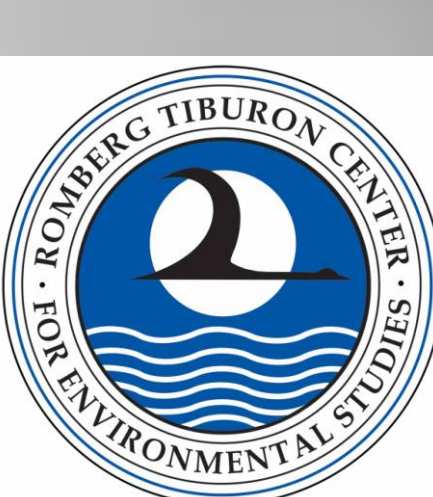# Evaluation of Hydrogen Storage in Metal Organic Frameworks by Bridged Hydrogen Spillover

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Abstract:

Hydrogen has the potential to be the next energy carrier. The ability to use hydrogen in fuel cell technologies depends largely on the ability to store hydrogen efficiently. Metal-Organic Frameworks (MOFs) belong to an interesting set of materials that consists of porous channels and have been shown to carry potential for hydrogen storage when added to metal catalysts. MOFs alone show no potential to store hydrogen, but when added to metal catalyst they can exhibit a spillover effect to increase hydrogen storage capacity. The key critical issues with MOFs are to validate the promises that MOFs can provide with spillover, since spillover intricately linked to more standard H_2 storage mechanisms. The current project focuses on the synthesis of Isoreticular Metal Organic Framework-8 (IRMOF-8) added to platinum on Activated Carbon (AC) and bridged together with sucrose to enhance the spillover effect. In order to reach hydrogen storage goals, a method must be proven to have enough capacity for the adsorption/resorption (reversibility) at ambient and 120 bar reasonable pressures. With the tremendous interest in spillover materials for hydrogen storage, NREL and DOE have dedicated resources to synthesize specific materials and to develop, perform, and validate the requisite measurements.

