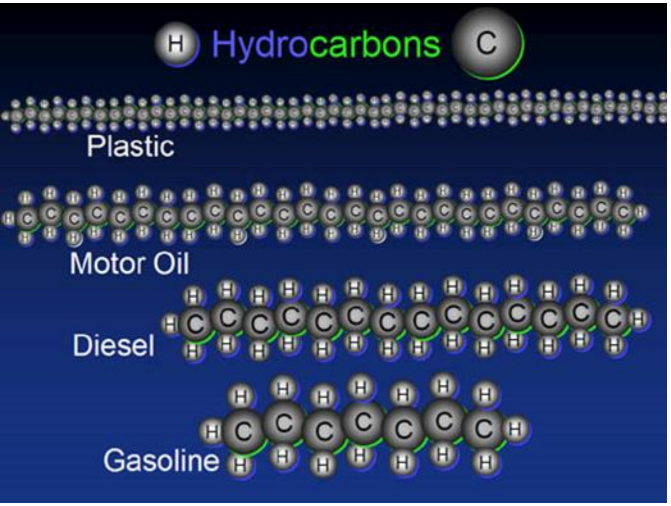
At standard temperature and pressure:

Hydrogen is a colorless, odorless, tasteless, non-toxic, non-metallic, highly combustible diatomic gas with the molecular formula H_2.

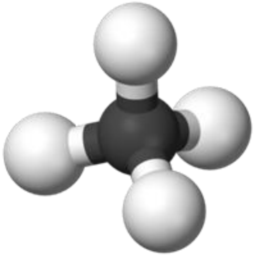
Hydrogen gas is very rare in the Earth's atmosphere (1 ppm by volume).

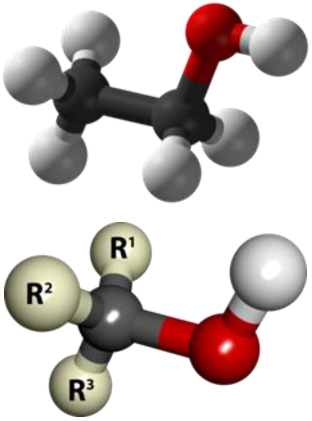
Natural occurrence
Earth

Hydrogen is the third most abundant element on the Earth's surface, in the form of chemical compounds such as hydrocarbons (methane) and the most simple, water.

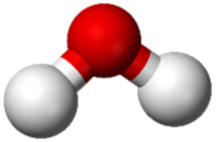


CH_4





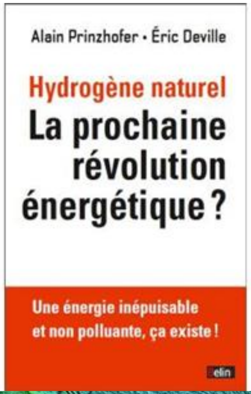
H_2O



Natural occurrence
Earth

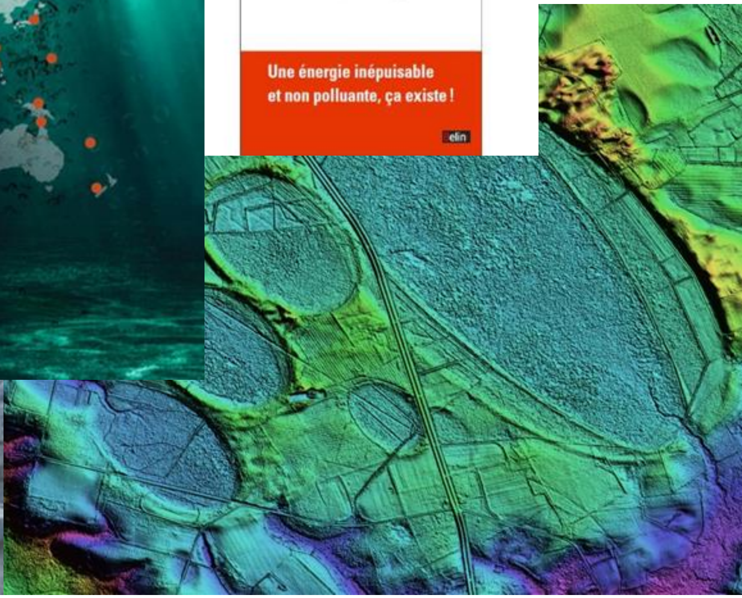
Recently some H_2 sources have been discovered

1.5 billion m^3
Bourakébougou, Mali



Russia

(methane & hydrogen)
Chimaera, Turkey

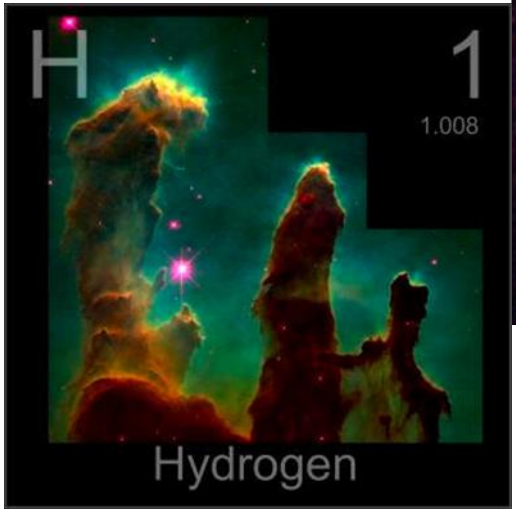


Carolina Bays, North Carolina, USA

Natural occurrence
Universe

Hydrogen, as atomic H, is the most abundant chemical element in the universe,

making up 75% of normal matter by mass and more than 90% by number of atoms.



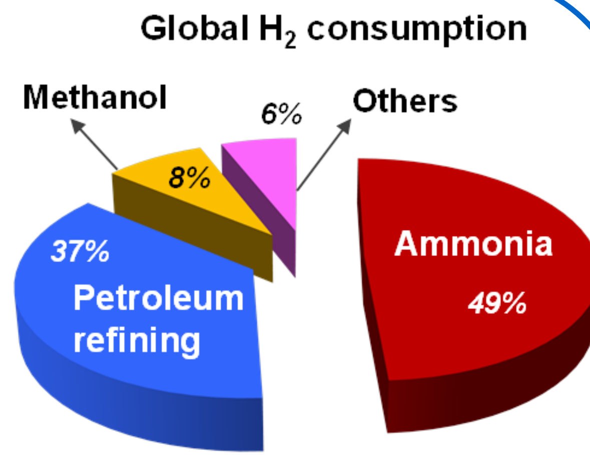
NGC 604, a giant region of ionized hydrogen in the Triangulum Galaxy

Today H_2 importance

H_2 is already:

- An important chemical product

  The industrial gas the most used,
  and the demand is increasing.



- An ideal fuel

  Clean because when it burns,
  combustion produces only water:

  $$2H_2 + O_2 \rightarrow 2H_2O$$

  No emission of pollutants

- H_2 : Energy of the future
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- Today H_2 production
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Possible classification

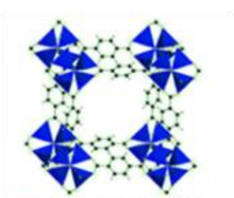
How is hydrogen stored?

Physical-based

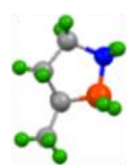
- Compressed Gas
- Cold/Cryo Compressed
- Liquid H_2

Material-based

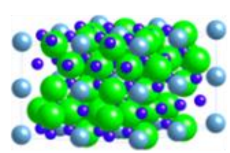
- **Adsorbent** – Ex. MOF-5



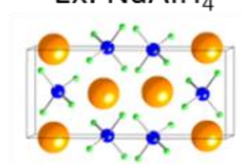
- **Liquid organic** – Ex. BN-methyl cyclopentane



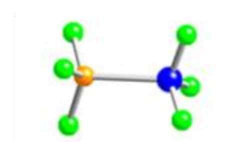
- **Interstitial hydride** – Ex. $LaNi_5H_6$



- **Complex hydride** – Ex. $NaAlH_4$



- **Chemical hydrogen** – Ex. NH_3BH_3



www.energy.gov/eere/fuelcells/hydrogen-storage

- Physical storage
  - CGH2 (Compressed gaseous H_2)
  - LH2 (Liquid H_2)
  - Cryoadsorption on high surface-area materials
- Chemical storage
  - Hydrides
  - Amine-Borane adducts
  - Amides/Imides
  - Hydrogenation/dehydrogenation of liquid hydrogen carriers
  - Reforming of liquid hydrogen carriers
  - Etc.

