

Molecular sieving of linear and branched C₆ alkanes by tannin-derived carbons

Supplementary Information

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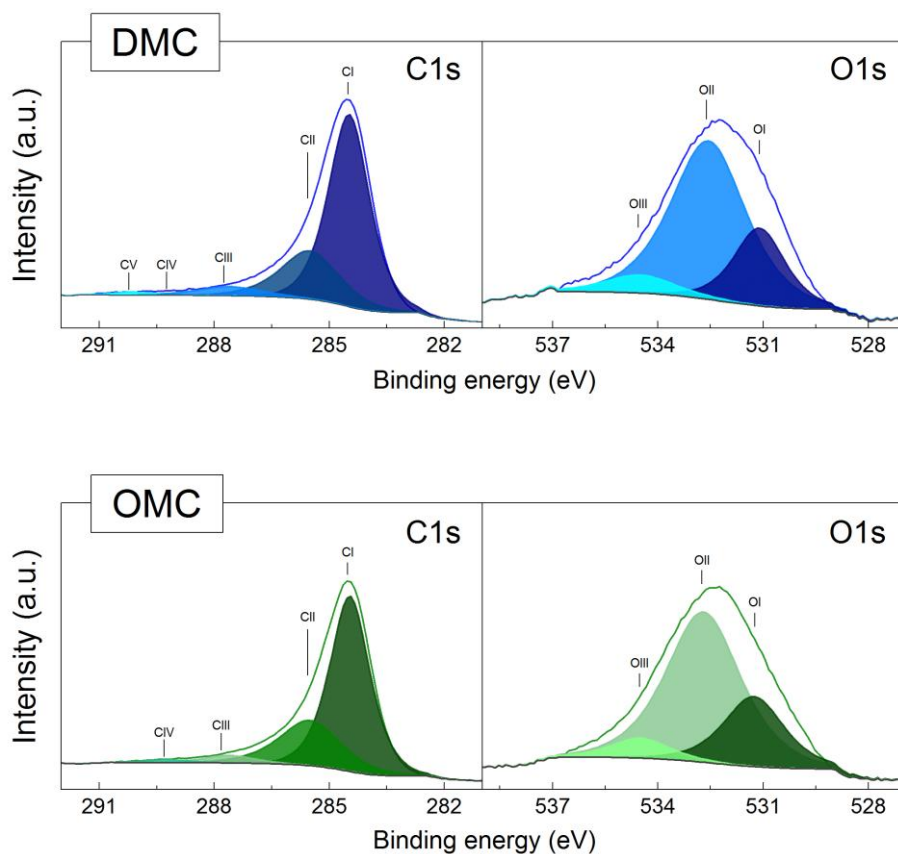


Figure S1. C1s and O1s high-resolution XPS spectra of DMC and OMC materials, along with their corresponding deconvoluted peaks.

Table S1. Peak assignment and relative contributions of surface functionalities obtained by XPS analysis.

Sample	C1s					O1s		
	C-I	C-II	C-III	C-IV	C-V	O-I	O-II	O-III
	Area [BE] (% [eV])	Area [BE] (% [eV])	Area [BE] (% [eV])	Area [BE] (% [eV])	Area [BE] (% [eV])	Area [BE] (% [eV])	Area [BE] (% [eV])	Area [BE] (% [eV])
DMC	68.4 [284.5]	24.8 [285.5]	5.3 [287.6]	0.3 [289.1]	1.2 [290.1]	23.4 [531.1]	69.2 [532.6]	7.3 [534.5]
OMC	68.3 [284.4]	26.9 [285.5]	3.6 [287.6]	1.2 [289.2]	--	25.6 [531.3]	67.4 [532.7]	7.0 [534.5]

