CO_2 Uptake

CO_2 capture

- ✓ Introduction
- ✓ Capture and separation technologies
- ✓ Materials as adsorbents for CO_2 capture

CO_2 capture

- Biggest challenge of the 21st century: to provide universal access to energy throughout the world in a safe, clean and sustainable way.
- Current energy systems are based on the use of fossil fuels.
- The extraction of energy generates significant environmental and social impact.

CO_2 capture

The International Energy Agency (IEA) forecasts that demand for energy:

- It will increase 40% by 2030
- An average annual increase of 1.5%
- Over 50% of the increase in demand comes from China and India

The analysis by the Intergovernmental Panel on Climate Change:

Indicates that emissions will increase until 2015 and could then fall below 2000 emissions if measures are taken to capture CO2

Sustainability: "Development that meets the needs of the present without compromising the ability of future generations to meet their needs".

UN Brundtland Report “Our Common Future”.

Report was made by Norway's former Prime Minister Gro Harlem Brundtland, with the purpose of analyzing, criticizing and rethinking globalizing economic development policies, recognizing that the current social advancement is taking place at a high environmental cost. The report was drafted by various nations in 1987 for the UN, led by Dr Brundtland

CO_2 capture

Until the mid-20th century (isolated news)

- ✓ Ordinances banning the use of coal in London at the beginning of the 14th century because of the great pollution they produced
- ✓ Measures taken in Talavera de la Reina (Spain) at the beginning of the 17th century to avoid the discomfort caused by emissions from ceramic kilns
- ✓ Study of the British Parliament of 1772 to analyze the serious problem of air pollution in London
- ✓ In 1911 is invented the word "smog" (mixture of smoke and fog)

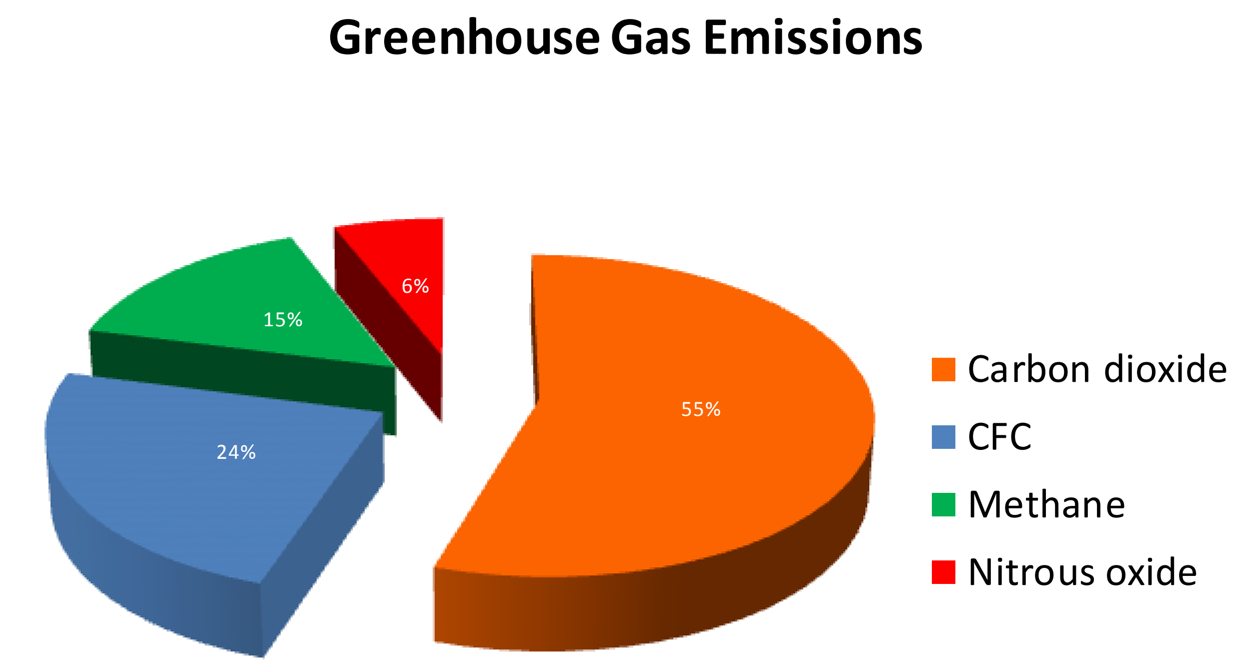
1952 Smog causes 4000 deaths in London

1970 The EPA (Environmental Protection Agency) is created in the United States and the first steps are taken to obtain clean air from the CAA (Clean Air Acta)

