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Neutron Diffraction Experiments in Metal-Organic Frameworks for Hydrogen Storage and Isotope Separation

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Metal-organic frameworks have attracted considerable attention during the last past decade because of their potential application such as hydrogen storage and gas separation. Deuterium can be used for various applications such as nuclear fusion reaction, pharmaceuticals and chemical analysis, his demand is anticipated to increase in the future. Although D2 is highly versatile, natural abundance of D2 is really small, and its extraction from nature is one of the challenges in modern separation technology due to their identical size, shape and thermodynamic properties. The conventional techniques for hydrogen/deuterium separation like cryogenic distillation, the Girdler Sulfide process, thermal diffusion, and centrifugation are highly energy consuming and possesses a low efficiency.

Recently our group has participated in the characterization of a novel material for separating (H2/D2) isotope mixture, exploiting the gating effect in Metal-Organic Frameworks [1]. MFU-4 (Metal-organic Framework Ulm University) is constructed from {Zn5Cl6}6+ secondary building units interconnected with BBTA linkers [2]. MFU-4 structure possesses a pore system of alternating small and large cavities connected by a small square-shaped aperture formed by four chlorine atoms. An adsorbed molecule has to pass for the small cavity (2.88 Å) to reach the large one. The small cavity and the aperture act as separation gates, and the large cavity (11.94 Å) offers the surface area for storing large amounts of deuterium. The narrow apertures between the small and the large cavities form a barrier using four atoms of Cl which is based on the Pauli repulsion between the Cl atoms and H2, making classical diffusion impossible.

Neutron powder diffraction (NPD) is a technique that may provide a fundamental insight of adsorption such as the exact adsorption sites of hydrogen isotopes within the framework and their occupancy as function of the pressure and loading temperature. The Physics Department at IFE possess the facilities (JEEP-II reactor, powder neutron diffractometer PUS) to perform this demanding type of measurements.

For this project, adsorption of two different gases (D2 and 1:1 H2/D2 mixture) on MFU-4 will be investigated. A background of the empty material will be first measured. Afterward, adsorption of D2 will be investigated using as loading temperatures 30K, 50K and 70K for a fixed loading pressure of 0.5 bar. A mixture 1:1 (H2/D2) will be used as loading gas at the temperatures 40K, 50K and 60K with a fixed pressure of 0.5 bar and evacuating the remaining gas in the sample cell after 20 min of loading. In all cases, after the loading process the sample will be cooled to 19.5 K and the neutron diffraction pattern will be collected. This investigation will provide key information on the preferential occupancy of the different

adsorption sites for hydrogen isotopes (H2 and D2). Moreover, the proposed STSM will establish a new line of collaboration between the Institute for Energy Technology (IFE) and the Max Planck Institute for Intelligent Systems.

[1] Teufel, J., H. Oh, M. Hirscher, M. Wahiduzzaman, L. Zhechkov, A. Kuc, T. Heine, D. Denysenko and D. Volkmer (2013). "MFU-4 - A Metal-Organic Framework for Highly Effective H-2/D-2 Separation." Advanced Materials 25(4): 635-639.

[2] DDenysenko, D., et al., Elucidating Gating Effects for Hydrogen Sorption in MFU-4-Type Triazolate-Based Metal-Organic Frameworks Featuring Different Pore Sizes. Chemistry-a European Journal, 2011. 17(6): p. 1837-1848.