

Gas Capture and Vapour Separation by Microporous Materials

DVS Application Note 51

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Metal Organic Frameworks (MOFs) as well as inorganic solids are of great importance due to their high adsorption capacity and surface reactivity and are used for various applications. Dynamic vapour sorption (DVS) methods have been a very useful tool for the characterization of these properties using water and organic vapours at process relevant temperatures.

Introduction

Microporous materials like Metal Organic Frameworks (MOFs) and zeolites have been a novel class of candidates for absorbents, catalysts and separation processes [1],[2],[3],[4]. For example, a highly flexible micro-porous metal organic framework material exhibits remarkable capability to capture and separate carbon dioxide from other small gases, including N₂, H₂, CH₄, CO and O₂, with a separation ratio of 294, 190, 257, 441 and 768 for CO₂/N₂, CO₂/H₂, CO₂/CH₄, CO₂/CO and CO₂/O₂ respectively at 0.16 atm at 25 °C [5]. Therefore, investigation of the sorption behaviour of these materials is of interest for gas and liquid capture and separation. This application note will present CO₂, SO₂ gas and ethanol/water vapour sorption in Zn-MOF, SiO₂ and zeolite, respectively.

Method

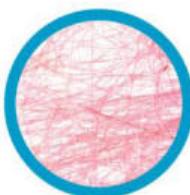
All measurements were conducted using the DVS Vacuum instrument. The Vacuum system with its 400°C pre-heater allows a complete emptying of

micro pores, which may not be easily achieved by thermal heating and dry gas flow alone.

Results

CO₂ sorption in Zn-MOF

A Zn based MOF sample as supplied with 88.4 m²/g BET surface was outgassed at 10⁻⁵ Torr for three hours at 25 °C prior to CO₂ sorption measurement. The CO₂ gas was then admitted into the system with a partial pressure ranging from 0 to 722 Torr and step duration of 20 minutes. Figure 1 shows the CO₂ sorption kinetics data in the MOF sample at 25 °C. The adsorption and desorption mechanisms are similar and a total uptake of 0.7462 mg can be seen. The corresponding isotherm is plotted in Figure 2, which shows Type I isotherm characteristics, verifying sorption behaviour in a microporous material. The isotherm has not plateaued to a constant value, indicating that more CO₂ can be captured at higher partial pressures, i.e., pressures above atmosphere. Apart from the relatively large surface area of MOF materials, their pore size can be specially designed for capturing or separating a specific gas by different preparation conditions.



The Total Sorption Solution

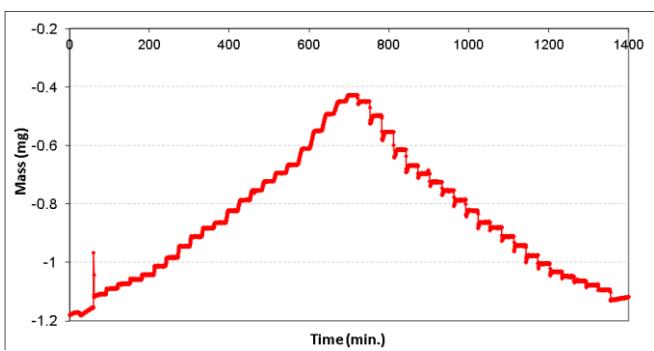


Figure 1. Dynamic sorption data of CO_2 gas on Zn-MOF material at $25\text{ }^\circ\text{C}$

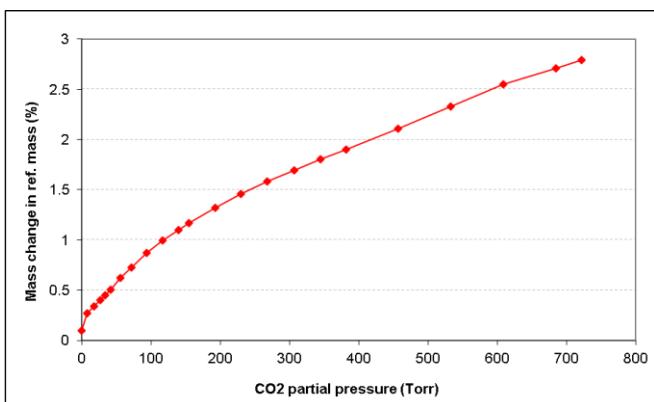


Figure 2. Adsorption branch of CO_2 gas on Zn-MOF material at $25\text{ }^\circ\text{C}$