Introduction

The use of hydrogen as the source of energy for fuel cell technologies relies on the development of an efficient and cost effective hydrogen storage system.[1] Porous metal-organic frameworks (MOFs) are potential candidates for hydrogen storage.[2] MOFs form a coordination network constructed by multidentate ligands and metal atoms joined by coordinate bonds. MOF's ability to have and retain a three dimensional structures gives them a unique network of channels and pores that are able to be filled with various gaseous species.[3] Unfortunately, MOFs also have the disadvantage that they can easily decompose in the presence of air or moisture.[7] In order to be demonstrated as feasible for hydrogen storage, a sorbent matrix must be proven to have enough capacity for the adsorption/desorption (reversibility) at ambient temperatures and up to 150 bar. Current MOFs with their low isosteric heats of hydrogen adsorption, fail to hold on to sufficient dihydrogen species at ambient temperatures, i.e. they have extensive physisorption at cryo temperatures.[3] Physisorption is specifically related to adsorption and shows that the involvement of weak intermolecular forces are involved between the hydrogen and metal catalysts.[7] Hydrogen spillover, also known as weak chemisorption, is the weak bonding that hydrogen can create with metal nanoparticles such as platinum and the migration of hydrogen atoms onto connecting surfaces.[4] According to Miller et al.[5], the spillover effect can be increased if there is a system of support between the MOFs and the platinum on activated carbon showing the possibility of increased hydrogen storage near ambient conditions. Previous work completed by Li and Yang[1], illustrates that up to 4 wt % hydrogen can be reversible adsorbed/desorbed on a bridged-MOF at room temperature and 100 atm (Figure 1). The goal was to focus on the replication of Li and Yang's results[1], to validate the potential of spillover when bridging was involved between IRMOF-8 and metal catalyst. The current project involves the synthesis of isoreticular metal-organic frameworks (IRMOF), specifically IRMOF-8 and combining it with Platinum on Activated Carbon using sucrose to serve as the bridge. The U.S. Department of Energy's (DOE) current goal to look into spillover materials is to validate spillover on metal organic frameworks or bridged framework materials.[6]
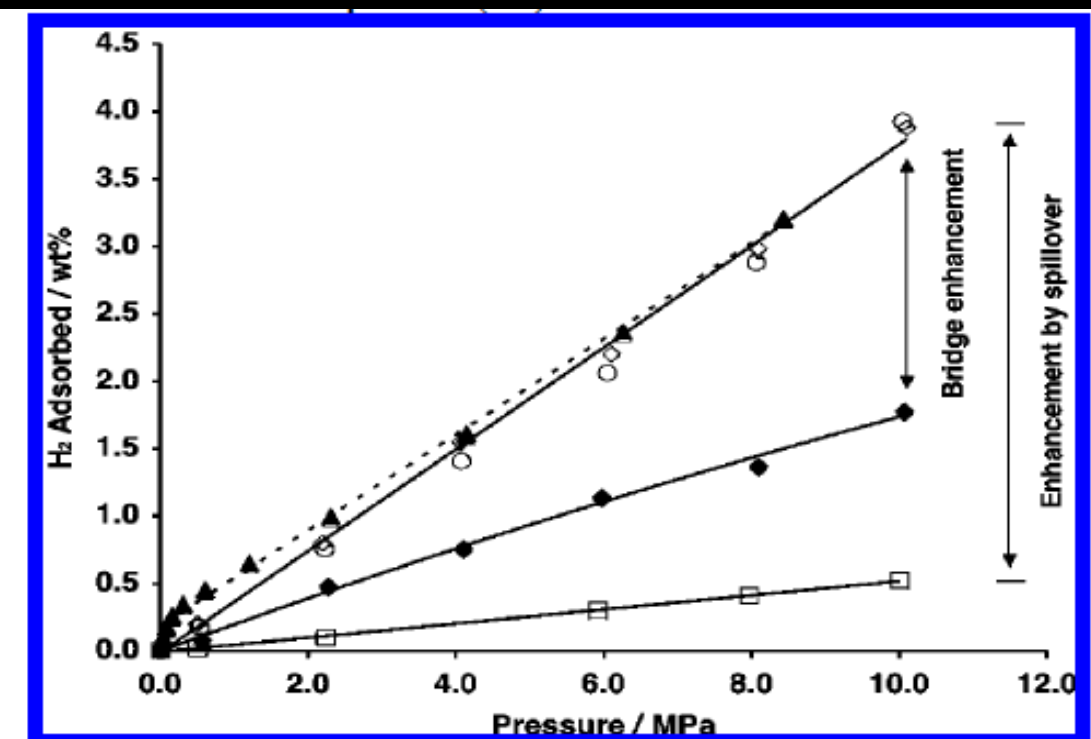

Figure 1.[1] High-pressure hydrogen isotherms at 298 K for pure IRMOF-8 (□), Pt/AC and IRMOF-8 physical mixture (1:9 weight ratio; ◆) and for a bridged sample of Pt/AC-bridges−IRMOF-8: first adsorption (○), desorption (▲), and second adsorption (◇).

Materials and Methods

To a 250 mL round bottom flask 1.19 g of zinc nitrate hexahydrate was added to .43 g of 2,6-napthalene dicarboxylic acid. About 50 mL of N,N-Dimethyl Formamide (anhydrous DMF) was added and stirred vigorously until completely dissolved. The reaction was performed in an inert N_2 atmosphere. To the stirring mixture, .15 mL of hydrogen peroxide was added to the round bottom flask. Subsequently, .2 mL of triethylamine was added every 5 minutes for 50 minutes. Next, .15 mL of triethylamine was added to the stirring mixture every 5 minutes for 10 minutes for a total volume of 2.3 mL. The reaction was allowed to stir for 1 hour and a half before filtering. The white precipitate was washed with 60 mL of DMF and then was washed with 60 mL of ethylene glycol dimethyl ether. The white precipitate was loaded onto a sample holder and heated to 180° Celsius for 24 hours at 10^{-6} torr then allowed to cool to room temperature and stored in a N_2 glove box.

