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ISIS

Temperature-programmed Isochoric Desorption

Adding Value to Neutron Studies on Nanoporous Materials

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I. Motivation and Objectives

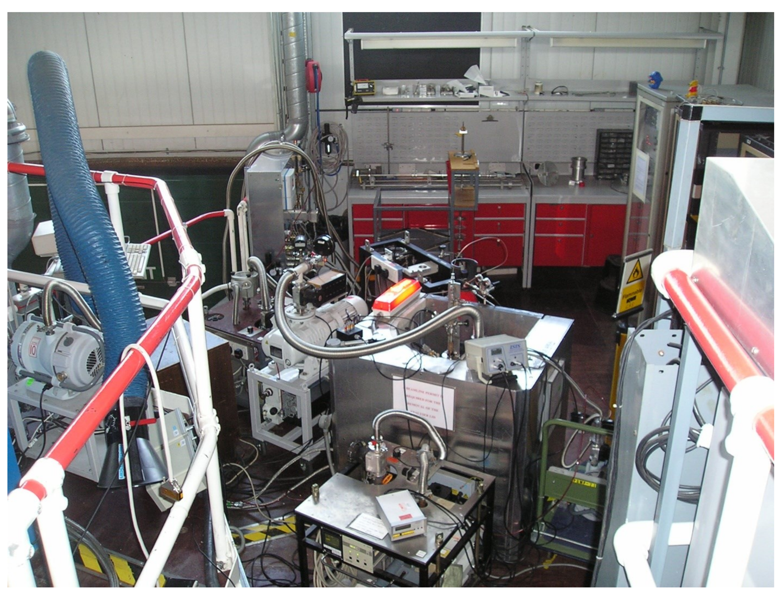
• Adsorption experiments using neutrons are valuable yet they can be time consuming and resource intensive [1,2].

• Adsorption behaviour typically measured *ex-situ*, and over a restricted set of temperatures [3]. Also, there is no guarantee that sorbent will behave in an identical way under neutron beam.

• Ideally, we would like to combine neutron and gas-adsorption studies into the same experimental setup.

• *Temperature-programmed Isochoric Desorption* (TIDES) circumvents many of the above difficulties.

II. Methodology



In a typical neutron experiment, we have:

• Gas-handling rig with calibrated volumes for manifold and sample cell.

• Temperature regulation and control down to liquid-He temperatures, e.g., use of a CCR.

The TIDES protocol involves:

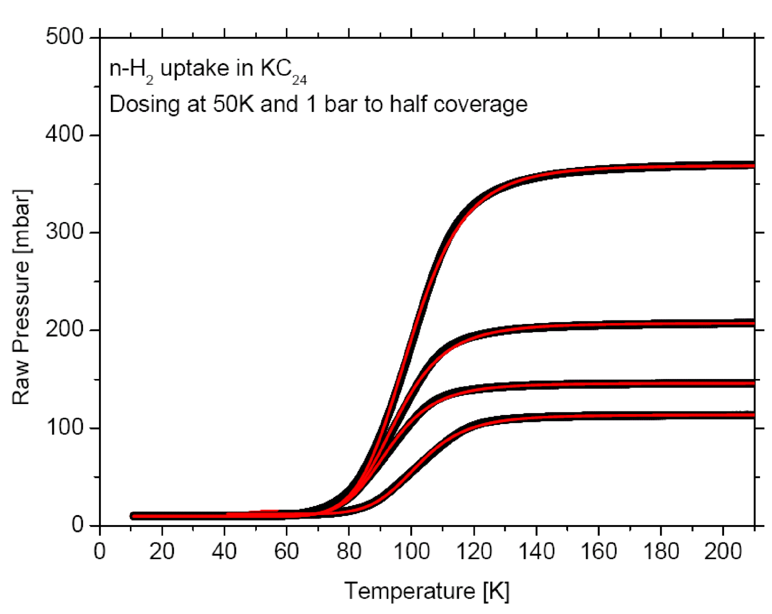
• Isothermal gas dosing.
• Sample isolation and cool down.
• Desorption run into a known volume with equilibration at each T step.
• For ideal gases in the Henry-law limit, desorption can be described using equation on the right.