Angew. Chem. Int. Ed. 2009, 48, 6608

- ➢ Gravimetric and volumetric densities
- ➢ Operating temperatures

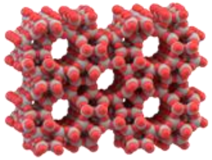
Physical storage

Under the term "Physical storage" of hydrogen, 3 technologies are usually categorized:

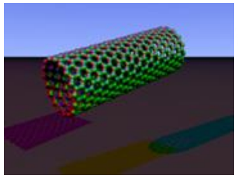
- CGH2 (compressed gaseous H_2)

- LH2 (liquid H_2)

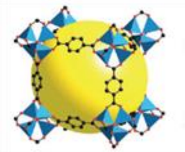
- Cryoadsorption on high surface area materials:
  - Zeolites



  - Carbon materials



  - Metal-Organic Frameworks (MOFs)



The physical storage technologies, in particular, CGH2 and LH2 are most mature.

Angew. Chem. Int. Ed. 2009, 48, 6608

Chemical storage
Hydrides

- Typical alloys for hydrogen storage are the AB_5 compounds,

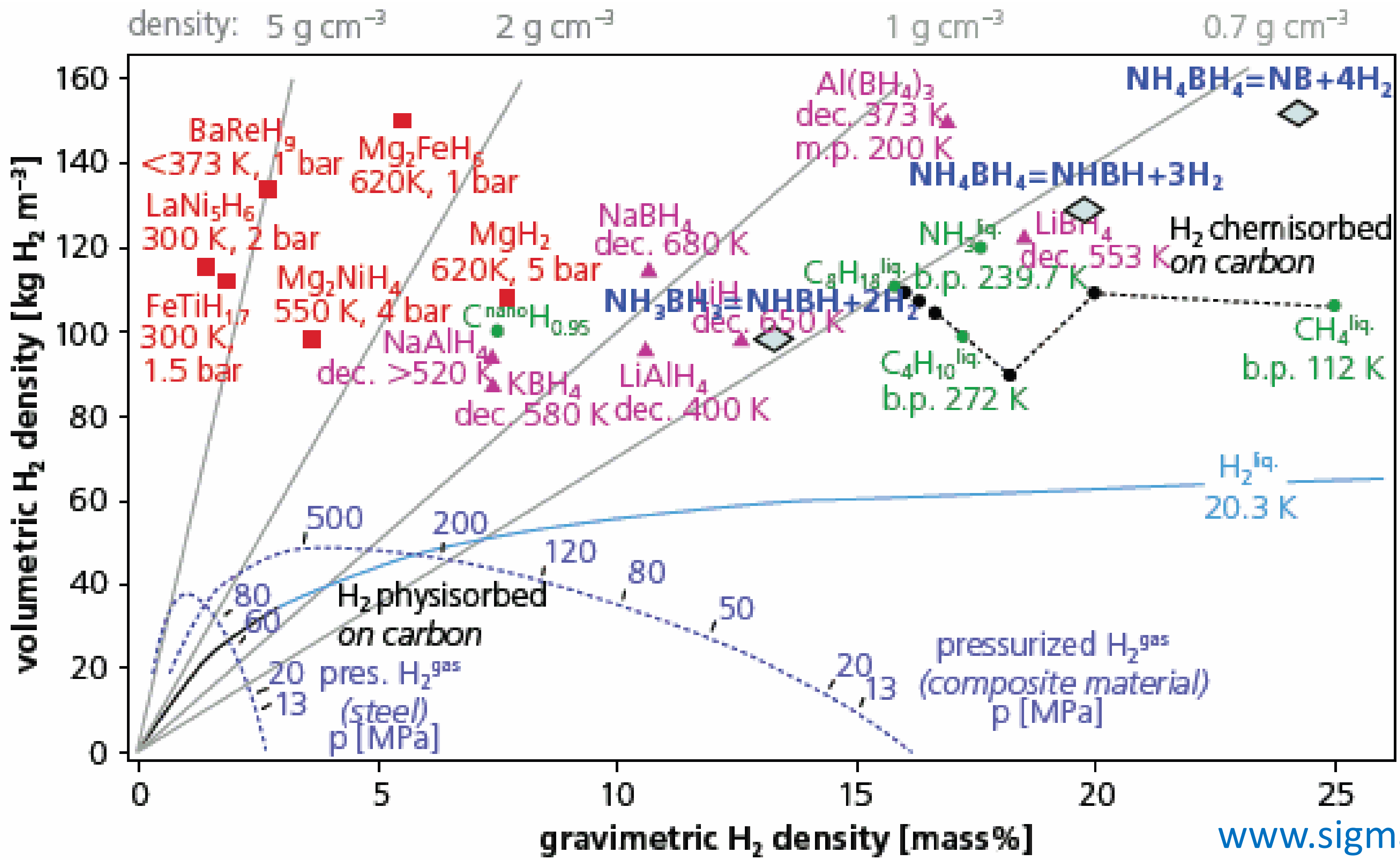
  such as $LaNi_5$ with a hydrogen content of roughly 1.4 wt%

  and an equilibrium pressure around 0.2 MPa at room temperature.

- MgH_2 : 7.6 wt%

  - With a hydrogen storage capacity of 7.6 wt%, low material cost, and good reversibility during the cycling process, MgH_2 is an interesting candidate.
  - MgH_2 is a typical high-temperature metal hydride with an equilibrium pressure of 0.1 MPa at temperatures of 300°C.

Gravimetric and volumetric densities



www.sigmaaldrich.com

Comparison of gravimetric and volumetric densities of various hydrogen storage materials

Operating temperatures

	Liquid hydrogen	Cryo-adsorption	Interstitial metal hydride	Compressed hydrogen	Alanate	Salt-like metal hydride	Water
	LH2	Activated carbon	Laves Phase Comp./ $FeTiH_x$ / $LaNi_5H_x$	CGH2	$NaAlH_4$	MgH_2	H_2O
	100 mat.wt%	6.5 mat.wt%	2 mat.wt%	100 mat.wt%	5.5 mat.wt%	7.5 mat.wt%	11 mat.wt%
Operating temperature	-253°C	> -200°C	0 - 30°C	25°C	70 - 170°C	330°C	>> 1000°C
Corresponding energy to release hydrogen in MJ per kg H_2	0.45	3.5	15	n/a	23	37	142

Several hydrogen storage technologies and their operating conditions

J. Power Sources 2007, 165, 833. Angew. Chem. Int. Ed. 2009, 48, 6608.

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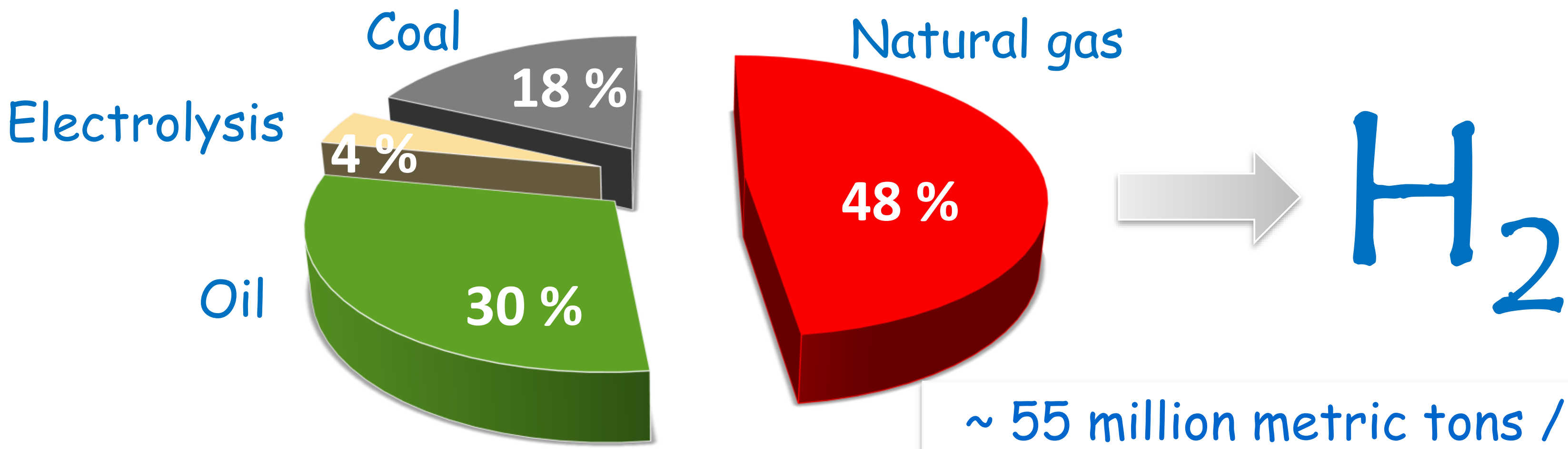
Production technologies

- Fossil fuels are the dominant source of industrial hydrogen.
- There are four main sources for the commercial production of hydrogen: natural gas, oil, coal, and electrolysis.

