Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information to:

On the potential of phase-change adsorbents for CO_2 capture by temperature swing adsorption

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1 Adsorption properties of zeolite 13X

The adsorption equilibrium data of CO_2 on zeolite 13X have been reported in Hefti et al.[1] and were described successfully with the Sips isotherm model:

$$n = \frac{n^{\infty}\,(bp)^{s}}{1+(bp)^{s}} \tag{S1}$$

where n is the adsorbed phase concentration, p is the CO_2 pressure, and n^{∞}, b, and s are functions of temperature as shown in equation (S2). The parameter values are listed in Table S1.

$$\begin{aligned} n^{\infty}(T) &= n^{\infty}_{\mathrm{ref}} \exp\left(\chi\left(\frac{T}{T_{\mathrm{ref}}}-1\right)\right) \\ b(T) &= b_0 \exp\left(\frac{Q_b}{RT}\right) \\ s(T) &= s_{\mathrm{ref}} + \alpha\left(\frac{T}{T_{\mathrm{ref}}}-1\right) \end{aligned} \tag{S2}$$

Table S1 Sips parameter estimates for pure component adsorption of CO_2 on 13X and heat of adsorption.[1]

n^{∞}	[mol/kg]	$n^{\infty}_{\mathrm{ref},i}$	[mol/kg]	7.268	±1e-3
		χ	[–]	-0.61684	±3e-4
b	[bar^{-1}]	$b_{0,i}$	[bar^{-1}]	1.129e-4	±1e-7
		$Q_{\mathrm{b},i}$	[kJ/mol]	28.389	±2e-3
s	[–]	$s_{\mathrm{ref},i}$	[–]	0.42456	±8e-5
		α	[–]	0.72378	±7e-5
$\Delta\overline{H}_{\mathrm{ads}}$	[kJ/mol]			37	

2 Temperature and composition profiles

Temperature and composition profiles for exemplary operating conditions resulting in an adsorption temperature of 305 K and in a desorption temperature of 410 K are shown in Figure S1. Let us start this analysis at the end of the adsorption step, i.e., with the column saturated with the feed mixture at 305 K. As it is heated, CO_2 desorbs until it completely step the nitrogen contained in the gas phase (see Figure S1). A plateau in the temperature profile is observed at about 380 K and 340 K for MOF-Mn and MOF-Fe, respectively. In fact, due to the presence of a step in the isotherm, most of the CO_2 is desorbed within a narrow temperature range in the vicinity of the step temperature at 1 bar ($T^{\mathrm{des}}_{\mathrm{step}}$). While the heating, cooling and pressurization steps are qualitatively similar for both materials, the exit composition profile of the adsorption step is noticeably different. In the case of MOF-Mn, a shock transition separates the initial state from the feed state, while in the case of MOF-Fe, a shock-wave-shock transition is observed (note that the wave is fairly flat). The corresponding performances are reported in Table S2. Since the bed density, the specific heat and the cyclic capacity for the chosen operating conditions are similar for both materials,

Table S2 Performance indicators of the cycles shown in Figure S1 predicted by the shortcut model.

		MOF-Mn	MOF-Fe
CO_2 purity, Φ	[−]	0.981	0.978
CO_2 recovery, r_{TSA}	[−]	0.986	0.56
Productivity, Pr	$[kg_{CO_2}/(m^3h)]$	67.3	61.1
Energy cons. e_{TSA}	$[MJ/kg_{CO_2}]$	3.34	3.68

the resulting purity, productivity and energy consumption are also similar. A striking difference is observed in the achieved recovery: while MOF-Mn recovers over 98 %, MOF-Fe achieves only a recovery of 56 % due to the disperse composition front that evolves during the adsorption step.

The shortcut model profiles are compared to those predicted by the detailed model for the same operating conditions. A good agreement between the two models is observed during the heating, cooling and pressurization steps for both MOF-Mn and MOF-Fe. There are, however, significant differences during the adsorption step, where the breakthrough of CO_2 occurs earlier according to the detailed model due to the dispersed front predicted by it because of the finite heat and mass transfer rates. Nevertheless, the rather good agreement supports the use of the shortcut model as a tool to perform a preliminary screening of the materials.

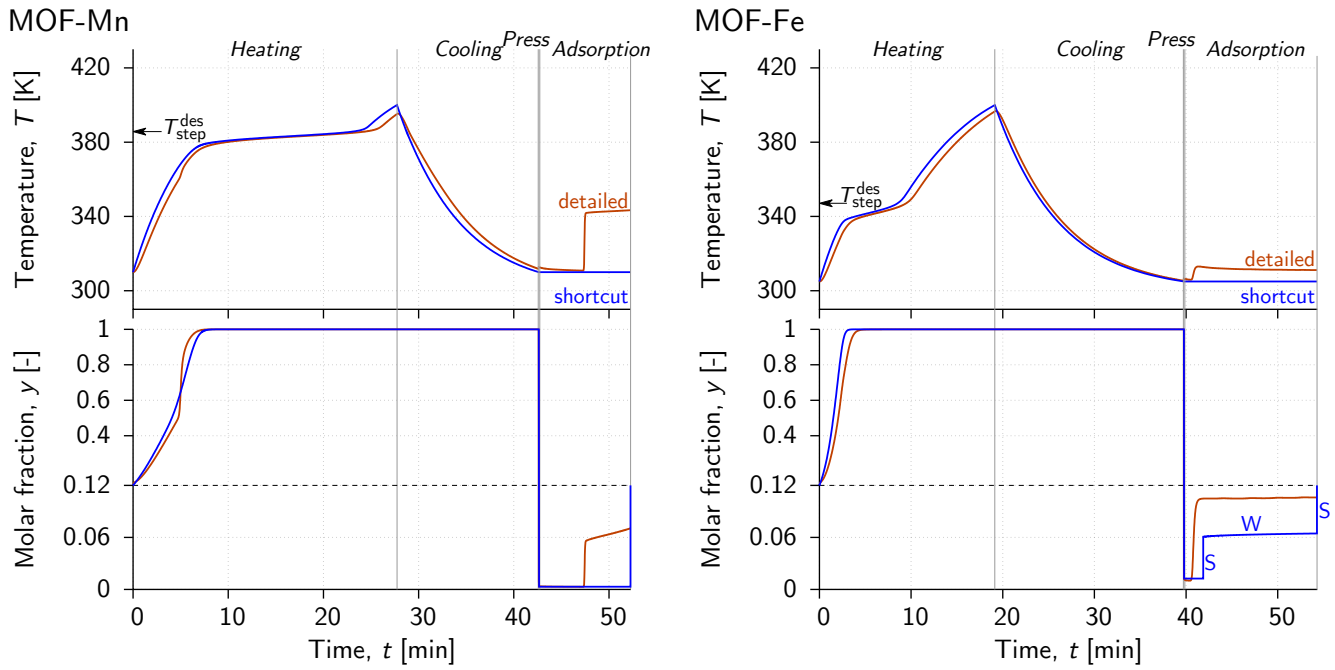

Figure S1 Temperature and composition profiles at cyclic steady state predicted by the shortcut and detailed model for MOF-Fe. The operating conditions are such that an adsorption temperature of $T_{ads} = 305\,K$ and a desorption temperature of $T_{ads} = 410\,K$ are achieved with the shortcut model.

References

[1] M. Hefti, D. Marx, L. Joss, and M. Mazzotti. Adsorption equilibrium of binary mixtures of carbon dioxide and nitrogen on zeolites ZSM-5 and 13X. *Microporous Mesoporous Mater.*, 215:215–228, 2015.