On the CO_2 Harvesting from N_2 Using Grazyne Membranes

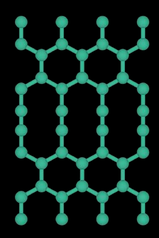
Adrià Calzada, Francesc Viñes, Pablo Gamallo

Departament de Ciència de Materials i Química Física, Institut de Química Teòrica i Computacional, Universitat de Barcelona, Martí i Franquès 1–11, 08028, Barcelona, Spain

Institut de Química Teòrica i Computacional UNIVERSITAT DE BARCELONA

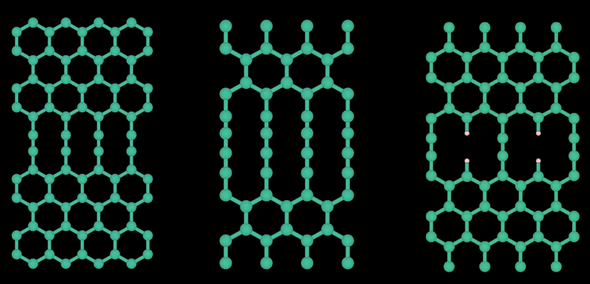
WE PROPOSE GRAZYNES

Grazynes are a subtype of graphynes, 2D single-layer C-based materials with sp and sp^2 C atoms hybridizations. In grazynes, graphene-like stripes with sp^2 hybridized C atoms are interconnected by acetylenic linkages with sp C atoms.



[1],[1]-grazyne

They can be modified in different ways

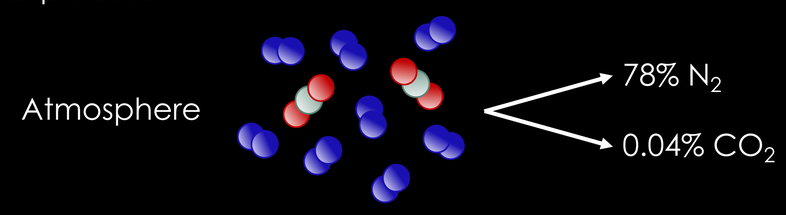


Modifying the graphene **width**

Enlarging acetylenic **linkages**

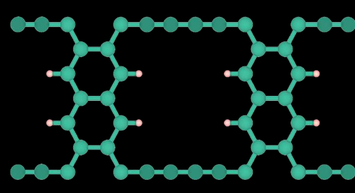
Creating acetylenic **vacancies**

The increase in the concentration of CO_2 in the atmosphere is one of the main drivers of climate change. In this context, the separation of CO_2 from N_2 is a critical process.



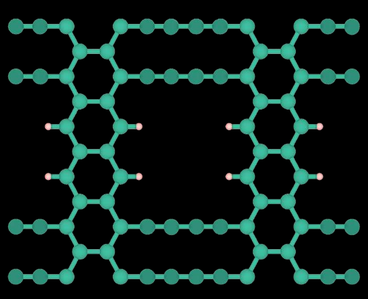
To effectively use this N_2, it must be in a high-purity state, which requires purification processes. Within the existing options, membrane-based separation stands out as a promising solution for CO_2 separation, boosting numerous benefits such as environmental friendliness, a high active surface area, and easy maintenance.

GRAZYNE MODELS



[1],[2]{2}⇨A

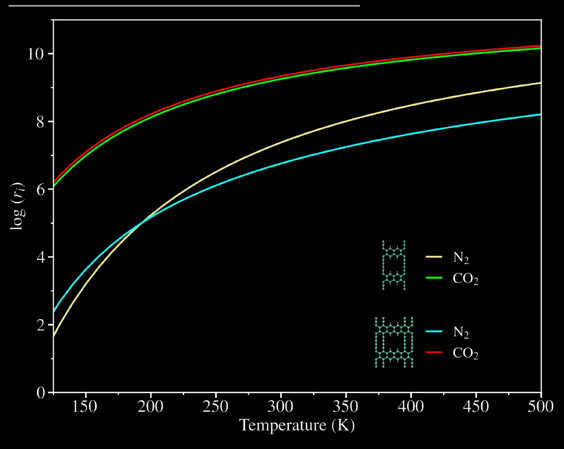
Composed of one-ring wide graphene stripes interconnected by acetylenic bonds, spanning a distance equivalent to two triple bonds, with two acetylenic vacancies.



[1],[2]{(0,0),2}⇨B

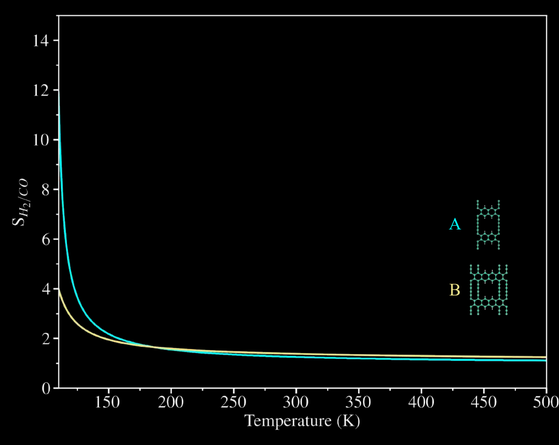
The difference between the structures lies in the A-grazyne containing a solitary acetylenic bond between consecutive pores, while the B-grazyne exhibits two adjacent acetylenic bonds followed by two vacancies.