$$P(T) = P_{max}\left[\frac{1}{1+\frac{P_{max}}{AT}e^{\frac{E_{ads}}{kT}}}\right]$$

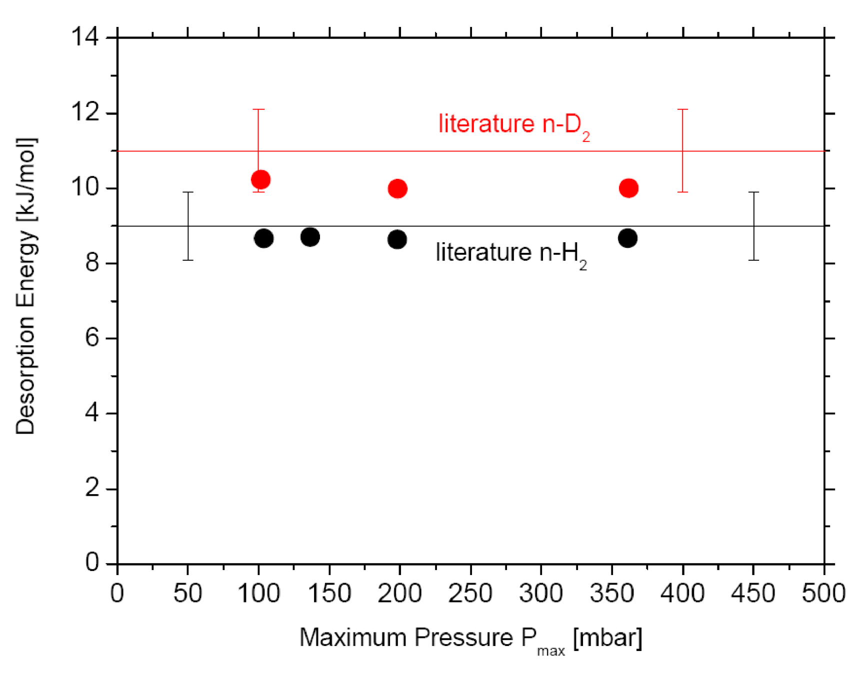
where

- E_{des} is the adsorption energy.
- lnA ~ adsorption entropy.
- P_{max} ~ initial load.

