



Unusually Low heat of Adsorption of CO₂ on AIPO and SAPO Molecular Sieves

Nuria González-Camuñas, Eduardo Pérez-Botella, Raquel Martínez-Franco, Ángel Cantín, Miguel Palomino, Manuel Moliner, Susana Valencia and Fernando Rey.



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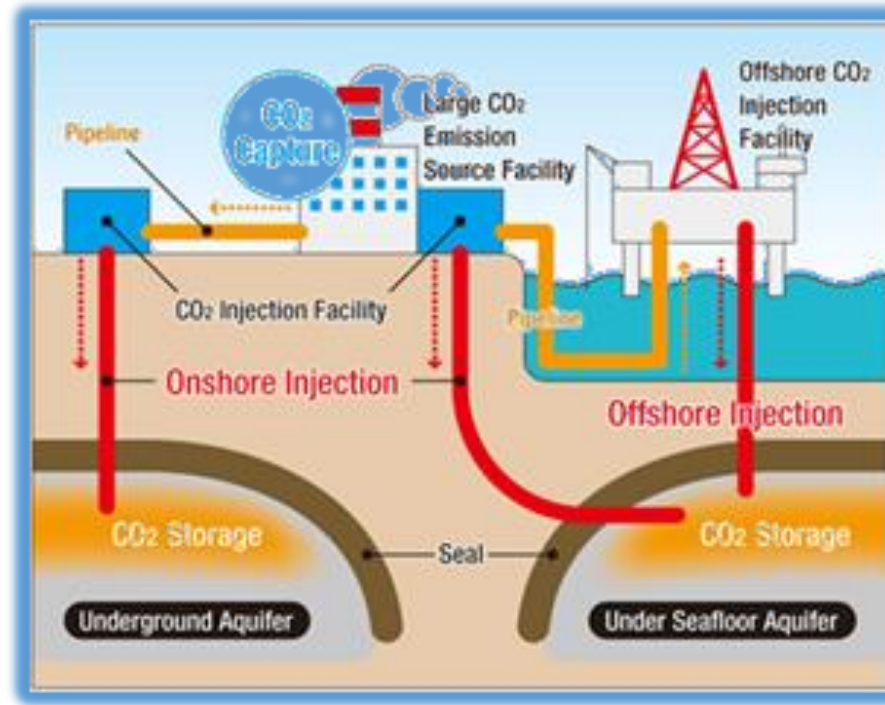
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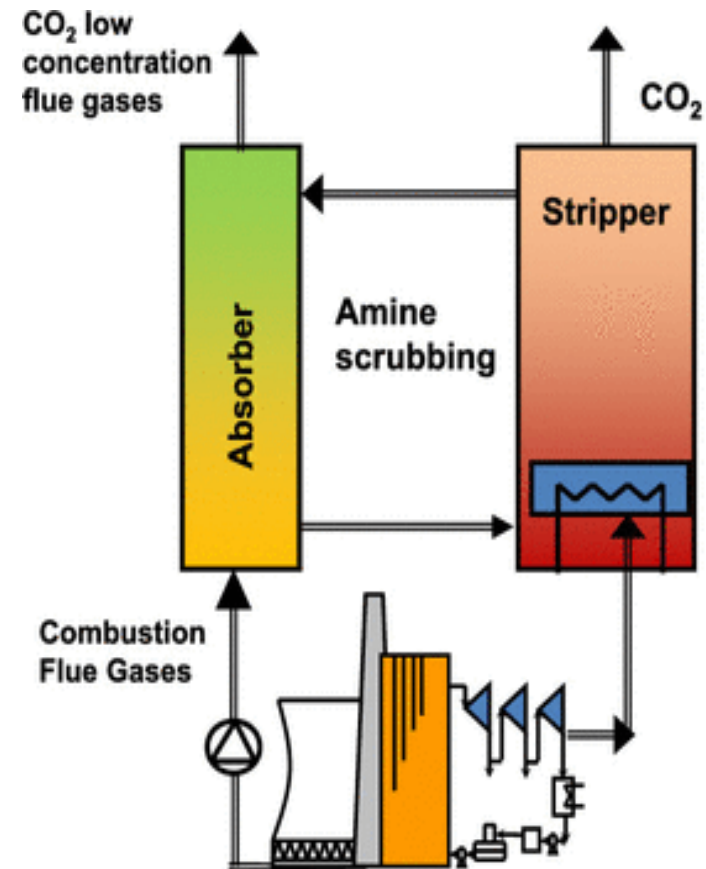


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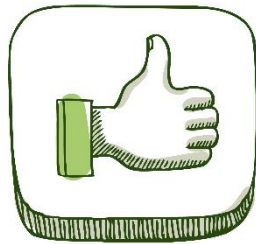
To mitigate CO₂ emissions and prevent the negative effect they have on climate change, **Carbon Capture and Storage (CCS)** technologies are being applied and developed.



