



Novel carbon nanomaterials for selective CO₂ capture

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Instituto Universitario de Materiales
Universidad de Alicante (Spain)***





✓ *Introduction*

Carbon Dioxide Pollution

CO₂ is a greenhouse gas which is a major contributor to global warming

Main Source

**Combustion of fossil fuel
(coal, oil, gas in power plants,
automobiles and industrial facilities)**





✓ Introduction

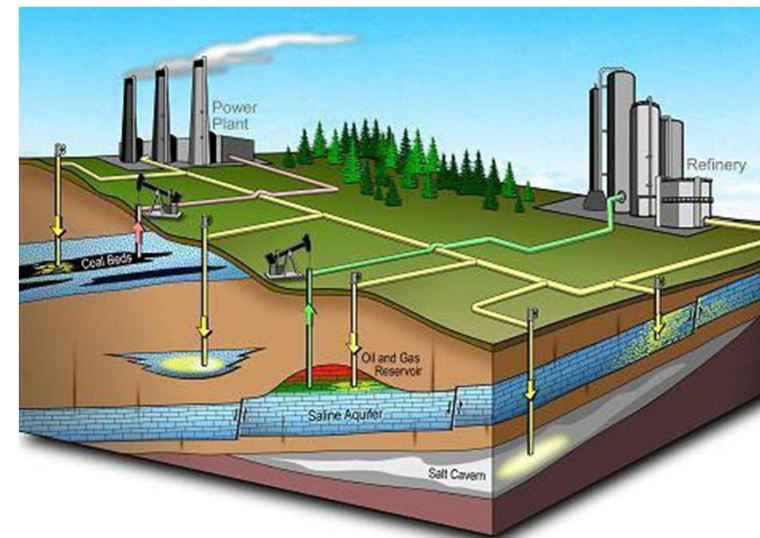
Carbon Dioxide Solutions

- Carbon Dioxide Sequestration (e.g. injection into deep underground reservoirs)

Requirements

Capture and concentration of CO₂ from large emission sources, such as power plants

!!!!CO₂ is accompanied by other gases: N₂, O₂, H₂O, NO_x, SO_x, particulate!!!!

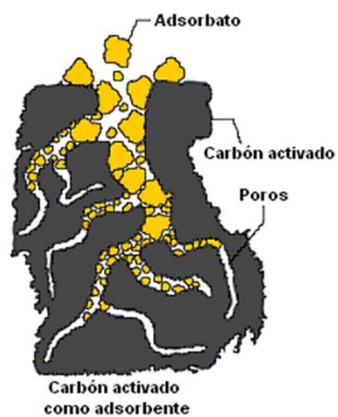




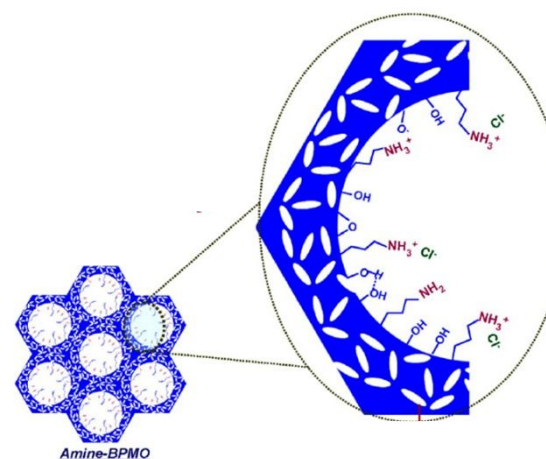
✓ Introduction

Selective CO₂ capture

Porous Structure



Surface Chemistry





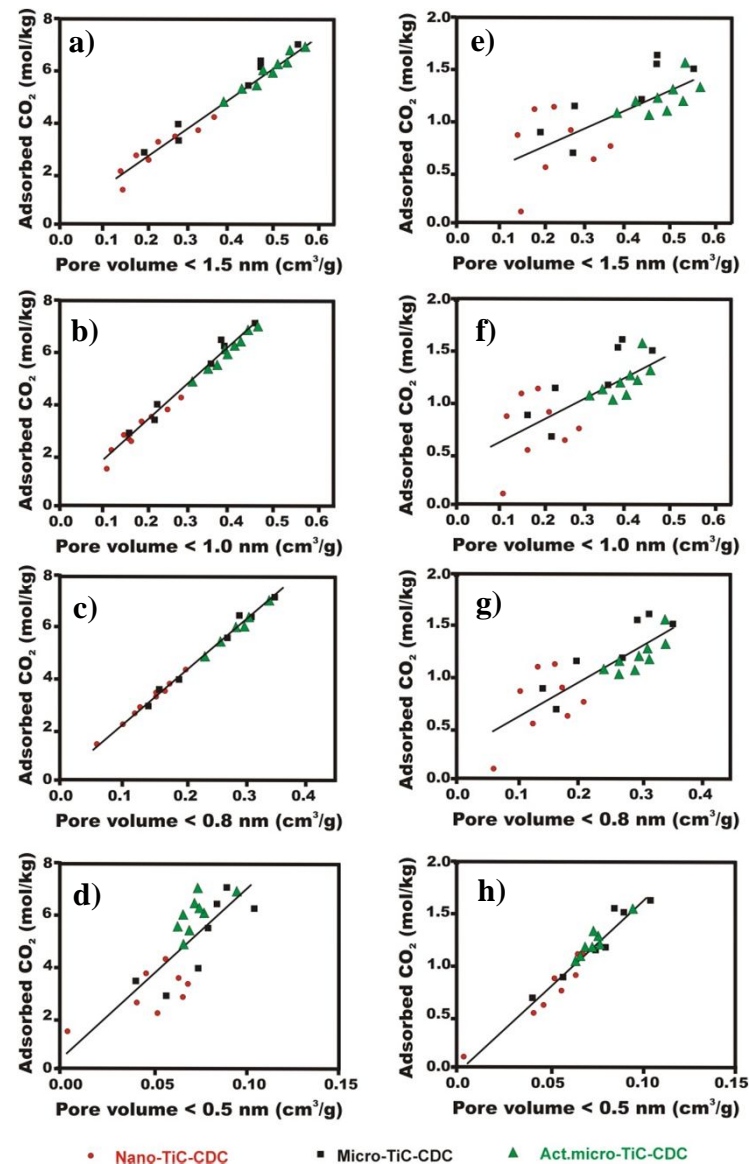
✓ Introduction

Effect of pore size

TiC-CDC
T=273K

(a-d) 1 bar
(e-h) 0.1 bar

*Presser et al. Energy & Environ.
Sci. 4, 3059-3066 (2011)*





✓ Introduction

Carbon Dioxide Solutions

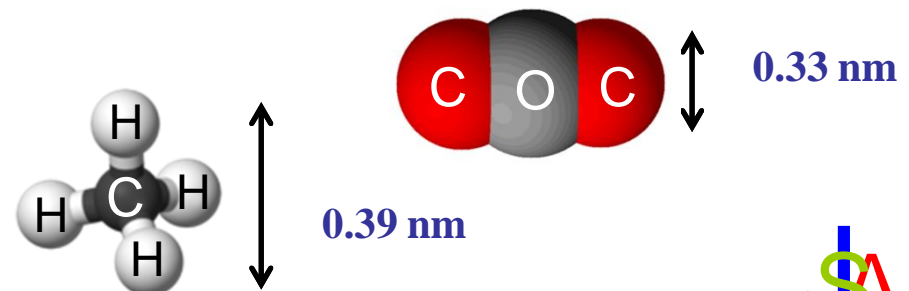
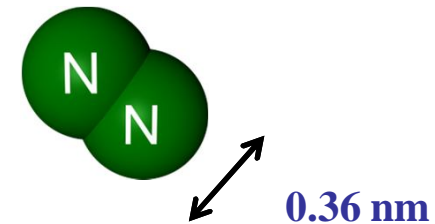
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2°SAASA, San Luis-2013





✓ *Introduction*

Molecular Sieves

Microporous solids with a very narrow pore size distribution, the dimension of micropores being similar to the molecules to be adsorbed/separated.

