Introduction to hydrogen chemistry

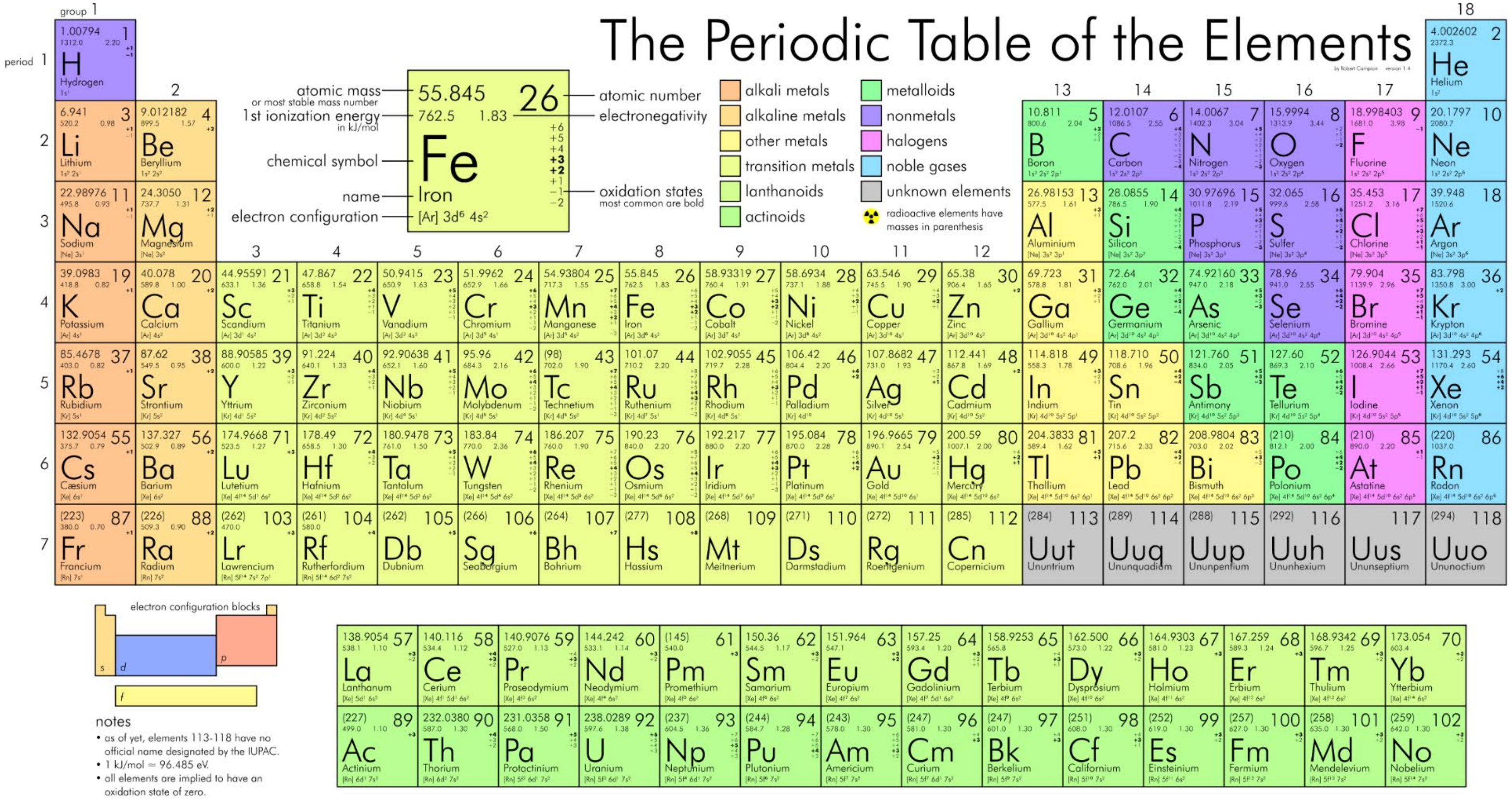
This lecture gives a short introduction to hydrogen (catalytic) chemistry and addresses the following issues

- Definitions of an atom and a molecule
- Basic properties of hydrogen
- Color coding of hydrogen cleaness levels
- Main industrial hydrogen production pathways
- Hydrogen production via steam methane reforming and water splitting
- Introduction to heterogeneous catalysis and its subclasses thermal catalysis and electrocatalysis
- Current and future usage of hydrogen.

