

Adsorption

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Adsorption selectivity of CO₂ over CH₄, N₂ and H₂ in melamine–resorcinol–formaldehyde xerogels

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Abstract

Sorptive selectivity of melamine–resorcinol–formaldehyde xerogels, towards CO₂, CH₄, N₂ and H₂, is reported, where all systems demonstrate potential for selective adsorption of CO₂ from corresponding binary gas mixtures. Selected gas mixtures represent important gas separation applications found in industry, i.e. CO₂ removal from power plant flue gases (CO₂–N₂), sour gas sweetening (CO₂–CH₄), and separation of species in the water–gas shift reaction (CO₂–H₂). All materials tested exhibit microporous character, enhancing adsorption of small molecules, however, it is the inclusion of a nitrogen-rich material into the gel matrix that results in enhanced selectivities for these systems. Despite the porous character of the gels, under the test conditions used to simulate industrial parameters, all three balance gases, i.e. H₂, N₂ and CH₄, showed low affinities for the xerogels, while CO₂ adsorption was notably higher and increased with the inclusion and increased concentration of melamine. Ideal adsorbed solution theory was used to demonstrate significant differences in adsorption uptake, especially for CO₂–CH₄, and high selectivities for CO₂ over N₂. In all cases, selected xerogels exhibited industrially relevant adsorption timescales for CO₂ over competitor gases, demonstrating the potential of these materials for the selective adsorption of CO₂ from process streams.

Keywords CCS · Sorbents · Gravimetry · Kinetics · IAST

1 Introduction

CO₂ is considered an important pollutant species, due to its major impact within global warming and climate change (IPCC fifth assessment report: climate change 2014 synthesis report 2014). According to the Emission database for global atmospheric research, the World's total CO₂ emissions in 2014 were 35.6 billion tonnes, which is 49% more than the total emissions in 1990. Power plants are one of the major contributors to CO₂ emissions; flue gases from power plants comprise varied compositions, depending on the type of fuel used but, typically, CO₂ levels will be 7–14% for coal fired and 4% for gas fired sources. The remaining

gas balance is composed mainly of N₂ and small quantities of other gas/vapour components. Flue gases from power plants are usually treated, using a series of chemical processes and scrubbers, to remove pollutants; while fabric filters or electrostatic precipitators are used to remove solid particles, specific units are used to remove sulphur dioxide (SO₂), which is typically a by-product of coal combustion. CCS technologies have been developed to remove CO₂ from these pre-treated flue gases before they are released to the atmosphere. Nowadays, most CO₂ removal processes use liquid absorbents, such as amines, to clean CO₂ from exhaust gases; however, these 'scrubbing technologies' are not without associated hazards (Rochelle 2012).

Within the design of experimental systems to determine the efficacy of developed carbon capture technologies, it is important to include real flue gas parameters, for example the fact that flue gases are composed of a mixture of different species, e.g. NO_x, SO_x, CO, CO₂, N₂ and solid particles, dependent on the fuel used and plant configuration. As stated above, NO_x and SO_x, as well as solid particles, are generally removed by ceramic filters, catalysed filters or dry scrubbers (Sinha 1999; Shemwell et al. 2002; Elliott

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and Startin 2010; Amrhein et al. 1993); however, multiple components still remain in the stream to be treated. Consequently, it is imperative that ‘real-life’ simulation includes competitive gas challenging of developed systems, where several components are used in the treatment stream. However, such adsorption studies cannot simply transition from single to multitudinous components, therefore, it is necessary to develop an understanding of the processes occurring during competitive adsorption by considering competing mixtures of two components, previously studied as single species. Working on the basis that the gas present at the greatest proportion, on all bases, is N_2 , this is chosen as the balance species to challenge the materials studied here. Consequently, in this study, CO_2 is always present, at a fixed proportion, and the balance is composed of N_2 , allowing the selectivity of the tested melamine–resorcinol–formaldehyde (MRF) xerogels, towards CO_2 over N_2 , to be determined. A complementary process to carbon capture is gas sweetening, where hydrogen sulphide (H_2S), which is considered sour gas, is separated from a process gas stream, and within such processes CO_2 removal is also required. Consequently, sour gas sweetening requires separation of H_2S and CO_2 from CH_4 .

Due to their inherent chemistry, which closely mimics that employed in amine scrubbing techniques, MRF xerogels could potentially be applied to separations such as those outlined above. Solvents currently used in sour gas sweetening and carbon capture processes are required to have specific characteristics, including a high selectivity for CO_2 , H_2S and other sulphur compounds, low uptake of hydrocarbons, high thermal stability, low energy penalty for regeneration, non-corrosivity, and low solvent vapour pressure in order to minimize solvent losses. MRF xerogels, by virtue of their form and chemistry, possess many of the aforementioned requirements (Principe et al. 2018). Notably, being solid sorbents, MRF xerogels offer minimal material losses, compared with liquid solvents and the ability to be regenerated by pressure swing techniques. Added benefits of immobilizing the nitrogen functionalities within the materials are reduced toxicity and a physical driving force for adsorption, reinforced by a low heat of adsorption for CO_2 (Principe et al. 2018). Due to the similar interactions exhibited between CO_2 and H_2S with amine solvents, it is reasonable to postulate that sorbents with enhanced performance for carbon capture would offer similar capacity for H_2S and other sulphur compounds, thereby removing the need for liquid amine sorbents in gas sweetening processes, where they currently play an integral role (Belmabkhout et al. 2009; Burchell et al. 1997; Huang et al. 2003; Sartori et al. 1987).

A third separation process to consider is that used in pre-combustion systems to remove CO_2 from H_2 ; example industries include gasification or steam reforming, where the fuel, natural gas or coal, is treated prior to combustion,

creating H_2 and CO , the latter being used to increase the yield of H_2 via the water–gas shift reaction, creating the by-product of CO_2 , up to 20% by volume, in the process. It is, therefore, necessary to separate CO_2 from H_2 before the stream is fed to the gas turbines, and industry again utilises scrubbing technologies to this end. Ideally it would be possible to displace this existing technology and the associated hazards (Rochelle 2012), by utilising an alternative sorption system, such as solid bed adsorption.

It has been suggested that any sorbent used for post-combustive CO_2 removal must demonstrate high adsorption capacity at low relative concentrations of CO_2 , while exhibiting selective adsorption in industrially relevant time-scales and a low heat of regeneration (Hao et al. 2013; Yang et al. 2017). This last factor has been previously reported for MRF xerogels (Principe et al. 2018), and this work seeks to address in the present study. It should be noted that, in addition to our own previous reports, other researchers have indicated that modification of sorbents to include nitrogen rich surface moieties can increase the uptake of CO_2 and other acidic gases (Heidari et al. 2014; Chen et al. 2016). While previous researchers have focussed on activation of synthetic mixtures rich in nitrogen-containing species and a carbon-based precursor (Chen et al. 2016; Adeniran and Mokaya 2016) or activation in the presence of nitrogen-rich gases (Heidari et al. 2014), this work looks to incorporate the nitrogen into the backbone of the structure akin to the modified linker chemistry utilised in MOF systems (Molavi et al. 2018a; Taylor et al. 2018). This work also provides evidence towards the ongoing dichotomy within the literature related to the usefulness of nitrogen incorporated into sorbent structures. Previous observations have been made that chemical modification is less useful for higher operating temperatures, where physically activated samples perform better (Manyà et al. 2018), while others (Molavi et al. 2018b) report that amine groups were observed to increase CO_2 adsorption with higher CO_2/CH_4 selectivity that increased with increasing nitrogen content in modified MOFs. Further still, earlier reports found negligible effects from the inclusion of nitrogen functionalities in sorbents (Adeniran and Mokaya 2016; Sevilla et al. 2013; Kumar et al. 2015), instead suggesting that ultra-micropores control CO_2 adsorption behaviour, including kinetic selectivity in CO_2/N_2 mixtures, while surface chemistry helps to control thermodynamics selectivity in such systems (Shahkarami et al. 2015). Consequently, the knowledge base requires additional evidence to develop a clearer understanding of the underlying mechanisms at play in competitive CO_2 adsorption systems.