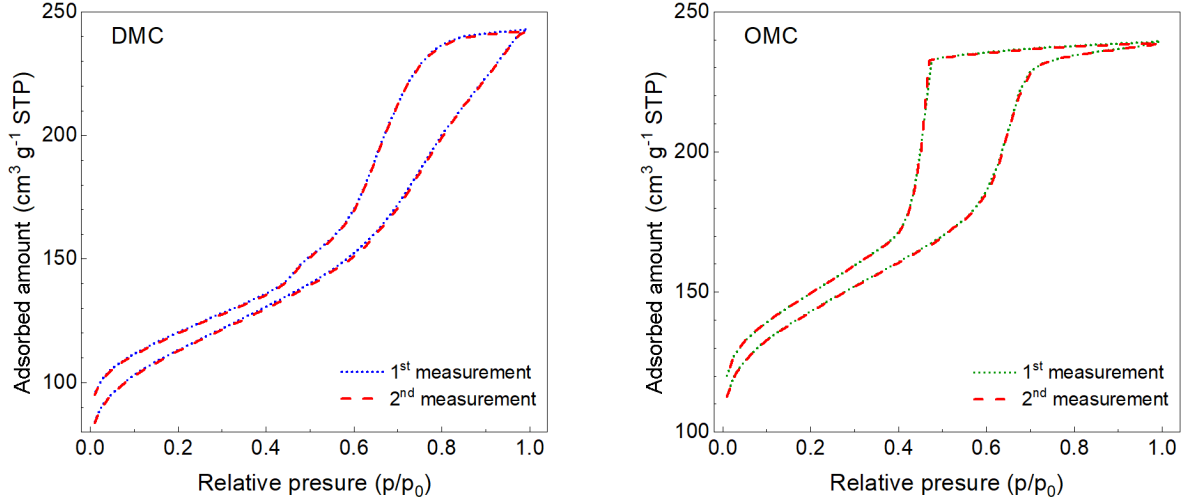


Figure S2. Nitrogen (N_2) isotherms at 77 K obtained by performing two consecutive measurements on the same sample of a disordered and an ordered mesoporous carbon (DMC and OMC, respectively).

Ideal adsorbed solution theory (IAST)

The IAST, initially proposed by Myers and Prausnitz [59], has become a good tool for predicting the adsorption of mixed gases on a material from single-component isotherms. This theory is based on an ideal relationship analogous to Raoult's law, represented mathematically by:

$$Py_i = P_i^0(\pi_i)x_i \quad (S1)$$

where P and P_i^0 are the total pressure and the hypothetical pressure in the standard state, respectively, y_i and x_i are the molar fractions in the gas and adsorbed phases, respectively, and π_i is the spreading pressure of component i in the mixture. The Gibbs adsorption isotherm is used to obtain π_i through:

$$z = \frac{\pi_i}{RT} = \int_0^{P_i^0} \frac{q_i^{pure}(P)}{P} dP \quad (S2)$$

where R is the universal gas constant, T is the temperature and q_i^{pure} is the molar concentration of component i in the adsorbed phase from the single-component isotherm. The latter can be calculated by different single-component equilibrium models such as Langmuir,

Freundlich, Sips, among others. Note that, at equilibrium, the spreading pressure of each component must be equal:

$$\pi_1 = \pi_2 = \dots = \pi_n \quad (\text{S3})$$

The total adsorbed amount, q_T , is calculated by:

$$\frac{1}{q_T} = \sum_{i=1}^n \frac{x_i}{q_i^0} \quad (\text{S4})$$

where q_i^0 is the amount absorbed at the hypothetical pressure in the standard state.

The algorithm implemented to apply the IAST is presented in the form of a flowchart in Figure S3. The fit of the single-component isotherms (normally carried out using the desorption branch because it is in equilibrium conditions) and the calculation of z were carried out using a combination of Langmuir and Sips models through the following equations:

$$q_i^{pure} = \frac{q_{max,i} b_i P_i}{1 + b_i P_i} + \frac{q_{max,i} (b_i P_i)^{1/n}}{1 + (b_i P_i)^{1/n}} \quad (\text{S5})$$

$$z = q_{max,i} \ln(P_i^0 b + 1) + q_{max,i} n \ln[(b P_i^0)^{1/n} + 1] \quad (\text{S6})$$