Molecular discrimination caused by:

- ↪ molecular dimension
- ↪ molecular shape
- ↪ kinetics of adsorption



✓ *Introduction*

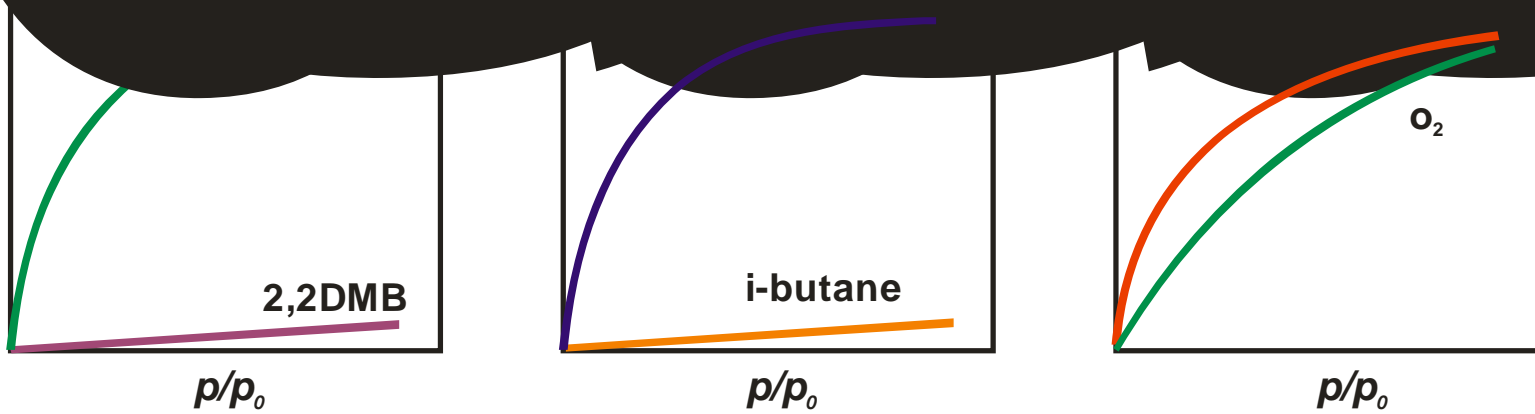


Molecular Sieves



✓ **Introduction**

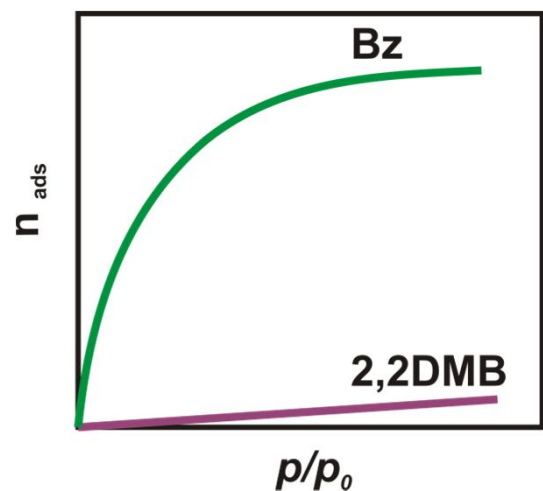
Molecular Sieves: Equilibrium adsorption isotherms



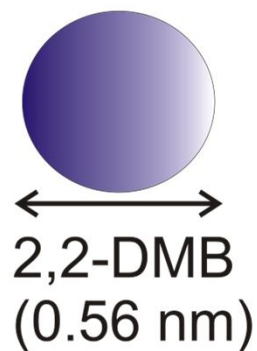


✓ Introduction

Selectivity by molecular shape



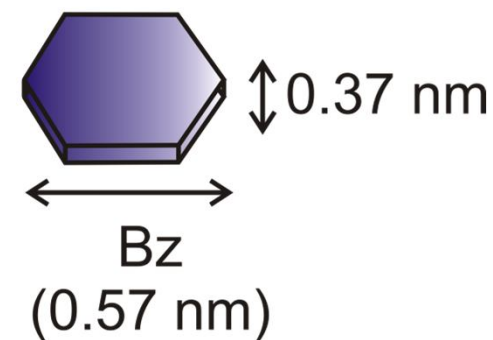
(a)



0.4 nm



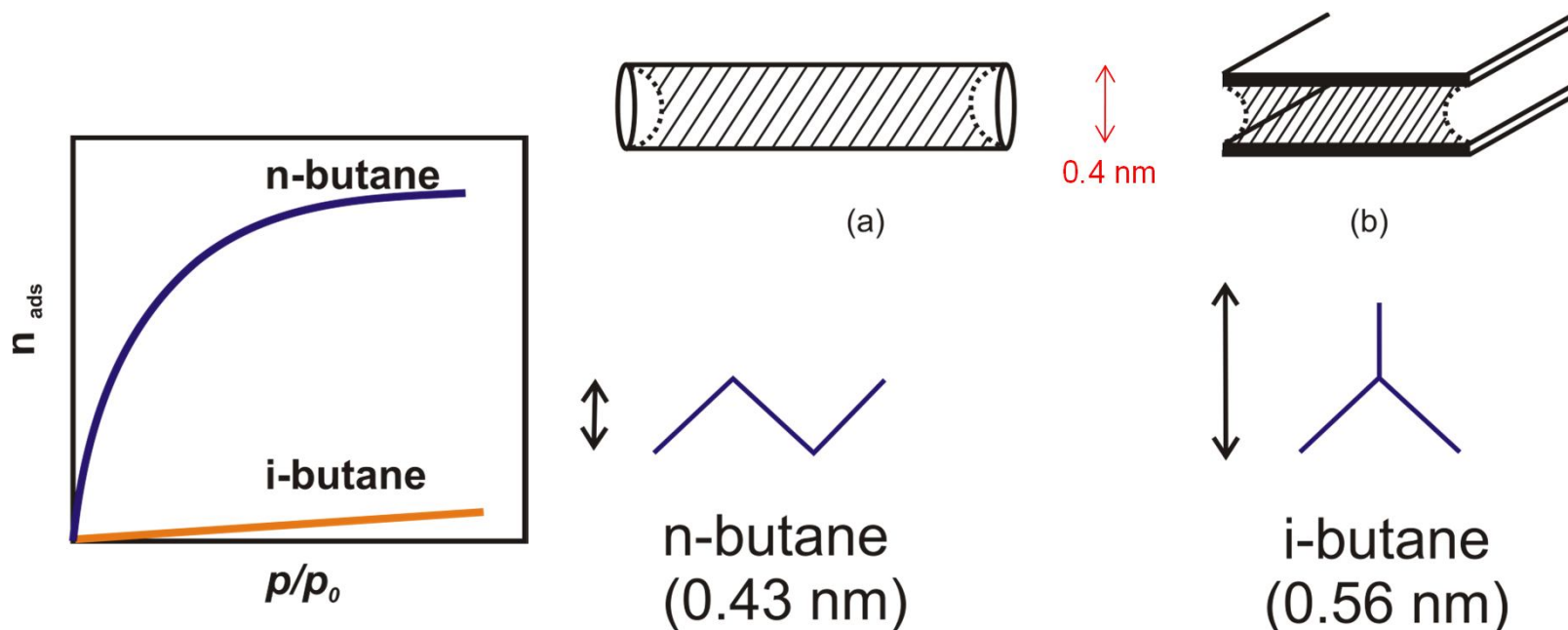
(b)





✓ Introduction

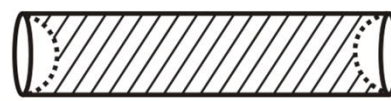
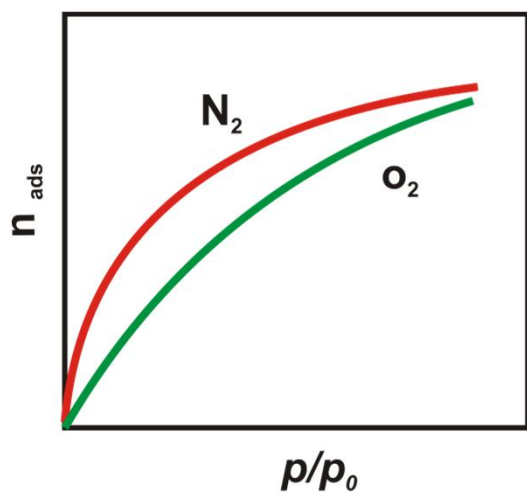
Selectivity by molecular size



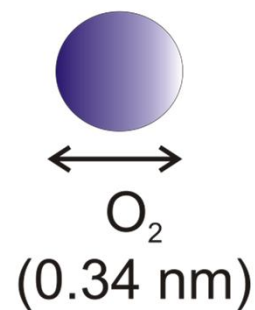


✓ Introduction

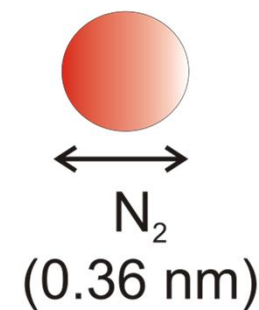
Selectivity by different kinetics



(a)



(b)





✓ Introduction

Why carbon molecular sieves?

Slit-shaped micropores

Porosity can be tailored

Rather "inert" surface

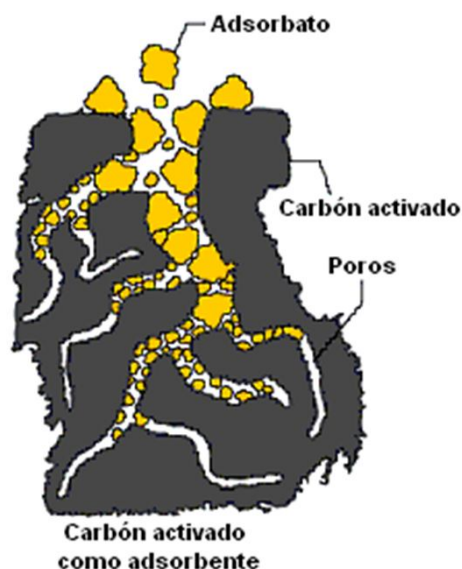
Adsorption of non-polar species favoured,

Surface chemistry can be easily modified,

Many physical forms (granular, pellets, fibres, cloth, felt, monoliths, etc.)