MRF xerogels are a modified form of formaldehyde–resorcinol (RF) resins; a family of organic materials that have potential application in a number of processes, including catalysis, thermal insulation, carbon capture, filtration and energy storage. The parent systems often

exhibit large pore volumes, low densities (which can affect requirements for packed beds), high surface areas but a non-crystalline structure. It has been shown that these characteristics can be tailored towards a specific application through control of the synthesis parameters and procedure (Mirzaeian and Hall 2009). The interconnected, solid structures arising from their growth and gelation pathways means that xerogels have received significant attention for their use in gas treatment processes, usually as a result of their adsorptive capacities. The incorporation of nitrogen-rich structures, such as melamine, into xerogels has been shown to modify the surface chemistry of the final solid material (Principe and Fletcher 2018), offering attractive interactions with acidic gases, by virtue of the basic functionalities incorporated by the amine precursor. Tuning the number and availability of these Lewis acid–base interactions can enhance acidic gas adsorption, e.g. CO₂ and H₂S, thereby increasing sorbent capacity for these gases. In all three of the applications described above, a major drawback to the separation methods currently employed is the high energy penalty for sorbent regeneration (Leung et al. 2014). MRF xerogels, by contrast, have been shown to be easily regenerable, with a low energy requirement and fast kinetics of sorption for CO₂, as well as good thermal stability for single gas components (Principe et al. 2018). However, in multicomponent gas separations, it is also necessary to demonstrate that these sorbents exhibit low affinities for the balance gases, i.e. N₂, CH₄ or H₂, to accomplish a high degree of separation; in this study, we present the results of binary challenges for MRF sorbents, selected on the basis of their previous affinity for CO₂ in a single component system, utilising ideal adsorbed solution Theory to determine the relative adsorbed phases from the mixtures used. The data obtained demonstrate the potential of these materials for multicomponent separations in a range of applications.

2 Experimental

2.1 Sample selection

Four xerogel samples, which all exhibited high thermal stability, were used in this study; selected for their promising CO₂ adsorption behaviour, as identified in an earlier study (Principe et al. 2018). As a series of materials, they represent three melamine loadings: zero, low (1%) and high (10%), where previous work has shown limitations to incorporation of higher quantities of melamine into the base RF gels (Principe and Fletcher 2018). The suits of materials also presented different catalyst quantities, and reactant ratios; sample nomenclature was in the form of MRF_X_Y_Z, where X is percentage of added melamine, Y is R/C ratio and Z is R/F ratio. The selected samples offer a range of surface areas and pore volumes but exhibit similar micropore volumes; more importantly, each was shown to exhibit moderate CO₂ uptake in static adsorption mode. Properties for the four samples are shown in Table 1, which presents data reported previously (Principe et al. 2018).

2.2 Materials and synthesis

Resorcinol (ReagentPlus, 99%), aqueous formaldehyde solution (37 wt% F, stabilized with 10–15% methanol, pH 2.8–4.0), sodium carbonate (anhydrous, ≥ 99.5%), melamine (99%) and acetone (ACS reagent, ≥ 99.5%) were all purchased from Sigma-Aldrich. Compositions of MRF solutions were calculated using the molar ratios of R/F and R/C, sodium carbonate was used as catalyst for all samples. Solution volume was fixed at 30 mL and total solid content (i.e. R, M, F and carbonate) was fixed at 20% w/v, which corresponds to a solid content of 6 g. The chosen parameters of study, R/C, R/F and [M], were varied as shown in Table 2. Note that [M] refers to the percentage of resorcinol substituted by melamine, therefore R/F denotes (R+M)/F, but for simplification it will subsequently be named R/F.

Table 1 Total (BET), non-micropore and micro surface area, total pore and micropore volume and pore size obtained for MRF xerogels synthesised in this study (Principe et al. 2018)

Sample	Surface area (BET and t-plot)			Pore volume		BJH	
	Total (m ² /g)	non-micropore (m ² /g)	Micropore (m ² /g)	Total (cm ³ /g)	Micropore (cm ³ /g)	Pore size (nm)	Density [†] (cm ³ /g)
MRF0_100_0.25	476	369	106	0.33	0.05	3	0.76 (03)
MRF0_200_0.25	464	365	99	0.60	0.04	5	0.81 (03)
MRF1_400_0.5	256	187	69	0.65	0.03	11	0.79 (03)
MRF10_200_0.25	194	143	61	0.44	0.03	12	1.43 (09)

Table 2 Melamine–resorcinol–formaldehyde synthesis variables studied in this work (resorcinol+melamine/catalyst ratio, resorcinol/formaldehyde ratio and melamine content)

Sample	(R+M)/C	R/F	[M]%
MRF0_100_0.25	100	0.25	0
MRF0_200_0.25	200	0.25	0
MRF1_400_0.5	400	0.5	1
MRF10_200_0.25	200	0.25	10

2.3 Xerogel characterization

A Micromeritics ASAP 2420 system was used to obtain surface areas and porosities via nitrogen sorption equilibrium measurements at 77 K, using ~0.5 g sample. The sample was first degassed, at 393 K for 120 min, before testing the nitrogen sorption capacity. Surface areas were calculated by applying Brunauer–Emmett–Teller (BET) theory combined with Rouquerol correction for BET application to microporous materials. Pore volumes were calculated from the equilibrium measurement of nitrogen adsorbed at ~0.98 bar (i.e. the saturation vapour pressure of N₂ at 77 K). The pore size distribution and average pore size were obtained by application of the Barret–Joyner–Halenda (BJH) method, while the t-plot method was used to calculate the micropore volume and micropore surface area of samples.

An intelligent gravimetric analyser (IGA) was used to perform adsorption capacity tests and to determine kinetics of adsorption. Both IGA models 001 and 003 supplied by Hiden Isochema Ltd were used in this study. Gas adsorption tests were performed on selected MRF samples using N₂, CH₄, H₂ and CO₂, the latter gas being that of major interest in this work, as a common factor in the three separation processes outlined above. Adsorption tests were conducted at two chosen temperatures (0 °C and 60 °C), with either a static or dynamic flowing arrangement.

