Determination of multicomponent mass transport processes for adsorptive environmental applications *

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Introduction

The study of the kinetics of the competitive adsorption of multicomponent gas mixtures on solid adsorbents is important for a range of practical adsorption processes. One such environmental application is carbon capture and storage (CCS) [1], which includes the use of geological CO_2 storage methods as well as the pre-combustion capture of carbon dioxide from syngas and post-combustion separation from flue gases [1-3]. The former include the storage of carbon dioxide in depleted oil and gas reservoirs and coal seams, while the latter use any one of a number of methods, including adsorption, to separate gaseous carbon dioxide from multicomponent gas flows. A range of porous materials are known to preferentially adsorb carbon dioxide over other species. These include activated carbons, zeolites and metal organic frameworks (MOFs), and these materials are therefore being considered for use in CCS technology [3]. The equilibria and kinetics of multicomponent adsorption from a number of different mixtures, including CO_2/CH_4, CO_2/H_2 and CO_2/N_2, are of fundamental importance to CCS technology, because the binary combinations mentioned above effectively represent a range of practical pre- and post-combustion gas streams. However, the experimental determination of the kinetics of multicomponent adsorption, in particular, is practically challenging.

In previous work, we have shown that the adsorption kinetics of multicomponent vapour mixtures can be determined by combining microgravimetry and dynamic sampling mass spectrometry [4]. This was demonstrated by measuring the adsorption of water/n-octane and water/n-butane vapour mixtures on BAX950 activated carbon (see Hiden Isochema Application Note 113 for further details). In this work, we use an alternative method to determine the time-dependent displacement of adsorbed methane by carbon dioxide in the same activated carbon at ambient temperature. We also measure the single component adsorption of both methane and carbon dioxide by this material in the range from room temperature to 45 °C and calculate the respective isosteric enthalpies of adsorption.

Experimental Details

The measurements were performed using a Hiden Isochema IMI-FLOW, as shown in Figure 1, which is a fully automated manometric-TPD gas sorption analyser that can be used to determine the gas sorption properties of materials up to pressures of 20 MPa (200 bar). This instrument combines the capabilities of a high pressure manometric sorption system with the ability to flow gases through the reactor and analyse the composition of the outlet stream using an integrated quadrupole mass spectrometer.
The standard system features two inlet gas streams; however, an optional third stream is available, which allows sophisticated binary gas mixture experiments to be performed, with the third

Figure 1: The IMI-FLOW high pressure manometric-TPD gas sorption analyser

stream used exclusively for the carrier gas. Helium is typically chosen as the carrier, since its presence is known not to significantly affect the isothermal uptake of other species during flowing experiments [4, 5]. It is also required for the determination of the dead volume of the sample reactor for manometric isotherm measurements. The accuracy of the IMI-FLOW for high pressure manometric isotherm measurement has been maximised by ensuring that the instrument has a very low internal volume, which is approximately 10 cm³. In addition, the temperature of the cabinet that houses the calibrated dosing volume is controlled to a stability better than ± 0.1 °C, while the pressure measurement accuracy is better than ± 0.05% of the range.

