

Supporting Material

A Novel Class of Nitrogen-rich Microporous Carbons for Highly Selective Separation of Light Hydrocarbons

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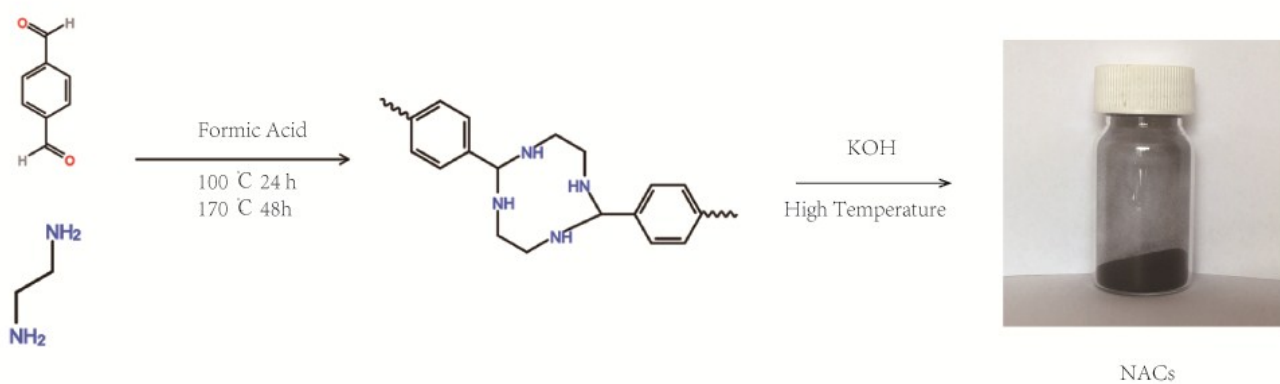
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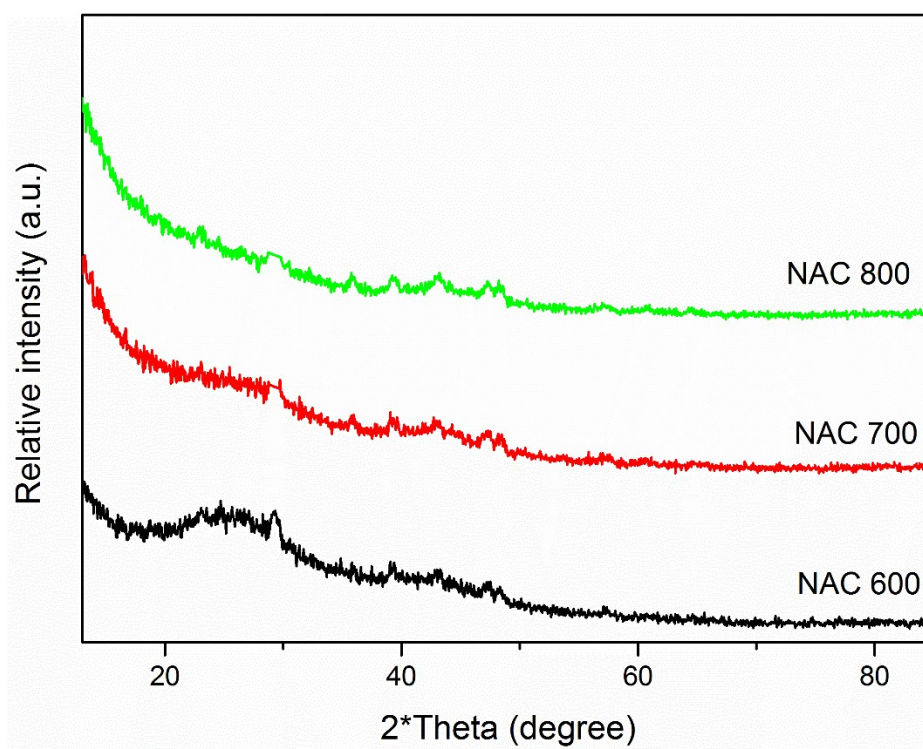
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Figure S1. Schematic illustration of synthesis process.