Thermodynamic analysis by ideal adsorbed solution theory (IAST) was used to determine the equilibrium composition of the adsorbed phase and bulk gas, for binary systems (Myers 1965; Hand et al. 1985). It is important to note that IAST is based on the thermodynamic equilibrium properties of the pure components of the system studied, and allows prediction of the selectivity of adsorbents, including porous materials, to separate a particular mixture. Based on Raoult's Law for vapour-liquid equilibrium of ideal solutions, which assumes negligible interactions between molecules and that, via consideration of the chemical potential of each phase, the components of an ideal mixture of liquids each exhibit a partial vapour pressure, P_i , equal to the product of the vapour pressure of the pure component, P_i^o , and its mole fraction, X_i , in the adsorbed mixture i.e. $P_i = P_i^o \cdot X_i$. Note that y_i is used to denote that mole fraction of species I in the

adsorptive phase. The adsorbed phase is assumed to behave as an ideal mixture, which is an accurate enough description of the mixture of simple gases adsorbed in microporous materials. Spreading pressure, ω , is a thermodynamic property of the adsorbed phase (J/m^2), used to define the vapour pressure, P_i^o :

$$\omega(P_i^o) = \frac{RT}{A_S} \int_0^{P_i^o} \frac{N_i^o(P)}{P} dP \quad (1)$$

where R is the universal gas constant, T is temperature, A_S is surface area of the material, and N_i^o is molar adsorbed amount (obtained from the adsorption isotherm) at pressure P . Applying this relationship to a binary system, in combination with Raoult's Law, gives two equations, one for each component. Adsorption data was processed here by applying the Langmuir isotherm model for each pure component to obtain the individual molar uptake, giving K (bar^{-1}), the constant of the Langmuir isotherm, and C_m (mol/g), the monolayer uptake. Combining this with Eq. 1 for a binary system, gives six equations with six unknown parameters (Eqs. 2 to 7):

$$Py_1 = P_1^o(T, \omega) \cdot X_1 \quad (2)$$

$$Py_2 = P_2^o(T, \omega) \cdot X_2 \quad (3)$$

$$y_2 = 1 - y_1 \quad (4)$$

$$X_2 = 1 - X_1 \quad (5)$$

$$\omega(P_1^o) = \frac{RTC_{m1}}{A_S} \ln(1 + K_1 P_1^o) \quad (6)$$

$$\omega(P_2^o) = \frac{RTC_{m2}}{A_S} \ln(1 + K_2 P_2^o) \quad (7)$$

Solution of these equations gives the adsorbed quantity for each component in the adsorbed phase as mole fractions (X_i):

$$\frac{1}{N_t} = \frac{X_1}{N_1^o} + \frac{X_2}{N_2^o} \quad (8)$$

where N_i^o is the amount adsorbed for each pure component in the adsorbed phase, and N_t is the total amount adsorbed. The selectivity, S , of the adsorption process is subsequently defined as:

$$S_{12} = \frac{X_1 y_2}{X_2 y_1} = \frac{P_2^o}{P_1^o} \quad (9)$$

It is important to highlight that pure component isotherms can generally be measured more accurately than binary mixtures, due to issues associated with determining the composite make-up of the adsorbed phase from a binary mixture. Pure adsorption isotherms can provide information for simple checks on the accuracy of binary equilibria isotherms via utilisation of appropriate isotherm models, such as IAST (Talu 1998). In such approaches, it is imperative that (1) the amount adsorbed for a binary mixture approaches the respective pure component value as the mole fraction approaches unity, and (2) as the pressure approaches zero, regardless of the binary composition, the selectivity approaches the ratio of the Henry's law constants of the pure components. It should also be noted that the accuracy of IAST is limited in the cases of (1) high surface heterogeneity, which may occur here with the targeted inclusion of nitrogen functionalities, and (2) of one component from a binary mixture being considerably more strongly adsorbed than another, which also may be related to surface chemistry (Myers 1965). However, the model does provide a comparative method to analyse the binary systems studied here, allowing selection of the most highly selective materials and potential directing of future materials development, while the absolute values determined for selectivity would require validation via analytical methods.

3 Results and discussion

3.1 Post-combustion carbon capture: adsorptive selectivity of CO₂ over N₂

The composition of the CO₂/N₂ gas mixture used for competitive adsorption was 15:85 on a pressure basis. This concentration of CO₂ sits at the higher end of the range of concentrations measured within flue gases but allows more accurate determination of competitive effects given that the higher CO₂ concentration will result in a smaller margin of error in the adsorption isotherm of the gas mixture.

All adsorption tests for CO₂ vs N₂ presented here were performed at 60 °C; as this temperature is indicative of the waste flue streams that require treatment within post-combustive gas processing. Also, at this temperature, the adsorption of N₂ is expected to be nearly negligible. N₂ possesses a quadrupole, but no defined charge moments, and the fluctuations of this quadrupole will increase with temperature, meaning that its adsorption potential for physisorption is very low. Contrastingly, CO₂ molecules are linear, and the two highly electronegative oxygen atoms attract electron density from the covalent bonds formed with the comparatively electropositive carbon atom, thereby creating dipoles within the molecule. This enhances interaction with the xerogel surface, which is composed of electron-rich

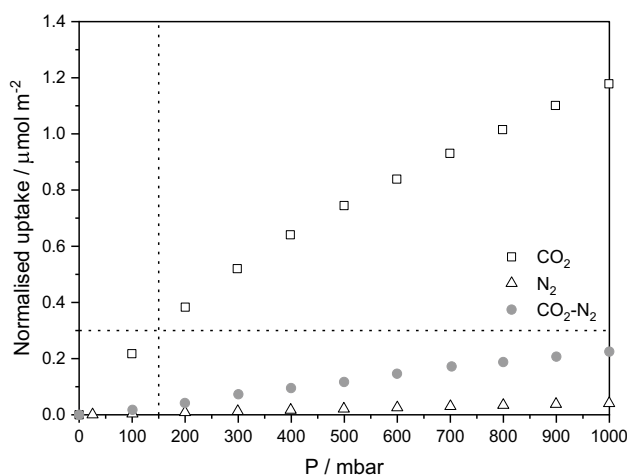


Fig. 1 Gravimetric gas adsorption uptake of single component gases (CO₂ and N₂) and a binary gas mixture (15% CO₂:85% N₂) at 60 °C under flow conditions of 200 cm³ min⁻¹ for MRF0_100_0.25. Uptake normalised by dividing molar uptake by S_{BET}; adsorption data only shown to simplify presentation (desorption data available in Electronic Supporting Information)

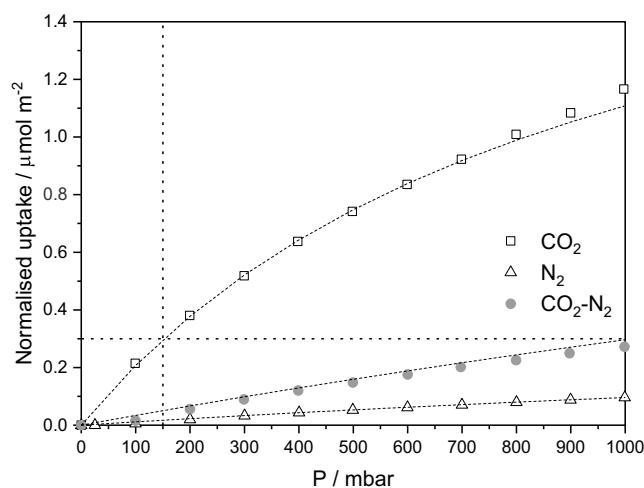


Fig. 2 Gravimetric gas adsorption uptake of single component gases (CO₂ and N₂) and a binary gas mixture (15% CO₂:85% N₂) at 60 °C under flow conditions of 200 cm³ min⁻¹ for MRF0_200_0.25. Uptake normalised by dividing molar uptake by S_{BET}; adsorption data only shown with associated fits (dashed lines) to simplify presentation (desorption data available in Electronic Supporting Information)

aromatic arrangements, while the incorporation of nitrogen in the xerogel structure, especially those in the ring (melamine), provide additional interaction sites for CO₂, through acid–base interactions, thus, enhancing adsorption. For these reasons, it is expected that low N₂ uptake would be observed at this temperature, favouring the comparative adsorption of CO₂.