SO_2 Sorption Studies on SiO_2 and zeolite

Approximately 50 mg of microsilica sample was first dried under vacuum (10^{-5} Torr) at $200\text{ }^\circ\text{C}$ for 2 hours using a pre-heater, and equilibrium mass was achieved. The experiment was performed in a temperature-controlled incubator at $25\text{ }^\circ\text{C}$, and the sample was first kept at low pressure (10^{-5} Torr and 0% P/P_0) to establish the dry mass, m_0 . Pure industrial SO_2 gas (purity > 99.98%; CAS No. 7446-09-5) was used as the adsorbate for the study. The sample was then exposed to the SO_2 gas environment from 0% to 60% P/P_0 in 10% steps. The range of partial pressures was based on a maximum pressure of 760 Torr, hence giving the range of applied pressure of 0 Torr to 456 Torr. The P/P_0 was then decreased in a similar manner to accomplish a full adsorption/desorption cycle.

A superimposed plot of the net percentage change in mass (based on dry mass) versus time is shown in Figure 3. It is clear that the two samples

with different densities resulting from different impurities exhibit similar SO_2 gas adsorption/desorption behaviour. Both samples adsorbed small amount of SO_2 with considerably fast sorption and desorption kinetics. Sample 1 with higher density has marginally higher adsorption capacity than Sample 2 (by merely 4.7% mass at 60% P/P_0).

The corresponding SO_2 sorption/desorption isotherm plots are combined and shown in Figure 4. The isotherm plot displays the percent change in mass (referenced from m_0) versus the target % P/P_0 . It can be clearly observed that both samples exhibit a similar isotherm profile. However, Sample 2 has an open-ended isotherm shape, indicative of an irreversible uptake of SO_2 molecules ($\leq 0.05\%$ mass).

Figure 5 includes the SO_2 isotherm of zeolite 5A, which was activated at $400\text{ }^\circ\text{C}$ in vacuum prior to the sorption measurement. Reported molecular diameter of SO_2 is approximately 6\AA [6], therefore zeolites with a pore size that is similar to the gas molecule should be more efficient. This is exemplified by the high adsorption capacity in the low partial pressure range (< 10% P/P_0), where pore filling process depends mostly on the pore adsorption potential. This makes zeolite 5A a potential candidate for SO_2 capture.

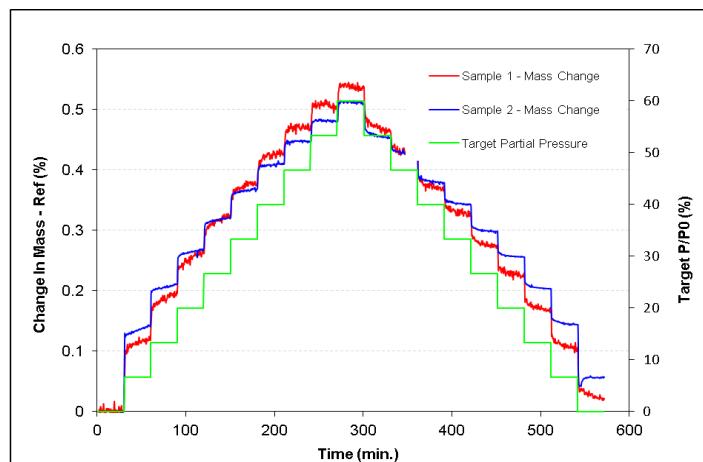


Figure 3. Dynamic sorption data on two different SiO_2 samples.

The Total Sorption Solution

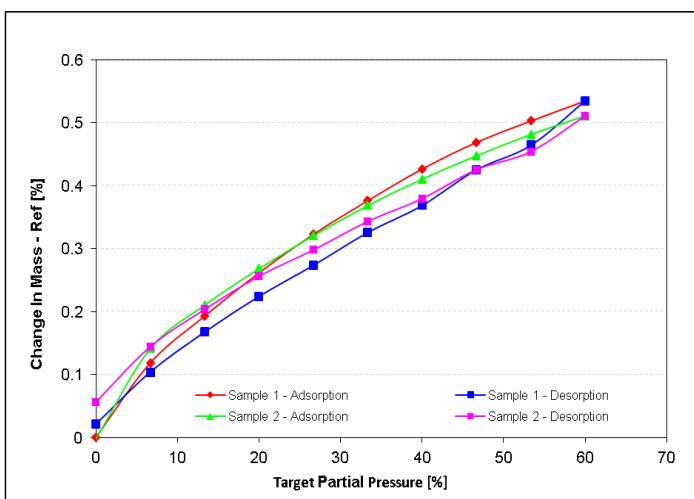


Figure 4. Isotherm plot of SO_2 on SiO_2 samples.