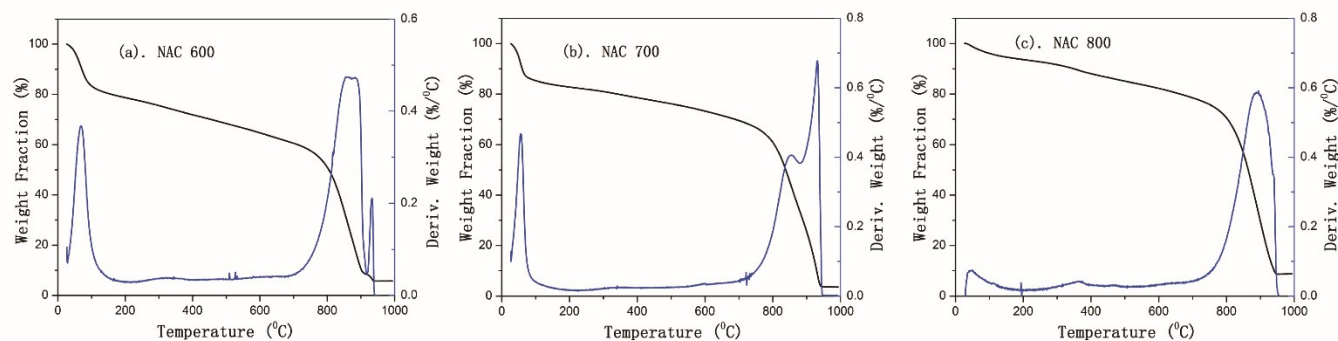
{Figure S1}

Figure S2. Wide XRD spectra of NACs.



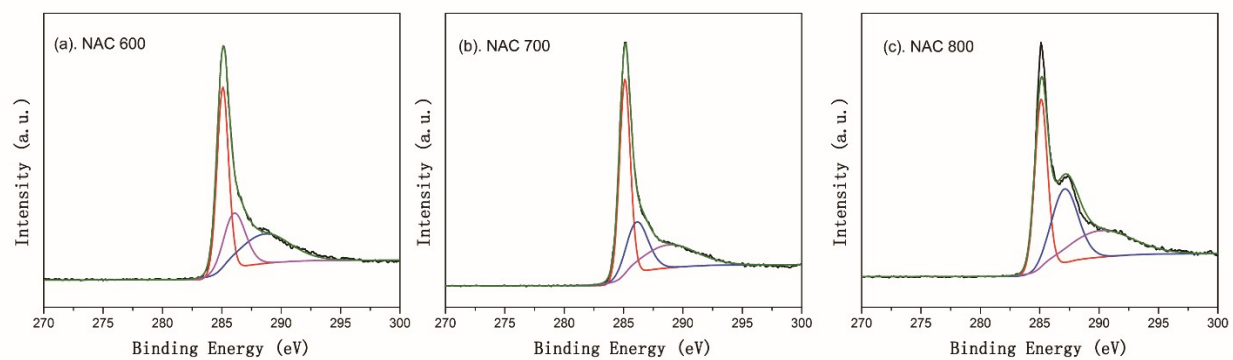
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Figure S3. TGA and DTG curves of (a). NAC 600, (b). NAC 700, and (c). NAC 800.



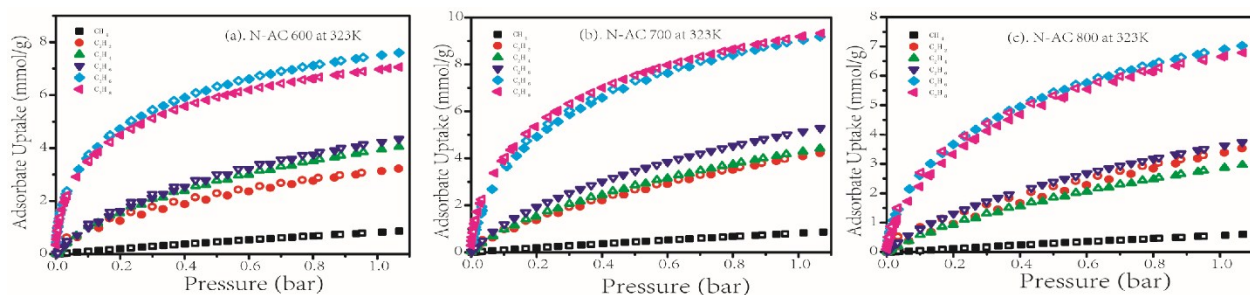
{Figure S3}

Figure S4. C 1s spectra for (a) NAC 600, (b) NAC 700, and (c) NAC 800.