96% from fossil resources



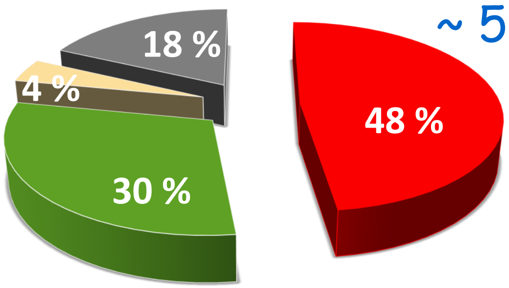
~ 55 million metric tons / year

Today H_2 production

Production technologies

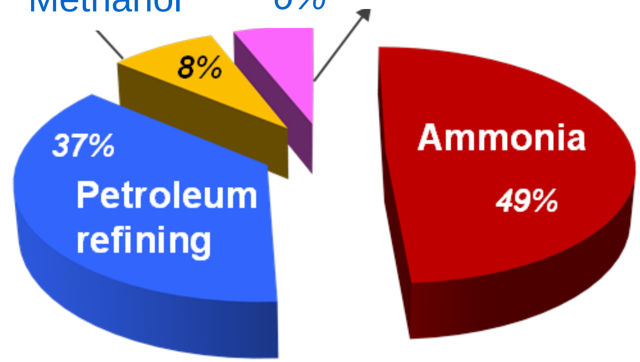
In the refining, chemical and petrochemical industries.
Most of the hydrogen produced in the world is captive

H_2 is the gas the most widely used and the demand is growing



~ 55 million tons /year

Global H_2 consumption



Mainly from natural gas reforming

Reaction at high temperature (> 600° C) over a Ni based catalyst. Usually, the reforming reaction is followed by a reaction in presence of water in order to transform carbon monoxide into carbon dioxide.

Steam reforming

Schematically:

Steam reforming reaction:

$$CH_4 + H_2O \rightarrow CO + 3\ H_2 \quad (700\text{–}1100°C)$$

Nickel catalyst

Water gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (\text{about } 360°C)$$

Iron oxide catalyst

Water gas shift reaction produces even more H_2

- The downside to this process is that its major by products are CO, CO_2 and other greenhouse gases.
- Depending on the quality of the feedstock (natural gas, rich gases, naphtha, etc.), one ton of hydrogen produced will also produce 9 to 12 tons of CO_2.

The hydrogen must be separated from the CO_2 to be able to use it.
This is primarily done by pressure swing adsorption (PSA), amine scrubbing, and membrane reactors.

Electrolysis

- Electrolysis is an established and well-known method, constituting the most effective technique for water splitting.
- The reaction is very endothermic thus the required energy input is provided by electricity.

$$2H_2O \rightarrow 2H_2 + O_2$$

Alkaline Electrolyser ELT, 760 m^3/h – 30 bars

http://www.afhypac.org

PEM Electrolyser Hydrogenics HyLYZER of 1Nm^3/h

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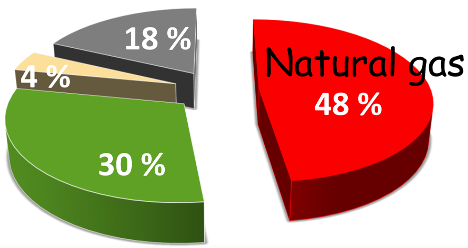
H_2 from bio-resources

Currently: 96%

Fossil resources



~ 280 millions tons of CO_2

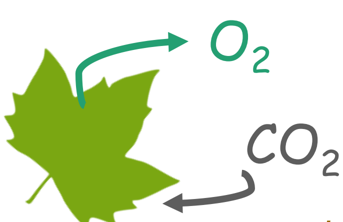
H_2

Forecast:

Needs in syngas could be multiplied by 10 in the next 30 years

Expected: **30%**

Renewable resources
Biomass



Biofuels 49%

Chemical industry 39%

Bio-resources

- Bio-resource: any resource of biological origin.
- Biological resources include agriculture, forestry, and biologically-derived waste, and there are many other renewable bio-resource examples.

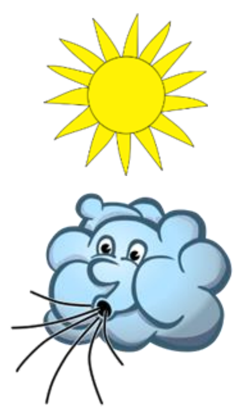
- Biomass is organic matter derived from living, or recently living organisms. Wood, agricultural crops, the waste of agricultural byproducts, animal waste, municipal solid waste (MSW), waste from food processing, aquatic plants and algae are the most important sources of biomass.

Renewable resources

A renewable resource can be totally replaced or is always available naturally, or practically inexhaustible. It has the ability to be renewed over a short period of time.

- It includes agricultural production, as in sustainable agriculture and to an extent water resources.

- Another type of renewable resource is renewable energy resources. Common sources of renewable energy include solar, geothermal and wind power, and biomass.

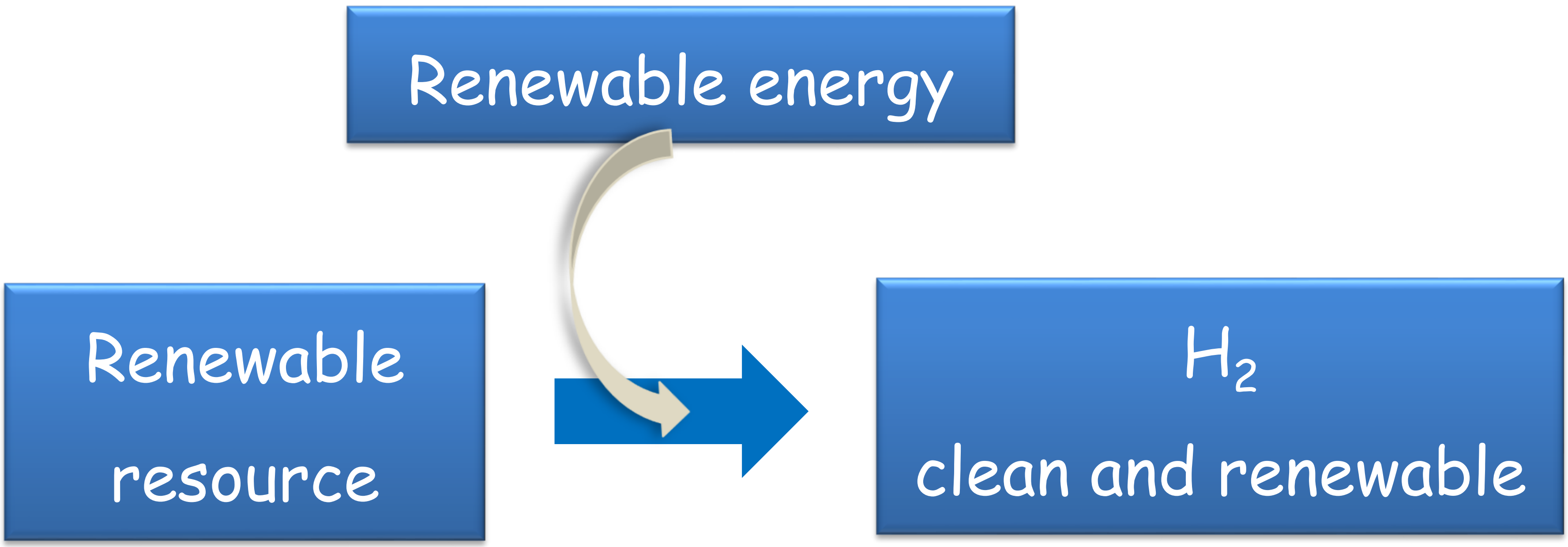


Water resources

- 97.5% of the water on the Earth is salt water,
- and 3% is fresh water;
- slightly over two thirds of this is frozen in glaciers and polar ice caps.

