CREG

Catalysis, Molecular Separations and Reactor Engineering Group

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Research lines:

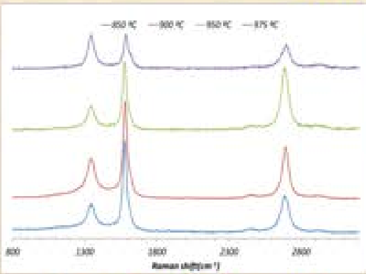
1. Catalytic synthesis of graphene
2. Synthesis and catalytic applications of biomorphic carbon
3. Catalytic decomposition of light HC and biogas: H_2 Production
4. Catalytic reduction of nitrates

http://www.unizar.es/creg/

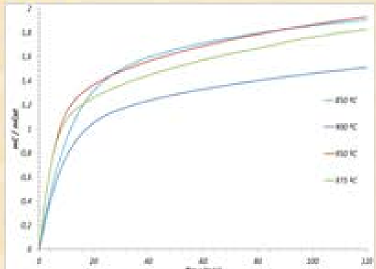
1. Catalytic synthesis of graphene

Influence of the operational conditions

Temperature



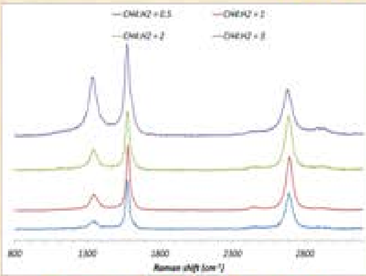
Raman spectra of the graphenic material prepared. Influence of temperature.



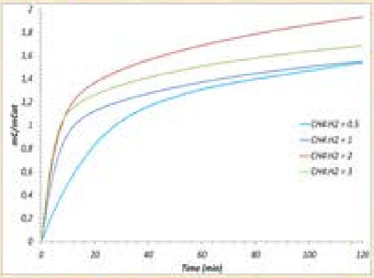
Evolution of graphenic material weight with time. Influence of temperature.

- ✓ *The D (~1350 cm^{-1}), G (~1580 cm^{-1}) and 2D (~2685 cm^{-1}) bands shown in the Raman spectra clearly indicate the formation of graphene and FLG.*
- ✓ *Graphenic material with the best quality is obtained at 950 °C. At this temperature, the I_{2D}/I_G ratio corresponds to 2-layer graphene [4]. When reaction temperatures are higher the presence of more carbon defects is observed.*
- ✓ *The evolution of carbon content along time indicates that there is a maximum, at ca. 950 °C, for the graphenic material productivity. This maximum is caused by formation of deactivating carbon (encapsulating) observed at high reaction temperatures.*

Feed composition



Raman spectra of the graphenic material prepared. Influence of feed composition.



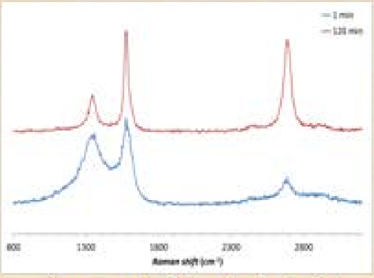
Evolution of graphenic material weight with time. Influence of feed composition.

- ✓ *The highest quality graphenic material (e.g. 2-3 layer graphene) is formed when the ratio CH_4:H_2 is 1:2. At elevated methane concentrations (e.g. CH_4:H_2>2), the graphene layers and the amount of carbon defects greatly increase.*
- ✓ *The evolution of carbon content along time indicates that there is also a maximum for graphenic material production given at CH_4:H_2 = 2. In this case, elevated concentrations of hydrogen inhibit the main reaction due to the competition with methane for the catalytic active sites.*

Influence of reaction time

TEM images of the sample after 1 min (left) and 120 min (right) of CCVD reaction time. CH_4:H_2= 2:1, Temp.: 950 °C.