{Figure S4}

Figure S5. Light hydrocarbons adsorption isotherms on (a) NAC 600, (b) NAC 700, (c) NAC 800 at 323 K and 1 bar.



{Figure S5}

Fitting of pure component isotherms

The experimentally measured loadings for CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8 were measured as a function of the absolute pressure at three different temperatures 273 K, 298 K, and 323 K.

The unary isotherm data for each guest molecule were fitted with the Langmuir-Freundlich model

$$q = q_{\text{sat}} \frac{bp^v}{1 + bp^v} \quad (1)$$

with T -dependent parameter b

$$b = b_0 \exp\left(\frac{E}{RT}\right) \quad (2)$$

The Langmuir-Freundlich parameters for adsorption of CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8 are provided in Tables S1, S2, and S3 for NAC 600, NAC 700, and NAC 800, respectively. For all guest/host combinations the isotherm fits are excellent.

Table S1. Langmuir-Freundlich parameters for adsorption of CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, and C₃H₈ in NAC 600.

	q_{sat} mol kg ⁻¹	b_0 Pa ^{-ν}	E kJ mol ⁻¹	ν dimensionless
CH ₄	4.9	2.28×10 ⁻⁹	18.2	1
C ₂ H ₂	12	4.38×10 ⁻⁷	17	0.63
C ₂ H ₄	9.2	1.8×10 ⁻⁹	23.7	0.96
C ₂ H ₆	9.9	7.04×10 ⁻⁹	22	0.9
C ₃ H ₆	12.7	3.12×10 ⁻⁶	14.3	0.69
C ₃ H ₈	12	4.77×10 ⁻⁶	17.4	0.53

{Table S1}

Table S2. Langmuir-Freundlich parameters for adsorption of CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, and C₃H₈ in NAC 700.

	q_{sat} mol kg ⁻¹	b_0 Pa ^{-ν}	E kJ mol ⁻¹	ν dimensionless
CH ₄	5.4	2.73×10 ⁻⁹	17.4	1
C ₂ H ₂	33.7	1.56×10 ⁻⁷	15.7	0.68
C ₂ H ₄	15.6	7.81×10 ⁻⁸	18.1	0.75

C ₂ H ₆	16.5	5.79×10 ⁻⁹	18.8	0.77
C ₃ H ₆	17.6	5.23×10 ⁻⁷	19.8	0.62
C ₃ H ₈	17	1.62×10 ⁻⁶	18	0.59

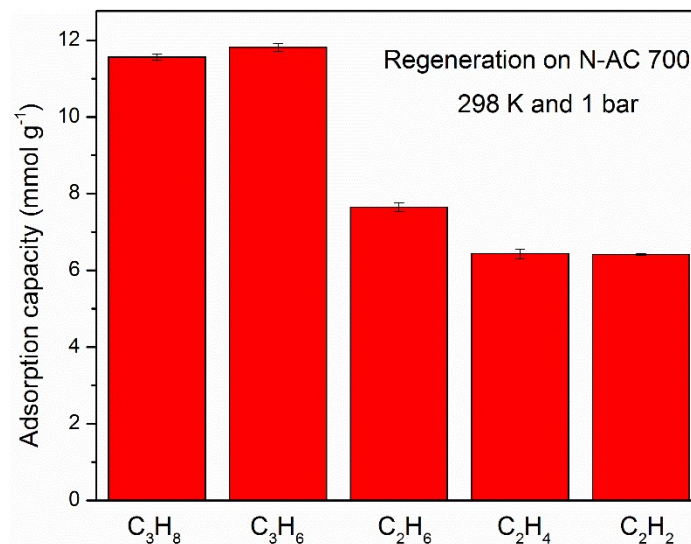
{Table S2}

Table S3. Langmuir-Freundlich parameters for adsorption of CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, and C₃H₈ in NAC 800.

