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Application Notes 5

使用 HPVA 研究金属有机骨架（MOFs）材料在高压下的储氢性能

摘要

确定 MOFs 材料和其他微孔材料的储氢性能是现代氢经济推进的一个重要任务。在发展氢燃料电池中，得到有效的储氢方法是一个非常重要的方面。而在压缩氢气中，单位质量上能量密度很高，单位体积上的能量密度很低，因此不利于氢气储存。以液态形式储氢（大气压下 20K）也不利用节能。只有将氢气通过被吸附存储在固体材料里是最好的选择。由于能够获取较高的氢能量密度和吸附的可逆性，将氢气作为吸附气，高压注入到高比表面的 MOFs 材料表面进行储存是一种非常理想的过程。本文主要使用美国麦克的高压气体吸附仪 HPVA 研究了由 BASF 生产的四种 MOFs 材料的储氢性能。

Application Note 5

Using the HPVA to Analyze Hydrogen Storage Potential of Metal Organic Frameworks at High Pressures

Determining the hydrogen storage capabilities of materials such as Metal Organic Frameworks (MOFs) and other highly microporous materials is an important undertaking in the modern push for a hydrogen economy. An efficient method of hydrogen storage is a critical aspect in the development of hydrogen fuel cells. Hydrogen gas has a high energy density by mass but a low energy density by volume when stored as a compressed gas, making it unfavorable for hydrogen storage. Maintaining hydrogen in a liquid state (20 K at atmospheric pressure) also is not energy efficient. Storing hydrogen in a solid material by adsorption is the best alternative, requiring less volume than compressed gaseous hydrogen and consuming far less energy than required to liquefy hydrogen. Dosing high pressure hydrogen onto high surface area MOFs for storage as an adsorbed gas is a highly desirable process due to the high hydrogen energy density obtained and the availability of reversible adsorption.

Four commercially available MOFs produced by BASF were analyzed with Particulate Systems' High Pressure Volumetric Analyzer (HPVA) to determine their hydrogen storage potential. Those MOFs are: Basolite C300, a copper-based organic framework; Basolite F300, an iron-based organic framework; Basolite Z1200, a zinc-based organic framework; and Basolite A100, an aluminum-based organic framework. Approximately 500 mg of each MOF was placed under vacuum and slowly heated up to 200 °C for a period of 12 hours (Z1200 was only heated to 100 °C to prevent degradation of the sample) using the HPVA degas port. All four samples were analyzed at liquid nitrogen temperature (77 K) in a liquid nitrogen bath, utilizing the cryogenic option for the HPVA, up to pressures of 100 bar. An isothermal jacket was used to maintain the cryogenic temperature zone of the samples during analysis. At 77 K, each MOF showed different amounts of hydrogen uptake; C300 adsorbed the most while F300 adsorbed the least. A plot of the isotherms generated from the analyses is shown in Figure 1.

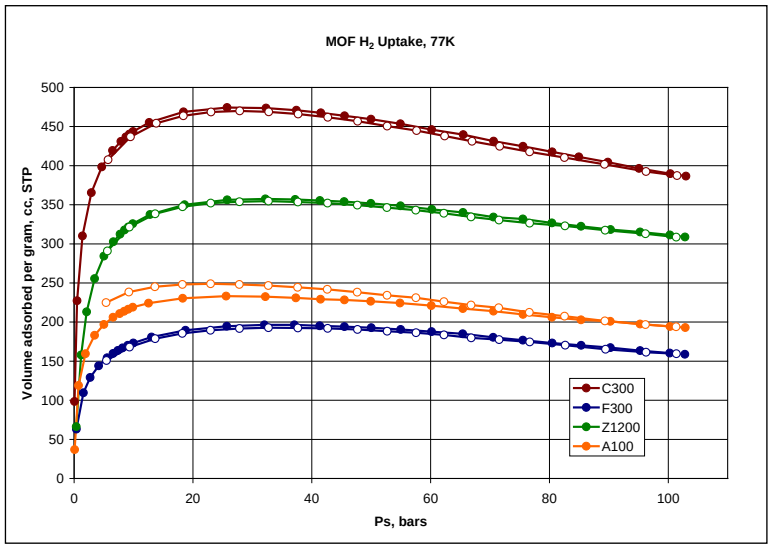

Figure 1: *An overlay of the excess isotherms generated from the analysis of various MOFs with hydrogen at 77 K. The solid circles represent the adsorption isotherms and the hollow circles represent the desorption isotherms.*

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The isotherms displayed in Figure 1 exhibit a phenomenon in which the adsorption reaches a maximum and then declines as the pressure increases. This phenomenon is due to the increasing density of the hydrogen in the pores of the material at elevated pressures. The density of the adsorbing gas (H_2) inside the pores (a function of pore size) is far greater than the density of a non-adsorbing gas (He). Since the calculated amount of gas in the sample cell is based on the density of helium and its resulting free-space volume (including the volume inside the pores), the amount of free gas in the sample cell is overestimated. When using the static volumetric method, like that of the HPVA, a maximum in the isotherm may be observed. This is used to create the excess isotherm as shown in Figure 1. To generate the absolute isotherm, the density of the gas and the volume of the pores must be included in the calculations. Since the pore size and distribution of these types of materials are not readily available to most users, the excess isotherm will suffice and is commonly reported for adsorption isotherms.

An alternative method to see the storage capacity of materials from the excess isotherm is to view the amount of gas adsorbed as a function of the sample weight. The target weight percentage of hydrogen uptake for storage purposes is between 7% and 8%. Figure 2 shows an overlay of the weight percentage plots based on the isotherms displayed in Figure 1.