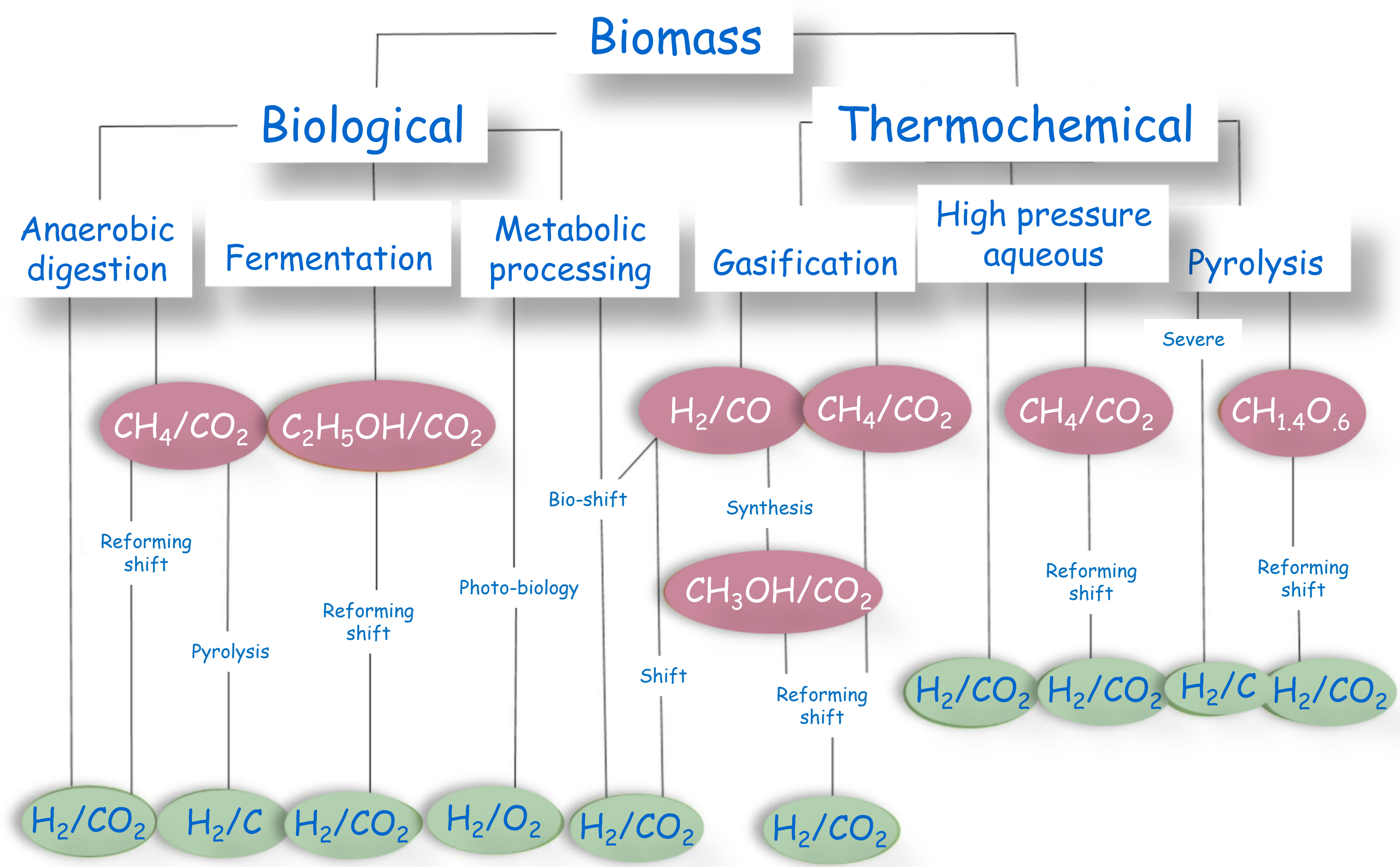
- Water can be considered a renewable material when carefully controlled usage, treatment, and release are followed.
- If not, it would become a non-renewable resource at that location.

Renewable resources and renewable energies



H_2 from renewable resources

H_2 production from biomass



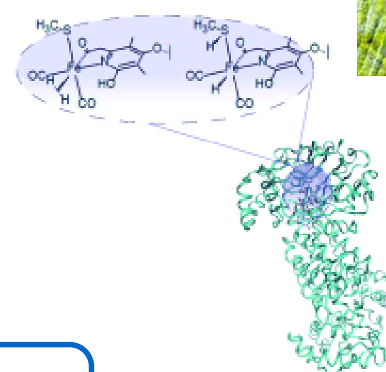
Pathways of biomass based hydrogen production. Renew. and Sust. Energy Rev. 2016, 57, 850

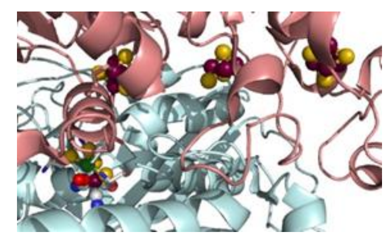
Biological H_2 production

- Most biological processes operate at ambient temperature and pressure, and they utilize renewable energy resources.

Plant Physiology, 127, 3, 2001

- Bio-hydrogen is produced from water by photolysis by some bacteria or algae directly through their hydrogenase or nitrogenase enzyme system.





$$2H_2O + \text{light energy} \rightarrow 2H_2 + O_2$$

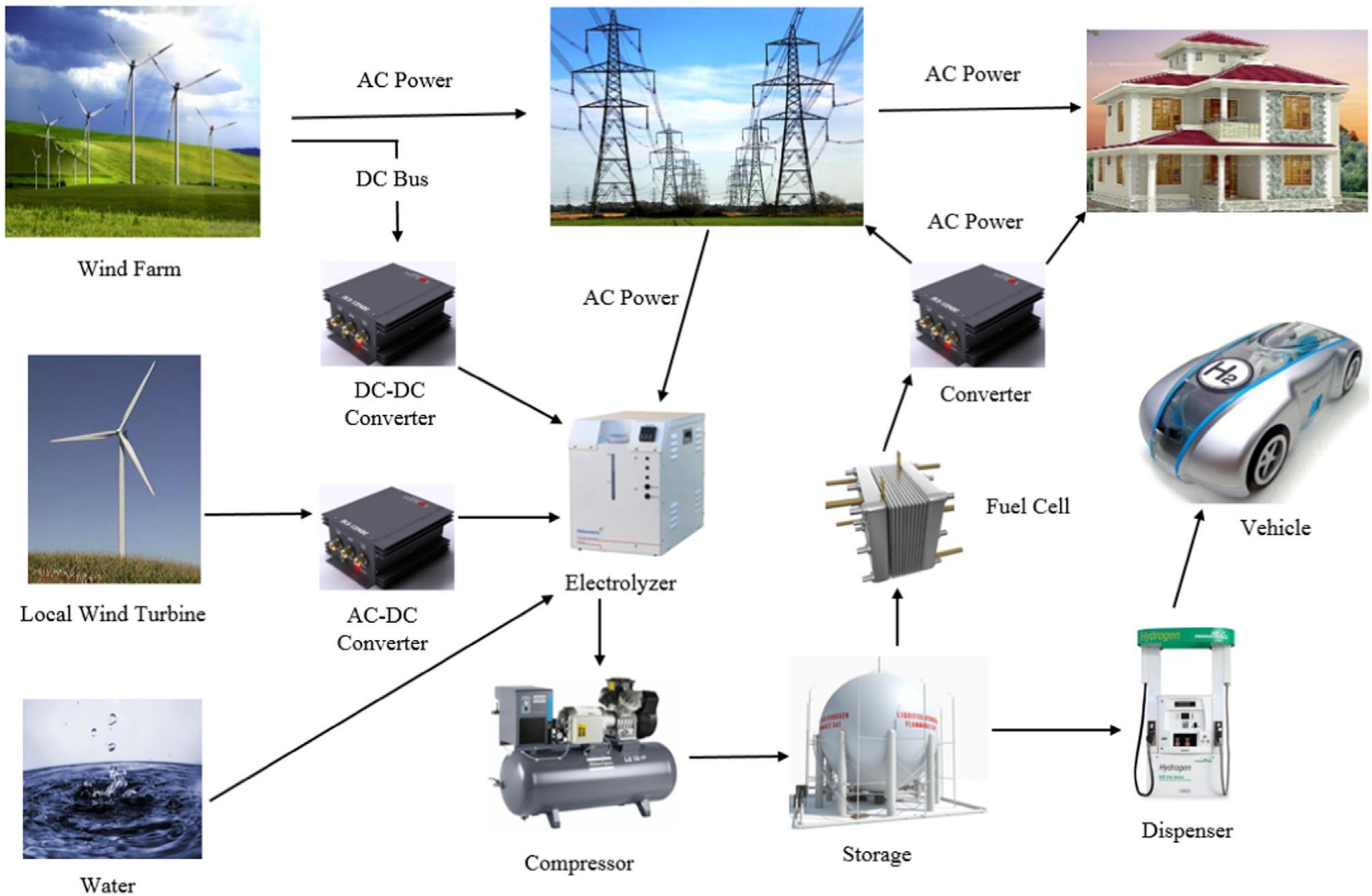
Sci. Adv. 2016; 2 : e1501014
Angew. Chem. Int. Ed. 2015, 54, 21, 6069