	q_{sat} mol kg ⁻¹	b_0 Pa ^{-ν}	E kJ mol ⁻¹	ν dimensionless
CH ₄	4.9	1.84×10 ⁻⁹	17.7	1
C ₂ H ₂	17	1.28×10 ⁻⁸	17.6	0.89
C ₂ H ₄	10.5	1.62×10 ⁻⁸	19	0.86
C ₂ H ₆	13.7	5.33×10 ⁻⁸	18.4	0.77
C ₃ H ₆	16	2.95×10 ⁻⁶	14.4	0.62
C ₃ H ₈	13.3	1.23×10 ⁻⁷	22.3	0.66

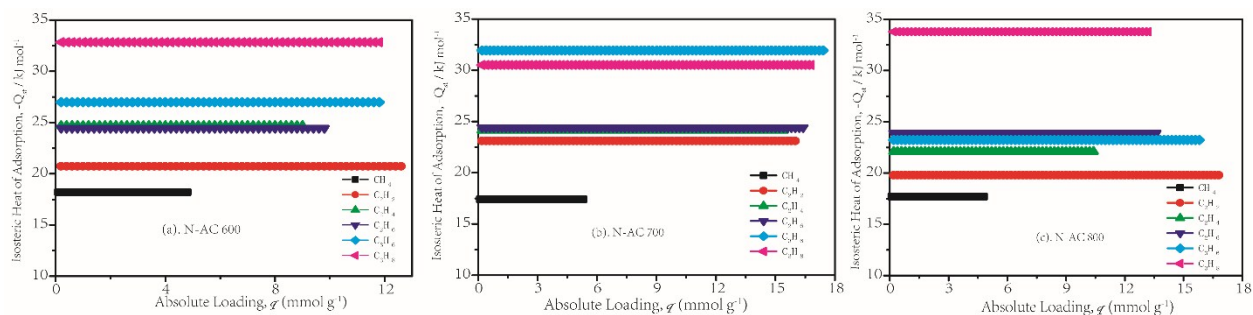
{Table S3}

Figure S6. Regeneration ability on N-AC 700 at 298 K and 1 bar.



{Figure S6}

Figure S7. Adsorption heat of light hydrocarbons on (a) NAC 600, (b) NAC 700, (c) NAC 800.



{Figure S7}

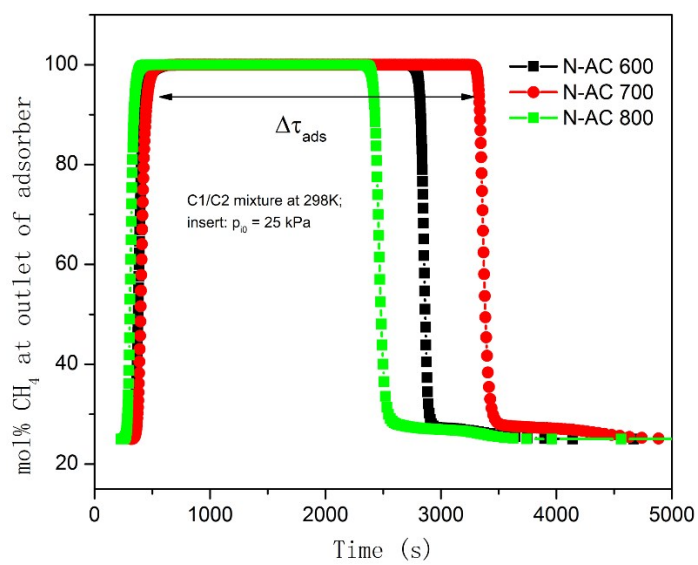
Table S4. Comparison of C₃H₈/CH₄, C₃H₆/CH₄, C₂H₆/CH₄, C₂H₄/CH₄, and C₂H₂/CH₄ selectivities of NAC 700 with other benchmark adsorbents.