The slides are mostly based on following literature: A.I. Osman et al. Environ. Chem. Lett. 20, 152 (2022); X. Zou & Y. Zhang Chem. Soc. Rev. 44, 5148 (2015);N. Rambhujun et al. MRS Energy and Sustainability 7, 1 (2020); El-Emam & Özcab J. Clean. Produc. 220, 593 (2019); L. Chen et al. Catalysts 10, 858 (2020)

What is an atom ?

- Atoms are basic building blocks of matter.
- They can not be broken down using chemical means.
- They make up all material in the universe.
- An atom consist of a positive nucleus surrounded by negative electrons.

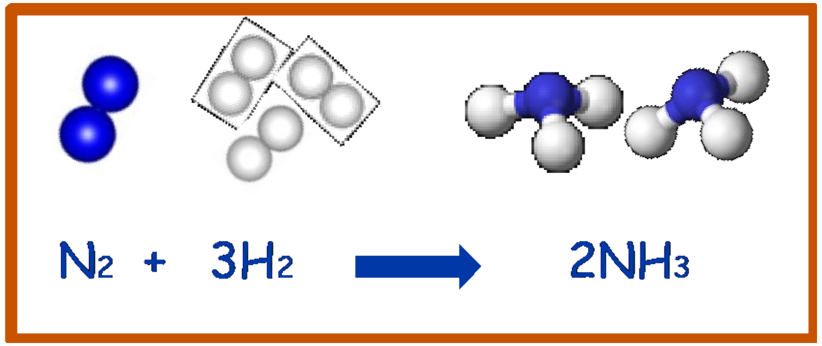


The periodic table is an organized array of all the chemical elements in order of increasing atomic number.

Periodic table from Wikimedia Commons

What is a molecule ?

- A **molecule** consists of two or more atoms held together by attractive forces known as **chemical bonds.**
- Some examples of molecules: H_2 (hydrogen), H_2O (water), CO_2 (carbon dioxide), CO (carbon monoxide), NH_3 (ammonia), O_2 (oxygen), N_2 (nitrogen), CH4 (methane), CH_3OH (methanol)
- Simple chemical reaction between hydrogen and nitrogen molecules to make ammonia:



Hydrogen and its basic properties

- A dihydrogen molecule (chemical formula H_2) is commonly called ***hydrogen*** and consists of two hydrogen (H) atoms.
- Most abundant element in the universe
- Highly reactive and therefore exists only in compounds such as water or organic materials (containing mainly carbon (C)).
- Hydrogen is odorless, flammale and colourless gas
  - Leads to safety concerns if the leak is not dected and gas is collected in a confined area. This may introduce explosion.
- Hydrogen gas has high energy density by weight but low energy density by volume compared to hydrocarbons and requires therefore a larger tank to store. For example, liquified hydrogen contains 2.4 times the energy of liquified natural gas but takes 2.8 times the volume to store.

Colour coding of Hydrogen cleaness levels

- Different color codings of hydrogen originate from the hydrogen production route.
  - Grey hydrogen is produced using fossil fuels such as natural gas, which primarly consists of methane (CH_4) but also other hydrocarbons.
    - Production of one tonne of grey hydrogen leads to 10 tonnes of carbon dioxide (CO_2) !
  - Blue hydrogen is also procuded from fossil fuels but with the combination of carbon capture and storage.
  - Green hydrogen is typically procuded via water electrolysis using 100 % renewable sources such as wind or solar energies.
  - Brown hydrogen is obtained by gasification of coal-based fuel.
  - Turquose hydrogen production relys on thermal decomposition of natural gas.
  - Pink hydrogen is made using nuclear energy.

The three main pathways for industrial hydrogen production

Technology	Process	Governing chemical reaction
Steam Methane Reforming	Methane, Steam → H_2, CO_2	$CH_4 + 2H_2O \longrightarrow 4H_2 + CO_2$
Coal Gasification	Coal, Steam → H_2, CO_2	$C + 2H_2O \longrightarrow 2H_2 + CO_2$
Water Electrolysis	Water, Electricity → H_2, O_2	$2H_2O \longrightarrow 2H_2 + O_2$

If nuclear energy is used, this is pink hydrogen production.