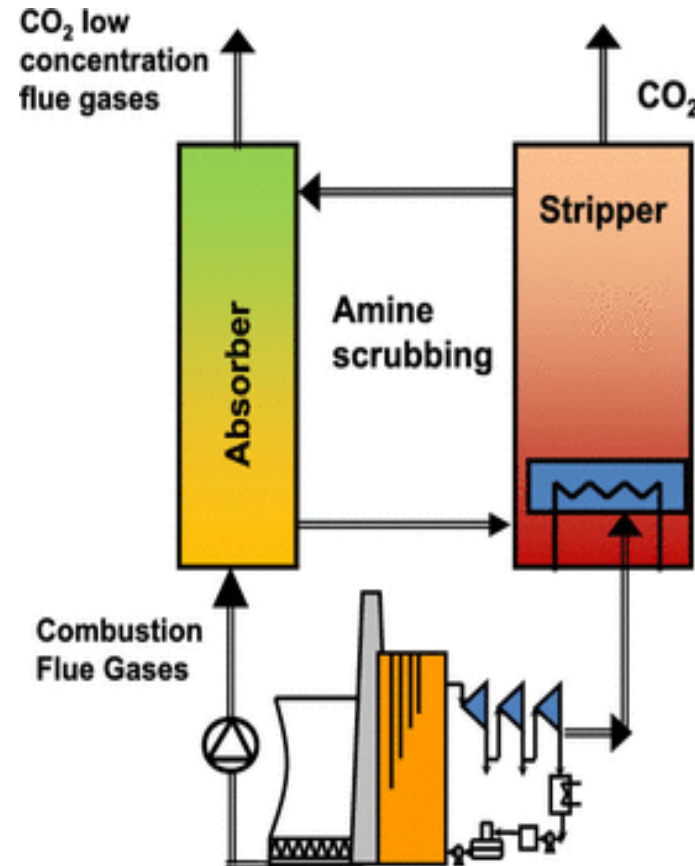
The most common technology for CCS from large point sources is **Amine Scrubbing**.



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High selectivity
High recovery
Well-established

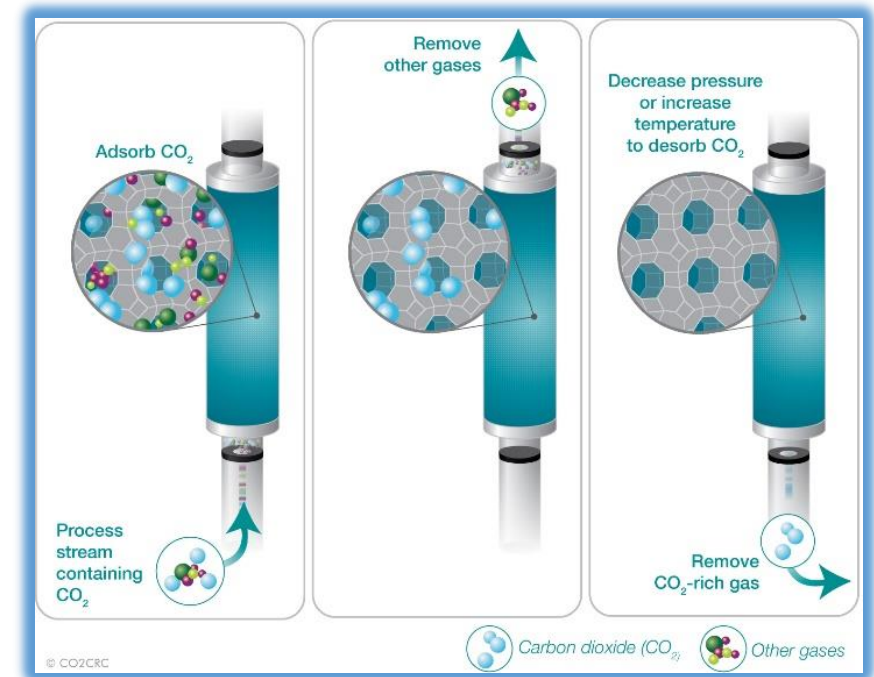


Highly energy demanding process
Reactant stability
Corrosion of the equipment

SEPARATION BY ADSORPTION

Adsorbents materials for CO₂:

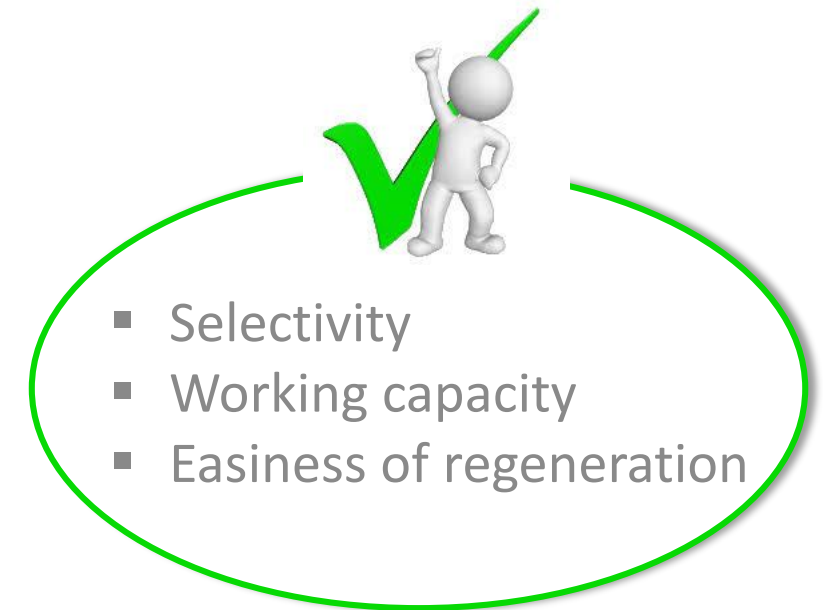
- Carbonaceous materials
- Metal Organic Frameworks (MOFs)
- Covalent Organic Frameworks (COFs)
- Supported Amines
- Zeolites
- **Aluminophosphates and Silicoaluminophosphates**



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➤ **Selectivity** : $\frac{Q_{CO_2}}{Q_{CH_4}}$ or $\frac{Q_{CO_2}}{Q_{N_2}}$