Figures 1, 2, 3 and 4 show the adsorption isotherms obtained, for both the single components and binary gas

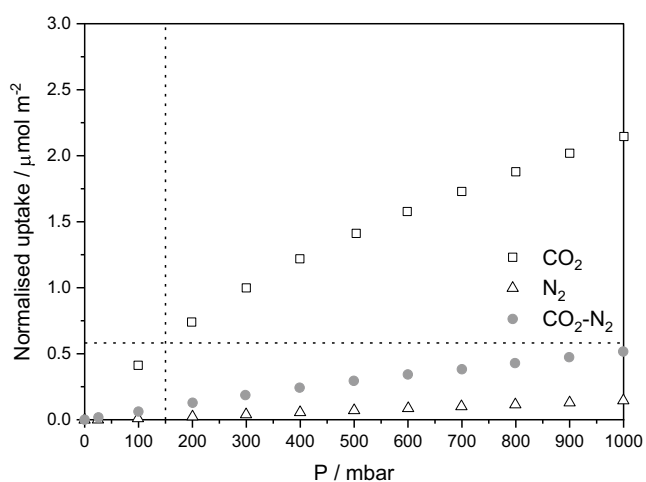


Fig. 3 Gravimetric gas adsorption uptake of single component gases (CO_2 and N_2) and a binary gas mixture (15% CO_2 :85% N_2) at 60 °C under flow conditions of $200 \text{ cm}^3 \text{ min}^{-1}$ for MRF1_400_0.5. Uptake normalised by dividing molar uptake by S_{BET} ; adsorption data only shown to simplify presentation (desorption data available in Electronic Supporting Information)

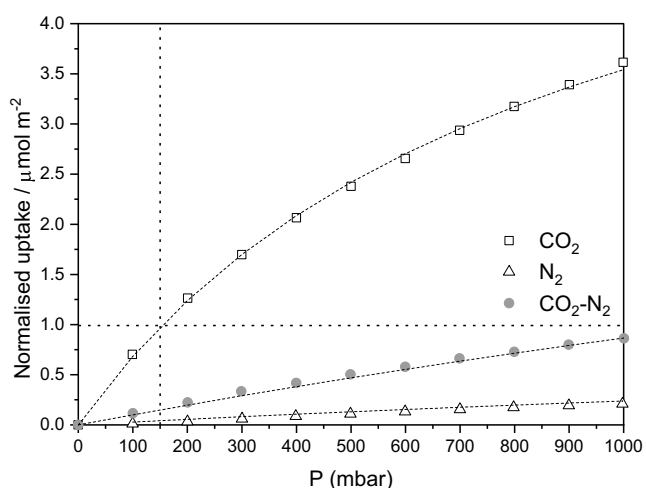


Fig. 4 Gravimetric gas adsorption uptake of single component gases (CO_2 and N_2) and a binary gas mixture (15% CO_2 :85% N_2) at 60 °C under flow conditions of $200 \text{ cm}^3 \text{ min}^{-1}$ for MRF10_200_0.25. Uptake normalised by dividing molar uptake by S_{BET} ; adsorption data only shown with associated fits to simplify presentation (desorption data available in Electronic Supporting Information)

mixture described above, for the four selected MRF xerogel samples. Gravimetric sorption measurements were corrected to account for the fact that they are conducted under flowing gas conditions rather than in a static environment (see Supporting Information for further details). These calibrations allow determination of corrected weight values, which account for the uplift generated at specific pressures. It is also important to note that the concentrations presented in these graphs have been normalized by dividing through

by the available surface area (m^2) for the selected material (Table 1). The intersection of the pure CO_2 isotherm curve, with a vertical line at 150 mbar, gives the concentration of pure CO_2 adsorbed at that pressure; this is relevant as gives a validity check between the uptake of the pure gas and that obtained, at a total pressure of 1000 mbar but a partial pressure of 150 mbar CO_2 .

Figure 1 shows adsorption isotherms for MRF0_100_0.25, tested with both pure CO_2 and N_2 , and the binary mixture (15 CO_2 :85 N_2). As expected, at the temperature used (60 °C), the pure N_2 uptake is very low compared to that of pure CO_2 . Therefore, it is expected that the xerogel would selectively adsorb CO_2 from the mixture. While the binary mixture gives an isotherm lower than that obtained for pure CO_2 , it should be borne in mind that the partial pressure of CO_2 is only 150 mbar within the mixture. Comparison of the uptakes at 150 mbar pure CO_2 and 1000 mbar of the binary mixture supports the hypothesis that N_2 adsorption is low for this system and it is not enhanced by the presence of CO_2 . Thermodynamically, the system is controlled by the pressure of CO_2 within the gas phase, for both single and binary component systems, however, it is also important to consider the effect that the competing gas has on the kinetic behaviour of the system. For pure CO_2 adsorption on MRF0_100_0.25, each pressure increment/decrement within the isotherm took an average of ~ 10 – 20 min to fully equilibrate, as observed from the relaxation to the plateau in the mass-time profile. By comparison, the equilibration times of the binary mixture (CO_2 – N_2), were of a comparable timescale, at ~ 10 – 12 min for most pressure increments/decrements. While it may be conceived that this equilibration time might be slightly increased due to the reduction in the mean free path of the targeted species, the results obtained here indicate that CO_2 is adsorbed selectively on the xerogel in a timeframe similar to the pure gas, which has positive implications for the commercial use of such materials.

Figure 2 shows that the total uptake at 1000 mbar, for adsorption of the binary gas mixture on MRF0_200_0.25, again corresponds to a similar mass to that of 150 mbar of the pure gas, and that the overall uptake is similar to the quantity adsorbed for MRF0_100_0.25. This is expected as the textural characteristics of the two materials are very similar. However, in this case, it was observed that N_2 sorption data, particularly that obtained for the desorption branch, did not equilibrate fully at low pressure within the maximum timescale used (3 h), hence, hysteresis is observed for this pure component isotherm. The results suggest that, for this material, while N_2 adsorption is small, there may be kinetic limitations that mean it is retained in the structure once adsorbed on a timescale beyond that which would be useful for cycling systems. Such behaviour is not observed for MRF0_100_0.25, which may be ascribed to individual differences in the specific micropore

dimensions for the small contributions of these pores in each material, and may exclude CO₂ during the sorption process (3.189 Å × 3.339 Å), while admitting, but retaining the smaller N₂ molecule (2.991 Å × 3.054 Å). Again, comparison of the equilibration times of the pure isotherm for CO₂ and those obtained for the binary mixture shows similar behaviour for MRF0_200_0.25. The pure CO₂ isotherm equilibrates averagely in < 3 min for most pressure increments/decrements, while the isotherm steps for the binary gas mixture achieve equilibrium in an even shorter timescale, on average (~2 min). This can be explained by considering only the low pressure equilibration times for pure CO₂; at pressures below 300 mbar, the equilibration time is ~ 1 min, therefore, the quicker equilibration can be ascribed to the lower relative concentration of CO₂ in the mixture.