Steam Methane Reforming and Coal gasification make about 96 % of all hydrogen production.

Grey hydrogen production: steam methane reforming (SMR)

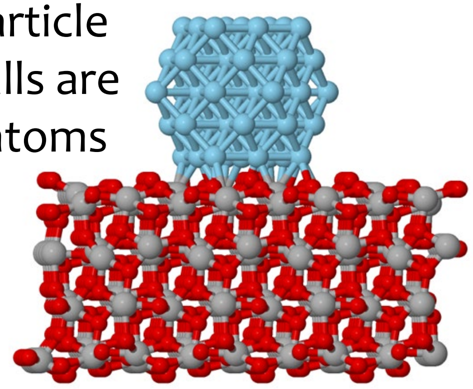
- In SMR, methane from natural gas is heated with steam in the presence of a **catalyst** to produce hydrogen and carbon dioxide.
- The SMR reaction has two chemical reaction steps:
  - Reforming reaction: $CH_4 + H_2O \longleftrightarrow CO + 3H_2$ and
  - Water gas-shift reaction: $CO + H_2O \longleftrightarrow CO_2 + H_2$
  - The overall reaction (including both reactions above) is

    $CH_4 + 2H_2O \longleftrightarrow CO_2 + 4H_2$
- SMR is the least expensive and most common method to produce H_2.
- What is a catalyst and what does it do for SMR ?

What is a catalyst and what does it do ?

- **A catalyst is a substance that speeds up the chemical reaction without being consumed itself in the process.**
- This means that after helping a chemical reaction to proceed with less energy (see the figure on the next slide) and relasing a product molecule , a catalyst has the chemical composition as before the reaction (does not react to another species).
- A typical catalyst used in industry consists of an (inert) support material (e.g., metal oxide or carbon) and an active component: metal nanoparticles residing on the support.

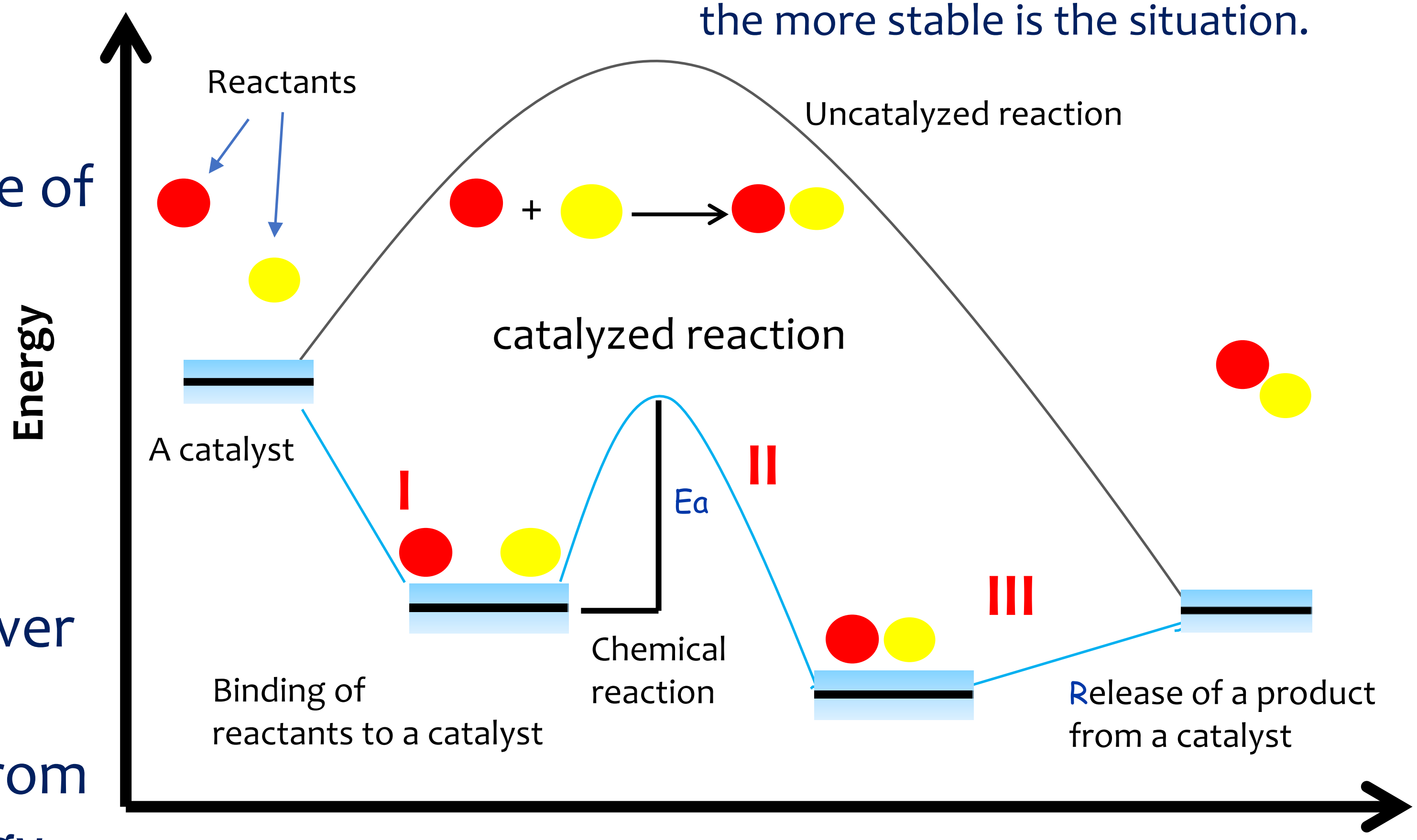
Schematic atomic level structure of a heterogeneous catalyst