1972 United Nations Conference on the Environment in Stockholm

CO_2 capture

1970-75	They are detected damage caused by acid rain
1972	The European Community decides to adopt an environmental policy
1985-86	The existence of the ozone "hole" in Antarctica is confirmed
1985-90	Alert on possible climate change caused by greenhouse gases
1986	Unleaded gasoline is marketed in Great Britain
1987	Montreal Protocol to Limit CFC Production
1992	United Nations Conference on Environment and Development in Rio de Janeiro


Greenhouse Gas Emissions
55%
24%
15%
6%
Carbon dioxide
CFC
Methane
Nitrous oxide

CO_2 capture

Carbon Oxides

CO_2 → It is generated by human activity, pollutant emitted in greater quantity to the atmosphere by non-natural causes

CO → About 90% that exists in the atmosphere is provided by naturally oxidation of methane (CH4) in photochemical reactions. It is eliminated by its oxidation to CO_2.

Sulfur Oxides

(SO_2) → More than half of what reaches the atmosphere is emitted by human activities, mainly by the combustion of coal and oil and metallurgy. Volcanic activity

(SO_3) → Secondary pollutant formed by oxidation of SO_2

NO_x (NO and NO_2)

- It has a great transcendence in the formation of photochemical smog, ozone destruction, both tropospheric and stratospheric, as well as in the phenomenon of acid rain.
- In high concentrations produces damage to health and plants and corrode diverse fabrics and materials. Combustion at high temperatures.
- More than half of the gases of this group emitted in Spain come from the transport.

Óxido nitroso (N_2O)

It comes mainly from natural emissions (microbiological processes in the soil and oceans) and less from agricultural and livestock activities (accounting for 10% of the total).

Amoniaco (NH_3)

The ammonia that is emitted to the atmosphere in Spain originates almost exclusively in the agricultural and cattle sector

Volatile organic compounds

Methane (CH_4)