The previous results, for MRF0_100_0.25 and MRF0_200_0.25, demonstrate a clear selectivity of CO₂ over N₂ with comparable adsorption kinetics for the relative proportion of gas for unmodified RF gels. Thereby providing a benchmark against which the incorporation of melamine can be tested by considering the results obtained for MRF1_400_0.5 and MRF10_200_0.25 xerogels. The incorporation of 1% melamine in MRF1_400_0.5 increases the concentration of CO₂ adsorbed to double that of MRF0_100_0.25 and MRF0_200_0.25; it can again be assumed that the gas adsorbed from the mixture is mostly CO₂, due to the limiting quantity being comparable to the pure system. The equilibration times for both the pure CO₂ isotherm and the mixture are similar. Most of the pressure steps for the pure CO₂ isotherm equilibrate in an average time of < 4 min, while the mixture does so in < 2 min, as detailed above this mirrors the faster times obtained at lower pressures for the pure gas. Hence, incorporation of a small quantity of nitrogen-rich melamine results in enhanced adsorption of CO₂ in a timescale comparable to the best performing unmodified material, which is of the order being sought by industry.

Continuing the trend of increased nitrogen content also increases the quantity of CO₂ adsorbed. The CO₂ uptake for MRF10_200_0.25 is approximately three times larger than that obtained for either MRF0 xerogels and 1.5 times that of the 1% melamine material. As for all other cases, the material exhibits a maximum uptake for the binary gas system, at 1000 mbar, close to that of the pure CO₂ isotherm at 150 mbar; gain suggesting negligible uptake of N₂ and selective adsorption of CO₂ MRF xerogels are, therefore, selective for CO₂ even in the presence of high concentrations of N₂. Equilibration times obtained for both the pure and binary gas mixture isotherms were again very similar, averaging < 3 min for CO₂ and ~ 1–2 min for the mixture, with the reduction ascribed to the lower concentration of CO₂. Again, the all N₂ equilibration times were observed to

be ~ 180 min on average, which is constant over all samples studied, where equilibration was obtained.

As detailed above, the adsorption uptakes for the gas mixture, at 150 mbar of CO₂ in a balance of N₂ are similar to the pure CO₂ results, for the same relative concentrations. Combined with the fact that N₂ is expected to exhibit a low uptake at 60 °C, an argument can be made for the assumption that CO₂ is selectively adsorbed from the gas stream. However, this should also be proven categorically, hence, ideal adsorbed solution theory (IAST), which relates the compositions of the adsorbed phase and the bulk gas phase, for binary systems, was used to confirm selectivity in these systems. IAST gives useful information about the selectivity of a given adsorbent in separating a desired component from a binary mixture; the model predicts the composition of the adsorbed phase in equilibrium, based on the thermodynamics of the process. The pure N₂ adsorption isotherms obtained in this study were fitted to the Langmuir isotherm in its linear form:

$$\frac{P}{C} = \frac{P}{C_m} + \frac{1}{KC_m}, \quad (10)$$

where P is the pressure at which the concentration (C) of gas adsorbed, K is the equilibrium constant of adsorption and C_m is the concentration adsorbed within the monolayer.

As stated previously, the system temperature was 60 °C, the mixture composition was 15% CO₂ and 85% N₂, and IAST was applied using the data obtained from the pure systems and using the parameters of the mixed adsorption measurement, allowing the equilibrium concentration at a system pressure of 1 bar to be obtained.

IAST could not be applied for MRF0_100_0.25 and MRF1_400_0.5 due to their significantly low N₂ uptakes where, as a consequence, the data did not fit the Langmuir isotherm well. Therefore, K and C_m could not be determined and IAST did not present a valid approach. The pure N₂ isotherm for MRF0_200_0.25 was fitted using Eq. 10 ($R^2=0.998$). The K and C_m values obtained were 0.2394 bar⁻¹ and 0.2304 mmol/g, respectively. Similarly, the pure CO₂ isotherm for this material was fitted ($R^2=0.998$), giving $K=1.071$ bar⁻¹ and $C_m=0.9946$ mmol/g.

The amount of CO₂ and N₂ adsorbed at equilibrium for MRF0_200_0.25, using IAST, were 0.127 and 0.027 mmol/g, respectively. Normalizing this value per m² of MRF0_200_0.25 surface area (464 m²/g), the concentrations were 5.8 × 10⁻⁵ mmol/m² for N₂ and 2.73 × 10⁻⁴ mmol/m² for CO₂. It is worth noting that the concentration calculated using IAST agrees with the CO₂ concentration calculated from the adsorption isotherm of the mixture, which was 2.72 × 10⁻⁴ mmol/m². The concentration of N₂ at equilibrium is very small, ~ 17.4% of the total adsorbed, which suggests that separation is also favoured thermodynamically,

giving a selectivity for CO₂ of 27%, and a mole fraction in the adsorbed phase of 0.824 for CO₂ and 0.176 for N₂.

The pure N₂ isotherm for MRF10_200_0.25 was fitted using Eq. 10 ($R^2 = 0.962$). The K and C_m values obtained were 0.2125 bar⁻¹ and 0.4615 mmol/g, respectively. Similarly, the pure CO₂ isotherm for this material was fitted ($R^2 = 0.999$), giving $K = 1.3316$ bar⁻¹ and $C_m = 1.1545$ mmol/g. IAST with MRF10_200_0.25 gives an adsorbed phase with mole fractions of 0.769 for CO₂ and 0.231 for N₂, and a selectivity of 18.9%. The concentration uptake (normalized for the sample surface area, 194 m²/g) is 9.09×10^{-4} mmol/m² at 150 mbar and 2.73×10^{-4} mmol/m² at 850 mbar, for CO₂ and N₂ respectively. The CO₂ concentration calculated with IAST agrees reasonably with the concentration obtained from the adsorption isotherm of the mixture, which was 9.52×10^{-4} mmol/m²; which is primarily comprised of CO₂ in the adsorbed phase. This shows that increasing melamine results in an increase of CO₂ uptake, and that MRF xerogels are potential materials for CO₂ separation from gas mixtures given their enhanced selectivity, both kinetically and thermodynamically.

Researchers have previously reported selective adsorption for CO₂ from N₂ for a wide range of materials. Chemically modified UiO-66 materials primarily adsorbed CO₂ via chemical interactions, some mildly reversible (Molavi et al. 2018a), and dependent on the specific nitrogen based moieties within the added structures; while providing enhanced interaction with the target gas, such interactions may impact on the recyclability of these materials. In contrast to the measurements undertaken in this study, the results reported were made at high pressures (up to 5 bar) and at ambient temperature (298 K); the materials showed better selectivity at lower pressure but total uptakes were markedly reduced. High selectivities have also been reported by other researchers for a variety of sorbents, for example binderless and exchanged microspheres (Yan et al. 2019), nitrogen-doped porous carbons (Wang et al. 2018), however, many systems have been tested at room temperature, i.e. subcritical conditions, which alters the adsorption mechanism and reduced the applicability of the results in higher temperature streams. Several reports have considered the supercritical conditions of real process streams, however, it is notable that the total uptakes were markedly reduced (Manyà et al. 2018; Deng et al. 2014; Hao et al. 2017), while other researchers have reported reduced selectivity at higher temperatures due to a greater temperature-dependence for CO₂ than N₂ at elevated temperatures (Landaverde-Alvarado et al. 2017). Such reduced CO₂ uptakes have also been observed for our systems, which will be limited to monolayer coverage and several of these materials exhibit uptakes in line with a single layer of adsorbate; these results suggest that the incorporation of nitrogen-rich precursors to the sorbent enhance CO₂ adsorption but, while there is excellent performance

in selective adsorption, improved uptake represents an area for improvement required for these materials to take them forward for deployment, however, this must be considered with respect to the limiting monolayer uptake under supercritical conditions.