A catalyst reduces energy cost of a chemical reaction

I: A catalytic reaction starts by binding of reactants to a surface of a catalyst. This step lowers the energy of system.
II: The reaction between the reactants. This is typically associated with an activation energy, which is significantly lower than without a catalyst.
III: Finally a product separates from a catalyst. This also needs energy.

Lower the energy in the energy diagram, the more stable is the situation.



Ea = activation energy

What kind of catalysts are there?

Catalysts can have multitude of forms varying from

- atoms
- molecules
- enzymes
- zeolites (microporous, crystalline material made out of aluminosilicate)
- metal nanoparticles

Metal nanoparticles, atoms, and molecules (called an active component) are typically attached to a solid material called support, which immobilizes and stabilizes the active component.

Optimal catalysts exhibit high activity, high selectivity towards desired products, low cost and long-term stablity to achieve economical industrial operation.

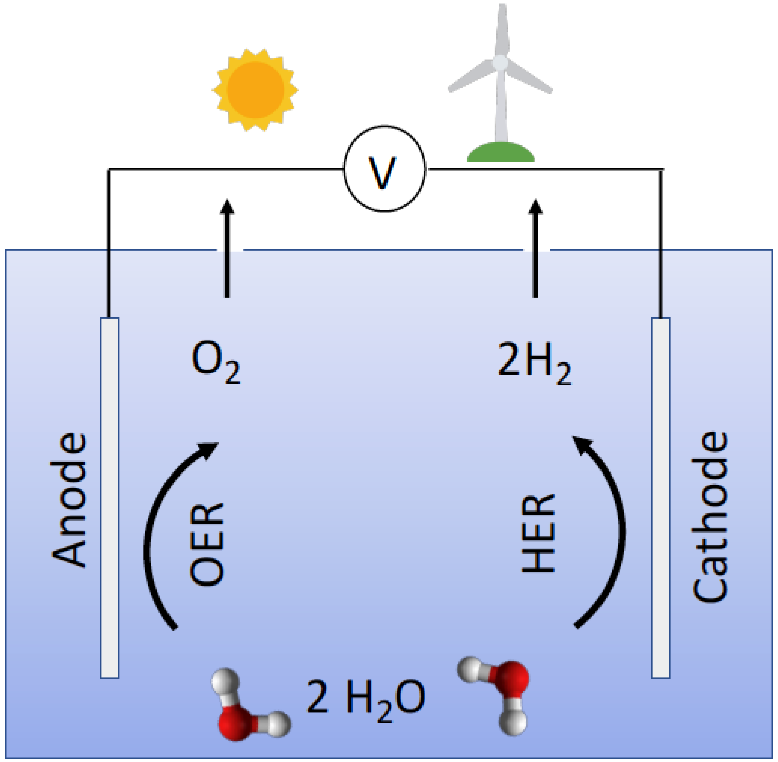
Different catalysis types

- So catalysis is a process where the speed of a chemical reaction increases by adding a catalyst.
- Three main types of catalysis
  - Thermal catalysis driven by temperature
    - Indusrially the most mature field
  - Electrocatalysis driven by electric potential
    - Offers attractive prospects for green transition when renewable electricity is used
    - Improvements are needed to become industrially viable
  - Photocatalysis driven by light (not addressed further in this lecture)

Heterogeneous catalysis

- In heterogeneous catalysis, the phase of a catalyst differs from that of reactants or products. Typically the catalyst is in the solid phase and reactants/products in gas or liquid phase. Metal nanoparticles on support materials are typical heterogeneous catalysts. The chemical composition and structure of a catalyst affects its catalytic activity (and selectivity).
- Examples of heterogenously catalyzed reactions
  - Thermal catalysis: steam methane reforming (SMR) reaction discussed earlier
  - Electrocatalytic water splitting, which produces hydrogen and oxygen via hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)
- A commercial SMR catalyst Ni/Al_2O_3 (Al_2O_3 = alumina) suffers from serious deactivation (= loss of activity during operation). Noble metals ruthenium (Ru) and rhodium (Rh) are more active and stable but more expensive and their availablity is limited.