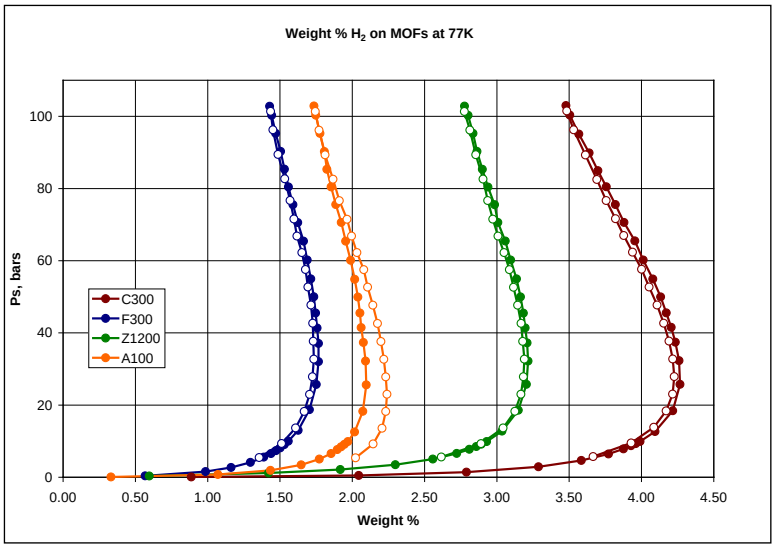

Figure 2: *Weight percentage plots of various MOFs analyzed with hydrogen at 77 K.*

Since the Basolite C300 adsorbed the most hydrogen at 77 K, it was also analyzed at two additional temperatures. For one analysis, an ice bath was used to maintain the sample at 0 °C. For the second, a recirculating water vessel was used to maintain the sample temperature at 30 °C. For these two experiments, the sample was dosed with hydrogen to pressures up to 200 bar, the full extent of the pressure range obtainable with the HPVA. The excess isotherms are shown in Figure 3 and the weight percentage plots in Figure 4.

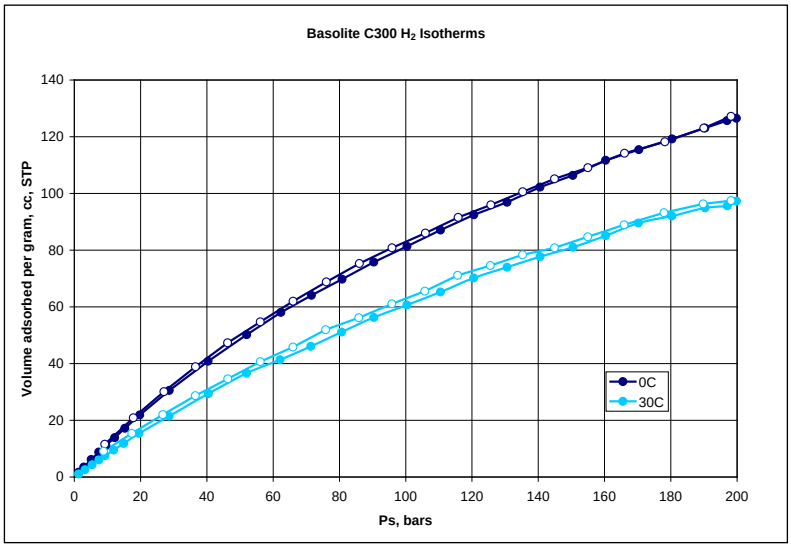

Figure 3: *Hydrogen uptake on Basolite C300 at 0 °C (dark blue) and 30 °C (light blue).*

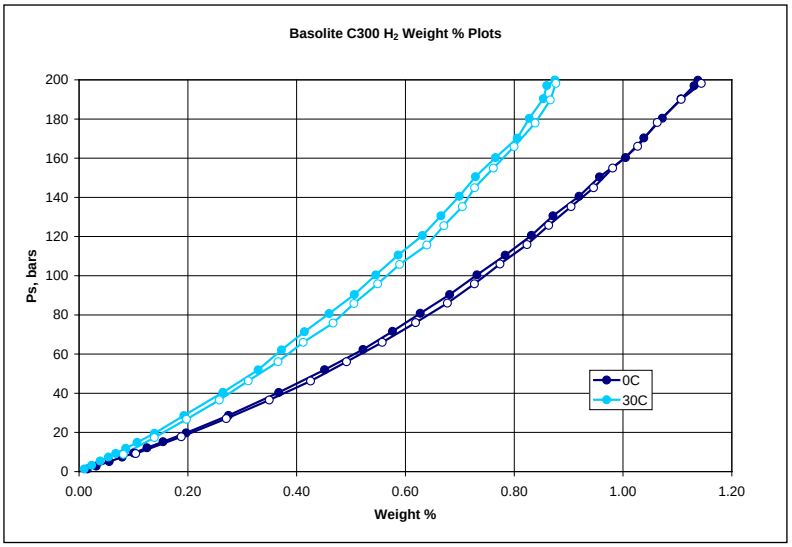

Figure 4: *Weight percentage plots of hydrogen on Basolite C300 at 0 °C (dark blue) and 30 °C (light blue).*

When reviewing the data in Figures 1 through 4, it is clear that the HPVA is a powerful tool for evaluating the hydrogen storage potential in MOFs and other microporous powders. The HPVA, with its wide temperature range (from cryogenic to 500 °C) and its ability to dose up to 200 bar of pressure, is perfect for analyzing samples under extreme conditions while providing accurate data.