Low temperature H_2 adsorption on metal-organic frameworks

using a top-loading Optistat™Dry cryostat from Oxford Instruments

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Introduction

This application note reports a new optical configuration to easily and accurately measure low-temperature diffuse reflectance infrared spectra using a top-loading sample-in-exchange-gas **Cryofree** cryostat system, **Optistat**Dry TLEX from Oxfrod Instruments (Figure 1) and a Bruker Vertex 70 FTIR. This setup has been used to study gas-metal interaction in metal-organic frameworks, a class of materials with potential application in hydrogen storage for automotive vehicles.

Background

Hydrogen has the potential to be an exceptional green fuel in motor vehicles as it may be produced from renewable energy in a carbon-free cycle. However, challenges remain in improving hydrogen storage capacity in vehicles in order to improve range and usability. Metal-organic frameworks present a possible solution due to strong yet reversible physisorptive interactions between hydrogen and unsaturated metal sites which may be engineered into the framework. Low temperature in-situ gas dosing FTIR spectroscopy represents an excellent method to study the interactions between hydrogen and these sites and to extract thermodynamic parameters associated with gas binding to the framework.

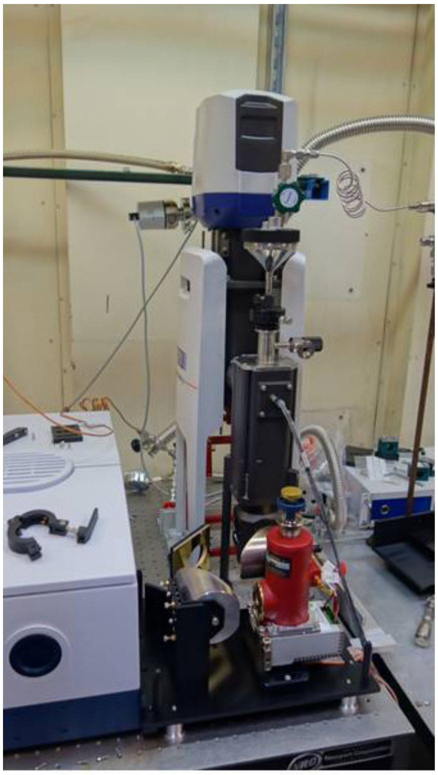

Figure 1. **Optistat**™Dry TLEX cryostat in the DRIFTS setup.

Experimental set-up

A Bruker Vertex 70 spectrometer equipped with a custom optical array (Bruker) was used to record IR spectra of Co2(dobdc) (dobdc = dioxidobenzenedicarboxylate), a metal-organic framework bearing unsaturated metal sites, in samples held in a custom gas-accessible cell held in the **Optistat**Dry TLEX cryostat. Infrared radiation from the Bruker spectrometer was to the sample in the cryostat by a system of mirrors, and diffuse reflectance was directed to a mercury cadmium telluride detector. The entire **Optistat**Dry TLEX system was mounted on a jig fixed to the optical table so the sample position could be adjusted while in the cryostat. A sample containing approximately 15 mg of Co2(dobdc) was loaded into a custom cell attached to the end of the sample probe which had been modified to incorporate a gas dosing capillary, and a gas manifold was attached. Diffuse reflectance spectra before and after dosing hydrogen into the sample cell were recorded at a variety of temperatures and pressures.

Experimental Results

Difference spectra for hydrogen-dosed Co2(dobdc) in relation to the evacuated material showed distinct features which may be attributed to ν(H–H) which become IR active once polarized upon interacting with the framework surface (Figure 2). The temperature of the OptistatDry can then by varied which leads to a change in the amount of hydrogen adsorbed on the material. Thermodynamic parameters of the adsorption process may then be extracted by quantifying relative integrated intensities of the signal of interest (Figure 3).

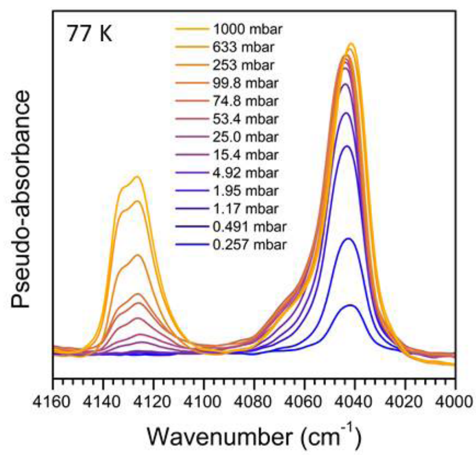

Figure 2. ν(H-H) of H_2 adsorbed in Co2(dobdc) at 77 K at various pressures.

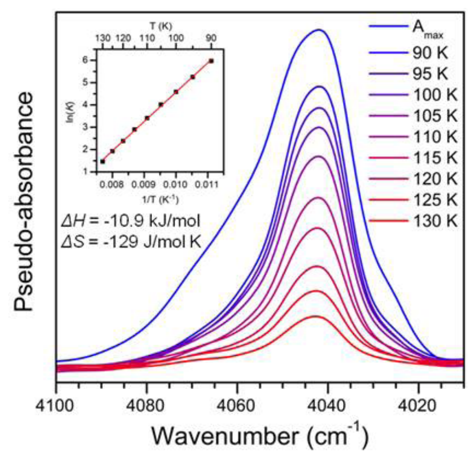

Figure 3. Variable temperature spectra of H_2 adsorbed on Co2(dobdc). Inset: Van't Hoff plot constructed from integrated peak intensities.

Conclusion and outlook

Diffuse reflectance spectra of hydrogen adsorbed on Co2(dobdc) were successfully recorded at a variety of temperatures using the OptistatDry cryostat. Precise control over temperatures in the sample chamber allowed for the determination of thermodynamic parameters of the adsorption process. This enables the spectroscopic study of site-specific gas-adsorbent interactions in these framework materials, which is of fundamental and practical interest in determining the gas storage properties of such materials.

About the **Optistat**Dry **Cryofree**® cryostat

OptistatDry provides a temperature controlled sample measurement environment within a **Cryofree** cryostat. It offers a range of top and bottom loading compact cryostats with optical access cooled by a closed cycle refrigerator. The system is capable of cooling samples to helium temperatures without the need for liquid cryogens. This provides significant benefits in terms of ease of use and running costs,. The system enables optical measurements to be carried out on your samples, as shown in this application note.

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