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Gravimetric adsorption measurements of helium on natural clinoptilolite and synthetic molecular sieves at pressures up to 3500 kPa

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ABSTRACT

We report helium adsorption capacities and the true specific impenetrable solid volumes of a clinoptilolite-rich Escott zeolite from Werris Creek (Australia), synthetic 3A and 4A zeolites, and carbon molecular sieve 3K-172 measured by a gravimetric method at pressures of (300–3500) kPa and temperatures in the range of (303–343) K. Our helium adsorption procedure extends the previous works by Gumma and Talu [1] to determine the impenetrable solid volume of the adsorbent, which in standard helium pycnometry is determined under the assumption that helium does not adsorb at room temperature. Our results confirm helium adsorption on these solids is small, but not zero: equilibrium helium adsorption capacities measured at 3500 kPa and 303 K were 0.067 mmol/g on Escott, 0.085 mmol/g on 3A, 0.096 mmol/g on 4A and 0.089 mmol/g on 3K-172. The specific solid volumes determined by the Gumma and Talu method were 10–15% larger than the specific solid volumes measured by standard helium pycnometry, and this error can result in uncertainties of 2.6–28% in the equilibrium adsorption capacities of CO_2 and N_2 measured at high pressures. The uncertainties were largest for N_2 on the Escott zeolite, which had the lowest equilibrium adsorption capacity for N_2. These results support the need to consider helium adsorption in the characterisation of adsorbents with narrow pore sizes, especially for adsorption processes that involve helium separations at low temperatures and/or high pressures.

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1. Introduction

To measure adsorption of gases on porous solids with a high degree of accuracy requires the adsorbent's impenetrable solid volume (V_s) to be determined precisely. The most common method used to determine V_s is by volumetric helium pycnometry [2–4] because helium is small enough to access narrow pores (kinetic diameter of 2.60 Å [5]) and helium has only weak interactions with solid surfaces. Typically, helium pycnometry is performed either in-situ within an adsorption measurement apparatus or in a separate pycnometer, and this procedure is based on the assumption that helium adsorption is negligible (i.e. mass helium adsorbed $m_{a,He} = 0$) [5,6]. This assumption is reasonable for many adsorbents and conditions of relevance to most industrial processes. However, there is evidence in the literature [2,7] that the uptake of helium on certain adsorbents may significantly affect the measurement of V_s at low temperatures and high pressures. Thus, at high pressure conditions the standard helium expansion methods may lead to significant errors in the determination of V_s [1,8], and these errors propagate as uncertainties in the estimation of the Gibbs dividing surface excess (GSE) [8,9] and consequently as uncertainties in equilibrium capacities of other species such as CO_2, CH_4 and N_2 measured at high pressures.

Although helium pycnometry is ubiquitous in the characterisation of porous materials, there are few reports of high pressure helium adsorption measurement techniques [1,2,7,8,10–14]. Most commercial adsorption instruments perform helium pycnometry at pressures close to 101.3 kPa or in some high pressure instruments at pressures close to 500 kPa. Some theoretical and experimental approaches have been used to avoid using the limiting assumption that helium adsorption is zero. For example, Herrera et al. [3] proposed an alternative dividing surface to the traditional Gibbs dividing surface. From an experimental perspective, Sircar [8] and Gumma and Talu [1] have sought to develop methods that allow the true GSE to be approached more closely than the assumption of zero helium adsorption allows. Sircar's [8] approach was to

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Nomenclature

H	Henry's constant, (mmol/g.kPa)
H_0	Entropy of adsorption, (mmol/g.kPa)
H_1	Isosteric heat of adsorption, (kJ/mol)
m_a	Adsorbed phase weight, (g)
m_b	True weight of sample basket and hook, (g)
m_s	True weight of solid adsorbent, (g)
m_{bal}	mass recorded by balance at measuring point 1, (g)
m_t^{Calc}	Calculated total weight, (g)
m_t^{Meas}	Measured total weight, (g)
MW_{ads}	Molecular weight of adsorbate, (g/mol)
n_a	number of moles adsorbed, (mole)
P	Pressure, (kPa)
Q_a	Amount of helium adsorbed per unit mass of the adsorbent, (mmol/g)
R	Molar gas constant, (kJ/K.mol)
V_a	Volume of adsorbed phase, (cm^3)
V_b	Volume of the sample basket and hook, (cm^3)
V_s	Impenetrable or inaccessible solid volume, (cm^3)
v_s	Specific inaccessible solid volume, (cm^3/g)
V_t	Total volume, (cm^3)
ρ_g	Fluid density, (g/cm^3)
Δm	Raw mass change, (g)

determine the impenetrable solid volume (V_s) and fix the Gibbs dividing surface by using helium as a probe molecule at temperatures where the Henry's Law constant (H) approached zero. Gumma and Talu [1] modified Sircar's method by relaxing the assumption that helium uptake at any temperature was zero, and instead measured helium uptake at a range of temperatures up to 515 K to estimate a value for the Henry's Law constant.