3.2 Gas sweetening: adsorptive selectivity of CO₂ over CH₄

The single component CO₂ capacities for all four selected samples have been presented in the previous section, but here they are contrasted with pure component CH₄ isotherms and data obtained for the binary mixture of 15 CO₂:85 CH₄. As for N₂ adsorption, the affinity of MRF xerogels for CH₄ is expected to be low, given it only exhibits London dispersion forces and its resulting non-polar character. Figures 5, 6, 7, 8 and 9 show a comparison of adsorption uptakes for pure CO₂, pure CH₄ and the binary mixture of 15% CO₂ and 85% CH₄. Firstly, it is important to note that the CH₄ uptake is low in all cases, which is a beneficial characteristic for a sorbent that is to be used for gas sweetening. The adsorption uptake, in all cases, is again normalised on the basis of available surface area (Table 1) to allow direct comparison between materials.

Figure 5 shows adsorption uptakes for the pure components, CO₂ and CH₄, and the corresponding binary mixture on xerogel MRF0_100_0.25, which contains no melamine. As for the N₂ balanced systems, the uptake at ~1000 mbar of the binary gas mixture is almost the same as that observed at 150 mbar of the pure component CO₂ isotherm. Additionally, the equilibration times for both pure

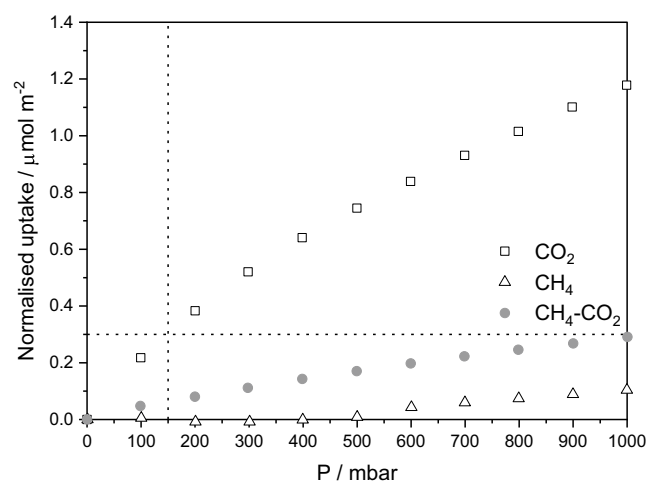


Fig. 5 Gravimetric gas adsorption uptake of single component gases (CO₂ and CH₄) and a binary gas mixture (15% CO₂:85% CH₄) at 60 °C under flow conditions of 200 cm³ min⁻¹ for MRF0_100_0.25. Uptake normalised by dividing molar uptake by S_{BET} ; adsorption data only shown to simplify presentation (desorption data available in Electronic Supporting Information)

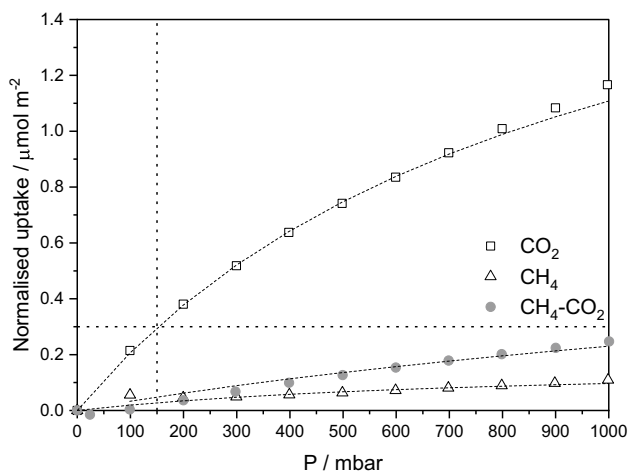


Fig. 6 Gravimetric gas adsorption uptake of single component gases (CO₂ and CH₄) and a binary gas mixture (15% CO₂:85% CH₄) at 60 °C under flow conditions of 200 cm³ min⁻¹ for MRF0_200_0.25. Uptake normalised by dividing molar uptake by S_{BET}; adsorption data only shown with associated fits to simplify presentation (desorption data available in Electronic Supporting Information)

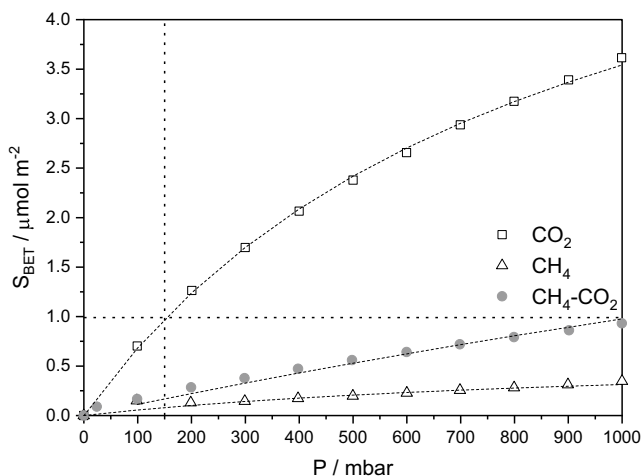


Fig. 8 Gravimetric gas adsorption uptake of single component gases (CO₂ and CH₄) and a binary gas mixture (15% CO₂:85% CH₄) at 60 °C under flow conditions of 200 cm³ min⁻¹ for MRF10_200_0.25. Uptake normalised by dividing molar uptake by S_{BET}; adsorption data only shown with associated fits to simplify presentation (desorption data available in Electronic Supporting Information)

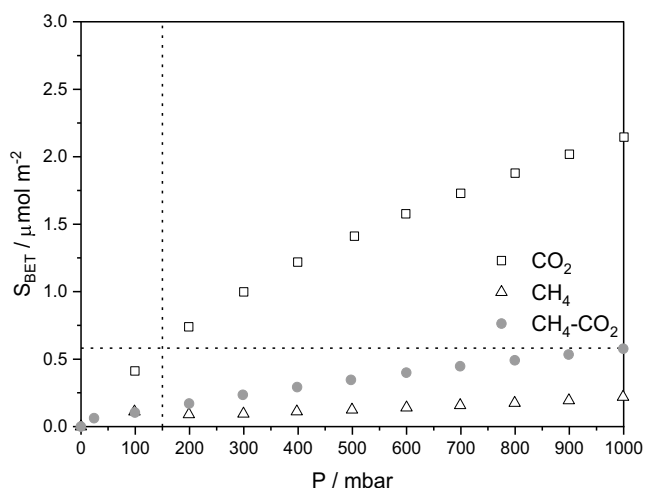


Fig. 7 Gravimetric gas adsorption uptake of single component gases (CO₂ and CH₄) and a binary gas mixture (15% CO₂:85% CH₄) at 60 °C under flow conditions of 200 cm³ min⁻¹ for MRF1_400_0.5. Uptake normalised by dividing molar uptake by S_{BET}; adsorption data only shown to simplify presentation (desorption data available in Electronic Supporting Information)