Unparalleled flexibility

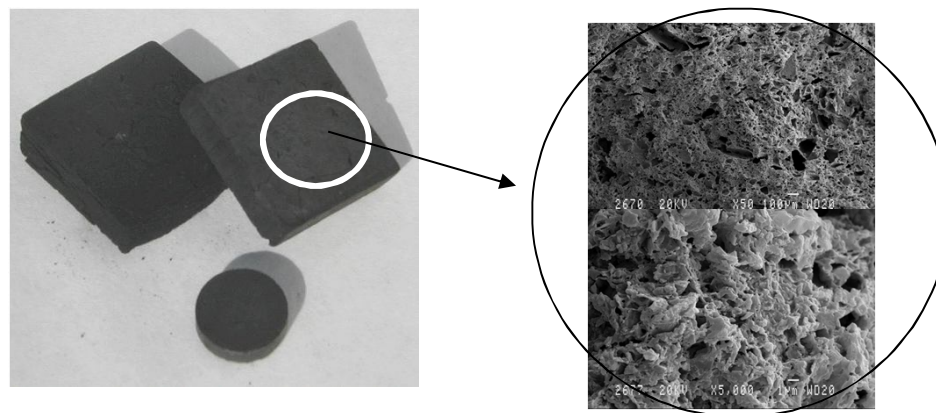


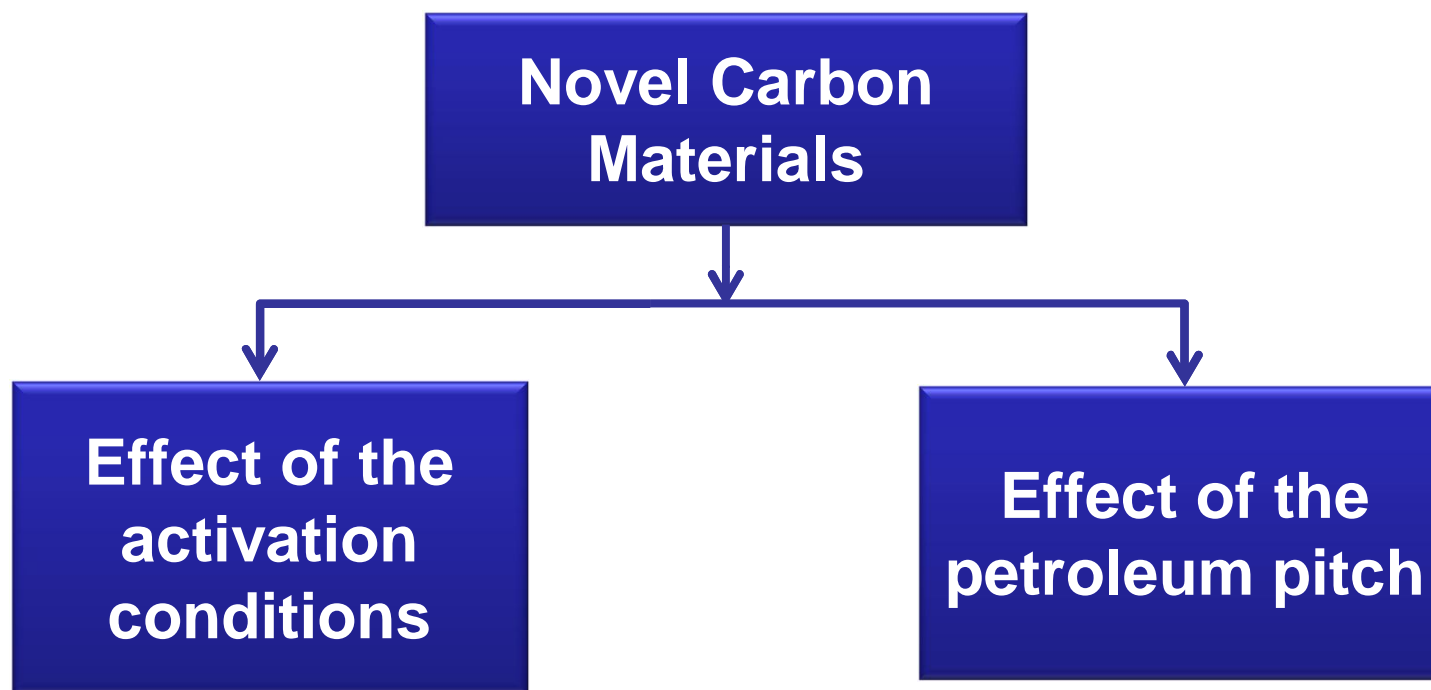


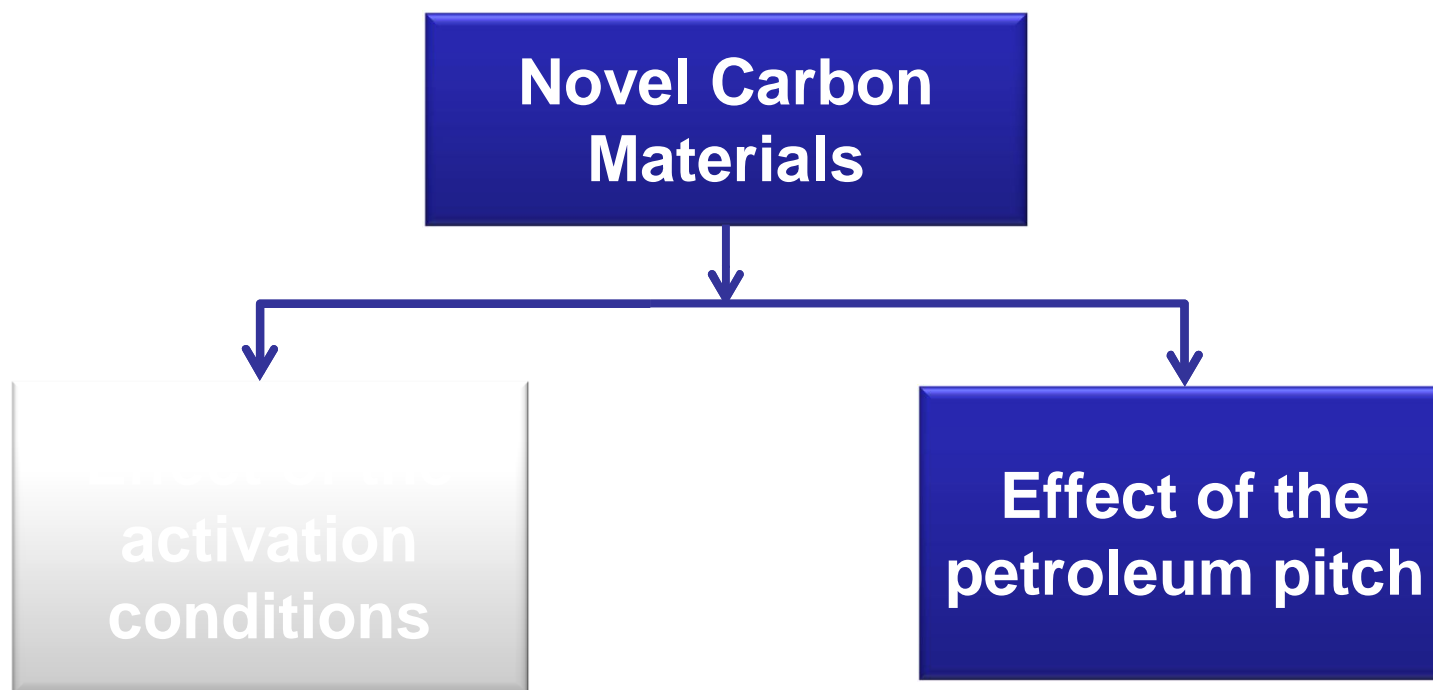
✓ *Objective*

Synthesis of very high porosity CMS from petroleum residues for selective CO₂ adsorption vs. other molecules of similar molecular dimensions (N₂ and CH₄)

Synthesis of monolithic CMS without the use of a binder:







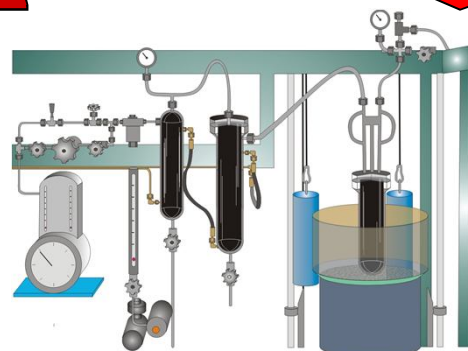


✓ *Experimental Section*

Ball Milling



440°C, 1 MPa,
2-4 Hours.