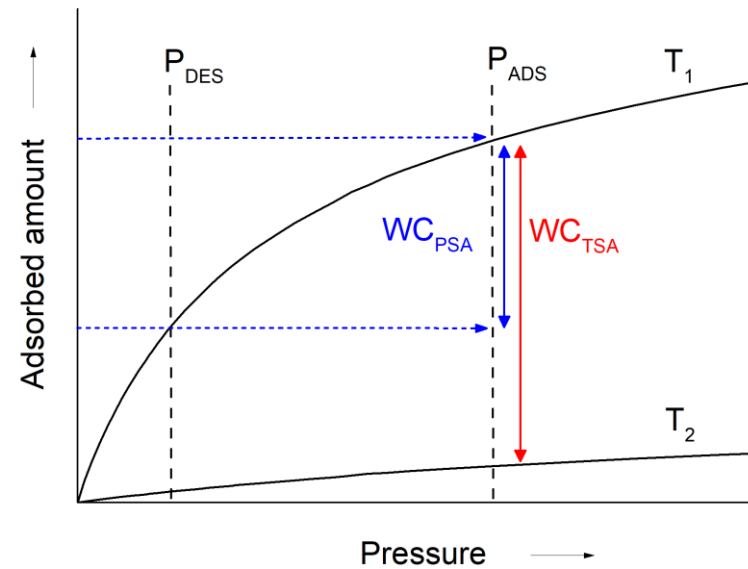
➤ Working Capacity

➤ Easiness of Regeneration

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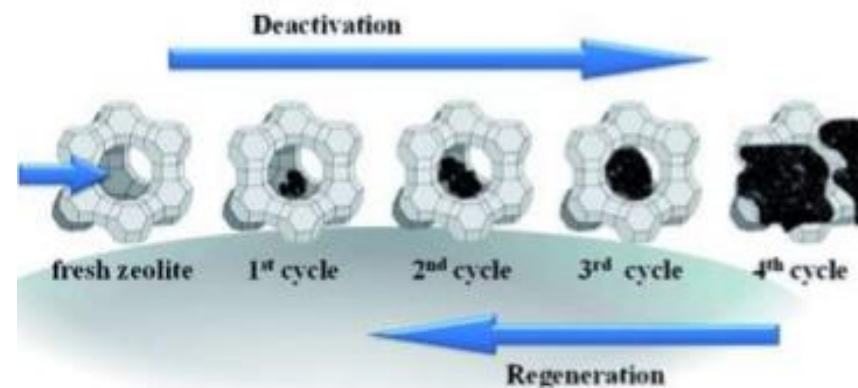
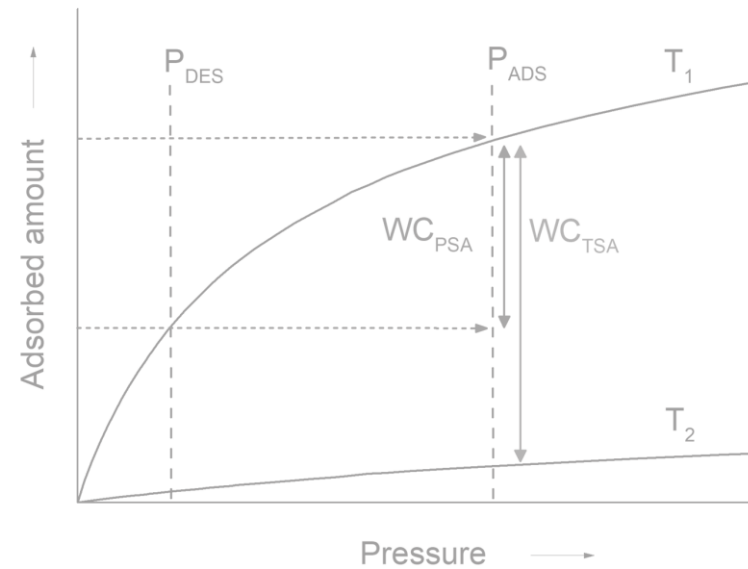
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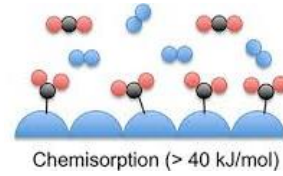
➤ Working Capacity

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Chemical interaction with CO₂ :

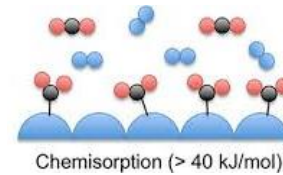
- Supported Amines
- MOFs
- Low silica zeolites



- High selectivity of CO₂/CH₄
and CO₂/N₂
- High energy of regeneration

Chemical interaction with CO₂ :

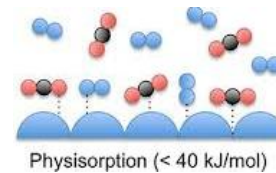
- Supported Amines
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Physisorption interaction with CO₂ :

- Carbonaceous
- MOFs
- High silica zeolites
- AlPOs and SAPOs



- Selectivity of CO₂/CH₄ and CO₂/N₂ can be high
- Lower energy of regeneration
- Higher working capacity

1.

Heat of Adsorption of CO_2 on AlPOs and SAPOs and compare with the zeolitic counterparts.

2.