Wind or Solar to H_2


Hydrogen production using wind (WTH) or solar energy (PV) strategy from water (electrolysis).

$$H_2O + Energy \rightarrow H_2 + 1/2O_2$$

The surplus electricity is stored as hydrogen and it can be transformed to electricity again in time so flow wind potential or when grid congestion has stopped.



Integrated system of electricity/hydrogen generation from wind power.

Renew. and Sust. Energy Rev. 2016, 57, 850

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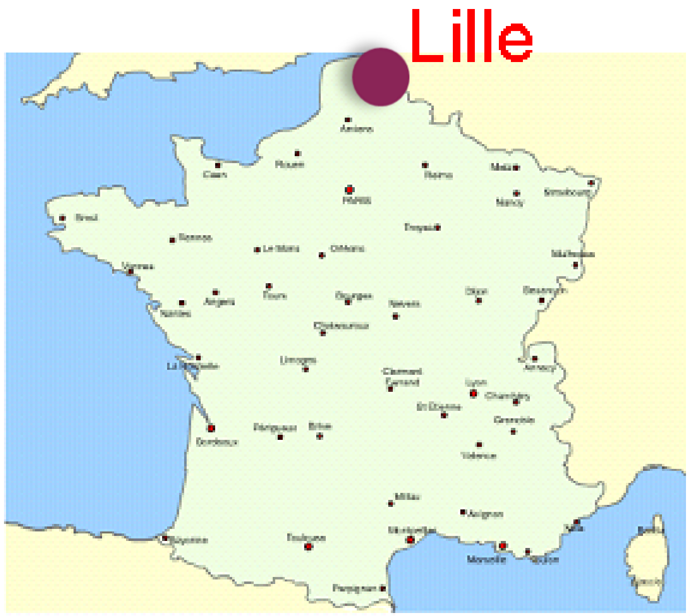

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H_2 from bio-resources

In theory, hydrogen production from biomass can be a neutral carbon-emission process since all carbon dioxide produced can be recycled back to plants.

Highly attractive routes for hydrogen production are catalytic transformation of:

- **Bio-ethanol**

easily obtained from transformation and fermentation of biomass.

- **Methane**

from biogas (mainly a mixture of CH_4 and CO_2). Agricultural and human waste, all release methane gas, also called landfill gas or biogas.

H_2 from ethanol

Steam reforming (SR)

$$C_2H_5OH + 3\,H_2O \longrightarrow 2\,CO_2 + 6\,H_2$$

endothermic

The endothermic nature of the steam reforming reaction makes the process energy intensive.

Partial oxidation (PO)

$$C_2H_5OH + 1.5\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2$$

exothermic

Oxidative steam reforming (OSR)

$$C_2H_5OH + a\,O_2 + b\,H_2O \longrightarrow c\,CO_2 + d\,H_2$$

One alternative way of supplying heat to the reforming of ethanol system is to add oxygen or air to the feedstock. The thermal neutrality of the reaction can be reached for specific values of a = 0.61 and b = 1.78.

H_2 from methane

Dry reforming (DR)

$$CH_4 + CO_2 \longrightarrow 2H_2 + 2CO$$

endothermic

Partial oxidation (PO)

$$CH_4 + 1/2O_2 \longrightarrow 2H_2 + CO$$

exothermic

Oxidative dry reforming (ODR)

$$CH_4 + aCO_2 + (1\text{-}a)/2O_2 \longrightarrow 2H_2 + (1\text{+}a)CO$$

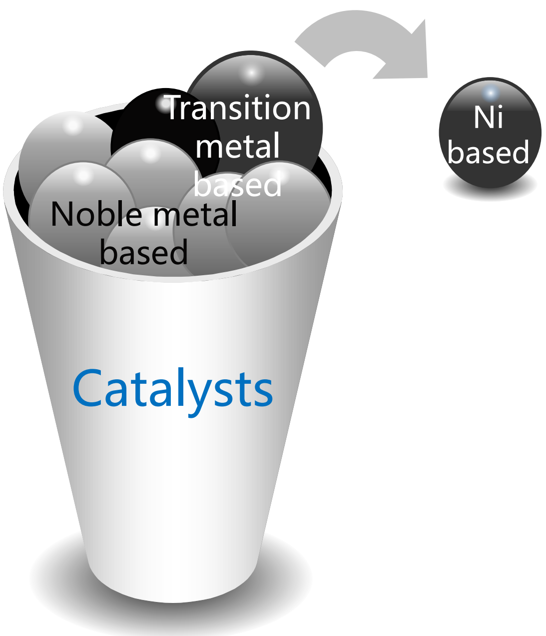
The oxidative biogas reforming process is a combination of dry reforming and partial oxidation of methane in a single reactor.

Catalyst

To perform the ideal transformation, very active and selective catalyst is required.

Ethanol C_2H_5OH → (Catalyst) → H_2

Methane CH_4 → (Catalyst) → H_2



- High activity
- Low cost
- Extensive availability
- Carbon formation
- Sintering

Objective: development of performant catalyst at low temperature in optimized conditions.

→ Influence of different parameters:

Catalyst ⟷ **Reaction conditions**

- Formulation
  - Ni content
  - dopant
- Preparation
- Treatment in H_2

- Temperature
- Reactants concentrations
- O_2/reactant ratio

- Catalysts : Ni based mixed oxides
  - Preparation
  - Characterizations
    - Oxidized state
    - Partially reduced state
- Ethanol transformation
- Methane transformation

Catalysts: Ni based compounds

Highly dispersed Ni species

$CeNi_X(Zr,Al)O_Y$ ⟺ Nanoparticles of NiO (10 nm), CeO_2 (5 nm), and/or Ce-Ni-(Zr,Al)-O solid solution

Angew. Chem. Int. Ed. 50, 2011, 10193
ChemCatChem 5, 2013, 2207
Appl. Catal. A 518, 2016,78
Appl. Catal. B 212, 2017, 159
WO2014108636, WO2015166182

$Mg_2AlNi_XO_Y$ ⟺ Nanoparticles (4-6 nm) of oxides and/or Ni-Mg-(Al)-O solid solution

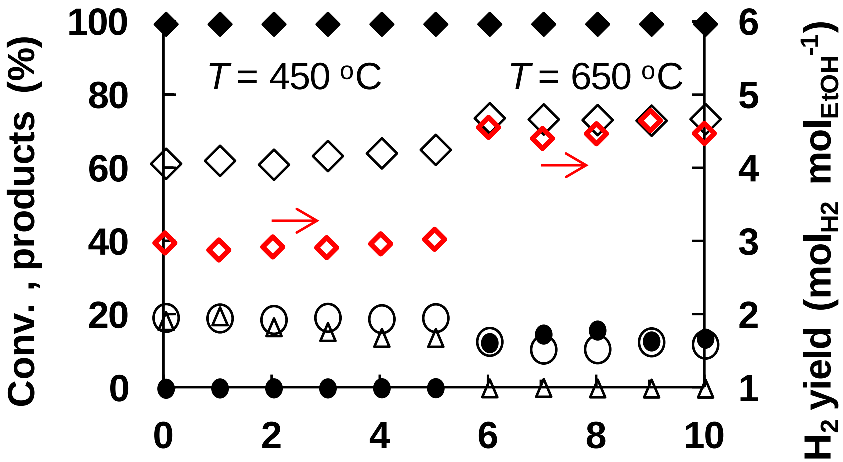
Appl. Catal. B 152–153, 2014, 370
Appl. Catal. B 166-167, 2015, 485
Int. J. Hydrogen Energy 41, 2016, 15443
Int. J. Hydrogen Energy 43, 2018 , 17643