- ✓ *When reaction time is short (~ 1 min), most of the carbon formed is found encapsulating the metal nanoparticles in form of graphite. However, after 120 minutes of reaction, the grown material mostly corresponds to "few layer graphene" [4].*
- ✓ *TEM images show that, for a short reaction time, the outermost layers of graphite surrounding the nanoparticles are partially exfoliated in unstructured carbonaceous films which, subsequently, may lead to FLG.*
- ✓ *The amount of FLG increases considerably with reaction time, while the presence of encapsulating graphite decreases.*
- ✓ *The growth of graphene implies the nucleation of graphite layers surrounding the nanoparticles, and then, the exfoliation of these graphite layers resulting in graphene sheets and FLG [5].*



Raman spectra of the graphenic material prepared. Influence of reaction time. CH_4:H_2= 2:1, Temp.: 950 °C.

2. Synthesis and catalytic applications of biomorphic carbons

Filter paper previously dried

Vine shoots

Impregnation with catalyst precursor: e.g. Pd(NO_3)$_2$

Drying at 80 ºC for 12 h; 2 ºC/min

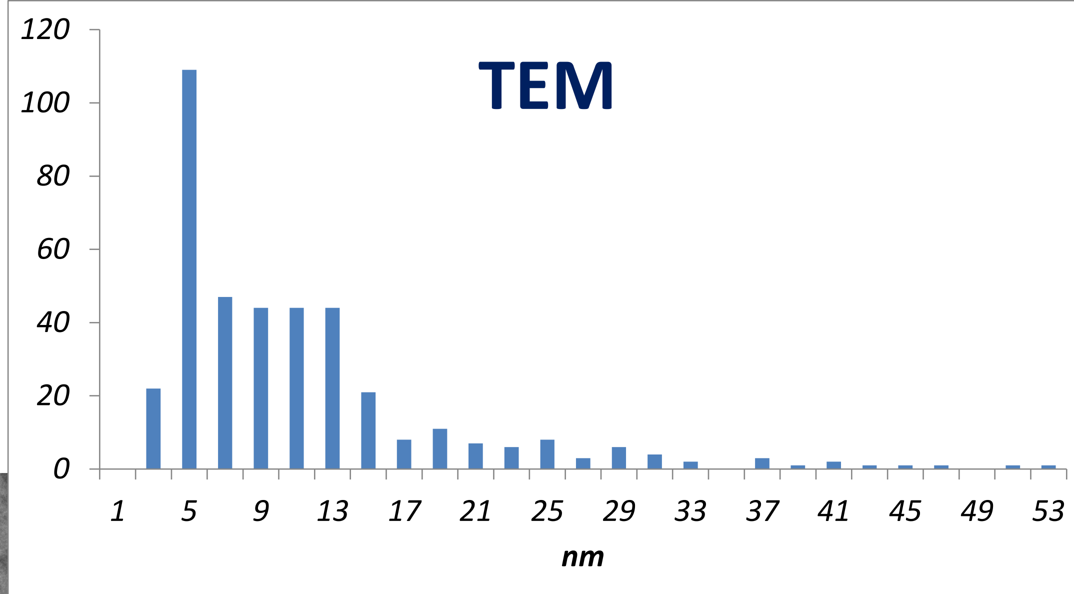
Formatting

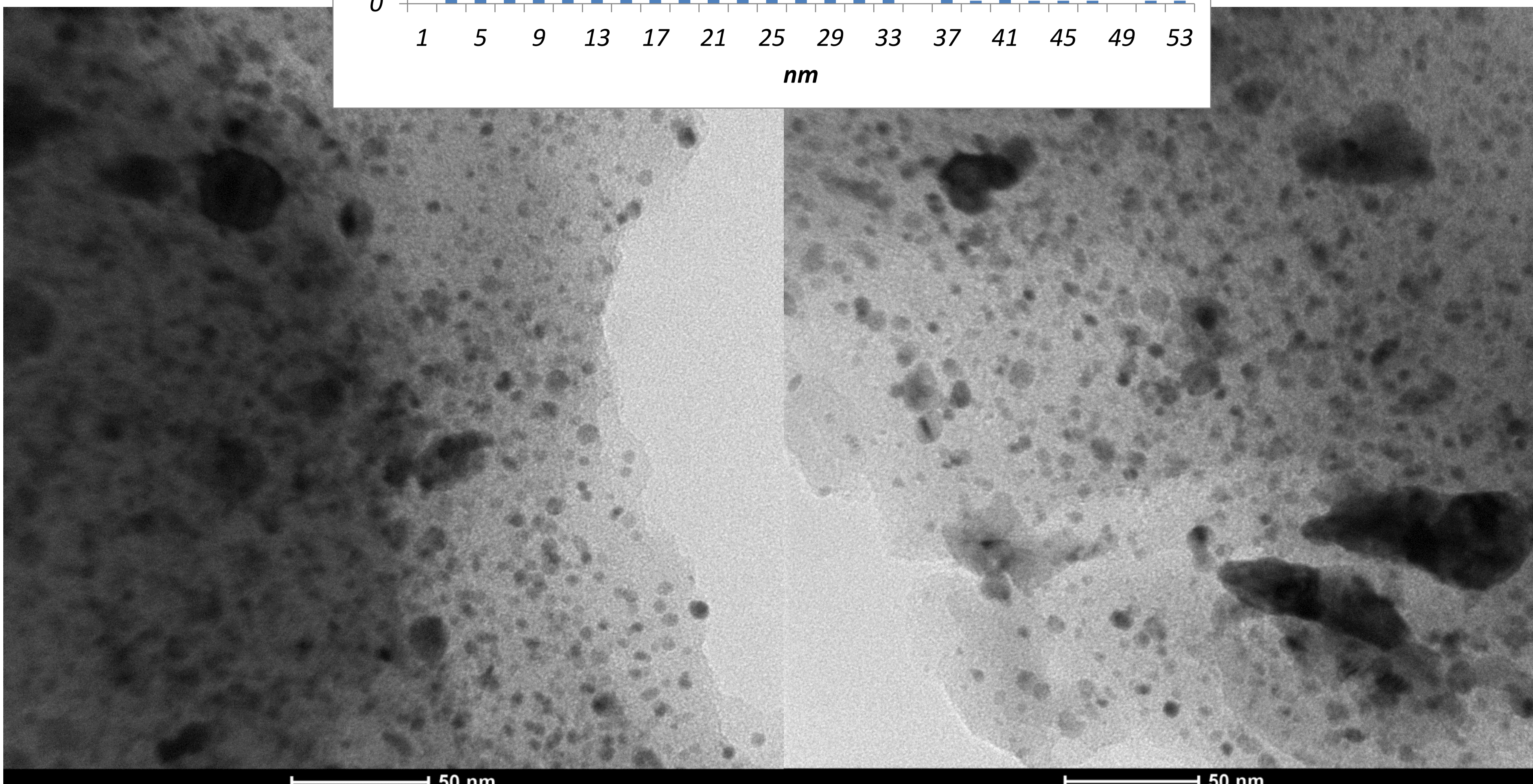
Thermal treatment: Carbonization
at HT (>600 ºC) during 30 min;
HR (≈50 ºC/min).
600 mL/min (5% H_2, 95% N_2)