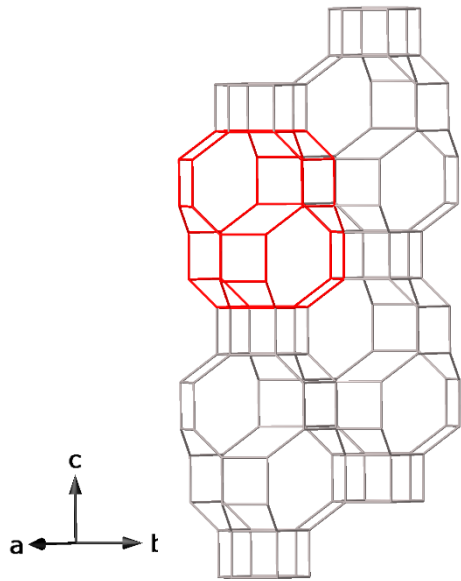
Dependence of the Heat of Adsorption with the Framework Negative Charge.

3.

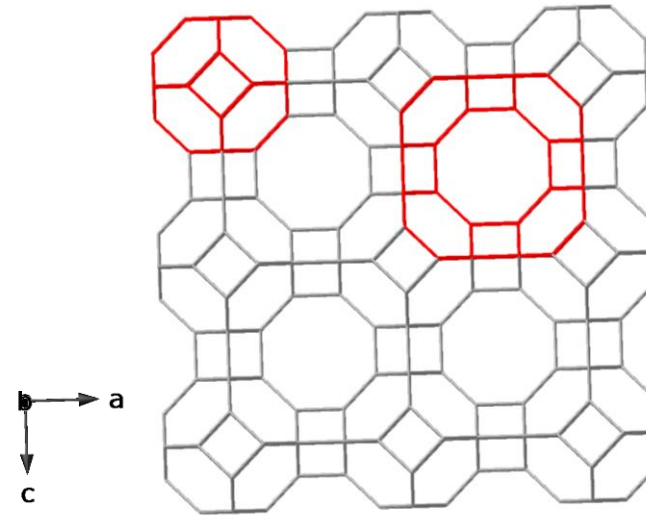
Trend of the Heat of Adsorption with the Selectivity of CO_2/CH_4 .

Small Pore Structure

CHA

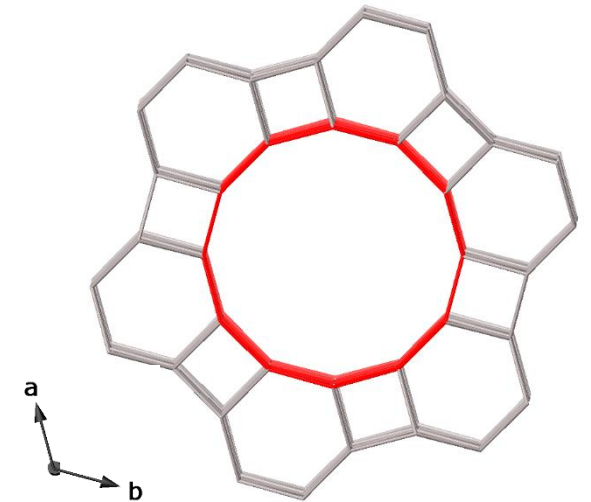


LTA



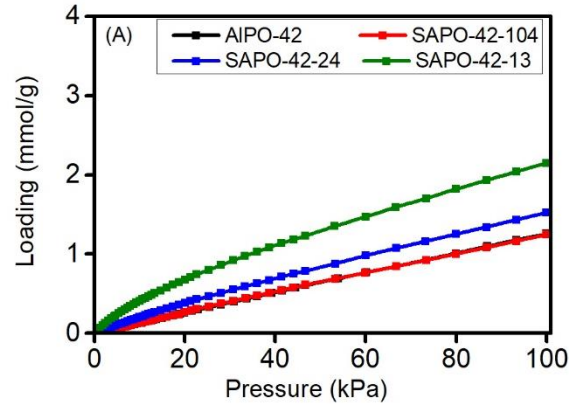
Large Pore Structure

AFI

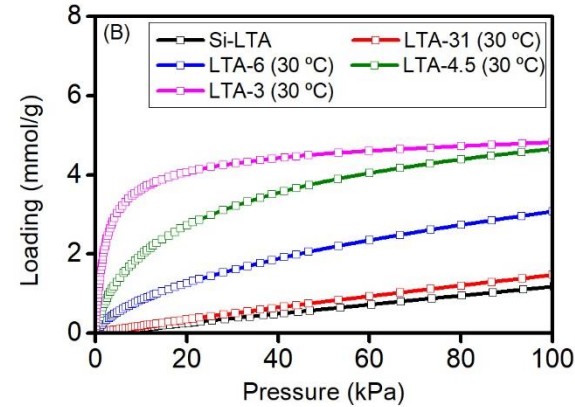


ISOTHERMS OF CO₂ ADSORPTION

ALPOs and SAPOs



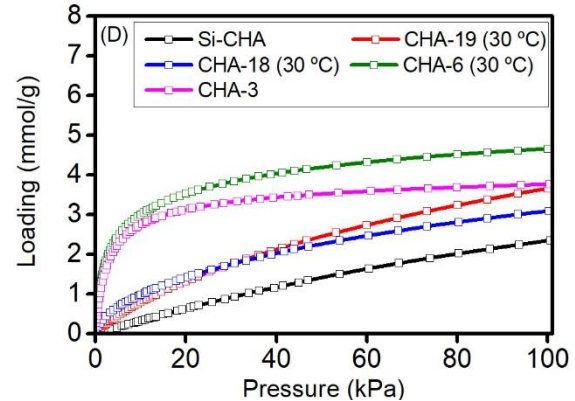
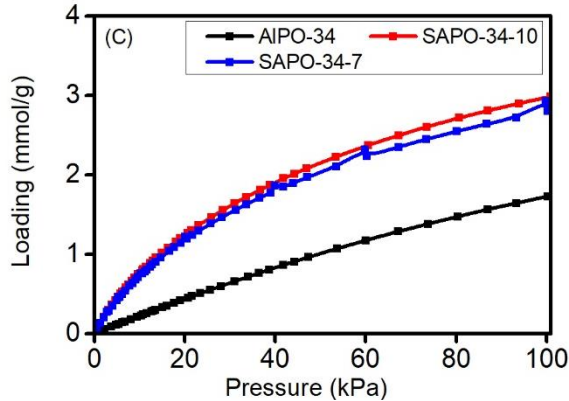
ZEOLITES