Mesophase pitch
 $\text{Ø} \leq 500 \mu\text{m}$



MP-2 (2 h)
MP-4 (4 h)

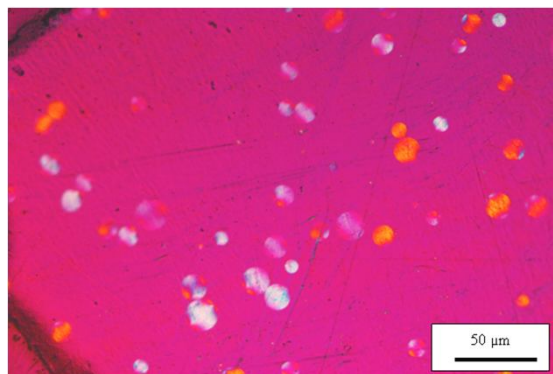
{
 VR-5; DO-10
 VR-93; DO-88

VR (vacuum residue)
DO (decanted oil)

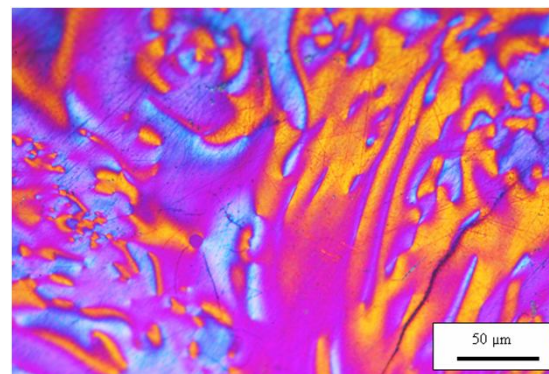


✓ *Experimental Section*

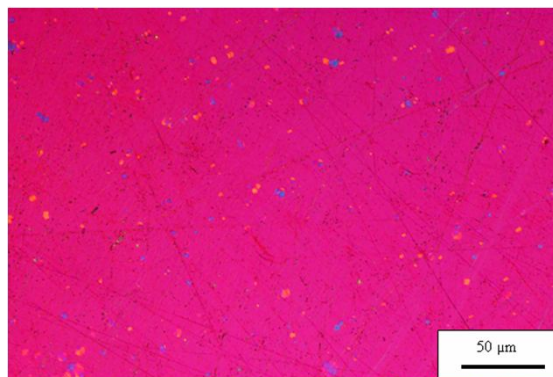
DO-10



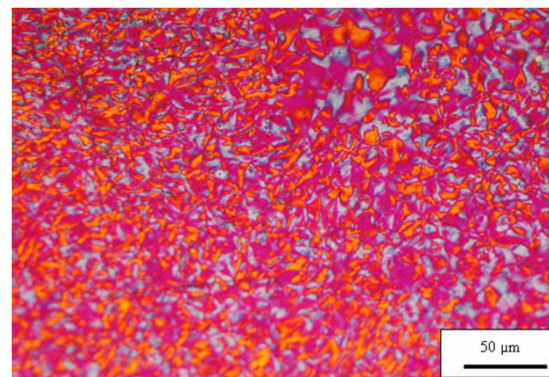
DO-88



VR-5

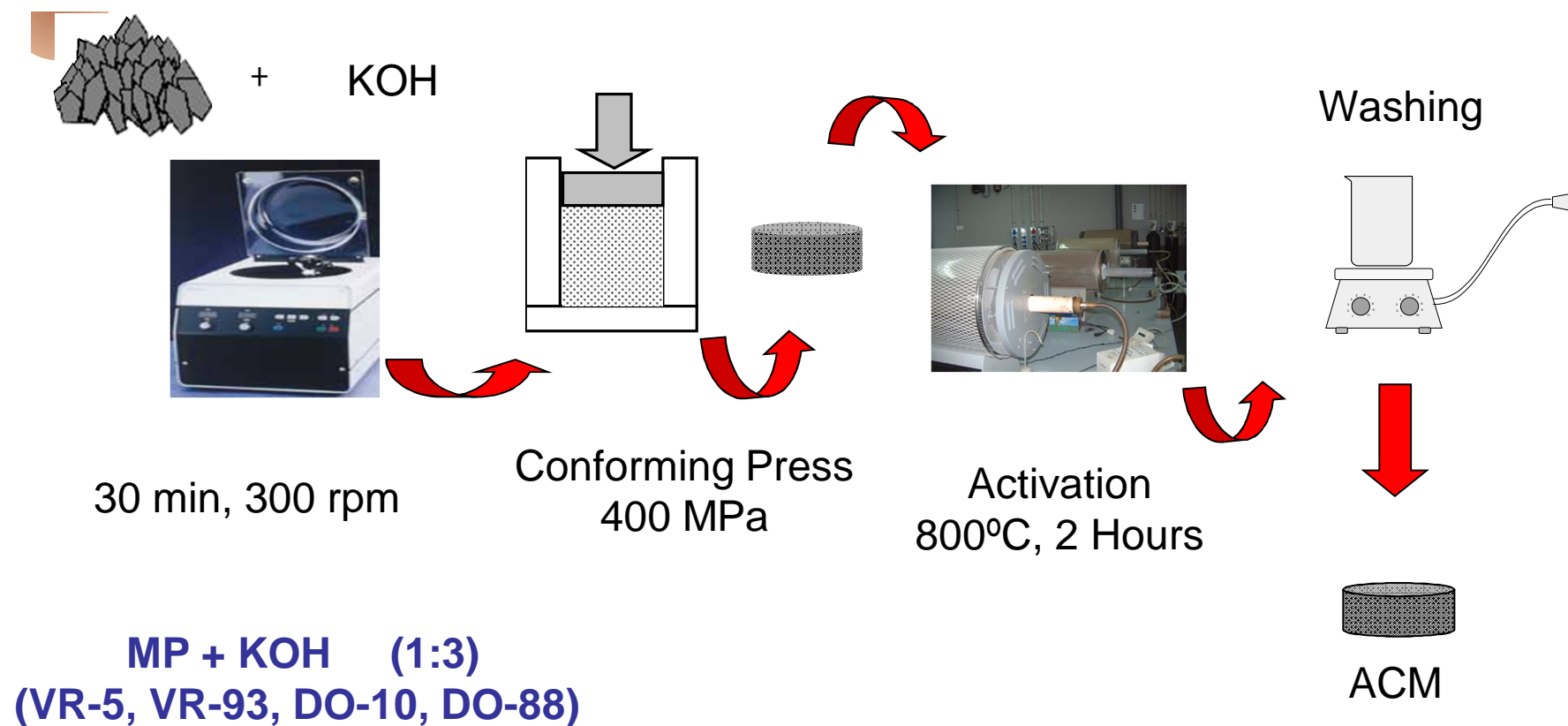


VR-93



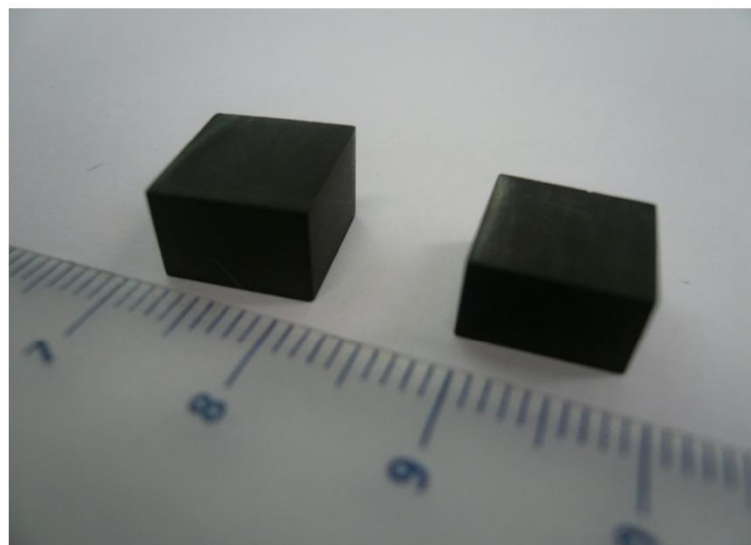


✓ *Experimental Section*





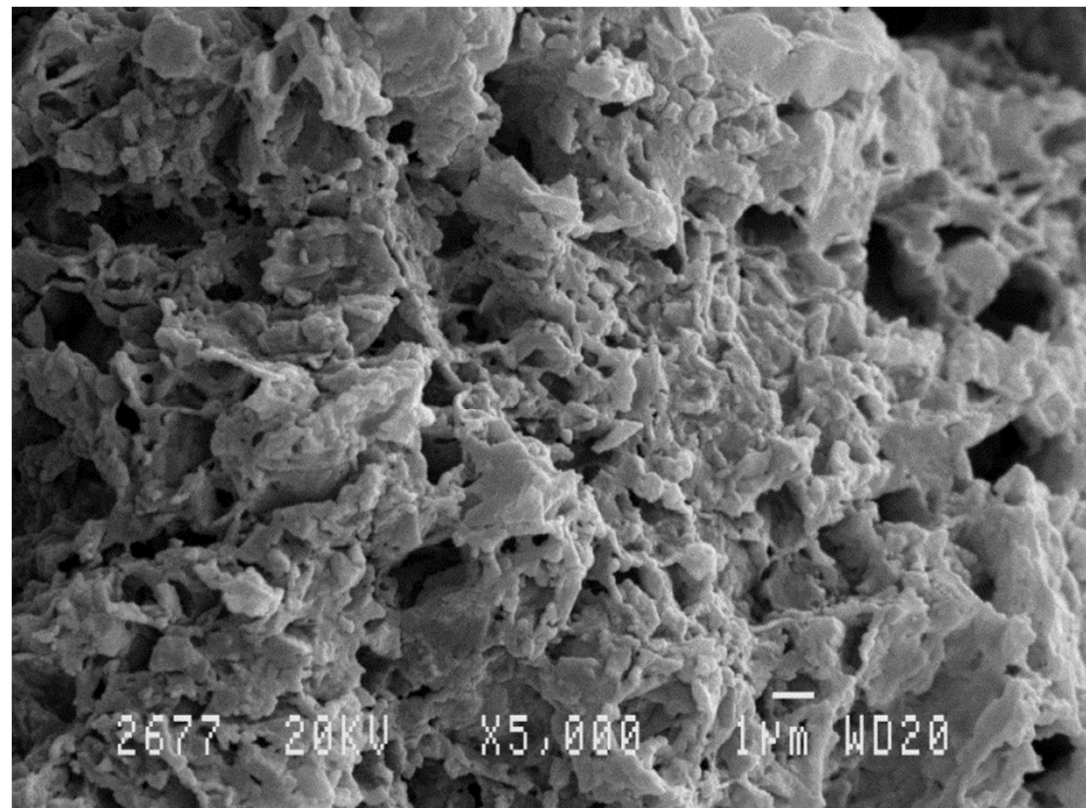
✓ *Results and discussion*





✓ *Results and discussion*

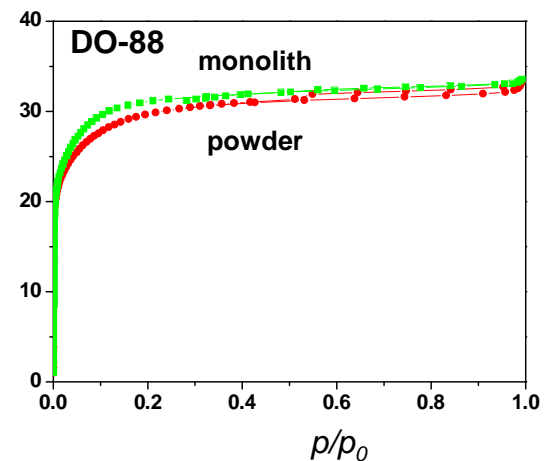
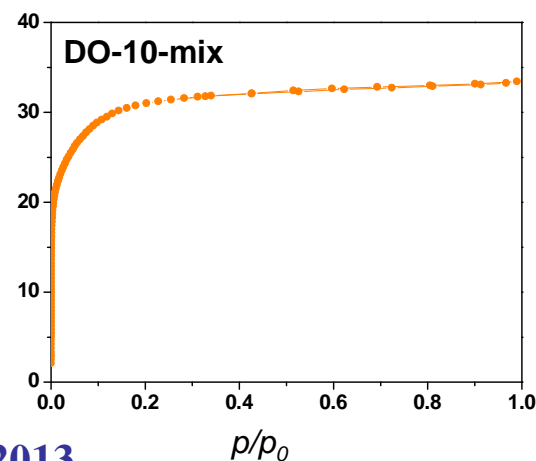
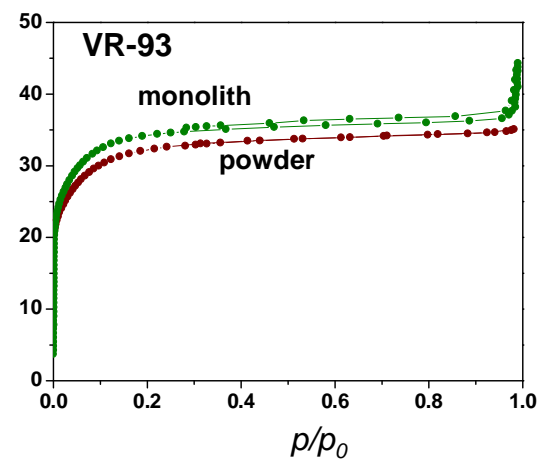