Figure 2 shows a schematic diagram of the set-up used in this study. It can be seen that the three stream configuration allows the supply of helium, methane and carbon dioxide to the sample reactor. Each stream is controlled by a mass flow controller (MFC) and the gas flow is directed through the packed sample bed. The system is also fitted with an integrated Hiden Analytical dynamic sampling mass spectrometer (DSMS), in order to sample the gas composition at the outlet of the reactor. A single MFC controls the flow rate at the outlet of the instrument, beyond the mass spectrometer sampling port, thus allowing precise control of the pressure and flow rates through the system.
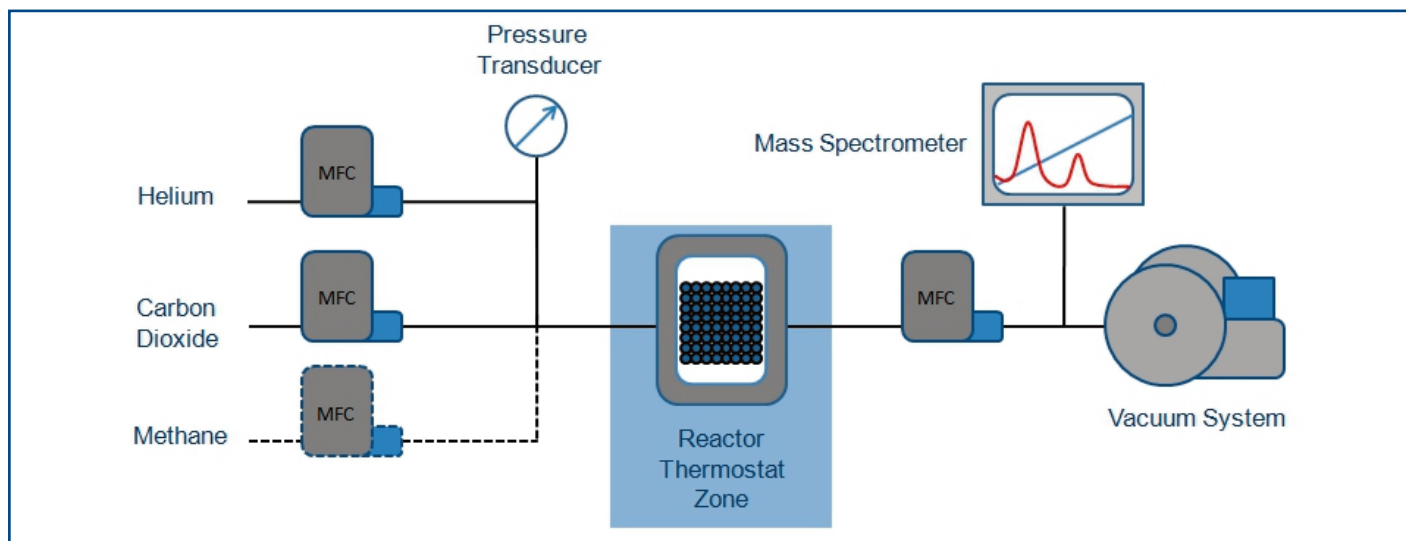
Figure 2: A schematic diagram of the IMI-FLOW instrument operating in dynamic flowing mode, with an integrated dynamic sampling mass spectrometer fitted to monitor the downstream gas composition. The inlet flow is regulated by the mass flow controllers (MFCs), while pressure is regulated using the outlet flow controller. The sample sits in a thermally isolated sample reactor with an in-bed thermocouple monitoring the sample temperature.

In this study, the IMI-FLOW was first used in static manometric mode to measure single component adsorption isotherms on a 416 mg BAX950 activated carbon sample using carbon dioxide and methane. The sample was degassed thoroughly and measurements were then performed at room temperature (RT), 35 °C and 45 °C.

For the determination of the exchange of carbon dioxide and methane, the measurements were performed in flowing mode by maintaining a constant flow of 45 ml min^{-1} of methane into the system throughout the experiment and a constant total combined inlet flow of 100 ml min^{-1}. The exchange experiment was then performed by increasing and decreasing the inlet flow of CO_2 in a stepwise fashion, with the remainder of the mixture consisting of helium. The low inlet flow rate of CO_2 was 1.5 ml min^{-1}, whilst the high rate was 45 ml min^{-1}. Throughout the experiment, the gas composition was monitored at the outlet of the reactor using the DSMS. In addition, the sample temperature was monitored continuously using athermocouple mounted in the reactor. The measurements were performed at RT, which was determined to be approximately 23.5 °C.

Results

Figure 3 shows the low pressure methane and carbon dioxide adsorption isotherms measured at 23.5 °C, 35 °C and 45 °C. It can be seen that the sample adsorbs more carbon dioxide than methane for any given temperature and pressure within the observed range. Isosteric enthalpies of adsorption calculated from these data using van 't Hoff plots, for uptakes in the range 50 to 300 micromoles, were in the region 19.4 to 20.4 kJ mol^{-1} for methane and 24.5 to 25.8 kJ mol^{-1} for carbon dioxide. These values are consistent with the isosteric enthalpies of adsorption at zero coverage of 23.8 ± 1.1 and 28.4 ± 0.7 kJ mol^{-1} obtained previously by Reid and Thomas [6, 7] for methane and carbon dioxide adsorption, respectively, on a carbon molecular sieve (CMS). The data set also suggests that BAX950 will preferentially adsorb carbon dioxide over methane due to the higher enthalpy of adsorption for the former. In addition, kinetic data recorded by the IMI-FLOW during the isotherm measurement show that the two sorbate species have similar rates of uptake and
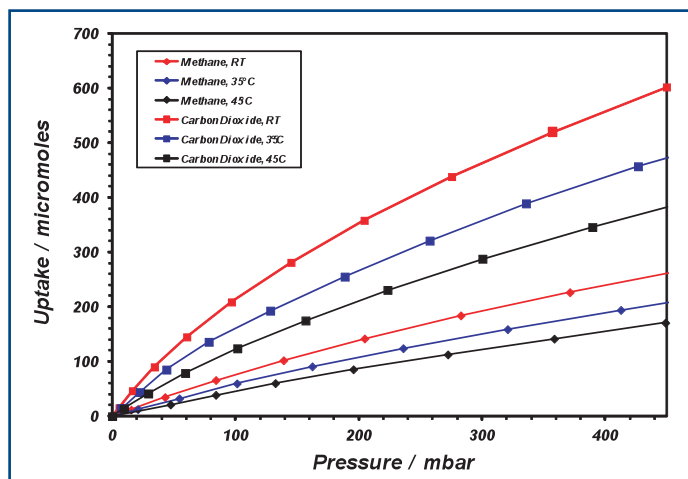