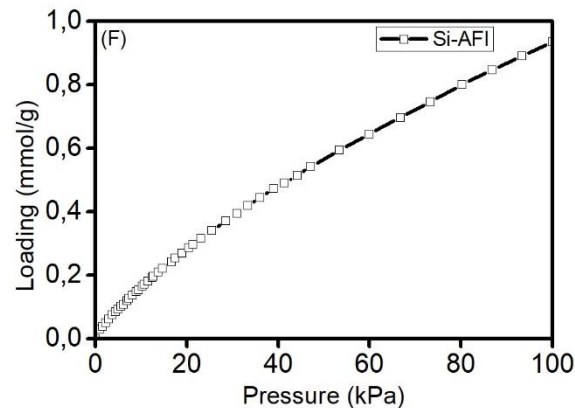
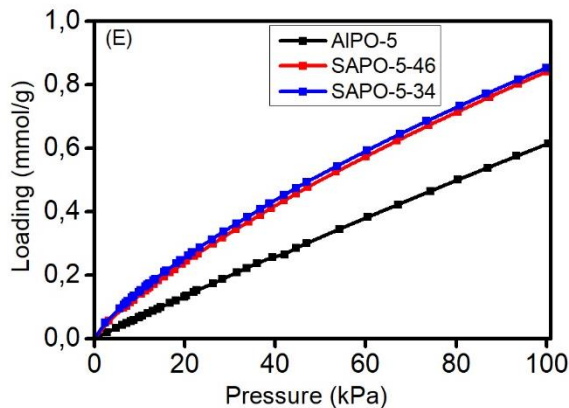
AlPOs and SAPOs present similar isotherms to high Si/Al zeolites and reach the saturation at higher pressures than low Si/Al Zeolites

LTA

CHA



AFI

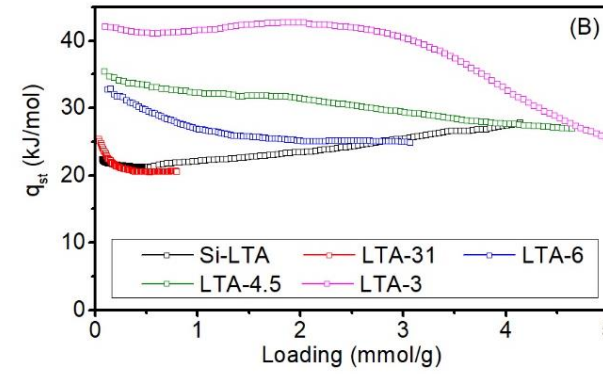
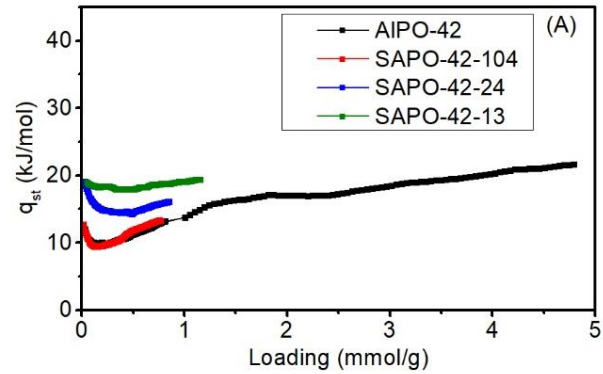


ISOSTERIC HEAT OF ADSORPTION OF CO₂

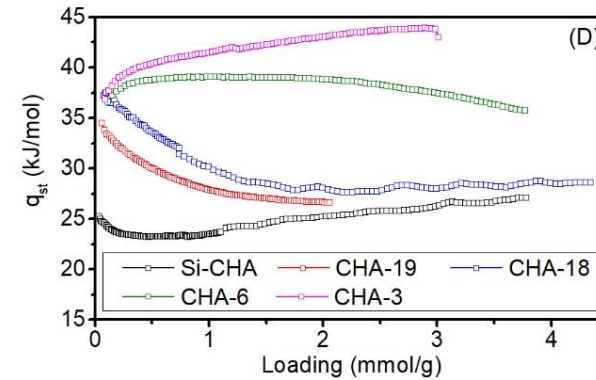
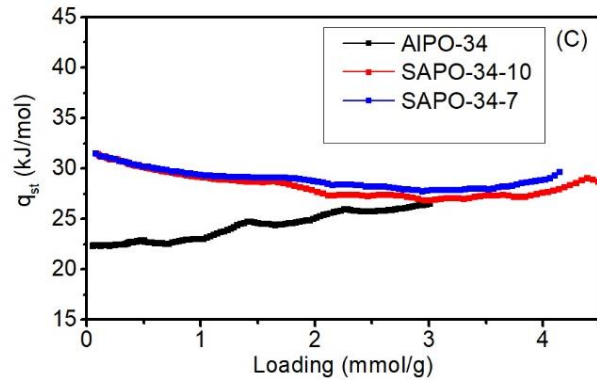
ALPOs and SAPOs