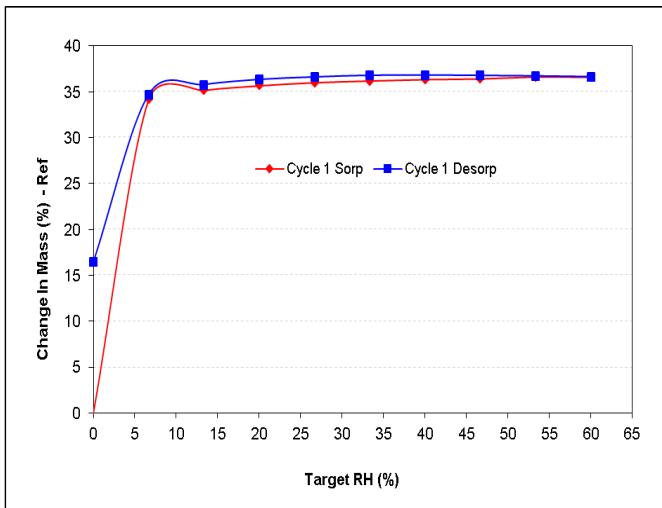


Figure 5. Isotherm plot of SO_2 in zeolite 5A.

Ethanol/water co-adsorption on Zeolite 3 \AA

Zeolite 3A sample was activated under the vacuum of 10^{-5} Torr at 400°C for four hours. The sorption measurements were conducted at 130°C using the pre-heater in order to avoid condensation, which would prevent vapours from further adsorption into the micropores. Water sorption isotherm at 130°C is plotted in Figure 6. The uptake of water at $20\% \text{P}/\text{P}_0$ is 8.29% with reference to the dry mass and obviously pores have not completely filled. Higher P/P_0 should result in higher water vapour uptake.

Figure 7 shows ethanol sorption isotherm at 130°C . At $20\% \text{P}/\text{P}_0$, the uptake is 0.90% which is much lower than uptake of 8.29% for water at the same P/P_0 . Even at $70\% \text{P}/\text{P}_0$, the ethanol uptake

is only 1.31%. The much lower uptake of ethanol compared to that of water is probably due to the difference in their molecular size. The molecular size of water and ethanol are reported to be 0.28 nm and 0.44 nm respectively. Obviously, the 0.30 nm pore size of the zeolite 3A is more favorable for the sorption of 0.28 nm water molecules.

Co-adsorption of multiple components has attracted more and more attention. This is simply because co-adsorption behaviour is of interest to filtration and separation processes. In order to generate a mixed vapour concentration of 95% ethanol and 5% water, 50 sccm ethanol and 2 sccm water were introduced to the zeolite 3A sample heated at 130°C . Figure 8 is the co-adsorption isotherm for the vapour mixture. The total uptake at $70\% \text{P}/\text{P}_0$ of the mixed vapours is 10.13% of the dry mass which is close to the uptake of water only if its isotherm is extrapolated to $70\% \text{P}/\text{P}_0$. This implies that the total sorption is mainly due to the water sorption for its smaller molecular size. The co-adsorption uptake at $20\% \text{P}/\text{P}_0$ is 2.75% which is lower than water only sorption of 8.29% at the same P/P_0 , but higher than the uptake of 0.90% for ethanol only. Although the sorption is mainly due to water sorption, the sorption behaviour was changed by the competition between the two vapours.

On the adsorption branch, one can see a maximum in uptake around $40\% \text{P}/\text{P}_0$. This results from the elimination of ethanol competition by purposely switching off ethanol flow. Beyond $40\% \text{P}/\text{P}_0$, the uptake gradually decreases, indicating that the higher uptake around $40\% \text{P}/\text{P}_0$ is probably due to surface adsorption, rather than pore filling. This additional surface adsorption was soon removed by the heating at 130°C .