Milling and sizing

Catalyst:
Me/BC

Calcined at 800 °C



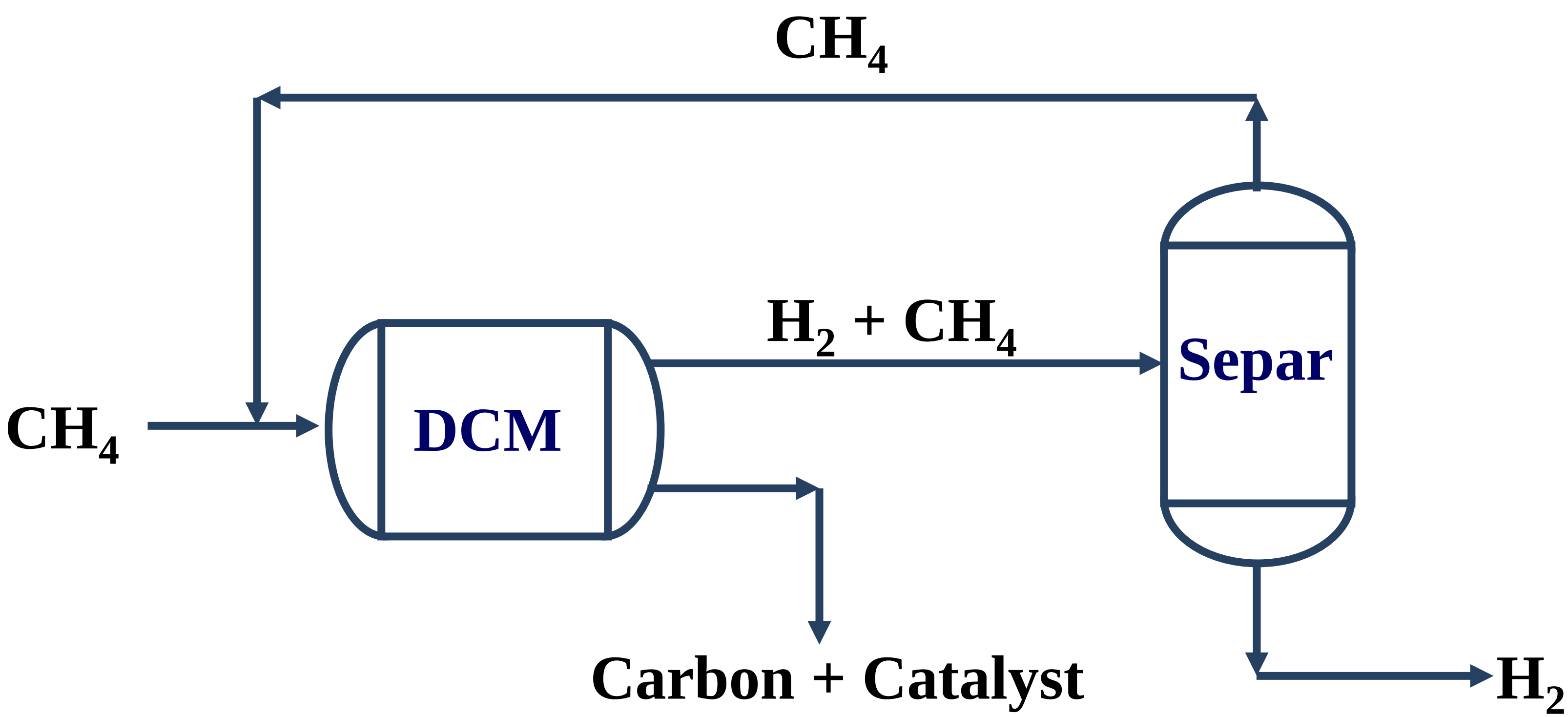


3. Catalytic decomposition of light HC and biogas: H_2 Production

Production

Catalytic Decomposition of Methane

$$CH_{4(g)} \Leftrightarrow C_{(s)} + 2H_{2(g)}$$



3. Catalytic decomposition of light HC and biogas: H_2 Production

Production

Catalytic Decomposition of Methane

$$CH_{4(g)} \Leftrightarrow C_{(s)} + 2H_{2(g)}$$

☺ Advantages:

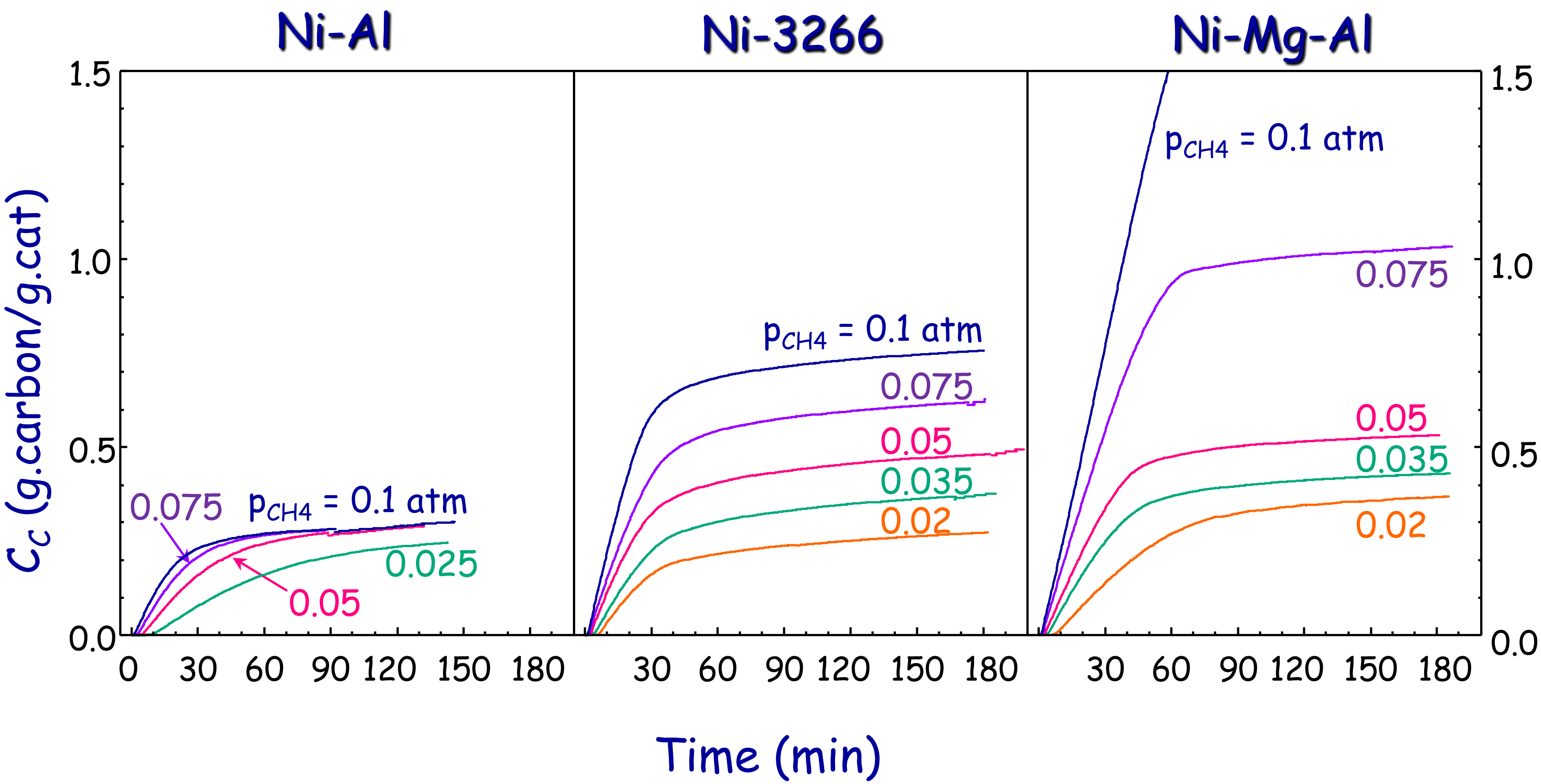
☺ Moderate reaction temperatures.
☺ Hydrogen production free of CO.
☺ Production of nanocarbonaceous materials.

Carbon nanotubes, Graphite, Graphene, etc.