ZEOLITES

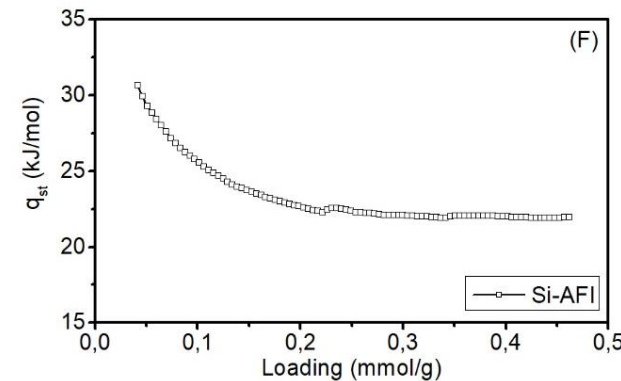
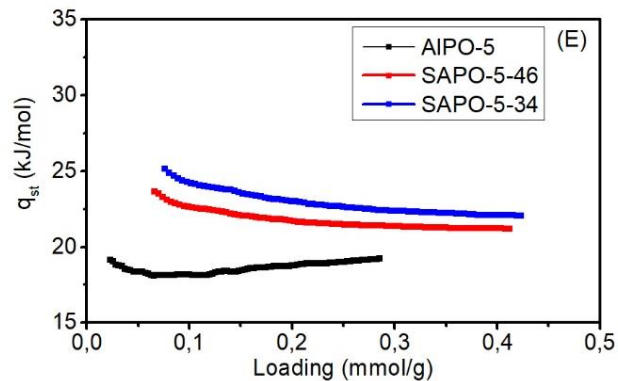
LTA



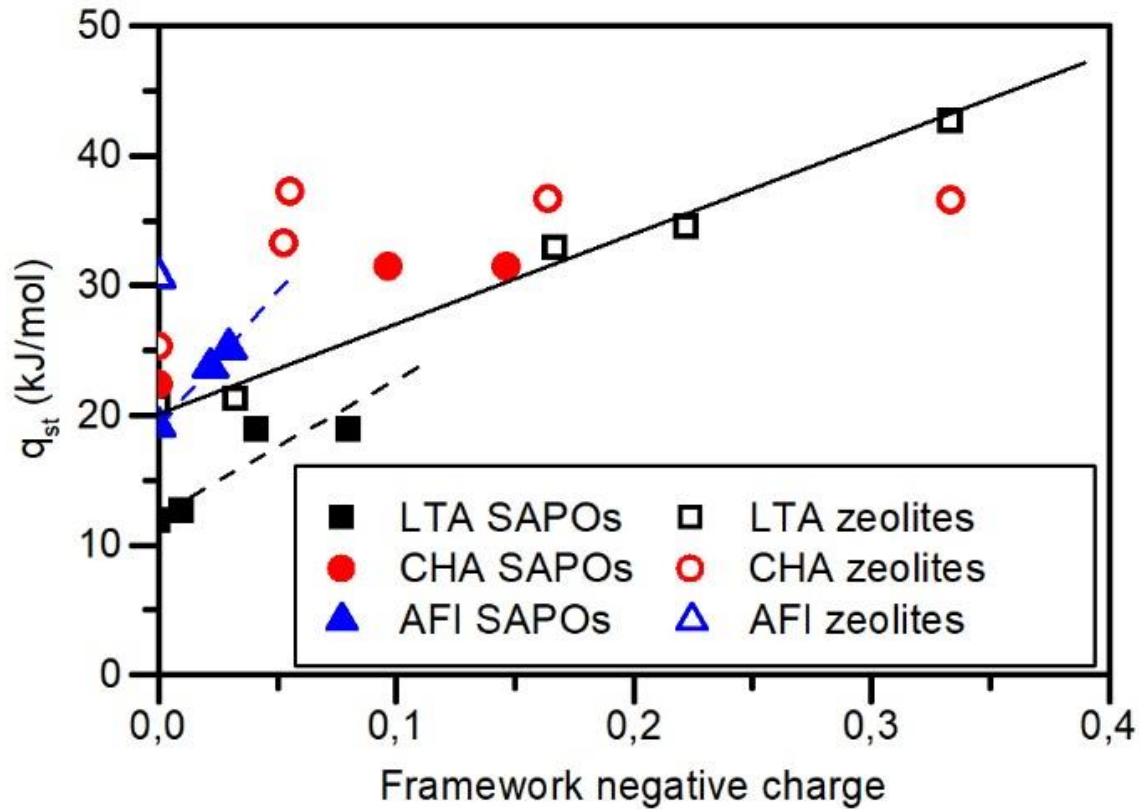
CHA



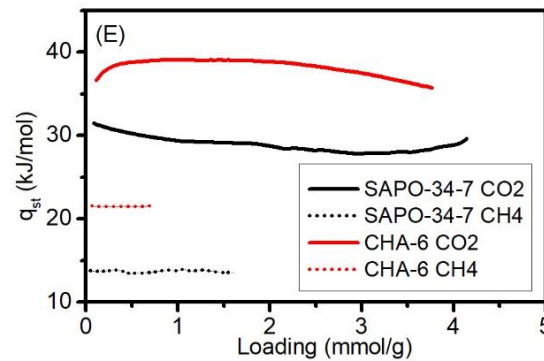
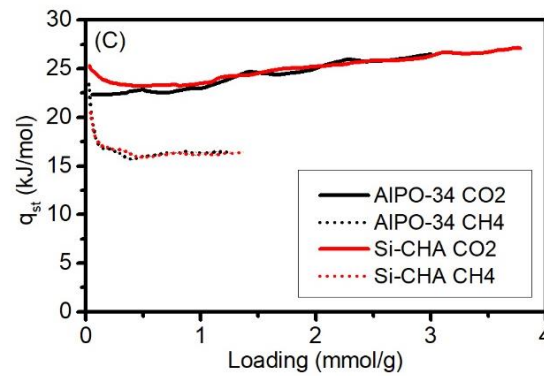
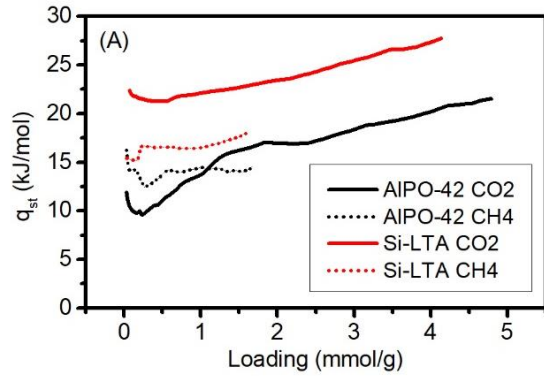
AFI