Samples	C ₃ H ₈ /CH ₄	C ₃ H ₆ /CH ₄	C ₂ H ₆ /CH ₄	C ₂ H ₄ /CH ₄	C ₂ H ₂ /CH ₄	References
NAC 700	501.9	419.8	65.7	45.1	47.1	This work
FJI-C4	293.4	-	39.7	22.1	51.0	1

UTSA-35a	80	-	13.5	8	19	2
UTSA-33a	-	-	16	12	18	3
JLU-Liu22	271.5	-	14.4	-	-	4
JLU-Liu5	107.8	-	17.6	-	-	5
JLU-Liu6	274.6	-	20.4	-	-	6
JLU-Liu18	108.2	-	13.1	-	-	7

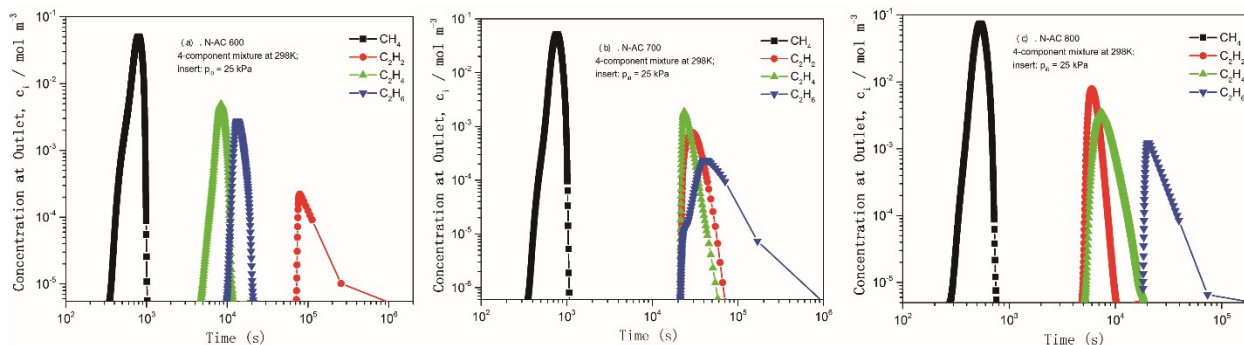
{Table S4}

Figure S8. Mole percentage of CH₄ in the exit gas stream as a function of time for NACs.



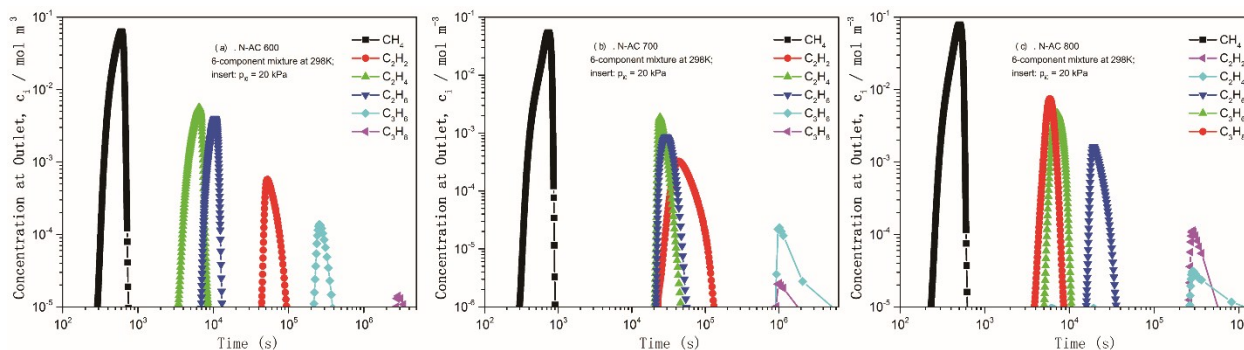
{Figure S8}

Figure S9. Pulse chromatographic simulations for separation of an equimolar 4-component $\text{CH}_4/\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ mixture on (a) NAC 600, (b) NAC 700, and (c) NAC 800 at 298 K and 1 bar.