In this study we tested Gumma and Talu's method with a gravimetric adsorption apparatus to measure the true void volumes and helium equilibrium adsorption capacities of a clinoptilolite-rich natural zeolite (Escott), synthetic zeolites 3A and 4A, and a carbon molecular sieve. To examine the sensitivity of the equilibrium adsorption capacities measured at high pressure on these narrow pore adsorbents to the value of true void volume, we measured CO_2 and N_2 adsorption isotherms at pressures up to 4990 kPa and temperatures in the range of (298–323) K.

2. Materials and materials characterisation

Natural clinoptilolite-rich Escott zeolite from the Werris Creek deposit (New South Wales, Australia) was provided from Zeolite Australia Pty Limited, the synthetic zeolite molecular sieves 3A and 4A were provided by Sigma-Aldrich (Australia), and the carbon molecular sieve 3K-172 was provided by Shirasagi (Osaka Gas Chemicals Co. Ltd., Japan). The Escott zeolite was used as-received as an un-purified powder with particle sizes of less than 76 μm. The synthetic zeolites were in the form of beads with mesh sizes of 4–8 for type 3A and 8–12 for type 4A. The 3K-172 carbon molecular sieve (CMS) was in the form of cylindrical, extruded pellets with diameter 1.8 mm and lengths in the range 1.18–2.8 mm (99% of particles in this size fraction according to technical specification sheet from Osaka Gas Chemicals Co. Ltd).

The Escott clinoptilolite was selected as a low-cost, natural adsorbent available in commercial quantities that features narrow pores that are just accessible to helium. Clinoptilolite has a typical unit cell of $Na_6[(Al_2O_3)_8(SiO_2)_{28}]$ $24H_2O$ and belongs to the heulandite (HEU) group [15,16]. This nanostructured material is composed of two parallel 10- and 8-membered ring channels of 0.72×0.44 nm and 0.47×0.41 nm, respectively that are connected to a third channel with the windows size of 0.55×0.40 nm [17]. Although the Werris Creek zeolite deposit is reported to be rich in clinoptilolite, thus natural material also contains other minerals such as mordenite, quartz, smectite clays and mica. We confirmed the presence of clinoptilolite in the Escott samples by powder X-ray diffraction (XRD, Bruker Advanced XRD) and MAS NMR spectra (AV-300 Brucker). The XRD pattern is shown in Fig. 3S of the Supporting Information (SI). The MAS NMR spectra collected at room temperature for the ^{29}Si, ^{1}H and ^{27}Al nuclei are included in Fig. 4S. $NH_4Al(SO_4)_2 \cdot 12H_2O$ was used as a reference for the chemical shifts. The ^{27}Al MAS NMR spectra was used to calculate a Si/Al ratio in the zeolite framework of $(Si/Al)_{fw} = 6.587$ (Table 2S). Further information on the composition of the Escott zeolite sample is available in the technical data sheet provided by Zeolite Australia Pty Limited [18] and we have included the X-ray fluorescence date from the data sheet in Table 1S of the SI. Table 1S shows that the principal cations identified in the Escott zeolite were K^+, Ca^{2+}, Fe^{3+} and Mg^{2+}, and as the cations affect the zeolite structure this data should be considered when comparing the Escott sorption capacities and selectivity to other natural or synthetic zeolites.

The synthetic zeolite molecular sieves 3A and 4A were selected for investigations because the structure of these materials is well characterized and the narrow pore openings of these zeolites allow only adsorption of small probe molecules such as like water, hydrogen and helium [19]. The structural framework of these zeolites is of the Linde Type A (LTA) cubically symmetric type. Zeolite 3A is a synthetic crystalline potassium aluminosilicate that is usually obtained by ion exchange from the sodium form of zeolite type 4A [20,21].

Pore textural properties of each adsorbent were characterized from sorption analyses of CO_2 at 273 K measured with a TriStar II 3020 apparatus (Micromeritics, USA). The adsorbents were degassed at 473 K at a pressure of 10^{-2} Torr for 24 h prior to sorption measurements on the TriStar II 3020. A summary of the pore volumes and surfaces areas measured is presented in Table 1, the CO_2 isotherms measured on the TriStar II 3020 and the calculated pore size distributions are included in the SI. These results indicate that the CO_2 equilibrium capacities at 273 K and 130 kPa rank in the order CMS > 4A > clinoptilolite > 3A.

The purities of gases used in this work, as stated by the supplier Coregas Australia, were Grade 5 (99.999%) for helium and nitrogen and grade 4.5 (99.995%) for carbon dioxide.

3. High pressure gravimetric adsorption apparatus

Adsorption isotherms of pure helium on the four adsorbents were measured at (303–343) K and pressures up to 3500 kPa using a BELSORP-BG high pressure gas adsorption instrument (BEL, Japan). A schematic of the BELSORP-BG instrument is shown in Fig. 1. Prior to adsorption measurements the sample was degassed in-situ at 423 K under an ultimate vacuum of 1×10^{-5} Torr, or lower, for 12 h. The sample mass is measured continuously during an adsorption experiment using a magnetic floating balance (RUBOTHERM, Germany).

The sample basket is connected to the permanent magnet and the volume of the magnetic coupling section excluding the sample

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