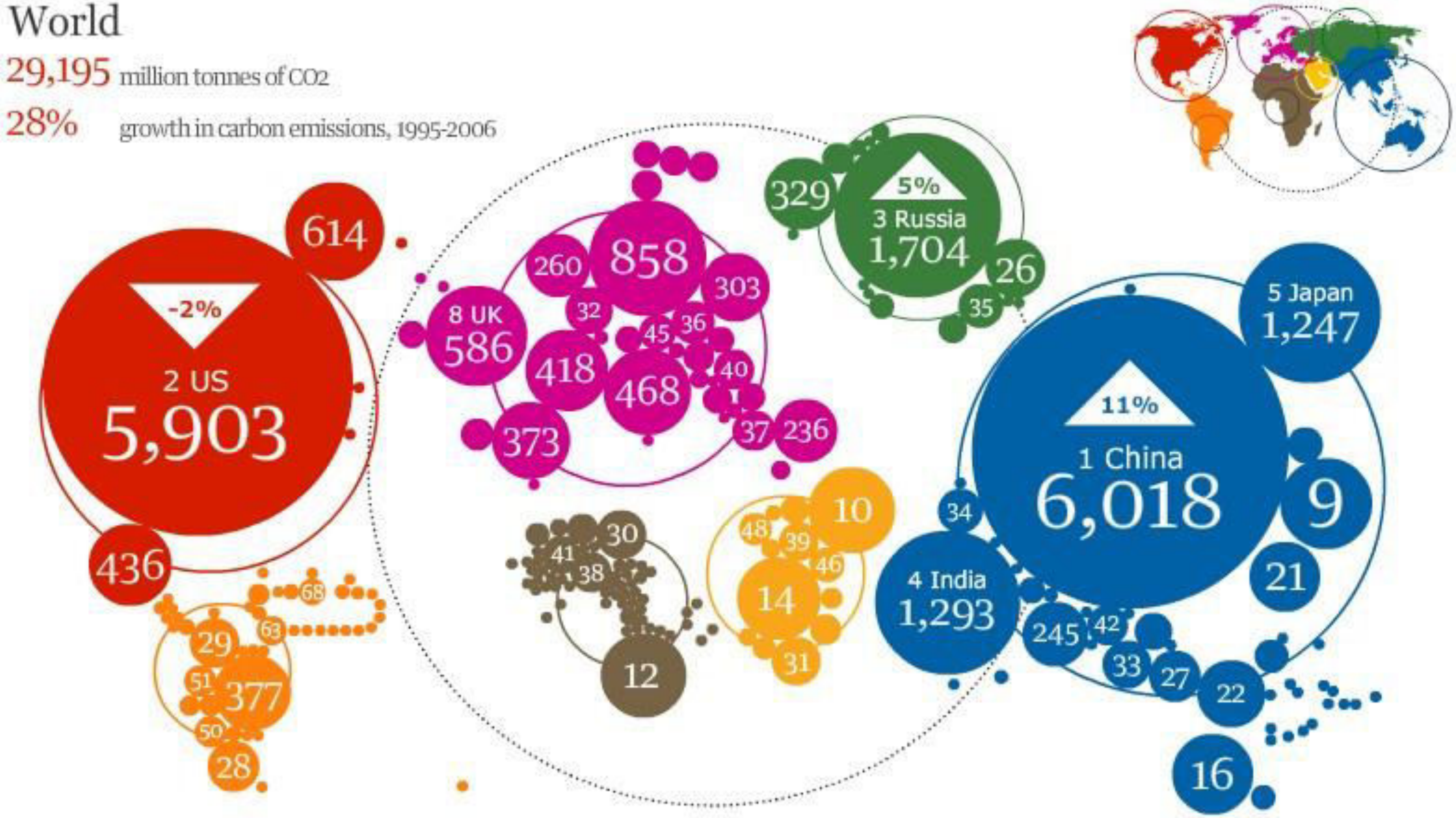
- It is the most abundant and most important of the atmospheric hydrocarbons.
- It is formed naturally in various anaerobic reactions of the metabolism of living organisms and also is derived from natural gas, which is a major component and in some combustion.
- Greenhouse effect

Volatile organic compounds

Other hydrocarbons

- Mainly from natural phenomena, but also from human activities, especially those related to the extraction, refining and use of oil and its derivatives.
- Its effects on health are variable.
- They intervene in an important way in the reactions that originate the photochemical smog.

CO_2 capture



Global CO_2 emissions by country. Data for 2006 indicate that emissions, compared to 2005, were reduced by 2.4%. (The Guardian, 2009)

Example 1:

The production of one ton of Portland cement emits between 0.6 and 1 ton of CO_2.

This represents 5% of total CO_2 emissions.

Part of the CO_2 is re-fixed by the cement base materials in the form of $CaCO_3$ in a reaction known as carbonation.

CO_2 capture

Example 2: One hour of combustion in a 660 MW coal-fired power plant, in the absence of any pollution-reducing system releases gases:

- 2.500 Tons of **N_2**
- 700 Tons of **CO_2**
- 1-20 Tons of **SO_2**
- 10-20 Tons of fly ash (particles)

NOx production is reduced if the bed temperature is kept below 1000 °C instead of 2000 °C of conventional plants

Fluidized beds also release particles although in much smaller amounts than pulverized fuel plants.

CO_2 capture

Elimination of gases produced in the combustion of coal by injecting crushed limestone at low temperature. The limestone reacts with the gases obtaining gypsum and other products that are periodically removed from the boiler.