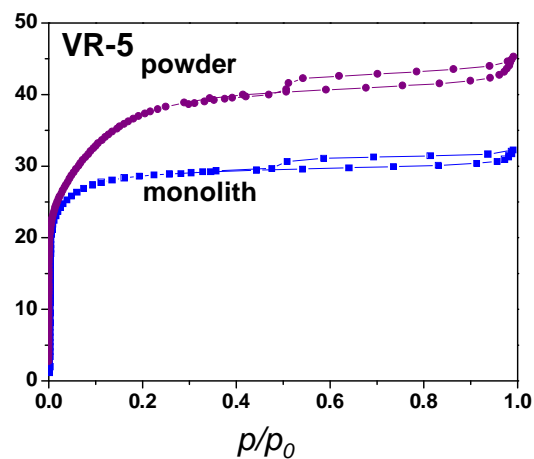
Scanning Electron Microscopy





✓ Results and discussion

N₂ adsorption/desorption isotherms at 77 K





✓ Results and discussion

Textural characteristics N_2 and CO_2 data

Muestra	S_{BET} (m ² /g)	V_0 (cm ³ /g)	V_t (cm ³ /g)	V_n (cm ³ /g)
VR-5-P	3100	1.45/1.02	1.57	0.85
VR-5-M	2450	1.03	1.12	0.95
VR-93-P	2895	1.28/1.06	1.42	0.80
VR-93-M	2720	1.21	1.22	1.08
DO-10-mix	2600	1.16/0.93	1.16	0.75
DO-88-P	2440	1.09/0.88	1.14	0.69
DO-88-M	2660	1.16/1.00	1.16	0.74



✓ Results and discussion

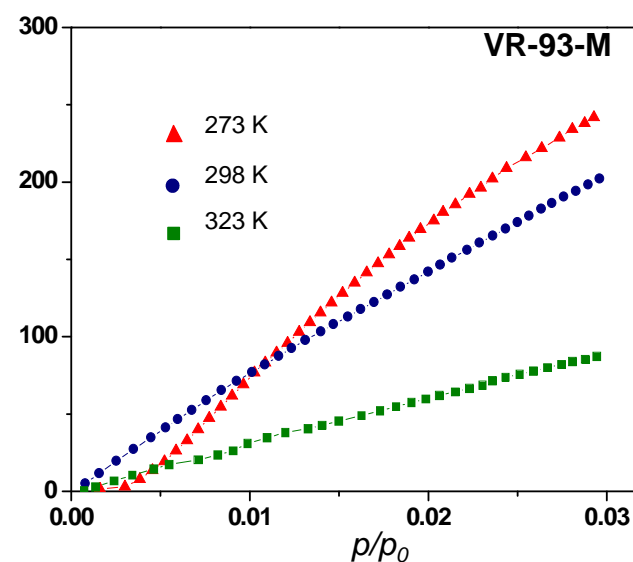
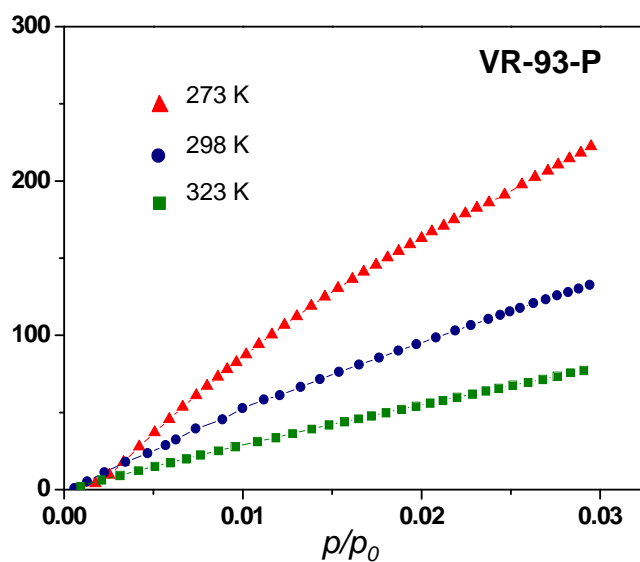
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✓ Results and discussion