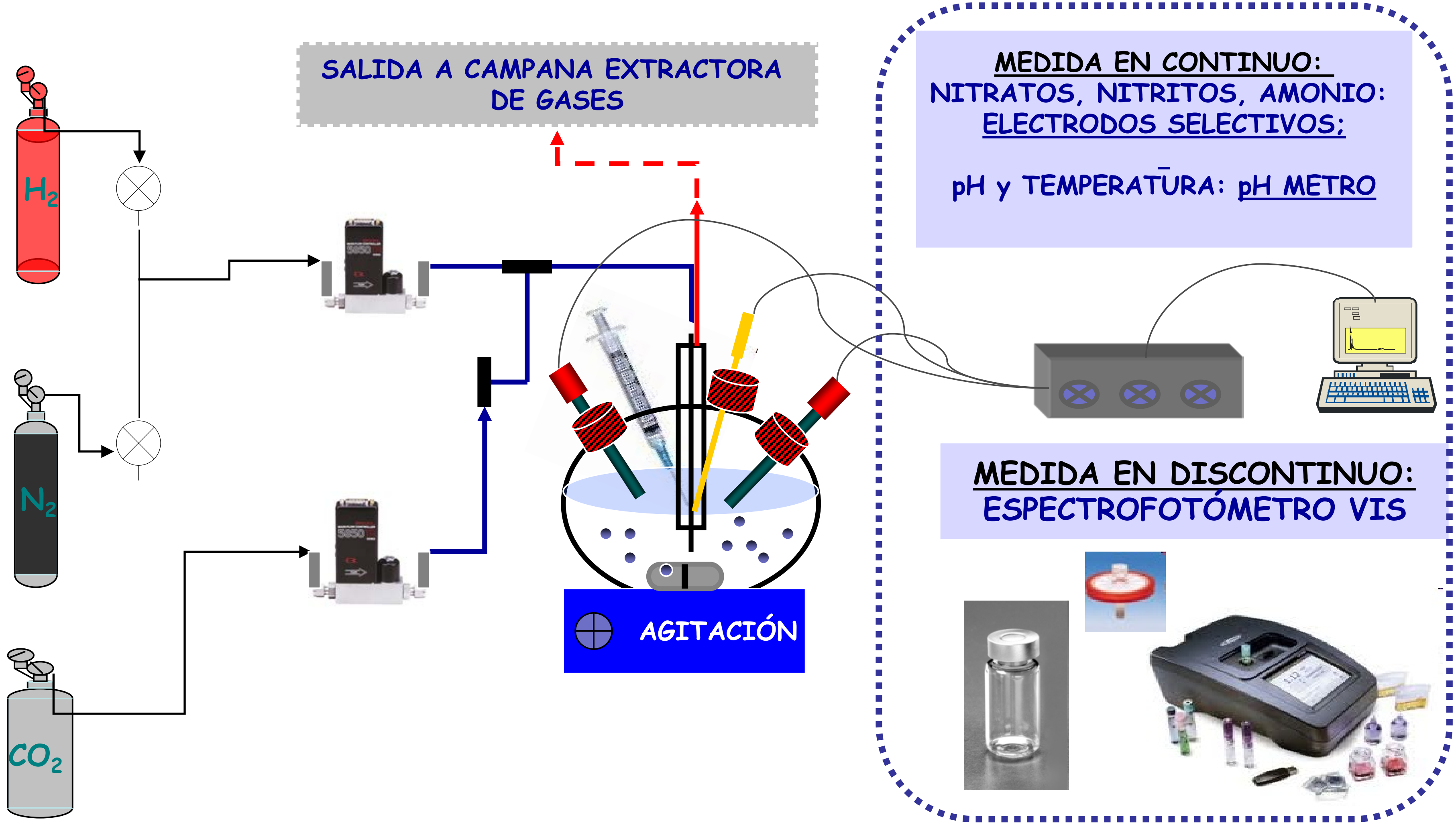
Experimental: Thermobalance

Results

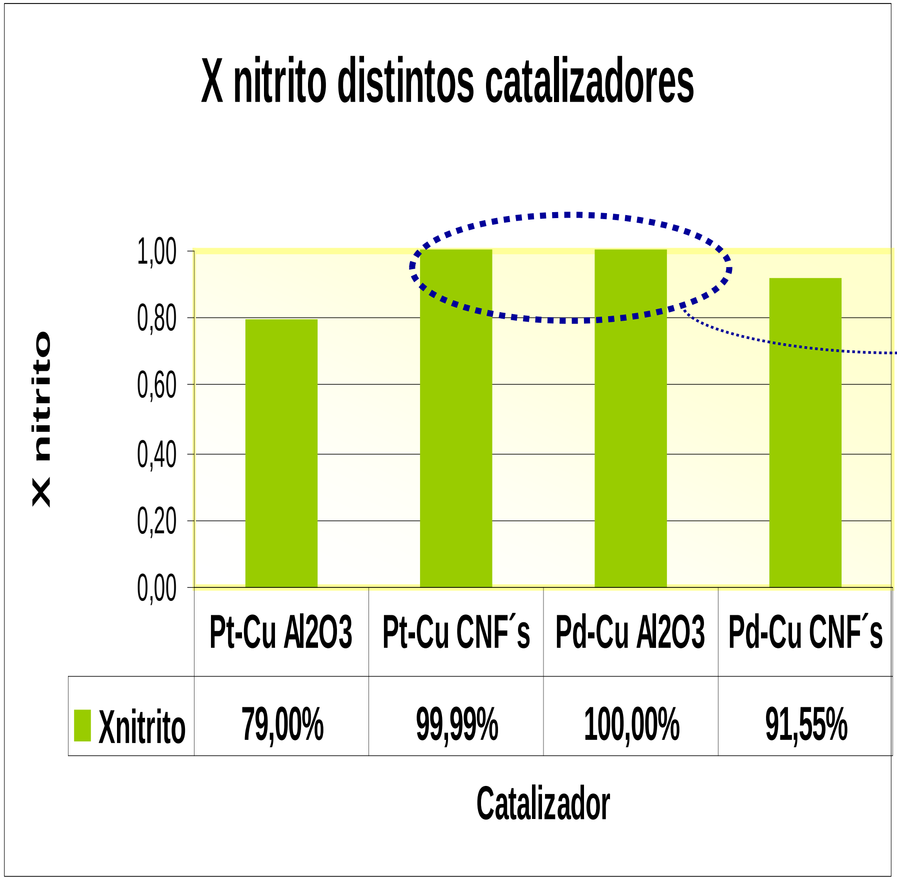
Influence of the Partial Pressure of CH_4

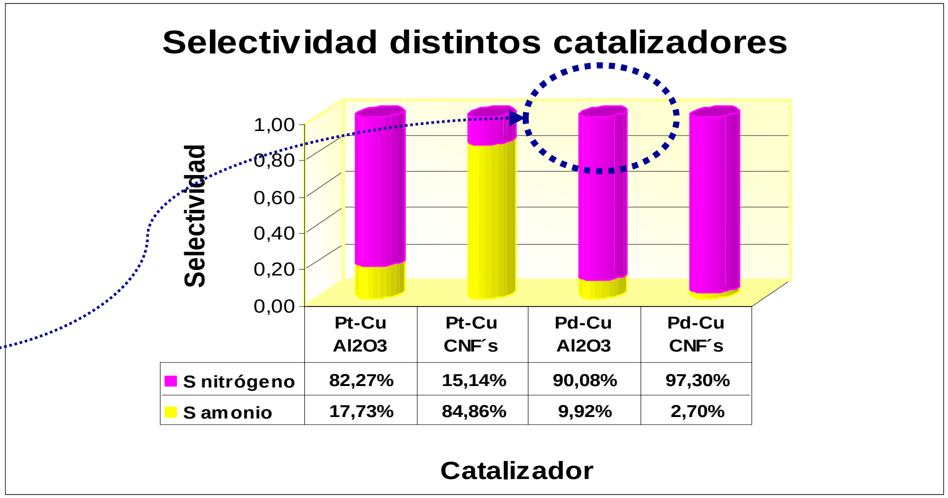


4. Catalytic reduction of nitrates



4. Catalytic reduction of nitrates





- Catalyst Pt-Cu/CNF´s: high activity but high selectivity to amonium.
- Catalyst Pd-Cu/Al_2O_3: high activity and high selectivity to nitrogen.