Protocol for Obtaining Reference Isotherm Using RM 8852 and Carbon Dioxide.[*]

Materials: The adsorbent is NIST Reference Material RM 8852[†] (ammonium ZSM-5 zeolite). The sample mass to be used should be optimized to achieve the best signal-to-noise ratio, according to the experimental parameters of the instrument being used. The adsorptive, carbon dioxide, should have a purity of not less than 99.999 %.

Sample Pretreatment: The zeolite should be outgassed using a turbomolecular pump and slowly heated to 350 °C (1 degree per minute, nominally) and held at that temperature for at least 12 hours under high vacuum (<1 cPa) with continuous pumping. If the outgassing is performed in a separate manifold, prevent contact with air when transferring to the analysis instrument.

Measurement of Adsorption Isotherms: Carbon dioxide adsorption isotherms should be measured at 20 °C over a pressure range of 1 kPa to 4.5 MPa. The same measurement is also to be done without the adsorbent to perform a "blank correction." This blank should be subtracted from the adsorption isotherm.[‡] The Span and Wagner[§] equation of state is to be used to determine the density/compressibility of the gas for the determination of surface excess uptake. RM 8852 has a skeletal density of ≈2.36 g/cm^3, which is to be used when performing buoyancy correction for gravimetric technique or void volume determination for volumetric technique.

Comparison to the Reference Isotherm Function to Measured Isotherms: Measured isotherms should fall within the 95% uncertainty interval of the reference isotherm function,

$$n_{ex} = \frac{d}{(1 + \exp[(-\ln(P) + a)/b])^c} \pm U_{k=2},$$

where n_{ex} is the excess uptake (mmol/g), P is equilibrium pressure (MPa); a, b, c, and d are fit parameters with values of a = -6.22 (0.08), b = 1.97 (0.01), c = 4.73 (0.21), and d = 3.87 (0.01); and $U_{k=2}$ = 0.075 mmol/g is the k = 2 uncertainty.

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[*] H. G. T. Nguyen et al., A Reference High-pressure CO_2 Adsorption Isotherm for Ammonium ZSM-5 Zeolite, *Adsorption* **2018**, *24*, 531. Available On-line.

[†] NIST Reference Materials, RM 8852 – Ammonium ZSM-5, Information On-line.

[‡] H. G. T. Nguyen, J. C. Horn, M. Thommes, R. D. van Zee, L. Espinal, Experimental Aspects of Buoyancy Correction in Measuring Reliable High-pressure Excess Adsorption Isotherms Using the Gravimetric Method, *Meas. Sci. Technol.* **2017**, *28*, 125802. Available On-line.

[§] R. Span, W. Wagner, A New Equation of State for Carbon Dioxide Covering the Fluid Region from Triple-Point Temperature to 1100 K at Pressures up to 800 MPa, *J. Phys. Chem. Ref. Data*, **1996**, *25*, 1509-1597. Available On-line.

In addition, the following recommendations for measuring of this high-pressure CO_2 adsorption isotherm are offered:

- Sample Activation: Sufficiently complete sample activation is crucial. RM 8852 requires special handling to ensure the sample is activated completely. As noted above, the zeolite must be activated at 350 °C for at least 12 h under high vacuum (≤1 cPa) to realize the reported reference isotherm. Care should be taken no to exceed 350 °C, to avoid deamination. If the sample is activated ex-situ, exposure to air and moisture must be avoided to obtain the correct sample mass.
- Sample Volume Determination: Proper determination of sample volume is needed both for buoyancy correction in a gravimetric system, as well as the void volume determination in a volumetric system. If required in data analysis, a skeletal density of 2.36 g/cm^3 should be used for RM 8852.
- Buoyancy Correction/Void Volume Correction: A buoyancy correction must be applied when using a gravimetric system. Although less important at low-pressures, buoyancy effects are significant for high-pressure measurements and cannot be overlooked. This is analogous to the use of void volume in a volumetric instrument to determine surface excess uptake, and the effect of using the wrong volume also becomes more significant with increasing pressure.
- Equation of State. In general, identify the equation of state used to calculate fluid density, and use critically evaluated equations, such as those contained in the NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP). The Span and Wagner equation of state should be used for CO_2 at 20 °C to replicate the results shown here.
- T, P, and m. Ensure good control and measurement of temperature, pressure, and sample mass, as these are important in accurate determination of the uptake.
- Blank Correction. A blank run subtraction should be performed whenever possible, as it corrects for small uncompensated transducer nonlinearities, effects of temperature heterogeneities coupled with the compressibility of the adsorptive, and other experimental effects.