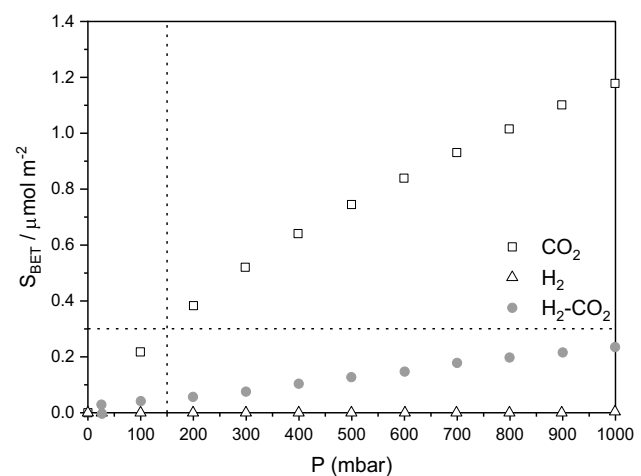


Fig. 9 Gravimetric gas adsorption uptake of single component gases (CO₂ and H₂) and a binary gas mixture (15% CO₂:85% H₂) at 60 °C under flow conditions of 200 cm³ min⁻¹ for MRF0_100_0.25. Uptake normalised by dividing molar uptake by S_{BET}; adsorption data only shown to simplify presentation (desorption data available in Electronic Supporting Information)

CO₂ and the gas mixture are very similar, being, on average, ~10–20 min for both systems. In contrast, the average equilibration time for pure CH₄ was ~35 min, this slower uptake of CH₄ may be due to the larger minimum cross-section of CH₄ (3.829 Å × 3.942 Å) compared with CO₂ (3.189 Å × 3.339 Å) (Webster et al. 1998). Therefore, the uptake observed at ~1000 mbar, combined with the low CH₄ uptake for the pure component system, and the similarity of

the equilibration times, suggest that mainly CO₂ is selectively adsorbed.

Figure 6 shows the uptake at 1000 mbar of the CO₂/CH₄ gas mixture is again significantly close to the uptake at 150 mbar of the pure CO₂ isotherm for MRF0_200_0.25. CH₄ adsorption, in the pure stream, was again observed to be low in comparison to CO₂. The equilibration times obtained for the pure isotherm show similar behaviour to those observed for the binary mixture; where the pure CO₂

isotherm steps equilibrate at an average time of < 3 min, while the mixture does so in ~ 1 min. This contrasts with an average time of ~ 180 min for pure CH_4 to equilibrate. The kinetics of adsorption of pure CH_4 are very slow compared to pure CO_2 , again this may be ascribed to the larger kinetic cross-section of CH_4 (Webster et al. 1998); overall, the mixture behaves in a very similar way kinetically to pure CO_2 , suggesting that separation of CO_2 from CH_4 is again favoured. This system also offers an industrially appealing timescale for separation.

The uptake observed for the binary gas mixture for MRF1_400_0.5 (Fig. 7) is approximately double that observed for the MRF0 samples, as is the pure CO_2 uptake. This is very similar to the behaviour observed for the CO_2 - N_2 mixture and is a direct consequence of the enhanced acid-base interactions afforded by the incorporation of melamine into the structure. The similar equilibration times observed for both pure CO_2 and the gas mixture isotherms, ~ 4 min and ~ 2 min, respectively, suggest that CO_2 is mainly adsorbed from the mixture. Additionally, the CH_4 equilibration time was ~ 180 min, similar to that for MRF0_200_0.25. Figure 8 shows that the total uptake of the mixture (at ~ 1000 mbar) is the same, or very close, to that observed for the CO_2 - N_2 mixture, which suggest that CO_2 is being selectively adsorbed from the mixture in both cases. The total uptake of CO_2 is again increased with additional nitrogen functionalities in the material and the equilibration times of both the pure CO_2 and CO_2 - CH_4 mixture are again similar. The average time for equilibration for pure CO_2 was ~ 3 min, while for the mixture it was ~ 1 min; CH_4 equilibration time was observed to be ~ 180 min, similar to the previous samples, and again ascribed to differences in the kinetic diameters of the two molecules.

Thermodynamic analysis of the isotherms obtained for the mixture of CO_2 and CH_4 was attempted using IAST, but failed due to the low uptake of CH_4 compared to CO_2 under the test conditions. The fitting of MRF0_100_0.25 and MRF1_400_0.5 CH_4 adsorption data with the Langmuir isotherm model was unsuccessful, again as a consequence of the low CH_4 uptakes obtained for these systems. Despite these negative results, it was possible to determine k and C_m for the isotherms obtained for the pure gases on the MRF0_200_0.25 and MRF10_200_0.25 samples. CH_4 isotherms, analysed using the Langmuir model, gave C_m values of 1.75×10^{-4} and 6.52×10^{-4} mmol/g, for MRF0_200_0.25 and MRF10_200_0.25, respectively, indicating the low uptakes observed experimentally. In contrast, C_m values for CO_2 adsorption on these materials were 0.995 and 1.287 mmol/g, respectively. It is important to note that the CO_2 uptake is > 8000 times that for CH_4 on MRF0_200_0.25 and ~ 2000 times for MRF10_200_0.25. This large difference, therefore, makes the vapour pressure for CH_4 very large (Eqs. 7, 8), which means that CH_4 would tend to stay

in the bulk gas phase, and not condense; while, due to its relatively higher condensate concentration, as determined from IAST, CO_2 would tend to condense on the MRF xerogel surfaces. Given that the uptakes obtained for adsorption of the CO_2 - CH_4 mixture on all xerogels are similar to those for the CO_2 - N_2 mixture, it is likely that similar selective effects occur within both systems, which may be expected to increase as $[M]$ increases as demonstrated for CO_2 - N_2 . It should be noted that dispersion forces would result in a higher MRF xerogel affinity for CH_4 compared to either N_2 or H_2 .

While previous results presented for adsorption of CO_2 / CH_4 gas mixtures on modified activated carbons suggest enhanced CH_4 uptakes in the presence of CO_2 , possibly as the result of a modified adsorption mechanism (Acar et al. 2018), the results shown here indicate no such enhancement. This difference may well be due to the difference in adsorption conditions (298 K vs. 333 K used here) and the resulting difference in scale of adsorption for the two systems, where the mass of CO_2 sorbed for the modified activated carbons (up to 110 mg/g at 1 bar pure CO_2) may alter the uptake of the second gas, while, here, the adsorption capacity does not extend beyond the monolayer. Despite the large CO_2 uptakes demonstrated for these modified carbons (Acar et al. 2018), they exhibited modest CO_2 / CH_4 selectivities, possibly as a result of this binary component enhancement.