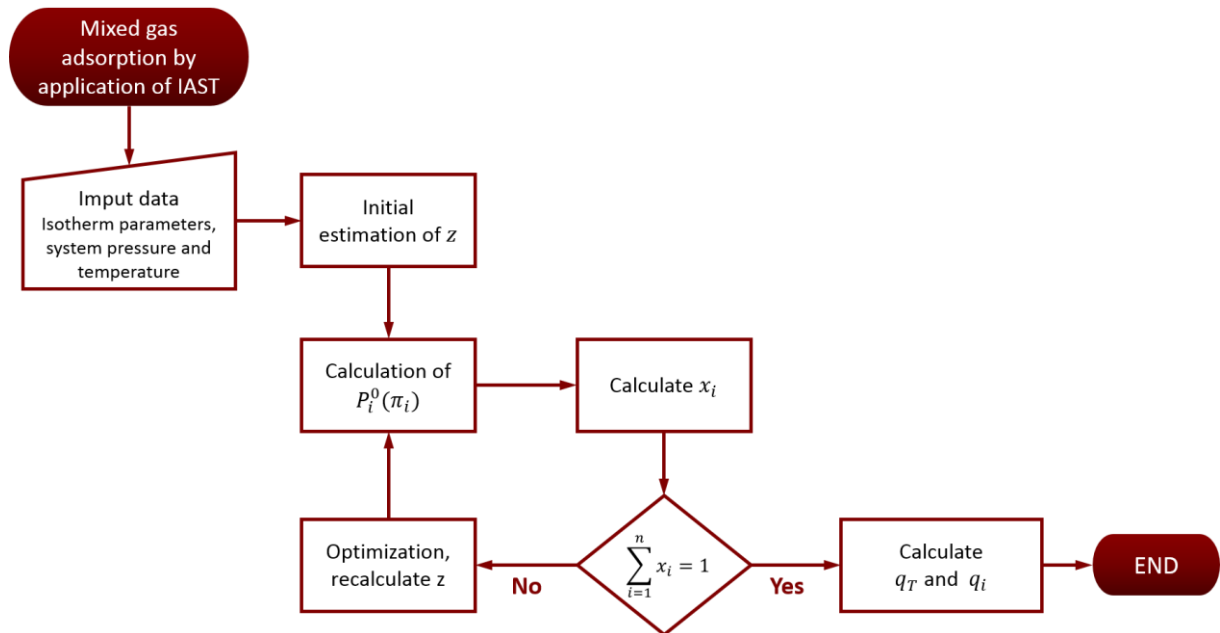


Figure S3. Flowchart of the algorithm used to apply the IAST to obtain the multi-component adsorption isotherms from the experimental single-component isotherms.

Finally, from the IAST data, it is possible to calculate the selectivity and the adsorption capacity, which are important parameters facilitating the evaluation of the performance of a material to be used as gas separator. Herein, for binary mixtures, the separation factor or selectivity is defined as:

$$S_{1/2} = \frac{x_1 y_2}{x_2 y_1} \quad (\text{S7})$$

where index 1 refers to nHEX, and index 2 refers to either 2MP or 22DMB. The adsorption capacity is then calculated by:

$$\text{Capacity} = q_1 = q_T x_1 \quad (\text{S8})$$

Equation S7 and S8 are adapted for ternary mixtures as follows:

$$S_{1+2/3} = \frac{(x_1 + x_2)y_3}{(y_1 + y_2)x_3} \quad (\text{S9})$$

$$\text{Capacity} = \frac{q_T(x_1 + x_2)}{2} \quad (\text{S10})$$

where index 1 again refers to nHEX, index 2 to 2MP, and index 3 to 22DMB. In this case, the selectivity and capacity are defined to evaluate the ability to separate the di-branched isomer from the linear and the mono-branched isomers.

For materials exhibiting a “reverse” hierarchy of adsorption of C₆ isomers in the order di-branched > mono-branched > linear, the selectivity and capacity for binary mixtures are calculated through:[64]

$$S_{1/2} = \frac{x_2 y_1}{x_1 y_2} \quad (\text{S11})$$

$$\text{Capacity} = q_2 = q_T x_2 \quad (\text{S12})$$

while for ternary mixtures, these values are obtained from:[64]