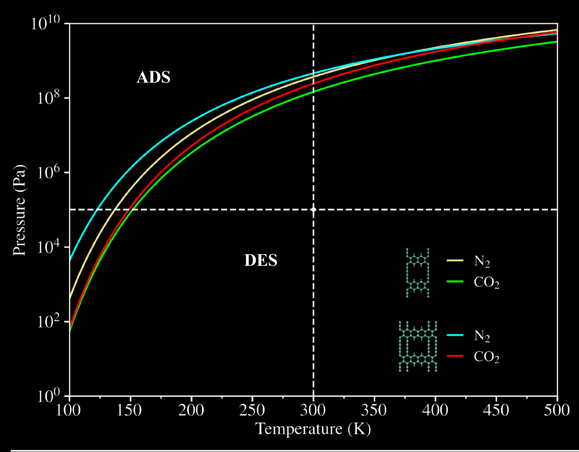
DFT RESULTS



CO_2 consistently shows higher membrane diffusion rates than N_2, regardless of the grazyne model. The figure highlights a key temperature range between 100 and 500 K, where diffusion rates, r_i, exceed 1 s^{-1}, suggesting the potential use of grazynes as molecular separation membranes.

The analysis of the selectivity confirms that CO_2 has a higher selectivity than N_2, but this decreases as temperature goes up, following the rate constants, with a clear trend toward unity at higher temperatures. Therefore, lower temperatures are better for separating CO_2 from N_2, though this comes with a lower permeation rate.



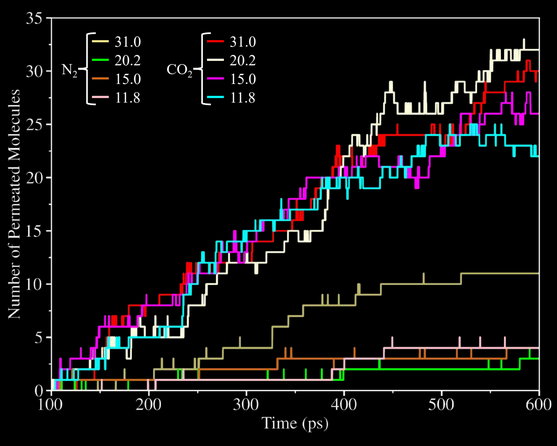


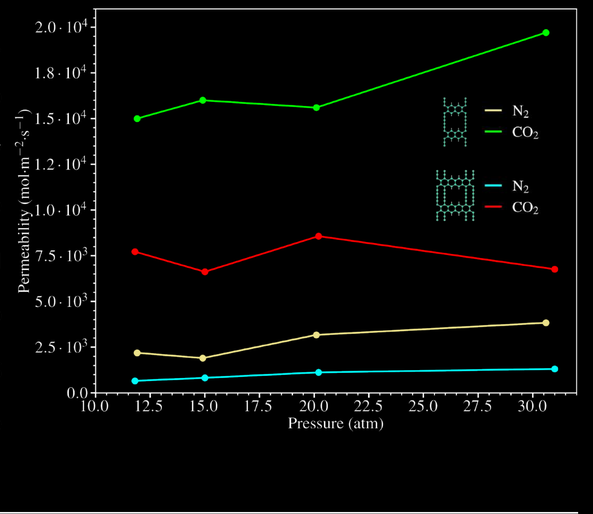
The KPD highlights two distinct regions: one where adsorption is favored, and another where desorption is preferred. CO_2 shows a wider adsorption range. At p=1 atm and T=300 K, neither CO_2 nor N_2 is inclined toward adsorption, making grazynes effective for separation membranes.

MOLECULAR DYNAMICS RESULTS

Grazyne		A				B			
Pressure (atm)		30.6	20.1	14.9	11.9	31.0	20.2	15.0	11.8
500 ps	#N_2	18	14	10	10	11	3	4	4
	#CO_2	39	41	30	30	30	32	26	22
1500 ps	#N_2	31	31	30	26	23	9	13	13
	#CO_2	41	38	30	28	45	38	35	33

The number of CO_2 (#CO_2) and N_2 (#N_2) molecules that passed through shows that CO_2 diffuses more easily through both grazyne membranes. CO_2 makes up about 65-75% of the total molecules permeating through A-grazyne and 70-90% for B-grazyne. These results suggest a potential CO_2 enrichment of *ca.* 90%. This trend is also seen in the time evolution of the number of molecules that passed through B-grazyne, while a similar trend is observed for A-grazyne (not shown). Generally, increasing the pressure leads to more permeation, though some trends may fluctuate. It is important to remember that the likelihood of a molecule passing through a pore depends on its arrival orientation. No parallel permeation has been observed, thus molecules approaching perpendicularly have a higher chance of crossing.





CONCLUSIONS

DFT and MD support the use of grazyne membranes for selective CO_2 separation from N_2. Grazynes are capable of physisorbing CO_2 and N_2, thus avoiding material poisoning by molecular decoration, while the diffusion of CO_2 through the pores is found to be rapid, yet easier than that of N_2, in the rate order of the s^{-1} in the 100-500 K temperature range. In addition, according to MD with equimolecular mixtures of CO_2:N_2, *ca.* 60-70% of CO_2 permeates the A-grazyne, with the remaining 30-40% being N_2. Conversely, B-grazyne achieves up to 90% CO_2 permeation.

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