The value of the heats of adsorption at low loading give information about the affinity adsorbent-CO₂

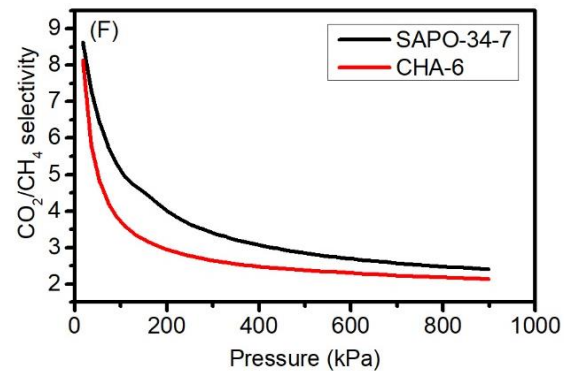
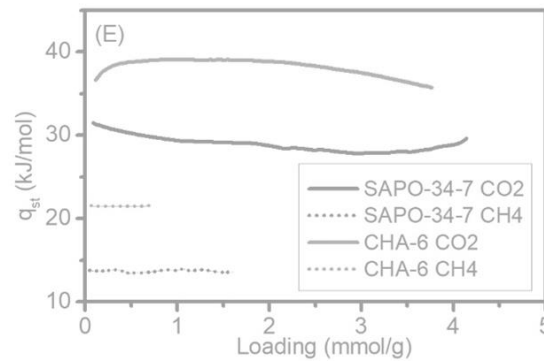
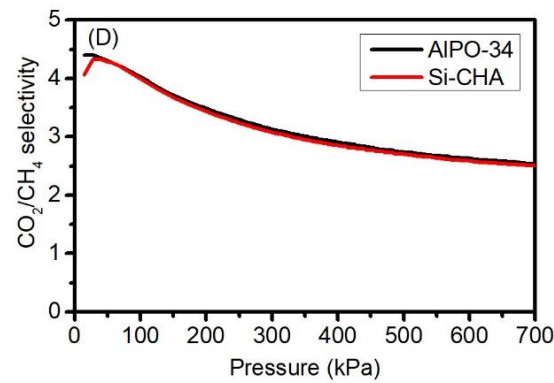
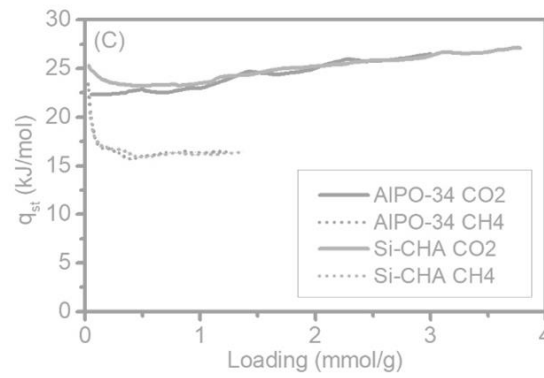
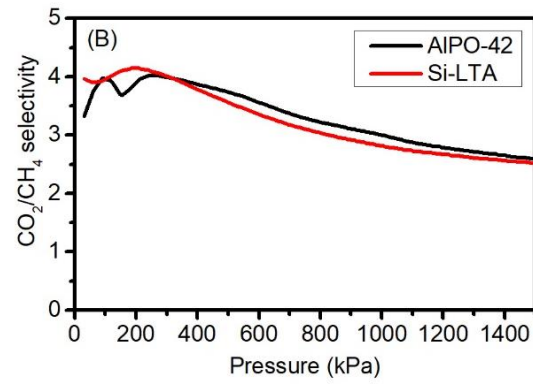
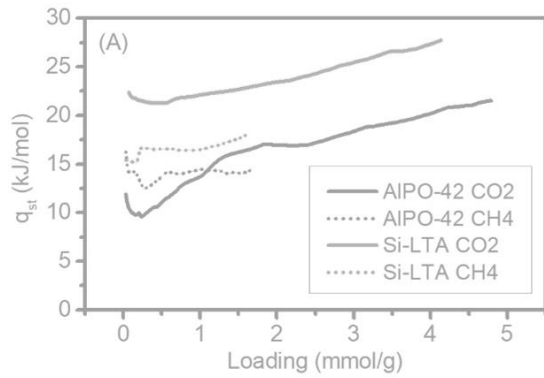


- AlPOs and SAPOs with LTA and AFI structure show lower q_{st} than the analogous zeolites.
- Lower q_{st} of adsorption results in an easy regeneration