Example:
Chemical reaction of the desulfuration process

$$SO_2 + CaCO_3 + \frac{1}{2} O_2 \rightarrow CaSO_4 \cdot 2H_2O + CO_2$$

Capture and separation technologies

Manufacturing of some fertilizers, natural gas processing and cement manufacturing produces large quantities of CO_2

In some industrial processes there is the emission of pure CO2 which can be captured and separated relatively economically.

Pre-combustion: remove CO_2 before combustion and use hydrogen

Post-combustion

Oxicombustion: Combustion with Oxygen to produce concentrated CO_2 without the presence of other gases, later the water is eliminated. High heaters are required

Capture and separation technologies

Type of combustion-capture system	Main compounds of the stream to be separated	Conventional carbon dioxide separation technology	New technologies of separation of carbon dioxide
Pre-combustion	Carbon dioxide, hydrogen	Chemical Absorption	Membranes. Physico-chemical adsorption
Post-combustion	Carbon dioxide, nitrogen oxides and sulfur oxides	Absorption	Capture of carbon by means of carbonated cycles. Membranes
Oxy-combustion	Oxygen, carbon dioxide, oxides of nitrogen, oxides of sulfur and water	Cryogenic Separation	Membranes. Absorption.

Capture and separation technologies

In the processes of pre and post combustion the gases are hot and humid

The development of **adsorbent systems** requires:

- Make it an economic material
- Not aggressive with the environment,
- Tolerant with water,
- Tolerant to impurities and
- That works at high temperatures

Adsorption systems operate in a three step cycle: adsorb CO_2, purge (remove impure gases) and evacuate (remove / desorb CO_2).

Capture and separation technologies

Absorption in dissolvent:

Cyclic processes: CO_2 is absorbed in a liquid.

Dissolvent more used: amine

The CO_2 is absorbed into the liquid and is processed to remove it and compress it for storage.

Capture and separation technologies

Membranes:

Polymers or ceramics act as CO_2 sieve in a stream of gas with a mixture of molecules

Different types of configurations:

- Single gas separation devices
- Incorporating different stages of absorption into liquids depends on the composition of the gas and temperature

Adsorption:

- Adsorption is based on cyclic processes
- The CO_2 is adsorbed from a stream of gas on a surface of a solid (mineral Zeolite)
- The solid is purified in different stages (pressure and temperature) and the CO_2 is compressed for storage

- Adsorption: process of accumulation of a gas on the surface of a liquid or solid (adsorbent)
- The accumulated gas is called adsorbate

Capture and separation technologies

Cryogenic techniques:

Very low temperatures are used to cool, condense and purify CO_2 from the gas stream.

Used for low CO_2 concentration in gas

Types of adsorption

CO_2 is absorbed by two types of adsorption: physical and chemical

Physicsorption:

- The adsorbate weakly binds to the adsorbent by combining Van der Waals and electrostatic forces.
- Covalent bonds are not formed and heat is released after adsorption
- The objective of developing new adsorbents is to increase adsorption capacity of CO_2 increasing the electric field and increasing the surface

Numerosos procesos de desorcion del CO_2

Types of adsorption

CO_2 is absorbed by two types of adsorption: physical and chemical

Chemisorption:

There is covalent interaction of the CO_2 and the surface of the adsorbent, allows to increase the capacity of adsorption.

The development of new adsorbents is based on improving the selectivity towards CO_2 and stability at high temperature: organic / inorganic hybrids, the functionality can produce increase of adsorption

Numerous CO_2 desorption processes

Materials as adsorbents for CO_2 capture

High adsorption capacity

Quick adsorption / desorption kinetics

Favorable adsorption / desorption temperatures

Cyclic stability

Physisorbents: zeolites and carbon active
T-sensitive, poorly selective and weak interaction with CO_2

Chemiadsorbents: Metal oxides, salts, hydrotalcites, organic / inorganic hybrid compounds.
High selectivity towards CO_2 and high adsorption capacity

Materials as adsorbents for CO_2

Classification according to temperature

Low temperature< 200 °C

Zeolites, MOFs and activated carbon

Intermediate temperatura 200-400 °C

Hydrotalcites

High temperatura >400 °C

CaO, MgO, Li_2ZrO_3, Li_4SiO_4

Materials as adsorbents for CO_2 capture

Metal Organic Frameworks (MOFs):

Hybrid materials combining organic ligands and metal ions or metal clusters.