The significant hysteresis (i.e. significant mass drop below $20\% \text{P}/\text{P}_0$) on desorption branch suggests that the hydration is formed to some extent or the water is trapped up in pores by capillary forces. All this indicates that zeolite 3A is a good candidate for water capture and for separation of water from ethanol.

The Total Sorption Solution

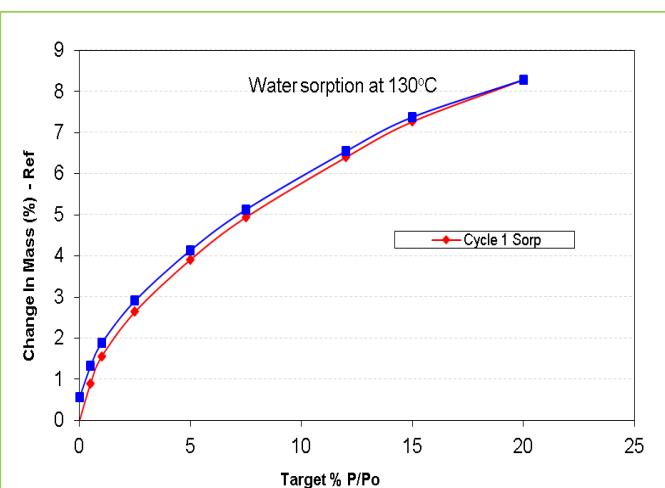


Figure 6. Water sorption isotherm at 130 °C.

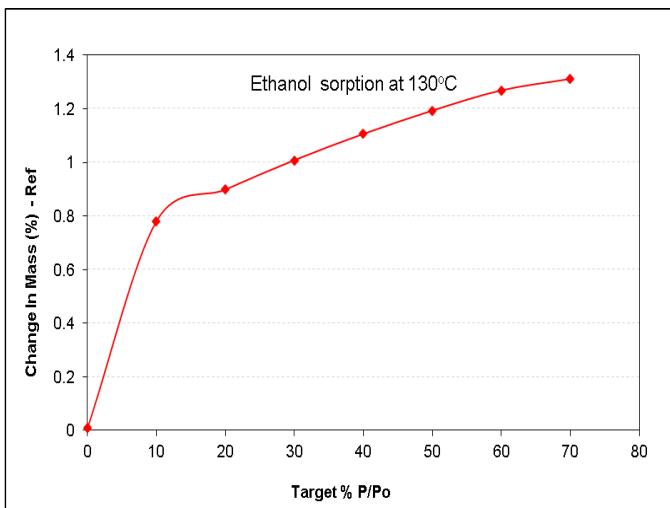


Figure 7. Ethanol sorption isotherm at 130 °C.

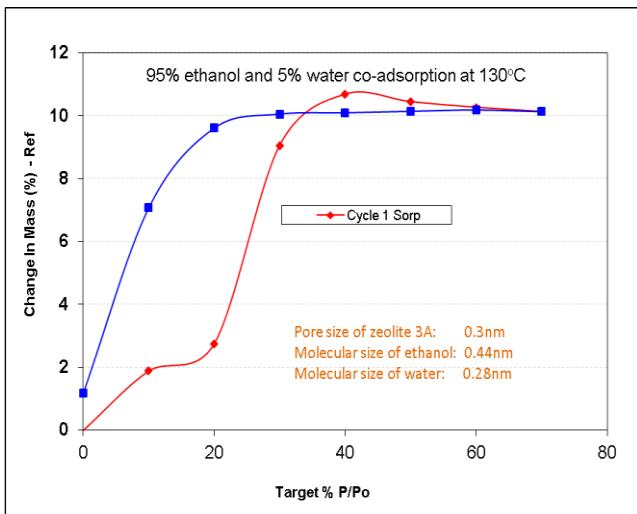


Figure 8. Co-adsorption of 95% ethanol and 5% water.

Conclusions

Gas and water/ethanol vapour mixture sorption isotherms were measured on microporous MOF samples and zeolites with different pore sizes over a range of temperatures. The surface area and pore size of MOF materials may be designed to optimise gas uptake. Microporous materials are better candidates than SiO₂ for SO₂ sorption. Considering the molecular size of water and ethanol the zeolite 3A would be more suitable for the separation of 0.28 nm water molecules from water/ethanol mixtures.

References

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