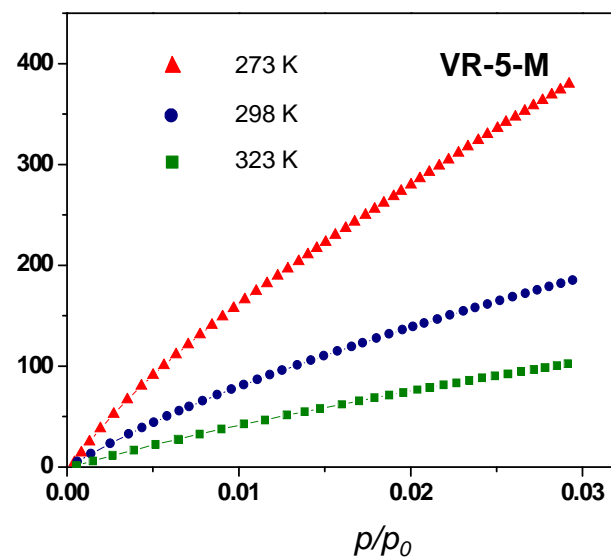
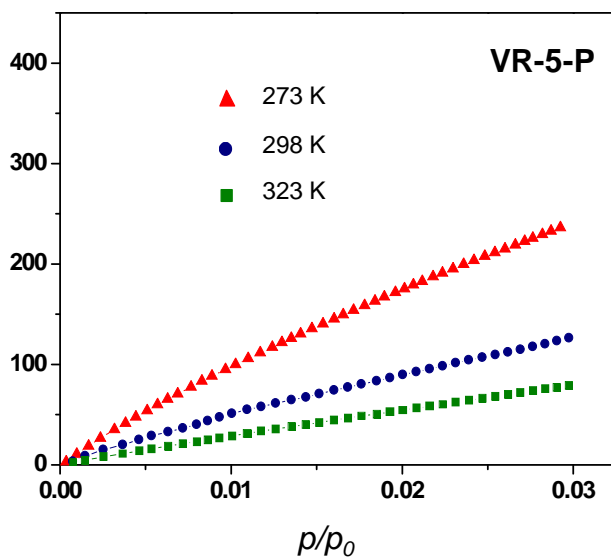
CO₂ adsorption isotherms at different temperatures (VR-93)





✓ Results and discussion

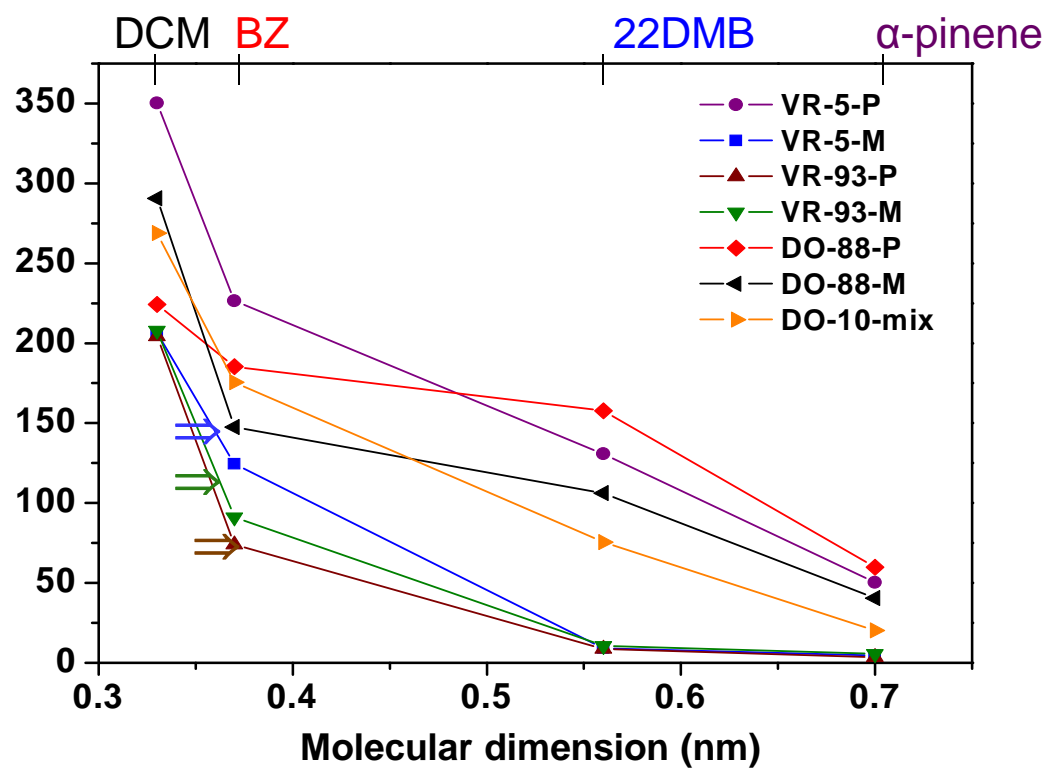
CO₂ adsorption isotherms at different temperatures (VR-5)





✓ Results and discussion

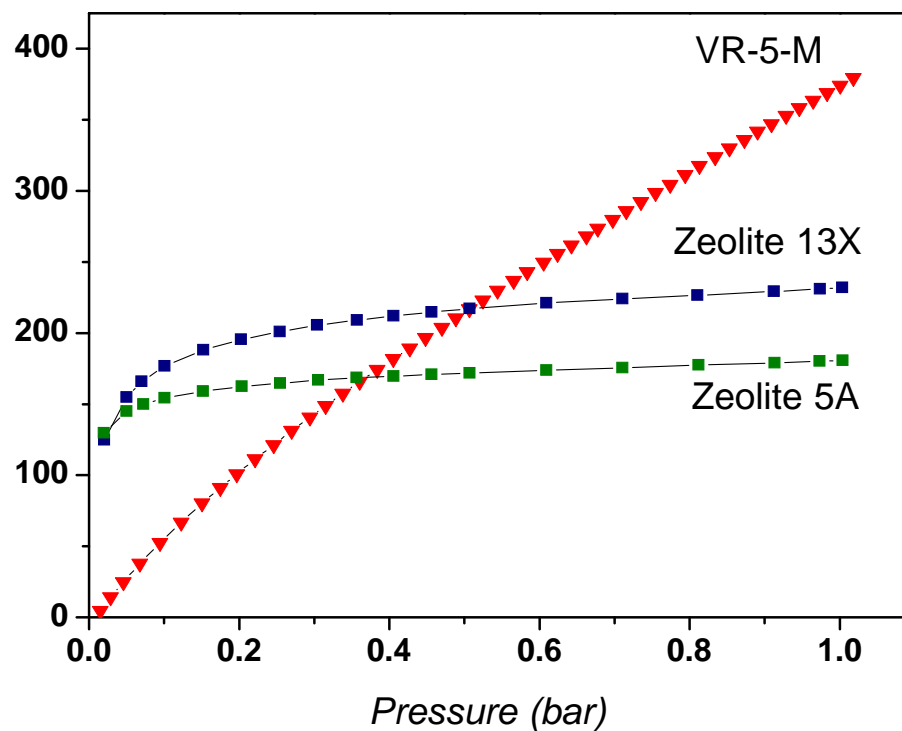
Immersion calorimetry into different liquids