- The best HER catalyst is platinum (chemical symbol Pt)

Electrocatalytic water splitting (water electrolysis)



Electrochemical cell

- Water splitting takes place in a **electrochemical cell,** which consits of two electrodes (anode and cathode) immersed in an electrolyte solution.
- The water splitting reaction consists of two half reactions: Hydrogen gas is formed on a cathode and oxygen gas on an anode. The reaction requires energy and external energy is provided by electricity.
- Electrocatalysts are located at the surface of the electrode. Half reactions take place at the interface of the electrode and electrolyte solution.
- Water splitting reaction is straightforward and environ-mentally friendly. Large scale production is still challenging due to low efficiency and high cost. **Therefore the development of efficient and cheap catalysts is a must.**

Electrocatalytic water splitting

- In water splitting electrical energy is converted into chemical energy that is to H_2 and O_2 molecules in hydrogen evolution (HER) and oxygen evolution reactions (OER) respectively.
- If renewable electricity is used, produced hydrogen is green and if nuclear power is applied produced hydrogen is pink.
- Both half reactions must take place efficiently. That is in order to make H_2 also OER must happen.
- Both HER and OER reaction have activation energy (see slide 10), but the activation energy (called overpotential) is higher for OER, so it is the "bottle neck" for the water splitting reaction. The electrocatalyst are developed to lower HER and OER activation energies. The lower activation energy leads to the faster and more efficient reaction.
- The performance of the electrocatalysts is determined by the chemical composition (what elements are used from the periodic table slide 2), the structure, and stability of a catalyst.

Hydrogen usage in (chemical) industry

Global hydrogen demand 90 Mt in 2020 (Global Hydrogen Review in 2021 by IEA)

- Ammonia production: $N_2 + H_2 \longrightarrow NH_3$ 34 Mt
- Petroleum refining 40 Mt
- Methanol production: $CO + 2H_2 \longrightarrow CH_3OH$ 9Mt
  - Methanol can be converted to dimethyl ether (DME) CH_3OCH_3
- Production of direct reduce iron (Fe) 5Mt.
- Some examples of new directions
  - Heavy industry: steel making
  - Hydrogen-based fuels
  - Synthetic fuels from captured CO_2 and H_2 e.g., jet fuel kerosene
  - Synthetic methane from captured CO_2 and H_2
- Increase in hydrogen use in existing applications such as ammonia synthesis and methanol production is expected.