Crystallographic structures defined 3D.

High specific surface and thermal stability.

- Zeolites
- Mesoporous carbon
- Silica gel
- Alumina

Materials as adsorbents for CO_2 capture

Zeolites

Open-structure aluminosilicates, with variable-sized pores acting as molecular sieves

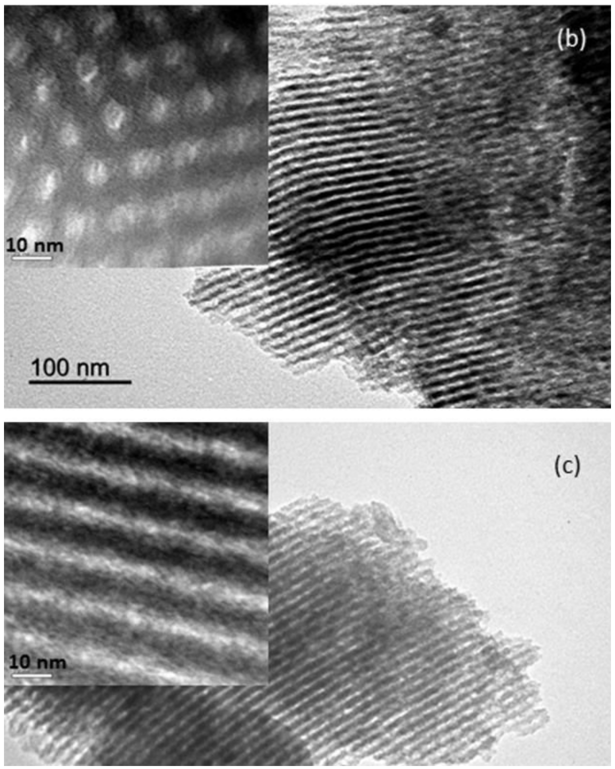
They can be modified to include the inclusion of a great variety of metallic cations by means of exchange process

Produces changes in CO_2 adsorption capacity, selectivity and water tolerance

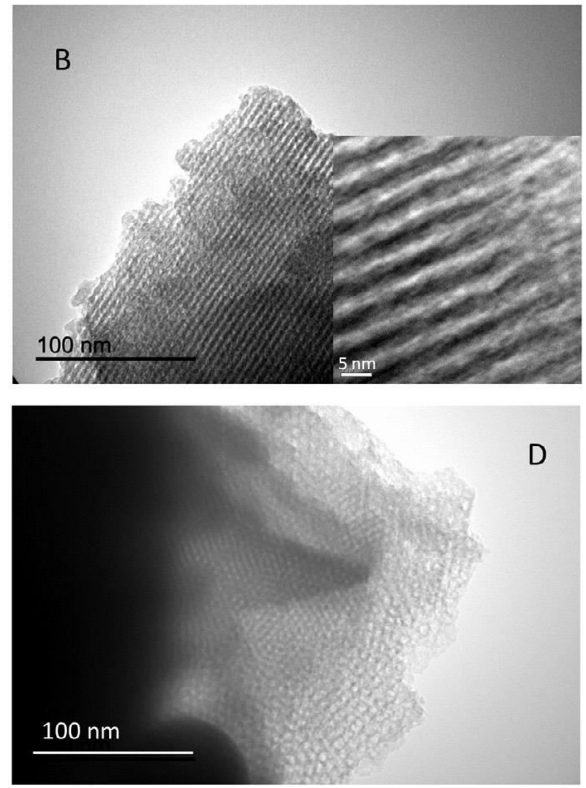
Mesoporous carbon

They are carbon with structure of mini boxes containing nanopores (diameters between 2nm and 50nm)