III. Case Study: Hydrogen Uptake in KC_{24}

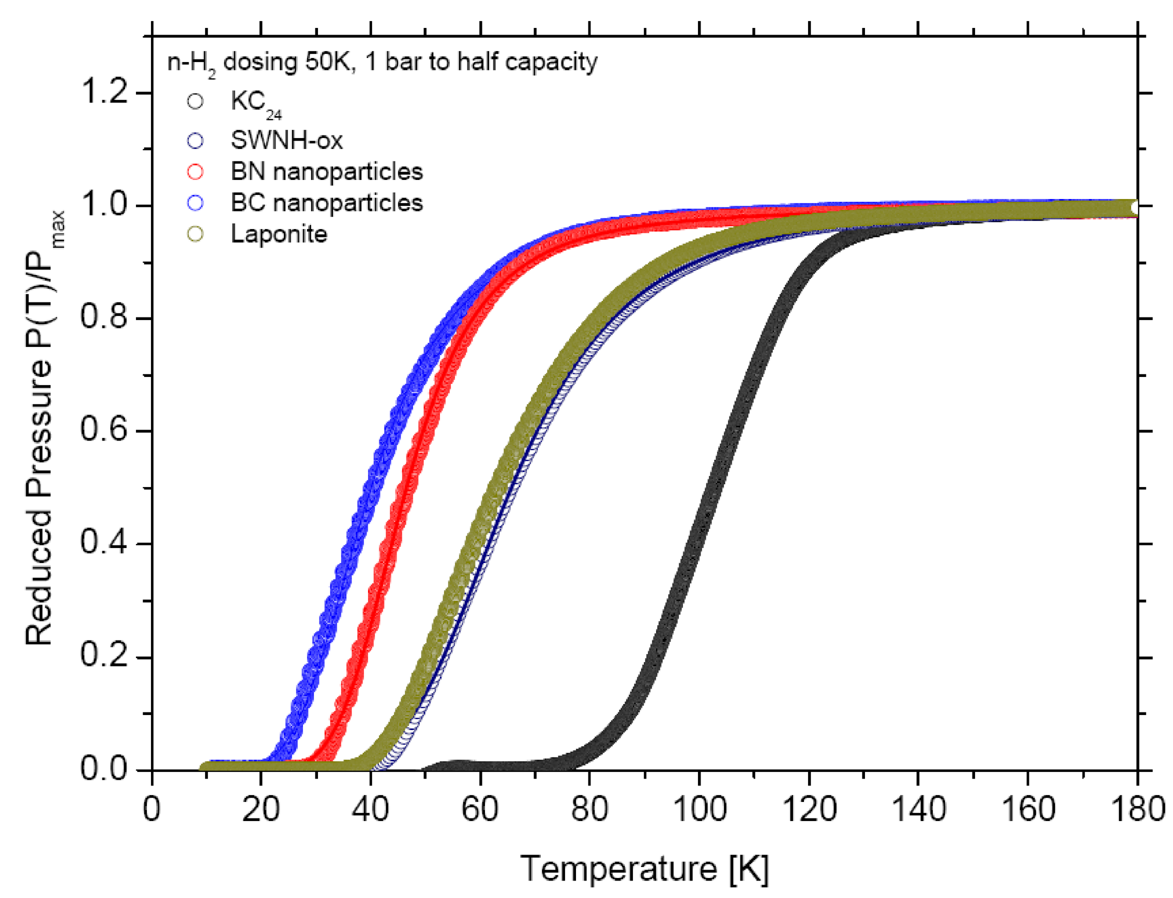


Left: TIDES runs under different isochoric conditions. The experimental data is adequately described by the equation above. The effects of non-ideal-gas behaviour and T-dependence of gas entropy are negligibly small.



Right: adsorption energies for H_2 and D_2 adsorption in KC_{24}. Agreement with literature values is excellent [4-7]. Practical desorption temperatures can reach up to ~150K at moderate pressures.