IRMOF-8 Bridging: In a mortar and pestle, 200 mg of IRMOF-8, 25 mg of Pt 5% on Activated Carbon and 33.2 mg of sucrose were gently grinded. It was added to a vial and heated for 3 hours at 185 °Celsius subsequently the temperature was raised to 250°Celsius in flowing Helium at 500 torr. About 140 mg of the cooled sample was then degassed at 200°Celsius for 24 hrs at 10^{-8} torr.
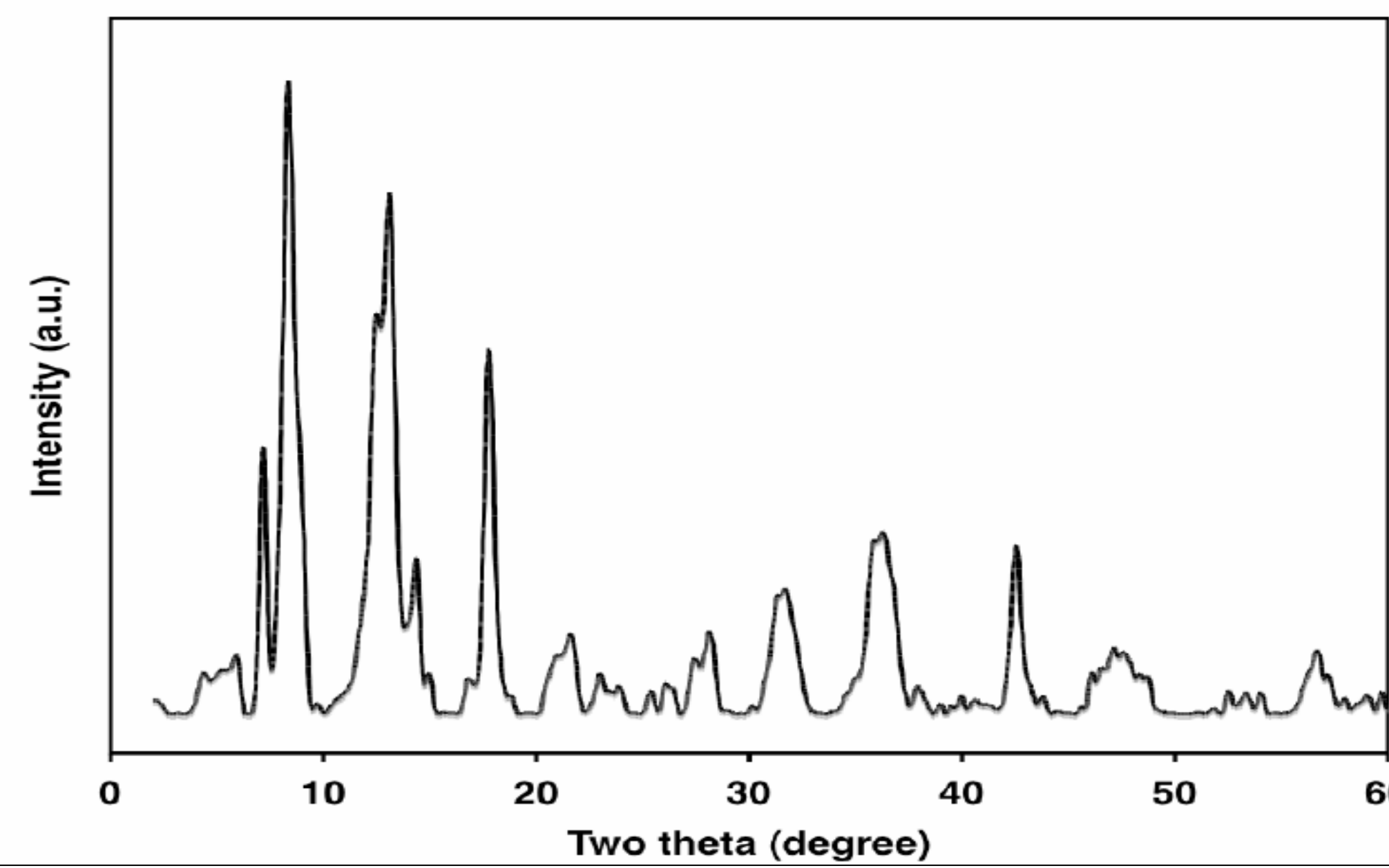
Characterization