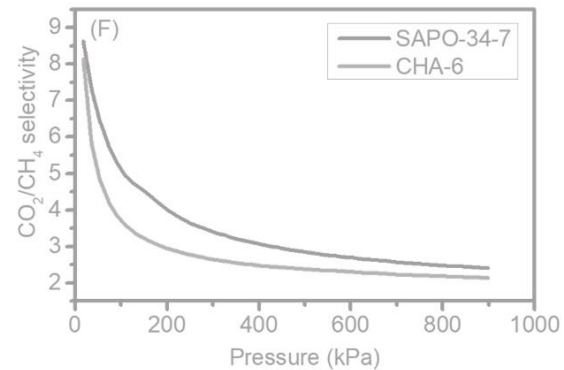
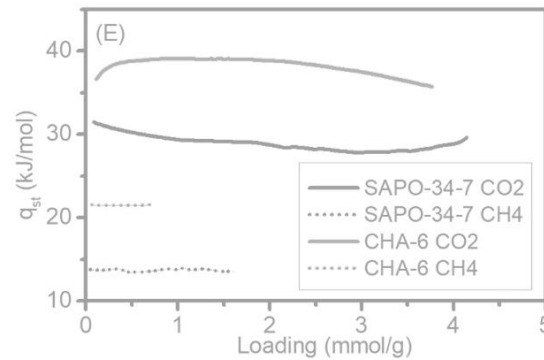
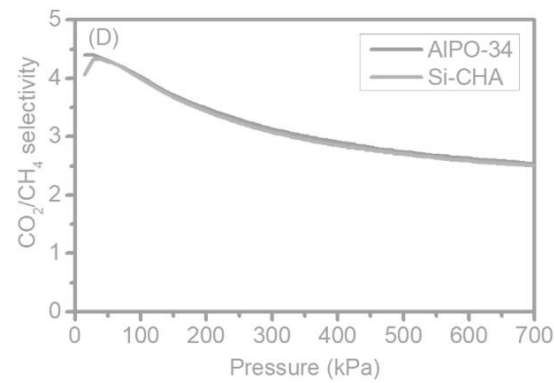
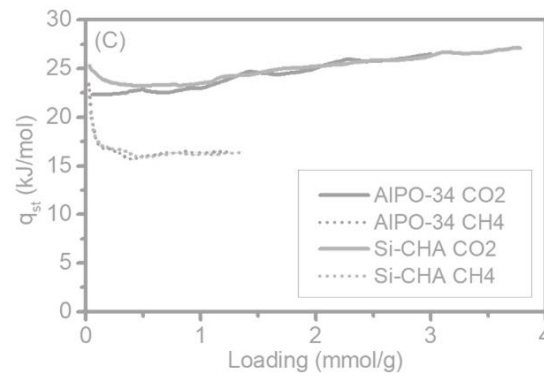
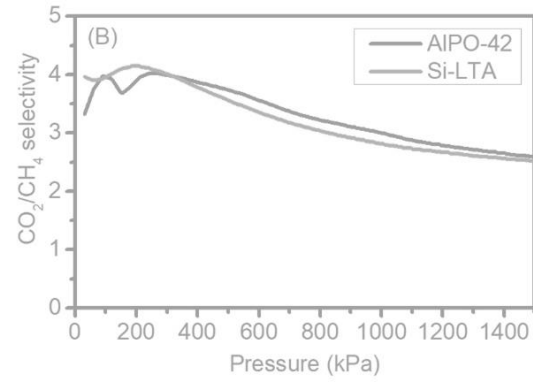
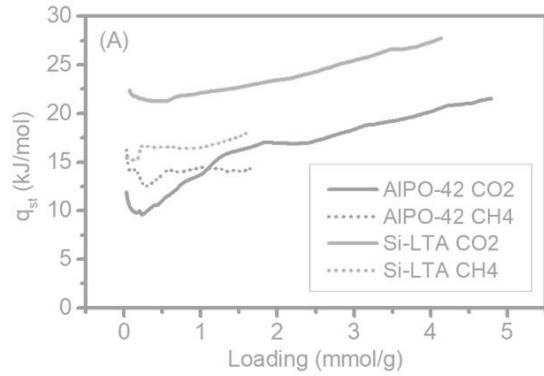
- Lower q_{st} of CO₂ and CH₄ on AIPOs and SAPOs

COMPARISON IN TERMS OF CO₂ AND CH₄ ADSORPTION



- Lower q_{st} of CO₂ and CH₄ on AIPOs and SAPOs
- Similar selectivity to CO₂/CH₄

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| | Working capacity (mmol/g) |
|-----------|---------------------------|
| AIPO-42 | 3.21 |
| Si-LTA | 2.99 |
| AIPO-34 | 1.90 |
| Si-CHA | 2.38 |
| SAPO-34-7 | 1.84 |
| CHA-6 | 1.01 |

- The isosteric heat of adsorption of CO₂ on AlPOs and SAPOs with AFI, LTA and CHA structures are lower than on the isostructural zeolites, even of pure silica composition.
- These results suggest that AlPOs and SAPOs can present major advantages in the field of CO₂ separation and adsorption in comparison to zeolites, if materials with structures that maximize selectivities over CH₄ or N₂ are found.

ACKNOWLEDGEMENTS

- Spanish Ministry of Sciences, Innovation and Universities (MCIU), State Research Agency (AEI), and the European Fund for Regional Development (FEDER) for their funding via projects Multi2HYcat (EU-Horizon 2020 funded project under grant agreement n°. 720783), Program Severo Ochoa SEV-2016-0683 and RTI2018-101033- B-I00 and also Fundación Ramón Areces for funding through a research contract (CIVP18A3908).
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- A- Team Adsorption from ITQ, in special Edi.



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