$$S_{1+2/3} = \frac{(y_1 + y_2)x_3}{(x_1 + x_2)y_3} \quad (\text{S13})$$

$$\text{Capacity} = q_3 = q_T x_3 \quad (\text{S14})$$

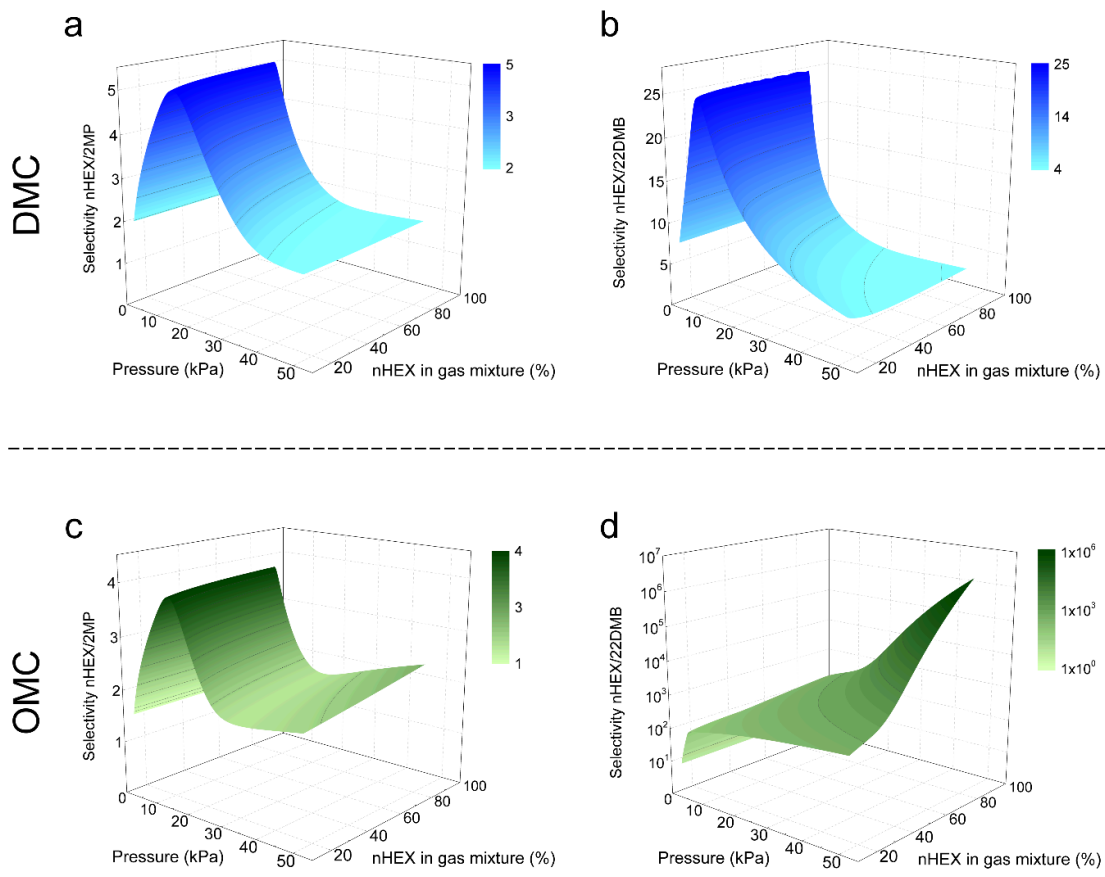


Figure S4. Selectivity of nHex for DMC and OMC materials from binary mixtures of (a, c) nHEX+2MP and (b, d) nHEX+22DMB at 45 °C.

Table S2. Adsorption performance of different materials tested for the separation of C₆ isomers. Sample names correspond to those of their source and reference numbers are those used in the main article.

Sample	Description	Temperature (°C)	Single-component adsorption capacity (mmol g ⁻¹)			Selectivity			Comments	Ref.
			nHEX	2MP	22DMB	nHEX/2MP [50/50]	nHEX/22DMB [50/50]	(nHEX+2MP)/22DMB [(25+25)/50]		
DMC OMC	Tannin-derived micro-mesoporous carbons	25	4.1	2.7	2.2	3.2	7.5	4.7	Adsorption capacity values at saturation pressure, selectivity obtained at 50 kPa from IAST calculations	This study
		45	3.8	2.8	2.1	1.9	3.8	2.9		
		25	3.6	1.8	0.2	40.9	6.1×10 ¹⁷	3.5×10 ¹⁰		
		45	3.3	1.9	0.5	2.2	1.9×10 ⁴	1.8×10 ³		
HKUST-1	MOF	25	5.5	5.5	5.1	1.3×10 ⁸	1.9×10 ⁴	7.0×10 ³	Adsorption capacity values at saturation pressure, selectivity obtained at 50 kPa from IAST calculations	[58]
UiO-66			3.5	4.2	4.3	1.5	45.6	12.9		
ZIF-8			4.3	3.7	0.9	9.9×10 ³	3.9×10 ³	1.7×10 ³		
Fe ₂ (BDP) ₃	MOF	200	0.9	0.6	0.3				Adsorption capacity values at 150 mbar	[4]
AC16	Activated carbon xerogels	30	1.4		0.1				Adsorption capacity values at saturation pressure	[20]
AC16X			1.1		0.6					
AC16X10			2.0		1.3					
AC16X40			2.4		2.4					
Zeolite-2	Zeolite	160				1.4			Selectivity (separation factor) calculated from correlation between vapor pressure and Henry constants	[21]
MCM-48	Ordered mesoporous silica					0.5				
CSM-19	Carbon-silica material	250					7.5		Selectivity (separation factor) calculated from the ratio of corresponding Henry constants	[22]
CSM-23							8.3			
CSM-24								6.4		
Carboxen-569	Commercial carbon molecular sieve						20			
MFI	Zeolite	160	0.7	0.6	0.5				Adsorption capacity values at 10 ⁴ Pa (fugacity) calculated from computer simulations	[65]
CoBDP			4.2	3.9	2.0					
UiO-66	MOF		1.4	1.7	1.7					
ZIF-77			0.7	0.3	0.0					
C ₂₁ H ₂₅ N ₄ O ₁₀ Zn ₂	Zinc (II) MOF	25	1.5		0.4				Adsorption capacity values at saturation pressure	[66]
C ₂₂ H ₂₅ N ₄ O ₉ Zn ₂			2.1		1.15					