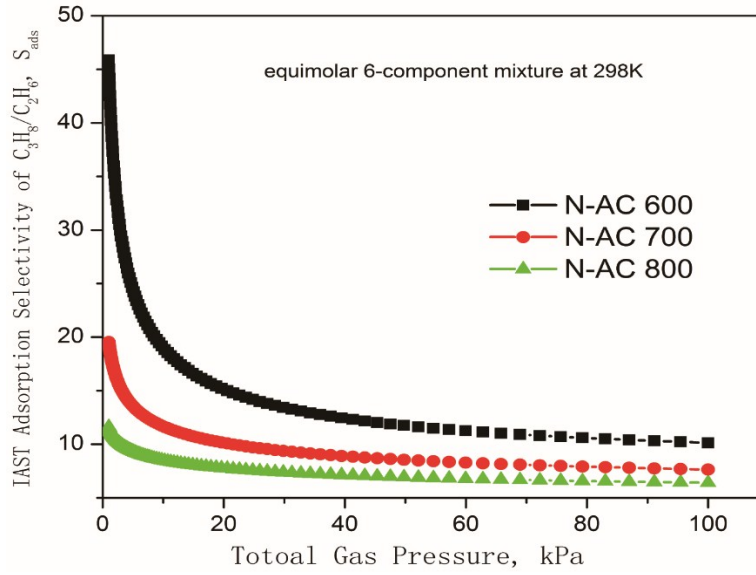
{Figure S9}

Figure S10. IAST calculations of C3/C1 and C2/C1 in an equimolar 6-component $\text{CH}_4/\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ mixture on (a) NAC 600, (a) NAC 700, and (a) NAC 800 at 298 K and 1 bar.



{Figure S10}

Figure S11. C₃H₆/C₂H₆ IAST calculations on NACs.



{Figure S11}

Transient breakthroughs in fixed bed adsorber

A brief summary of the breakthrough simulation methodology, essentially the same as that presented by Krishna [8,9], is provided below.

Assuming plug flow of an n -component gas mixture through a fixed bed maintained under isothermal conditions, the partial pressures in the gas phase at any position and instant of time are obtained by solving the following set of partial differential equations for each of the species i in the gas mixture.

$$\frac{1}{RT} \frac{\partial p_i(t, z)}{\partial t} = - \frac{1}{RT} \frac{\partial (v(t, z) p_i(t, z))}{\partial z} - \frac{(1 - \varepsilon)}{\varepsilon} \rho \frac{\partial \bar{q}_i(t, z)}{\partial t}; \quad i = 1, 2, \dots, n \quad (3)$$

In equation (3), t is the time, z is the distance along the adsorber, ρ is the framework density, ε is the bed voidage, v is the interstitial gas velocity, and $\bar{q}_i(t, z)$ is the *spatially averaged* molar loading within the crystallites of radius r_c , monitored at position z , and at time t .

At any time t , during the transient approach to thermodynamic equilibrium, the spatially averaged molar loading within the crystallite r_c is obtained by integration of the radial loading profile

$$\bar{q}_i(t) = \frac{3}{r_c^3} \int_0^{r_c} q_i(r, t) r^2 dr \quad (4)$$

For the breakthrough simulations presented in this article, we assume that intra-crystalline diffusion is of negligible importance. With this assumption the entire crystallite particle can be considered to be in thermodynamic equilibrium with the surrounding bulk gas phase at that time t , and position z of the adsorber

$$\bar{q}_i(t, z) = q_i(t, z) \quad (5)$$

The molar loadings at any position z , at time t in Equation (5) are calculated on the basis of adsorption equilibrium with the bulk gas phase partial pressures p_i at that position z and time t . The adsorption equilibrium can be calculated on the basis of the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz [10]. In all the simulation results we present in this article, the IAST calculations use Langmuir-Freundlich isotherm fits.

The *interstitial* gas velocity is related to the *superficial* gas velocity by

$$v = \frac{u}{\varepsilon} \quad (6)$$

In industrial practice, the most common operation is with to use a step-wise input of mixtures to be separation into an adsorber bed that is initially free of adsorbates, i.e. we have the initial condition

$$t = 0; \quad q_i(0, z) = 0 \quad (7)$$

At time, $t = 0$, the inlet to the adsorber, $z = 0$, is subjected to a step input of the n -component gas mixture and this step input is maintained till the end of the adsorption cycle when steady-state conditions are reached.

$$t \geq 0; \quad p_i(0, t) = p_{i0}; \quad u(0, t) = u \quad (8)$$

where u is the superficial gas velocity at the inlet to the adsorber.