The pores can be added functionality to increase the capture capacity



Mesoporous carbon



Benzene-PMO

Materials as adsorbents for CO_2 capture

Oxidos metálicos :

MgO: low adsorption capacity

CaO: high adsorption capacity decreases with cycles

Al2O3: low capacity, improvement with carbonate and metal oxides

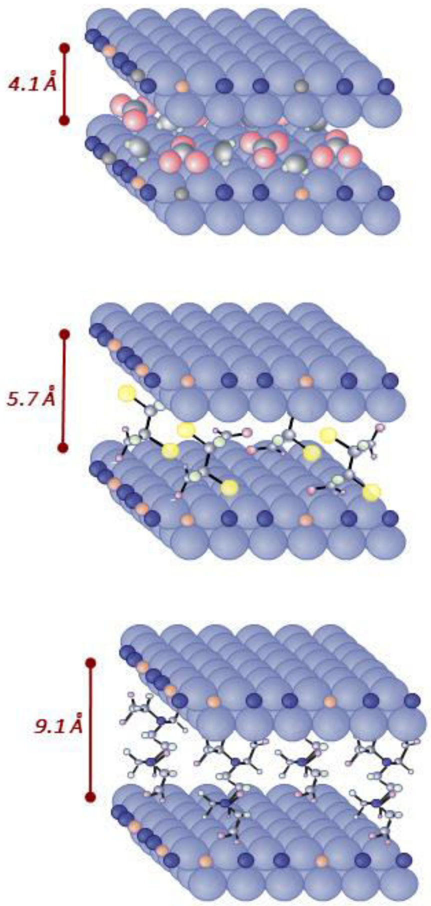
CaO-Al2O3: Increases the adsorption capacity

MgO-Al2O3: Good adsorbent at low T

Materials as adsorbents for CO_2 capture

Hydrotalcite type compounds:

- The adsorption capacity depends on the Al content, interlaminar anion, heat treatment.
- Hydrotalcites supported on zeolites increases the surface and the adsorption capacity.
- Nanoparticles: of MgAlO, CoAlO, MgCaAlO and CoMgAlO (Disadvantages: more complicated method than the oxides and relative low adsorption)



CaO

The use of the carbonation reaction of CaO to $CaCO_3$ as reversible adequate CO_2 separation process is possible. In carbonation, a flow of CO_2 gas is contacted with a CaO stream at temperatures above 600 °C being carried out the carbonation reaction to forms $CaCO_3$. The calcination takes place at higher temperatures, at around 900-950 ° C, to regenerate the adsorbent [1].

[1] J.C. Abanades, The maximum capture efficiency of CO2 using a carbonation /calcinations cycle of CaO/CaCO3. Chemical Engineering Journal 90 (2002) 303-306.

Hydrotalcite

Hydrotalcite is a good high temperature adsorbent for removing CO_2 in the presence or absence of water vapor. The total capacity is CO_2 adsorption to 1.16 mmol / g in the range of 450-500 ° C. Total adsorption capacities have been found very similar both in the presence and absence of water vapor. [2]

[2] Yong Z., Mata V.,. Rodrigues A. E., Adsorption of carbon dioxide at high temperature-a review, Separation and Purification Technology 26 (2002) 195–205.

In order to develop good CO_2 adsorbents at high temperature is required even investigate aspects: [3]

- Understanding the mechanism of CO_2 adsorption on different kinds of adsorbents
- Finding the best adsorbent for modifying chemical reagent to improve the adsorption capacity
- Study adsorption and desorption kinetics of CO_2 in the adsorbent,
- The choice of the optimal conditions for the industry.

[3] Ficicilar B., Dogu T., Breakthrough analysis for CO2 removal by activated hydrotalcite and soda ash, Catalysis Today 115 (2006) 274–278.

Finally, two aspects can be highlighted:

The first, relating to the capture of CO_2 in energy production and in cement production

The second one, related to the CO_2 capture improvement of the cement base materials by the addition of some additive like CaO or Hydrotalcite.

THANK YOU FOR YOUR ATTENTION

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