Figure 3: Carbon dioxide and methane adsorption isotherms for BAX950 activated carbon measured on the IMI-FLOW at the temperatures indicated in the legend.

release. The data recorded in dynamic flowing mode are shown in Figures 4 and 5. It can be seen in Figure 4, which shows the cyclic carbon dioxide flow, that there is a delay between the change in the composition of the flow at the inlet and the response to this change measured at the outlet. This delay results in curvature of the outlet flow or, in other words, the deviation of the outlet flow signal from the step change seen at the inlet. This indicates that the sample adsorbs carbon dioxide when the inlet flow is increased, because the measured outlet signal would otherwise more closely match the inlet flow. The time taken for the inlet and outlet flows to reach parity is approximately 1 min. Similarly, when the carbon dioxide flow is reduced, the carbon dioxide signal at the outlet decreases at a slower rate than the inlet flow. In this case, the time taken for theinlet and outlet carbon dioxide flows to reach parity is approximately 2 min.

The upper plot in Figure 5 shows the methane flow during the same experiment. The blue line shows the constant methane
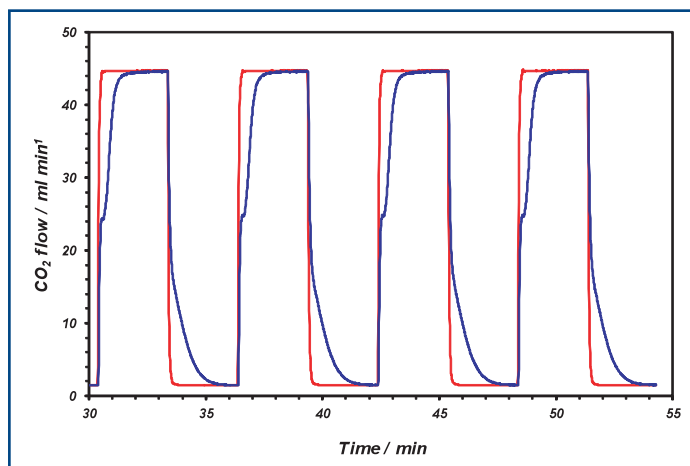
Figure 4: The inlet (red trace) and outlet (blue trace) CO_2 flows through the BAX950 activated carbon sample at ambient temperature during the cyclic addition of CO_2 with a constant CH_4 flow of ~45 ml min-1. The inlet signal is the flow through the CO_2 MFC and the outlet signal is the flow detected by the DSMS. A constant net flow of 100 ml min^{-1} is maintained using helium.
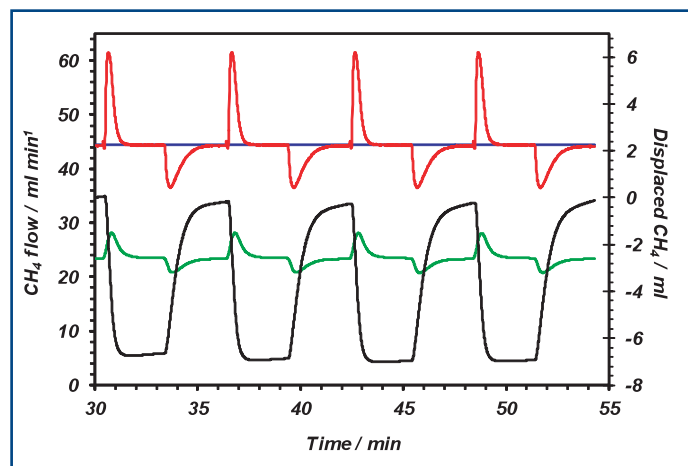