H_2 from bio-resources

H_2 from ethanol

Ethanol steam reforming (SR)

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$$



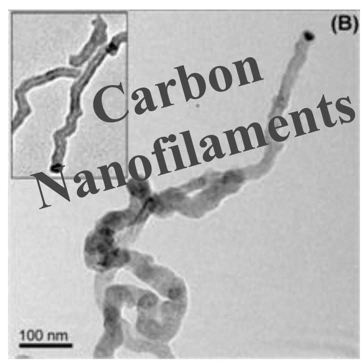
Time (h)

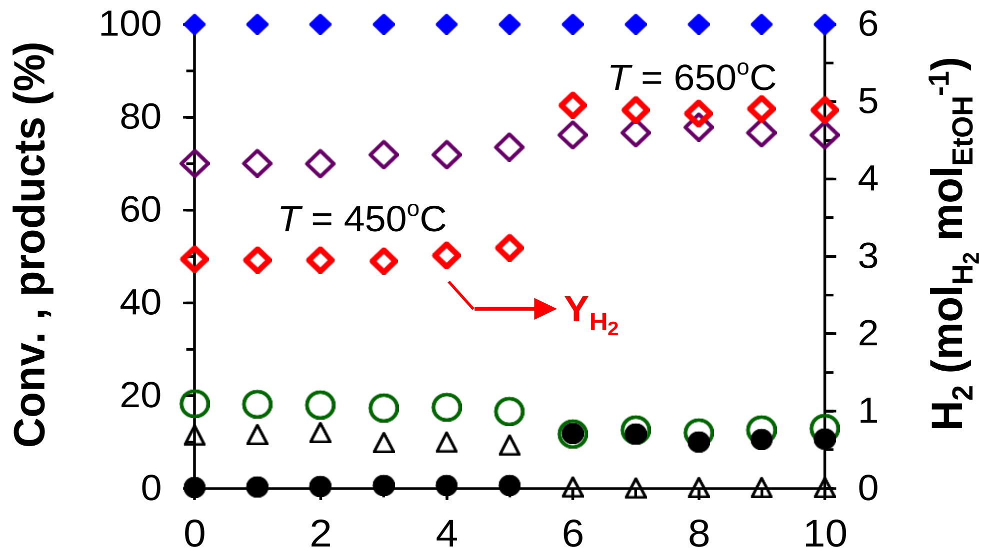
$CeNi_1O_y$ treated in H_2 at 250°C

Ethanol Conv. (◆), H_2 yield (◇), and products distribution:

H_2 (◇) CO_2 (○) CO (●) CH_4 (△).

$EtOH/H_2O/N_2$ = 3/9/88





Time (h)

$Ni_3Mg_2AlO_y$ treated in H_2 at 450°C

$EtOH/H_2O/N_2$= 1/3/N_2

$$C_2H_5OH \rightarrow H_2 + CH_4 + CO$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

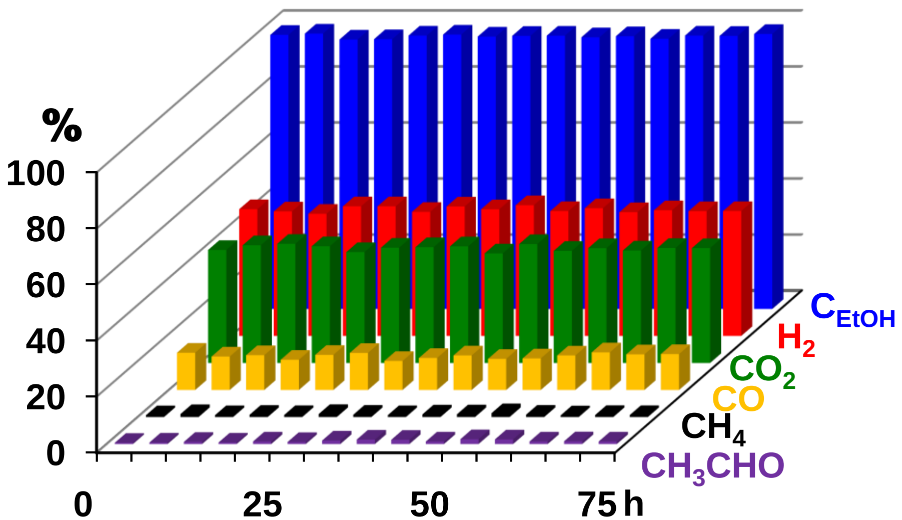
Int. J. Hydrogen Energy 35, 2010, 12741. RSC Adv. 2, 2012, 9626. Appl. Catal. B 152–153, 2014, 370. Appl. Catal. B 166-167, 2015, 485. Int. J. Hydrogen Energy 43, 2018 , 17643.

Ethanol oxidative steam reforming (OSR)

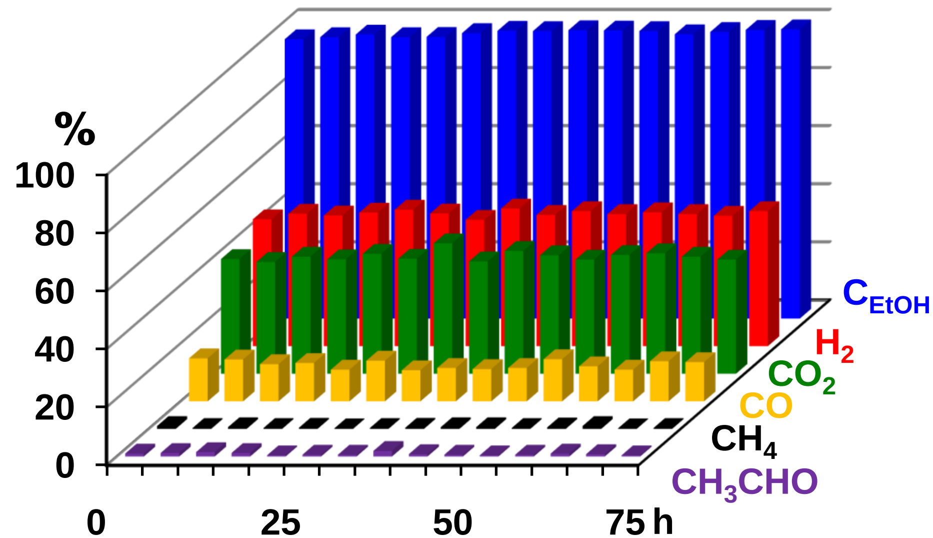
H_2 from ethanol

On Ni based oxyhydride catalysts

Catalyst: 30 mg Oven: 50°C Ethanol Conversion: 100%.