✓ *Results and discussion*

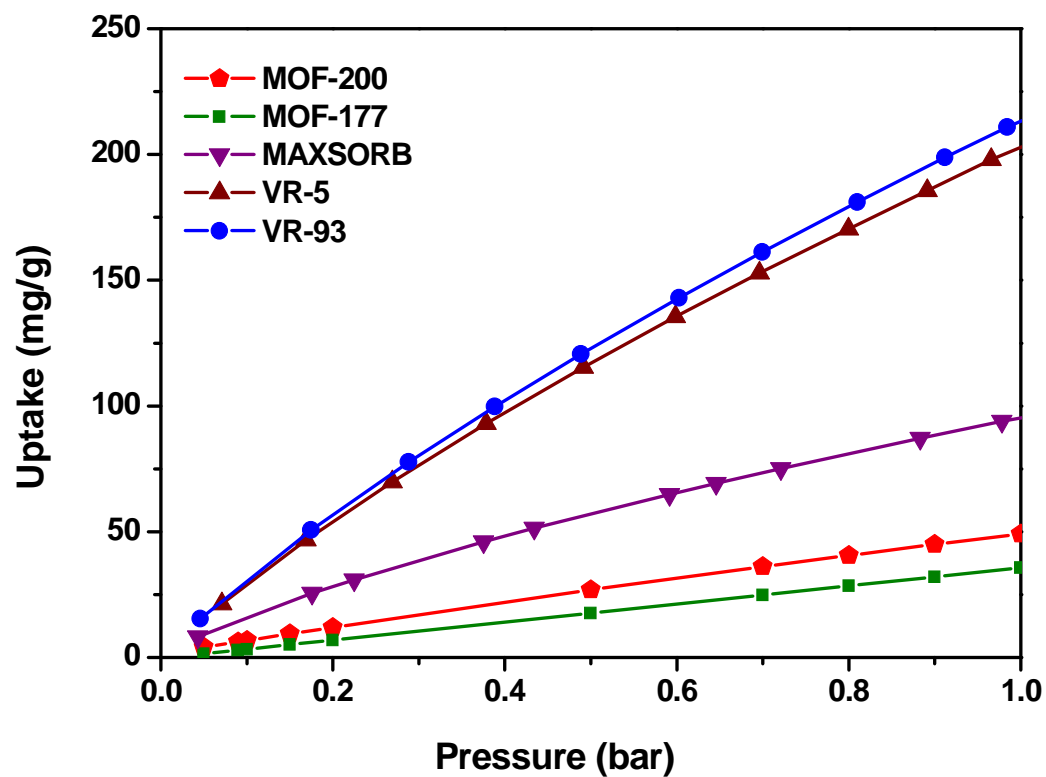
Carbon Molecular Sieves vs. Zeolites





✓ Results and discussion

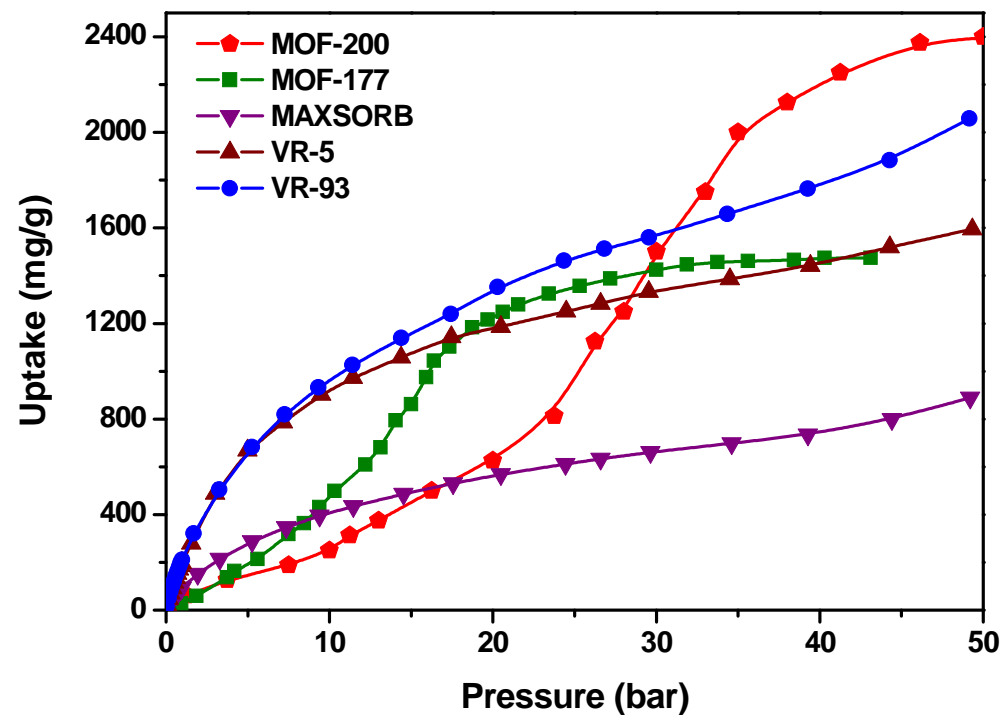
Carbon molecular sieves vs. MOFs materials





✓ Results and discussion

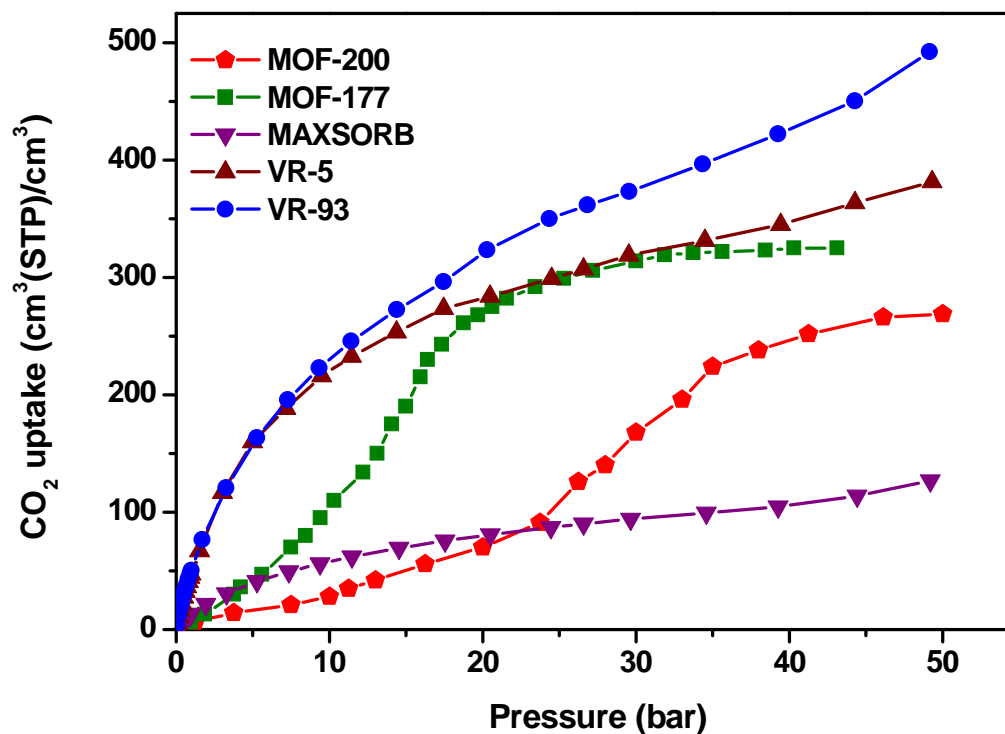
Carbon molecular sieves vs. MOFs materials





✓ Results and discussion

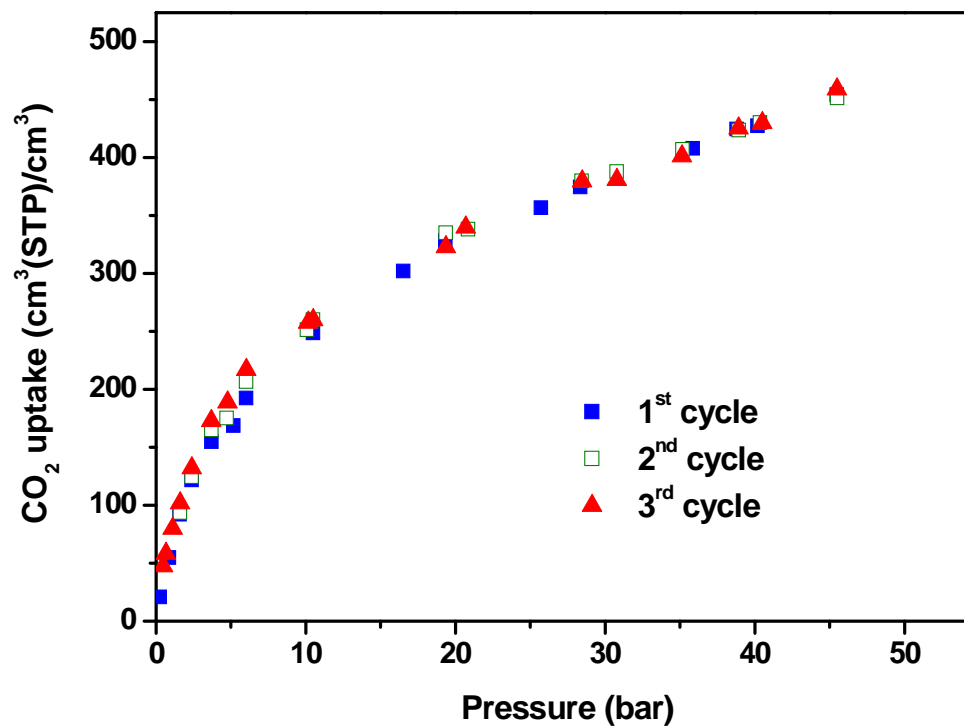
Carbon molecular sieves vs. MOFs materials





✓ *Results and discussion*

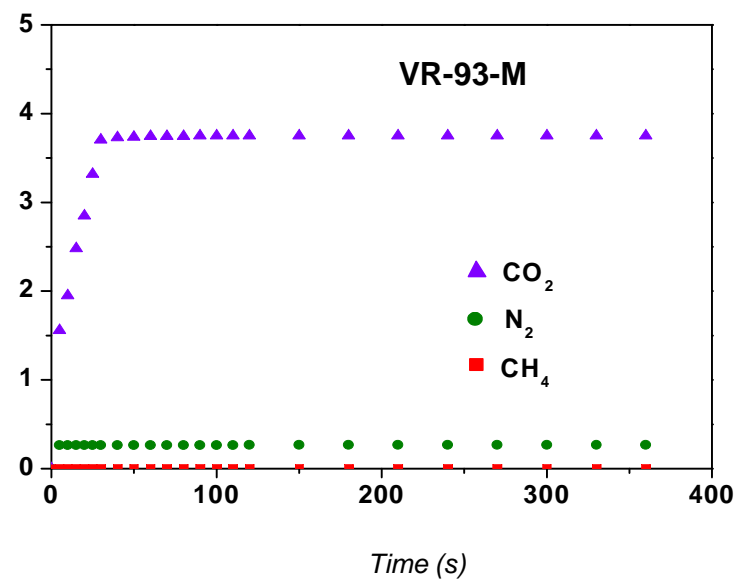
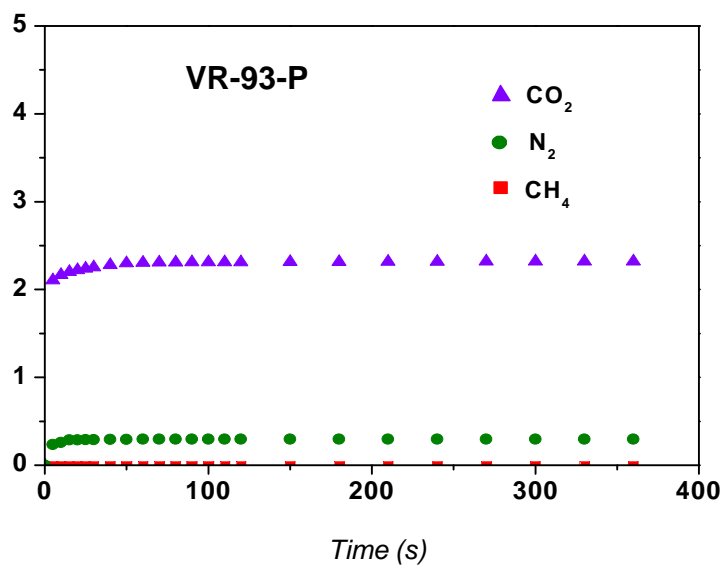
Regeneration of the carbon molecular sieves