Besides, the breakthrough simulations with a step-input (8), we also carried out simulations for a packed bed adsorber with injection of a short duration pulse of the mixture to be separated. This type of simulation is particularly useful to demonstrate the fractionating capability of adsorbents. For simulation of pulse chromatographic separations, we use the corresponding set of inlet conditions

$$0 \leq t \leq t_0; \quad p_i(0, t) = p_{i0}; \quad u(0, t) = u \quad (9)$$

where the time for duration of the pulse is t_0 .

In order to evaluate the different N-ACs, breakthrough calculations were performed taking the following parameter values: inside diameter of tube = 50 mm; bed length, $L = 1.8$ m; voidage of bed, $\varepsilon = 0.5$; superficial gas velocity, $u = 0.05$ m/s (at inlet), interstitial velocity, $v = 0.1$ m/s. The mass of adsorbent packed in the tube is 2 kg. For the pulse chromatographic simulations, a pulse injection time $t_0 = 10$ s was used. We use the dimensionless time, $\tau = \frac{tu}{L\varepsilon}$, obtained by dividing the actual time, t , by the characteristic time, $\frac{L\varepsilon}{u}$, when plotting simulated breakthrough curves [8].

Notation

b	Langmuir-Freundlich constant for species i at adsorption site A, $\text{Pa}^{-\nu}$
c_i	molar concentration of species i in gas mixture, mol m^{-3}
c_{i0}	molar concentration of species i in gas mixture at inlet to adsorber, mol m^{-3}
E	energy parameter, J mol^{-1}
L	length of packed bed adsorber, m
p_i	partial pressure of species i in mixture, Pa
p_t	total system pressure, Pa
q_i	component molar loading of species i , mol kg^{-1}
Q_{st}	isosteric heat of adsorption, J mol^{-1}
R	gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
t	time, s
T	absolute temperature, K
u	superficial gas velocity in packed bed, m s^{-1}

Greek letters

ε	voidage of packed bed, dimensionless
ρ	framework density, kg m ⁻³
ν	Freundlich exponent, dimensionless
τ	time, dimensionless

References

- [1] Li L, Wang X, Liang J, Huang Y, Li H, Lin Z, et al. Water-Stable Anionic Metal–Organic Framework for Highly Selective Separation of Methane from Natural Gas and Pyrolysis Gas. *ACS Appl Mater Interfaces* 2016.
- [2] Krishna R, Long JR. Screening Metal–Organic Frameworks by Analysis of Transient Breakthrough of Gas Mixtures in a Fixed Bed Adsorber. *J Phys Chem C* 2011;115:12941–50.
- [3] He Y, Zhang Z, Xiang S, Fronczek FR, Krishna R, Chen B. A Microporous Metal–Organic Framework for Highly Selective Separation of Acetylene, Ethylene, and Ethane from Methane at Room Temperature. *Chem – A Eur J* 2012;18:613–9.
- [4] Wang D, Liu B, Yao S, Wang T, Li G, Huo Q, et al. A polyhedral metal-organic framework based on the supermolecular building block strategy exhibiting high performance for carbon dioxide capture and separation of light hydrocarbons. *Chem Commun* 2015;51:15287–9.
- [5] Wang D, Zhao T, Cao Y, Yao S, Li G, Huo Q, et al. High performance gas adsorption and separation of natural gas in two microporous metal-organic frameworks with ternary building units. *Chem Commun* 2014;50:8648–50.
- [6] Yao S, Wang D, Cao Y, Li G, Huo Q, Liu Y. Two stable 3D porous metal–organic frameworks with high performance for gas adsorption and separation. *J Mater Chem A* 2015;3:16627–32.
- [7] Myers, A. L.; Prausnitz, J. M. Thermodynamics of Mixed Gas Adsorption, *A.I.Ch.E.J.* **1965**, *11*, 121-130.
- [8] Krishna, R. Methodologies for Evaluation of Metal–Organic Frameworks in Separation Applications, *RSC Adv.* **2015**, *5*, 52269-52295.

[9] Krishna, R. The Maxwell-Stefan Description of Mixture Diffusion in Nanoporous Crystalline Materials, *Microporous Mesoporous Mater.* **2014**, *185*, 30-50.