Figure 5: The inlet (blue trace) and outlet (red trace) CH_4 flows through BAX950 activated carbon sample at ambient temperature during cyclic addition of CO_2. The inlet signal, at a constant flow of ~45 ml min^{-1}, is the flow through the CH_4 MFC and the outlet signal is the flow detected by the DSMS. The running integral of the displaced CH_4 (black trace) is also shown in ml (indicated on the right axis). The in-bed sample temperature (green trace), indicating the exo- and endothermic responses to the CH_4 displacement, is displayed on the left hand axis, with units of °C.

flow into the system, whilst the red line shows the flow at the outlet, as determined using the DSMS. The peaks and troughs in the methane signal at the outlet clearly indicate that the methane is displaced by the carbon dioxide, as the carbon dioxide inlet flow is increases, and then subsequently replaces it when the flow is decreased. The running integral calculation for the methane is shown by the black line in the lower plot in Figure 5. It can be seen that this retains a fixed baseline as the initially displaced methane is replaced following the subsequent reduction in the carbon dioxide inlet flow. It can also be seen that the kinetics of the re-adsorption or replacement of methane are slower than the kinetics of the original desorption or displacement. This is consistent with the slower carbon dioxide desorption kinetics shown in Figure 4, and probably originates from the stronger adsorption affinity exhibited by CO_2.

The in-bed sample temperature was also recorded during the exchange experiment, using a temperature sensor mounted in the reactor. The measured temperature is shown by the green line in the lower plot of Figure 5, which is displayed against the left hand axis, using units of °C. This clearly shows that heat is evolved as part of the carbon dioxide/methane displacement process, while the sample cools when the carbon dioxide flow is reduced. This is consistent with the isosteric enthalpies of adsorption that were determined from the various isotherms shown in Figure 3.

Conclusions

Methane and carbon dioxide adsorption isotherms for BAX950 activated carbon were determined using an IMI-*FLOW* manometric-TPD gas sorption analyser in the temperature range from RT to 45 °C and in the pressure range from vacuum to 500 mbar. The data show that, for a given temperature and pressure in the measured range, more carbon dioxide than methane is adsorbed by the sample. The isosteric enthalpies of adsorption calculated from these data were in the region 19.4 to 20.4 kJ mol^{-1} for methane and 24.5 to 25.8 kJ mol^{-1} for carbon dioxide. These values are

consistent with the observationthat more CO_2 than CH_4 is adsorbed at any given temperature and pressure.

In addition, the kinetics of the displacement of adsorbed methane by carbon dioxide on BAX950 have been determined using a combined mass flow/mass spectrometry method. At ambient temperature, adsorbed methane is clearly displaced by carbon dioxide, as expected from the equilibrium uptakes and the relative isosteric enthalpies of adsorption. The exothermic nature of the displacement predicted by the isosteric enthalpy calculations is confirmed by the temperature changes measured in the sample cell during the exchange process. The kinetics of the re-adsorption or replacement of the displaced methane were found to be slower than the original desorption or displacement.

Using the example of carbon dioxide capture by an activated carbon, from a mixed CO_2/CH_4 gas stream, this study has clearly demonstrated the ability of the IMI-FLOW manometric-TPD gas sorption analyser to determine both single component equilibria and the kinetics of multicomponent adsorption by porous materials for practical adsorptive applications.

References

[1]   J-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H-K. Jeong, P. B. Balbuena, H-C. Zhou. Coord Chem Rev 255(15-16 (2011), 1791-1823

[2]   N. Hedin, L. Chen, A. Laaksonen. Nanoscale 2 (2010), 1819-1841

[3]   S. Choi, J. H. Drese, C. W. Jones. ChemSusChem 2 (2009), 796-854

[4]   A. J. Fletcher, M. J. Benham, K. M. Thomas. J Phys Chem B 106 (2002), 7474-7482

[5]   I. P. O'koye, M. Benham, K. M. Thomas. Langmuir 13 (1997), 4054-4059

[6]   C. R. Reid, K. M. Thomas. Langmuir 15 (1999), 3206-3218

[7]   C. R. Reid, K. M. Thomas. J Phys Chem B 105 (2001), 10619-10629