✓ Results and discussion

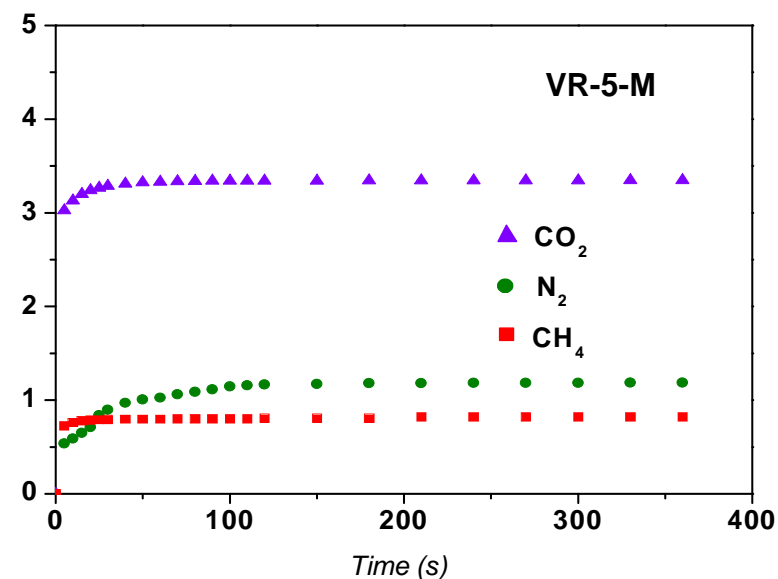
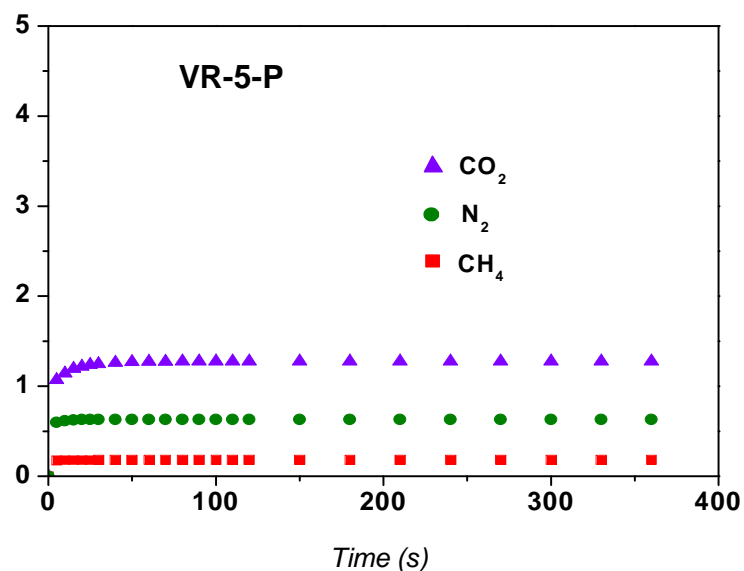
Kinetics of adsorption of CO_2 , N_2 and CH_4 at 298 K (VR-93)





✓ Results and discussion

Kinetics of adsorption of CO_2 , N_2 and CH_4 at 298 K (VR-5)





✓ *Summary*

- ✓ **High surface area (up to 3000 m²/g) carbon molecular sieves can be prepared from petroleum pitch using KOH as activating agent.**
- ✓ **These carbon molecular sieves exhibit an extremely high CO₂ adsorption capacity (up to 380 mg/g).**
- ✓ **The size of the pore entrance on these CMSs highly depends on the petroleum residue, the pyrolysis conditions used and the activation degree. For samples VR it is below 0.56 nm.**
- ✓ **Either at low (1 bar) and high (50 bar) pressure, CMSs are able to overcome the incomparable adsorption behavior described for MOFs materials.**
- ✓ **CMSs are able to discriminate CO₂ for molecules of similar dimensions (e.g. CH₄ and N₂).**



✓ *Acknowledgement*

Laboratorio de Materiales Avanzados



National Projects:


NAN2004-09267-C03-03

MAT2007-61734



EU Projects: FRESP (Advanced
First Response Respiratory
Protection)



An aerial photograph of the Alhambra in Granada, Spain. The image shows the complex's various towers and courtyards, including the prominent Giralda tower on the left. The Alhambra is situated on a hillside, surrounded by lush green trees. In the background, the Sierra Nevada mountains are visible under a clear sky. The text is overlaid on the top half of the image.

10th International Symposium on the Characterization of Porous Solids (COPS-X)

Granada (Spain)
11-14 May 2014

Location



Granada is located in the South of Spain in the "Andalucia Region"

How to arrive:

- Granada is located 434 Km south from Madrid. There are several daily trains from Madrid to Granada (4h 25 min; shorter time in 2014)
- Granada's airport is 17 Km from the city. There are direct national flights to Madrid (Iberia), Barcelona (Vueling) and Palma de Mallorca (Iberia, Air Europa). There are also International connections with Paris (Vueling), Milano (Ryanair) and Bologna (Ryanair)
- International airport of Malaga is located 125 Km from Granada.

The City of Granada



The "Alhambra"
Palace



The Cathedral



Generalife Palace



Albaicín

Granada Congress Centre



The "Tapas"

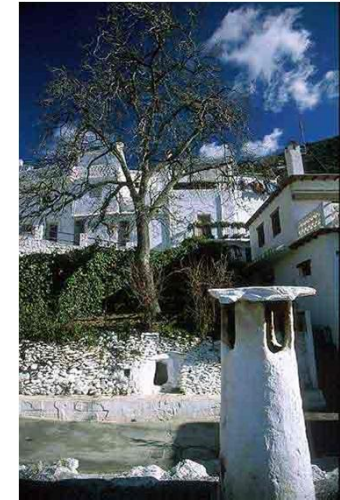


Around Granada

Sierra Nevada



The Alpujarras



Organization

Local Scientific Committee:

- Dr. Francisco Carrasco-Marín, University of Granada
- Dr. Agustín F. Pérez Cadenas, University of Granada

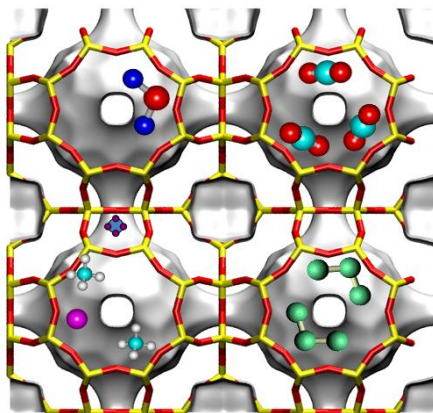
International Scientific Committee:

- Dr. Tina Düren, University of Edinburgh, UK
- Dr. Stefan Kaskel, TU Dresden, Germany
- Dr. Philip Llewellyn, University of Provence, France
- Dr. Joaquín Silvestre-Albero, University of Alicante, Spain

Honorary Scientific Committee:

- Prof. Dr. Francisco Rodríguez-Reinoso, Spain
- Prof. Dr. Jean Rouquerol, France
- Prof. Dr. Kenneth Sing, UK
- Prof. Dr. Klaus K. Unger, Germany

Materiales en Adsorción y Catálisis



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ISSN:2173-0253

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scalero@upo.es
joaquin.silvestre@ua.es
tvaldes@incar.csic.es

A photograph of the interior of Antelope Canyon, showing smooth, undulating sandstone walls. Several bright, vertical beams of light stream down from an opening at the top, creating a dramatic, ethereal atmosphere. The light illuminates the textures of the sandstone and creates a sense of depth and wonder.

**Thank you very much for
your attention!!!**

email: joaquin.silvestre@ua.es

*Antelope Canyon-Reserva de los
indios navajos (USA)*