$CeNi_1H_ZO_Y$ catalyst



$Mg_2AlNi_3H_ZO_Y$ catalyst

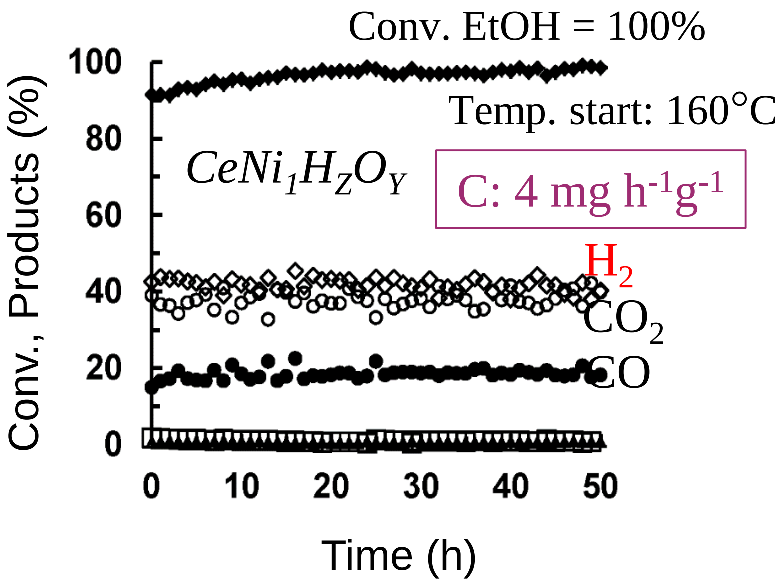
$EtOH/H_2O/O_2/N_2$= 1/3/1.6/1.3. Ethanol conversion and gas phase products: H_2 CO_2 CO (CH_4 and CH_3CHO < 1%), solid carbon formed

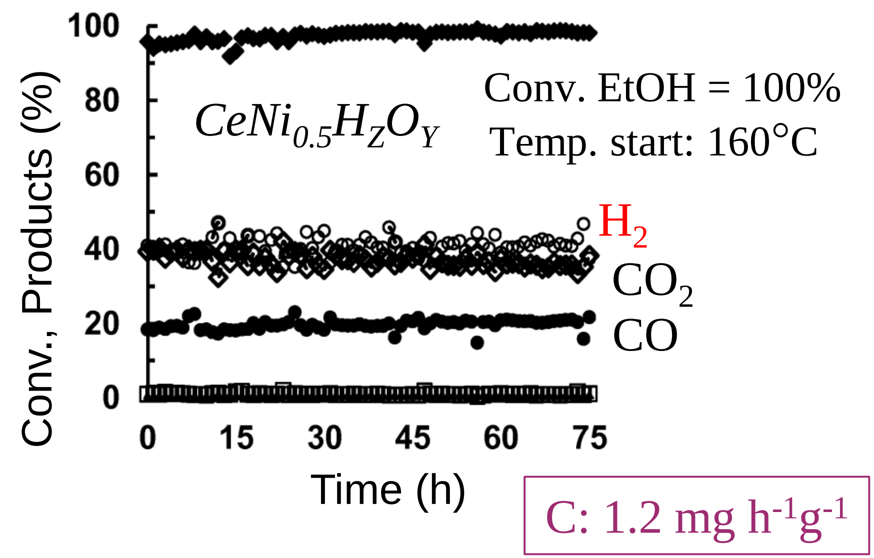
Patent WO2014108636. Angew. Chem. Int. Ed. 50, 2011, 10193. ChemCatChem 5, 2013, 2207. Appl. Catal. A 518, 2016,78. Int. J. Hydrogen Energy 41, 2016, 15443. Int. J. Hydrogen Energy 43, 2018 , 17643.

H_2 from bio-resources

H_2 from ethanol

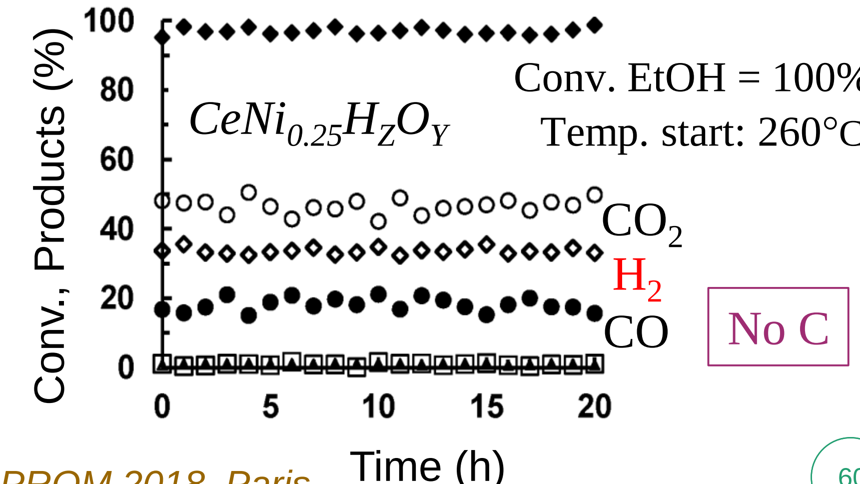
Ethanol oxidative steam reforming (OSR)





Catalyst: 30 mg,
Oven Temp: 50°C
Carbon formation largely decreased

$EtOH/H_2O/O_2/N_2$ = 1/3/1.6/1.3



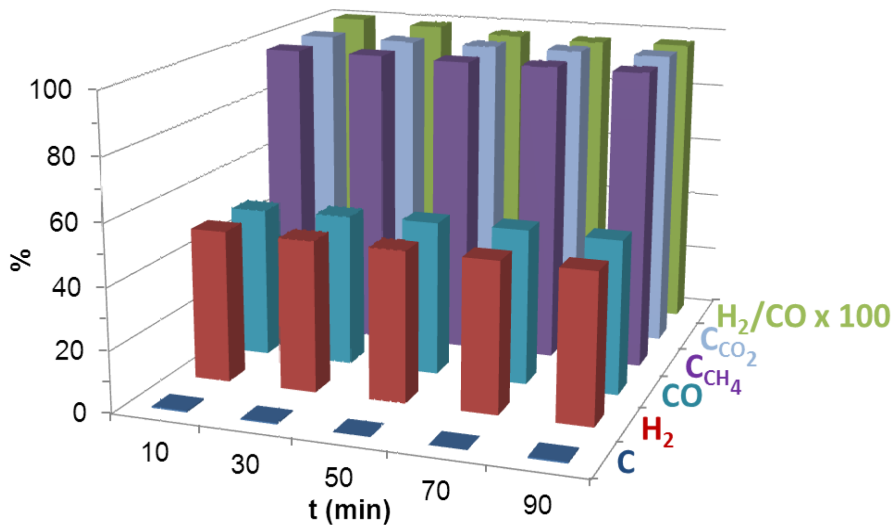
Patent WO2014108636.

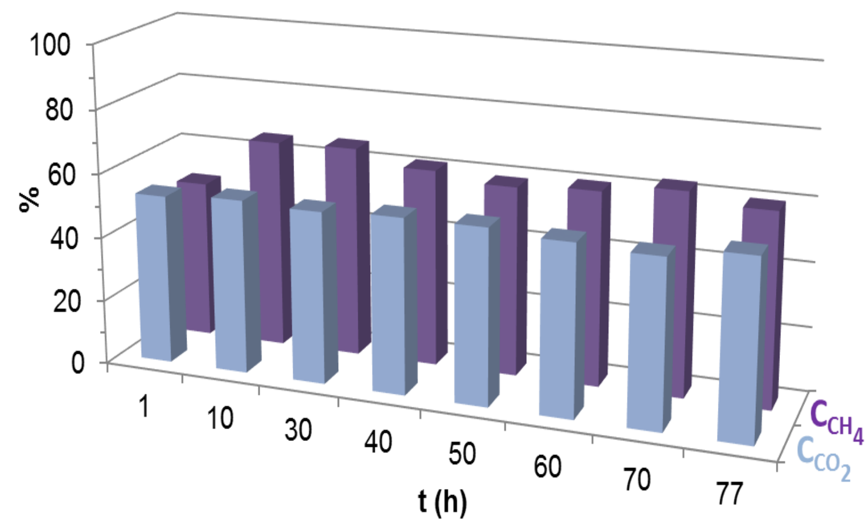
Methane dry reforming (DR)