Again, previous works have indicated high levels of selectivity for CO_2 from CH_4 streams for a range of materials (Yan et al. 2019; Taylor et al. 2018), however, the move to higher operating temperatures means that direct comparison with these results should be made with caution. Recent work conducted at a range of temperatures did show enhanced adsorption of CO_2 for amine modified MOFs, and ultrahigh selectivity of CO_2 over CH_4 (Babaei et al. 2018); however, it should be noted that the adsorption uptake was markedly reduced at higher temperatures (348 K was the highest temperature studied) and at lower, relevant pressures (i.e. 150 mbar). The mechanism of adsorption for these modified MOFs was also found to be a hybrid of chemi- and physisorption, which may have implications for recyclability of such materials. Consequently, MRF xerogels present an option within the current sorbent landscape providing a combination of reasonable uptake, fast kinetics and easy regeneration.

3.3 Pre-combustion carbon capture: adsorptive selectivity of CO_2 over H_2

The separation of CO_2 from H_2 is very common in gasification and steam reforming processes, where the fuel, natural gas or coal, is treated prior to combustion. Previous works have predicted (Cao and Wu 2005; Yang and Zhong 2006a, b) or experimentally determined (Belmabkhout and Sayari

2009) reasonable selectivities across a range of materials for CO_2/H_2 , hence, it is plausible to separate these two gases. The final stage of this process is the water–gas shift reaction, which aims to oxidise CO to CO_2 using steam, giving a product gas stream rich in CO_2 (over 20%) and H_2 . One of the major drawbacks, of the technologies available for CO_2 separation from H_2 for such gas streams, is the high energy requirement for sorbent regeneration (Leung et al. 2014), while MRF xerogels have demonstrated easy regeneration abilities (Principe et al. 2018), in tandem with fast kinetics of CO_2 adsorption. Hence, determining the affinity of MRF xerogels for H_2 , in competition with CO_2 , will establish the suitability of these materials to separate CO_2/H_2 gas streams.

Figures 9 and 10 show a comparison of uptakes for pure CO_2 , pure H_2 and a mixture of 15% CO_2 and 85% H_2 for samples with and without melamine; from the samples studied here these offer the two limits of no melamine present (MRF0_100_0.25) and high [M] (MRF10_200_0.25). This should provide a marked contrast for the sample with melamine added, as observations from the data presented for the other two mixtures tested, suggest that the higher [M] content will increase selectivity for CO_2 . It is important to note that the H_2 adsorption uptake at 60 °C and ~1 bar is expected to be very low. Again, the adsorption uptake, in all cases, has been normalised to account for the available surface area (m^2) for each material (Table 1).

Figure 9 shows the adsorption isotherms obtained for the pure components, CO_2 and H_2 , and the analogous gas mixture on xerogel MRF0_100_0.25. The uptake at ~1000 mbar of the gas mixture adsorption isotherm is again observed to be close to that observed at 150 mbar of the pure component

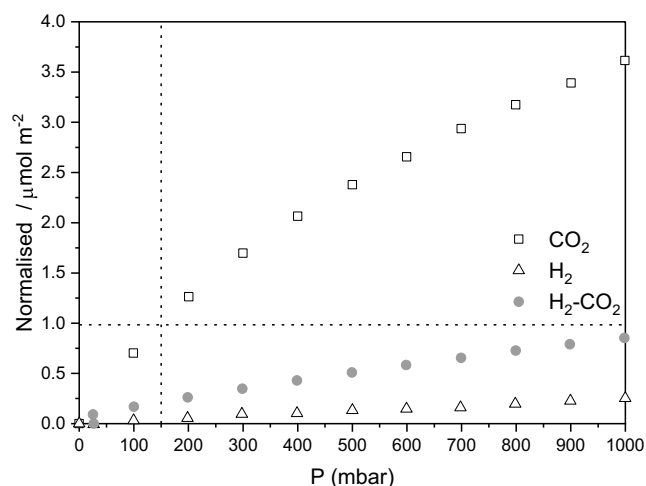


Fig. 10 Gravimetric gas adsorption uptake of single component gases (CO_2 and H_2) and a binary gas mixture (15% CO_2 :85% H_2) at 60 °C under flow conditions of $200 \text{ cm}^3 \text{ min}^{-1}$ for MRF10_200_0.25. Uptake normalised by dividing molar uptake by S_{BET} ; adsorption data only shown to simplify presentation (desorption data available in Electronic Supporting Information)

(CO_2). As for the other two systems studied, the equilibration times for both pure CO_2 and the mixture are very similar, ~10–20 min for both systems. Therefore, the uptake observed at ~1000 mbar, combined with the nearly negligible H_2 uptake (pure), as well as the similarity of the equilibration times, suggests that CO_2 is mainly adsorbed selectively by this material.

Figure 10 shows that the total uptake of the binary mixture (at ~1000 mbar) is again very close to that observed for CO_2 at 150 mbar, which suggests that CO_2 is selectively adsorbed from the mixture. The equilibration times of both pure CO_2 and the mixture are again similar. The average time for equilibration of pure CO_2 was ~3 min, while for the mixture it was ~1 min, while the H_2 equilibration time was observed to be ~240 min on average; as a consequence of the short timescales for adsorption of the binary mixture, despite the larger H_2 uptake for this material, it suggests that little H_2 is adsorbed. Again, these are industrially relevant timescales for this gas mixture allowing selective separation of the two gas components.

Previous researcher have reported that care is required when reporting H_2 related selectivities due to buoyancy effects in the adsorbed phase (Belmabkhout and Sayari 2009) and it should also be noted that it was not possible to perform thermodynamic analysis by IAST due to the very low uptakes of H_2 , similar to the situation encountered for CO_2 - CH_4 mixture, indicating a low affinity of these materials for H_2 . However, it is notable that the uptakes from the CO_2 - H_2 mixture, for both materials, were comparable to those for the CO_2 - CH_4 and CO_2 - N_2 mixtures; therefore, while H_2 adsorption increases with the incorporation of nitrogen content, both gases are enhanced, and selectivity can again be assumed to increase as [M] increases for this gas mixture. This indicates that MRF xerogels again provide a feasible route to sorbent development for pre-combustion carbon adsorption.

4 Conclusions

The ability of MRF xerogels to selectively adsorb CO_2 from binary mixtures has been demonstrated, using N_2 , CH_4 and H_2 as balance species. It was found that, as [M] increases, the selectivity of MRF xerogels for CO_2 from the binary mixtures is also increased. Experimental results were contrasted with data obtained using Ideal Adsorbed Solution Theory for the CO_2 - N_2 mixture. In this case, the sample made without melamine, and offering micropore structure only, exhibited a selectivity of 27% for CO_2 , while the sample comprising 10% modification with melamine showed a significant increase in selectivity of 52%. CO_2 - CH_4 and CO_2 - H_2 mixtures showed similar results, however, CH_4 demonstrated a higher affinity for the MRF xerogels, hence

the selectivity would be compromised compared to N₂ or H₂ mixtures. It has been previously reported (Nicholson and Gubbins 1996) that, for porous sorbents, adsorption selectivity of CO₂ over other gas species is controlled by a combination of pore size/shape, thermodynamics and relative gas densities of adsorbed species. It is also thought that, for the gas separation studied here, microporous sorbents exhibit a lower dependence on pressure, at near ambient temperatures, than mesoporous sorbents. This indicates that the separation selectivities observed here would be favourable across a range of pressures for subcritical conditions. At the higher temperatures required in many of CO₂ separations, the gas will be supercritical, and the gases will only adsorb to a monolayer, making wider pores redundant in terms of adsorption capacity, hence, the materials here offer high selectivity and relevant pore dimensions for these conditions.

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