IV. Hydrogen Uptake Beyond KC_{24}



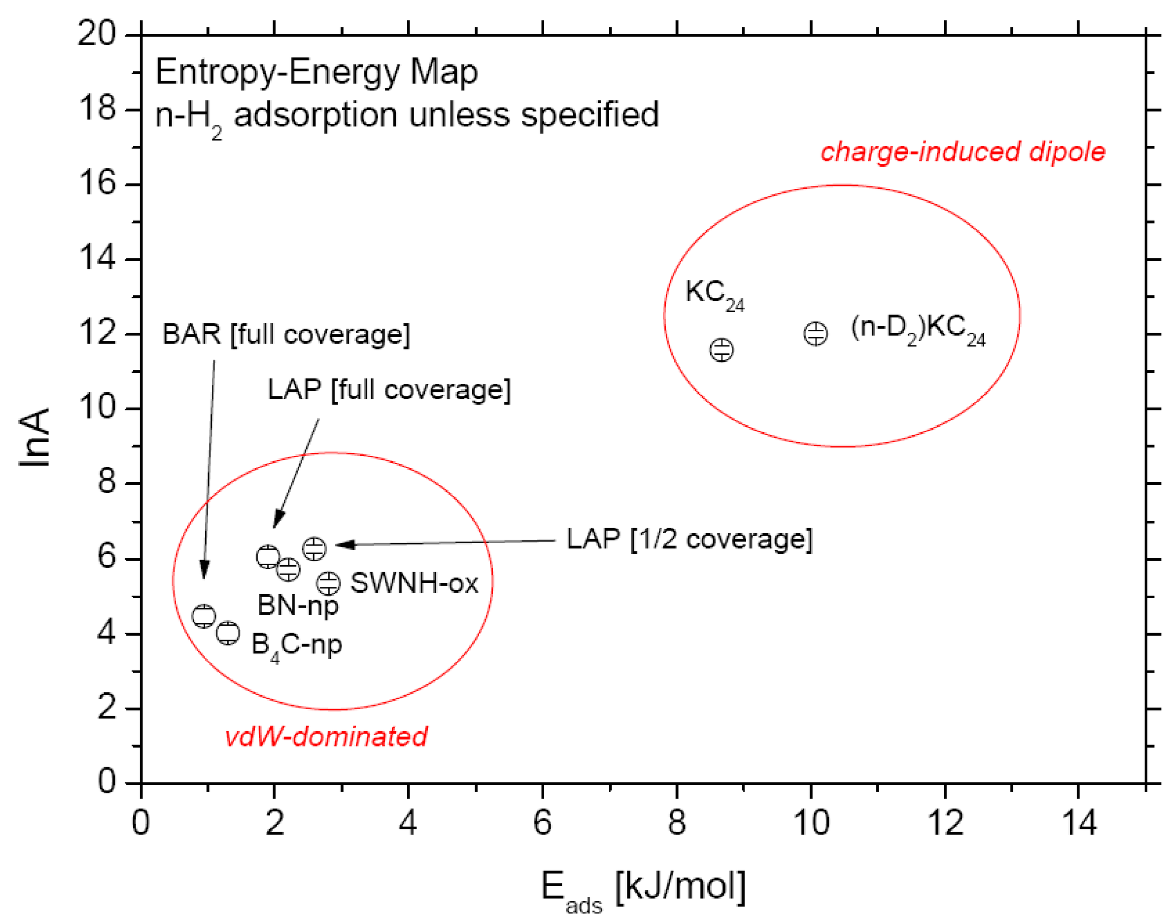
• Method has been applied to supercritical H_2 uptake by several sorbents, including carbon nanohorns, boron-based nanostructures, and clays.

• Highest desorption T's are found for metal-doped graphite (~3T_c), followed by carbon nanostructures and clay minerals (~2T_c).

• TIDES parameters can be used to construct "entropy-energy maps" to classify the thermodynamics of gas uptake for a given adsorbate.

• For H_2, materials tested so far are grouped into two classes, according to the underlying mechanism of H_2 physisorption.

• High desorption T (>2T_c) requires activation and dominance of charge-induced-dipole interactions.



Outlook

• We have developed a simple method to characterise atomic and molecular uptake by nanoporous substrates.

• Our methodology is well-suited for use in conjunction with neutron-scattering studies, including diffraction and spectroscopy. A quantitative description of TIDES data is facilitated by the strong (exponential) dependence of TIDES profiles on adsorption energy.

• Next steps: extension of TIDES method to pseudo-isobaric conditions and higher operating pressures (tens of bar).

References

[1] F Fernandez-Alonso et al, in *Handbook of Nanophysics*, KD Sattler Eds; CRC Press, 2010; vol 5, pp 1-29.
[2] A.J. Ramirez-Cuesta et al, *Materials Today*, 2009, **12**, 54.
[3] F Rouquerol et al, *Adsorption by Powders & Porous Solids*, Academic Press, San Diego, 1999.
[4] T Enoki et al, *Graphite Intercalation Compounds and Applications*, Oxford University Press, Oxford, 2003.
[5] JJ Purewal et al, *Phys Rev B*, 2009, **79**, 05435
[6] A Lovell et al, *Phys Rev Lett*, 2008, **101**, 126101.
[7] M Krzystyniak et al, *Faraday Discuss* (in the press).