H_2 from methane

$CH_4 + CO_2 \longrightarrow 2H_2 + 2CO$ $H_2 / CO_{theo.} = 1$

$T_{reaction} = 800^oC$ $H_2 / CO_{exp.} = 0.96$ $T_{reaction} = 650^oC$



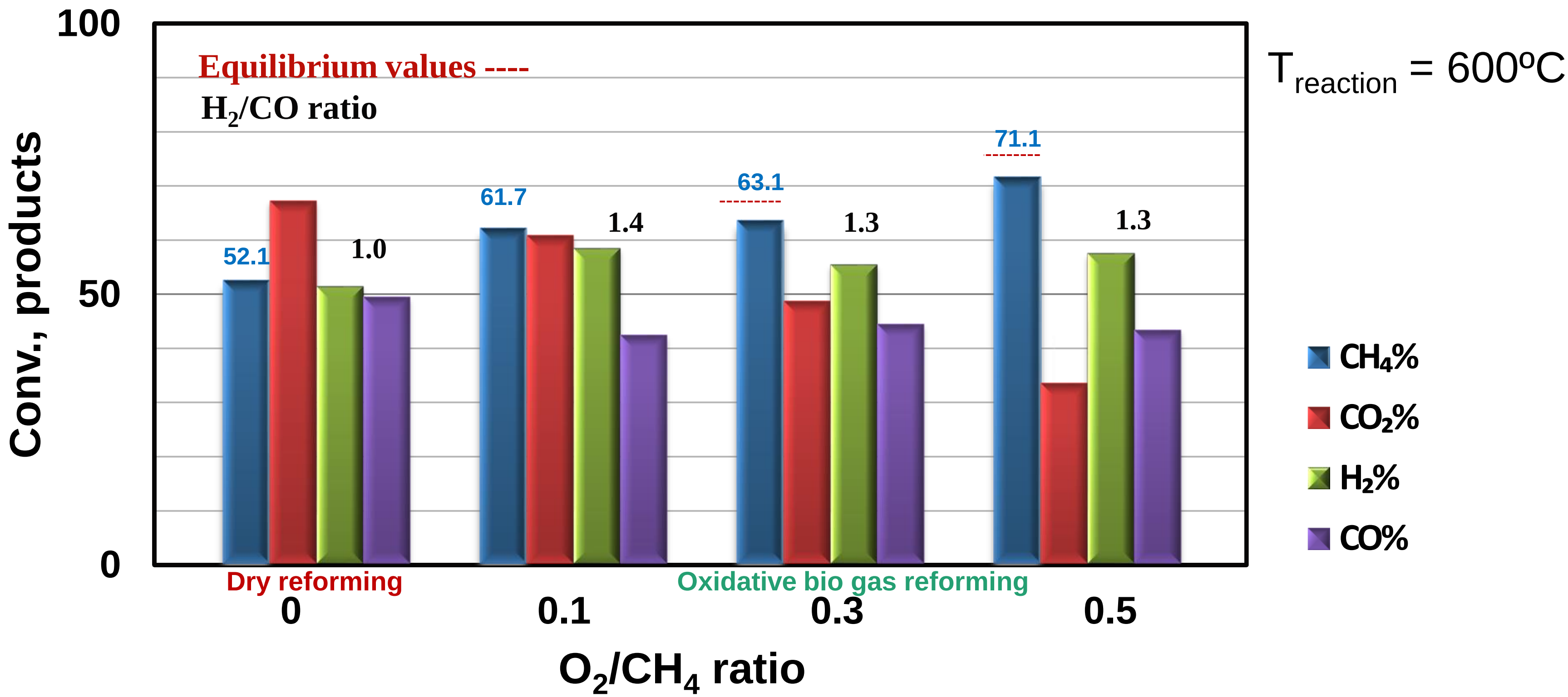


CH_4 and CO_2 conversions and products formed on Ni-Mg-Al-O catalyst.

Patent WO2015166182. Appl. Catal. B 212, 2017, 159. Chem. Eng. Proc. 122, 2017, 523.

H_2 from methane

Methane oxidative dry reforming (ODR)

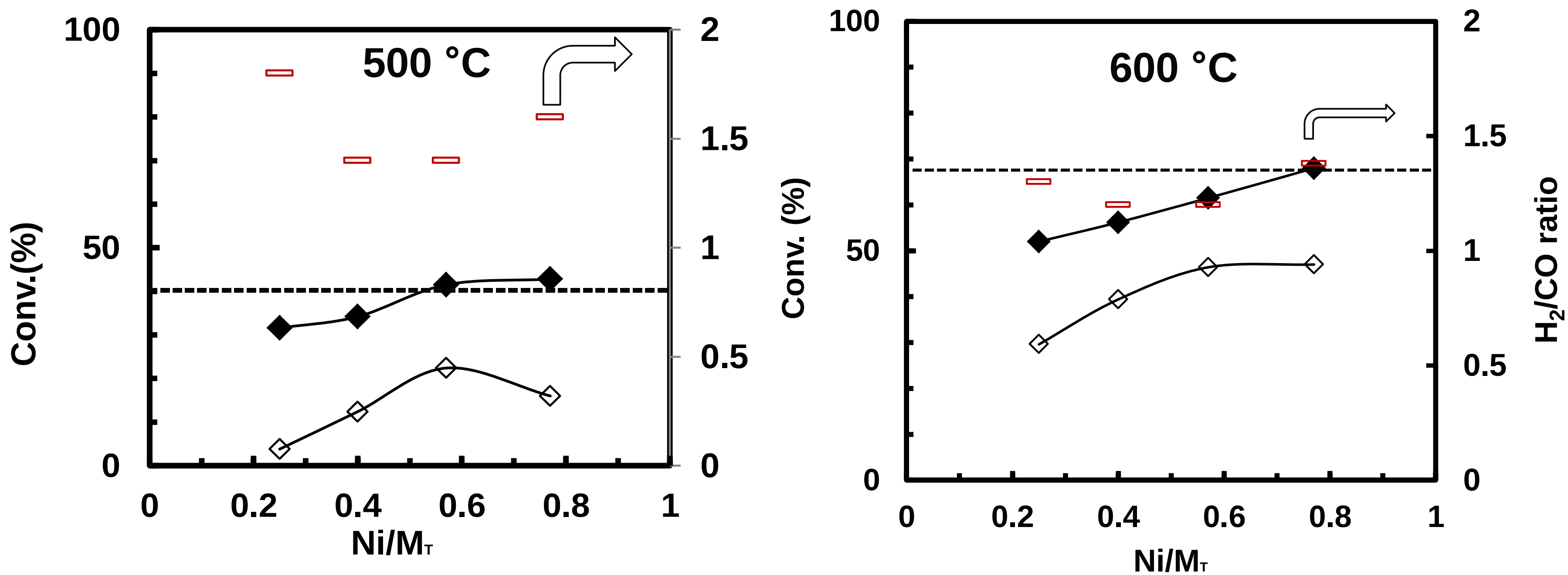


CH_4 and CO_2 conversions and products distribution (H_2, CO in mol %) on Ce-Ni-Al-O catalyst pretreated in H_2. $CH_4/CO_2/O_2/N_2$ =1:0.7:X:N_2

Addition of O_2 increases CH_4 conversion and H_2/CO ratio but decreases CO_2 conversion.

H$_2$ from methane

Methane oxidative dry reforming (ODR)



CH_4 (◆) and CO_2 (◇) conversions and H_2/CO ratio (▭) versus Ni content over $CeNi_XAl_{0.5}O_Y$ catalysts. (CH_4 conversion thermodynamic limit ----). $CH_4/CO_2/O_2/N_2$ =1:0.7:0.3:N_2. M_T is total metal: Ni + Al + Ce. Carbon formed.

Conversions globally increase with Ni content.
On high Ni content catalysts: values close to the predicted equilibrium.

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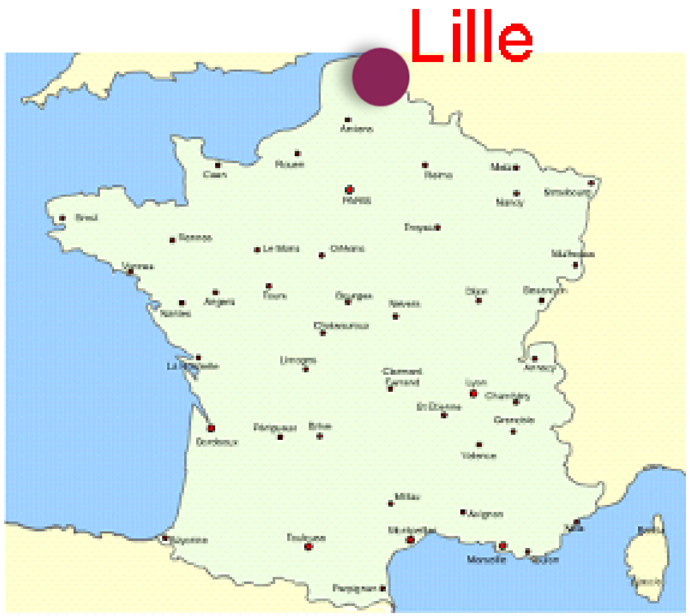
UNITÉ DE CATALYSE ET CHIMIE DU SOLIDE



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