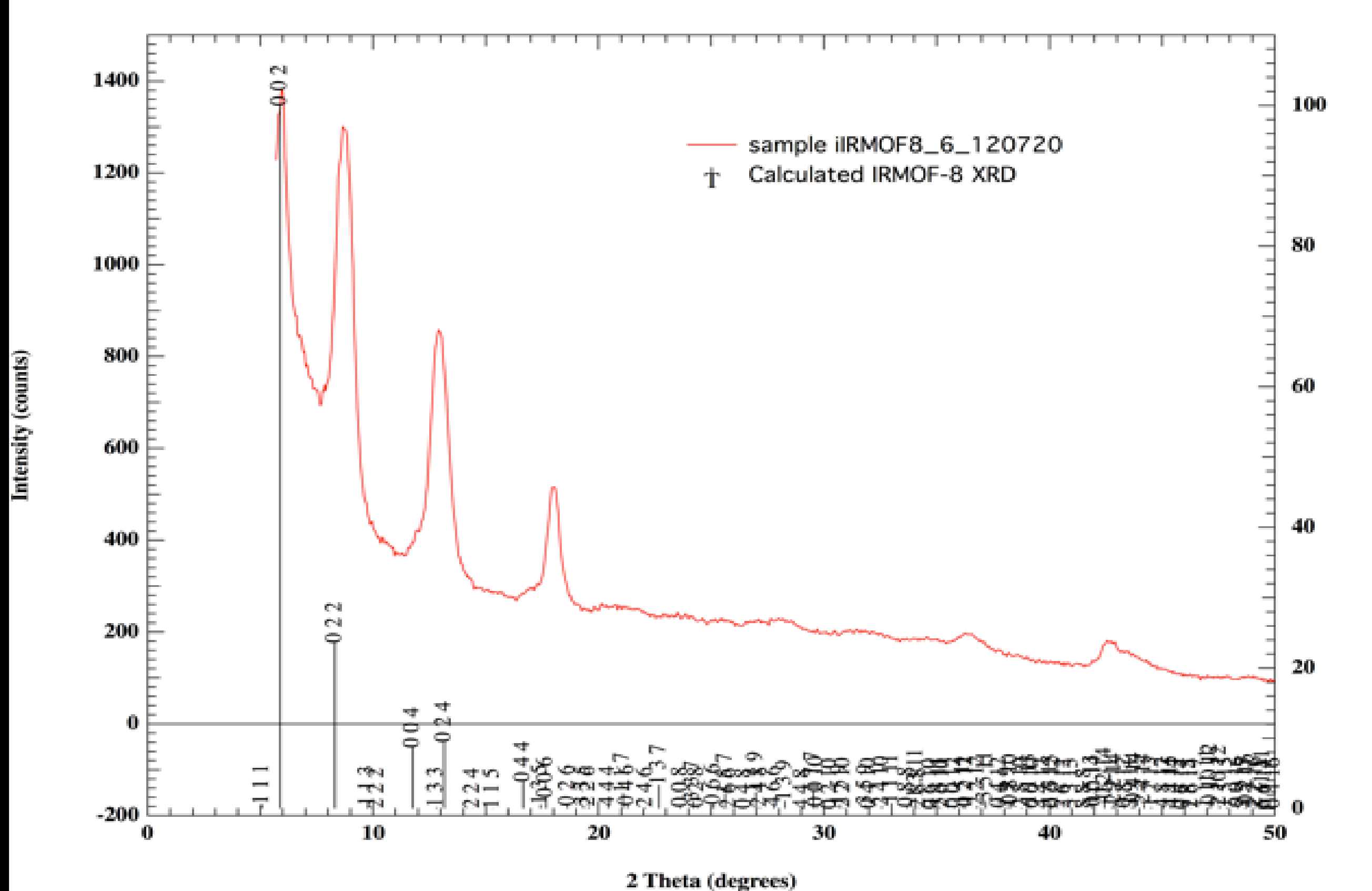Figure 2.[1] XRD IRMOF-8 Literature

Figure 3. XRD IRMOF-8 Experimental
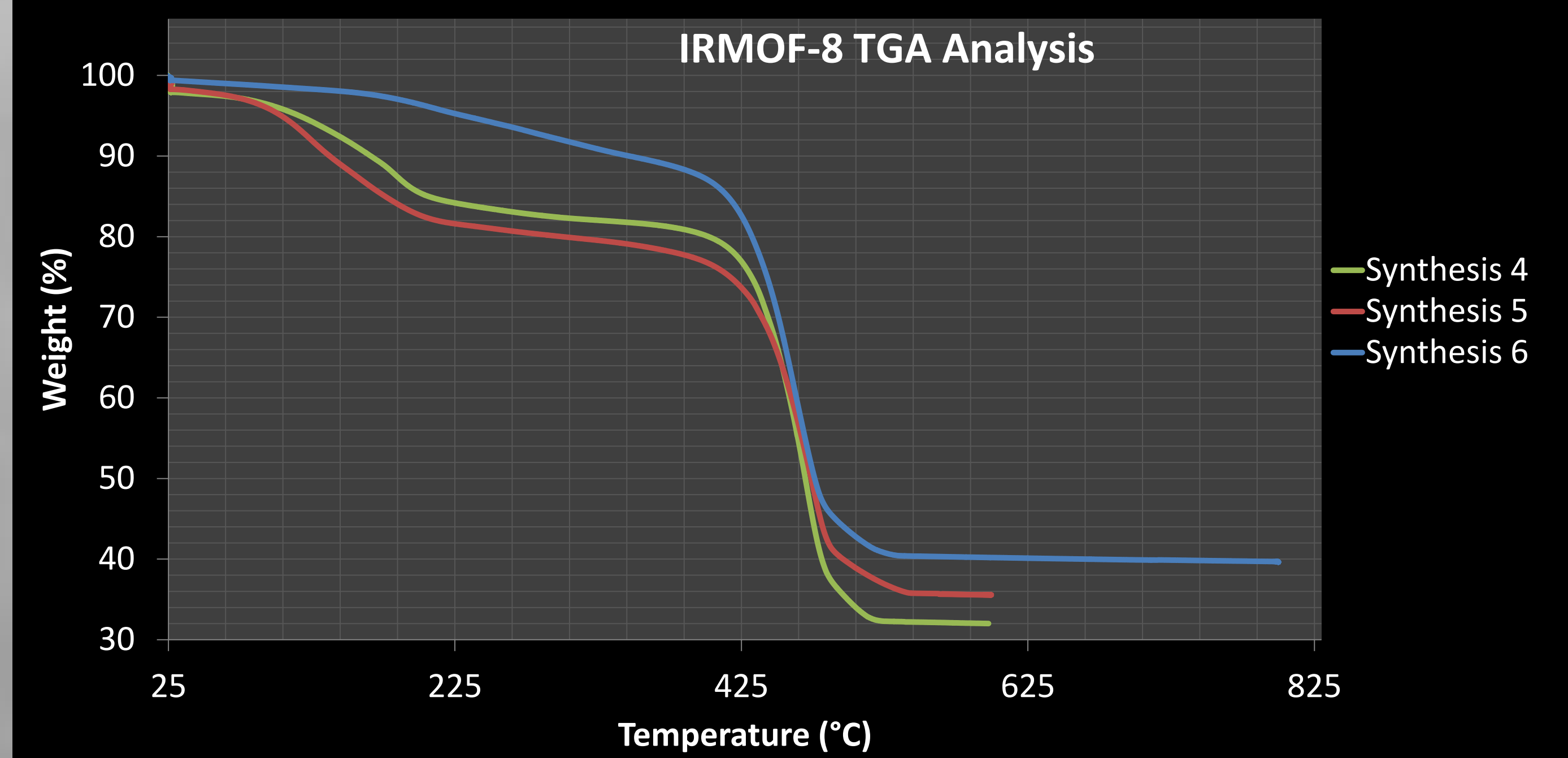
Characterization (continued)

Figure 4. Thermal Gravimetric Analysis of IRMOF-8. (Ramp 5°C/min to 600°C in flowing N_2)
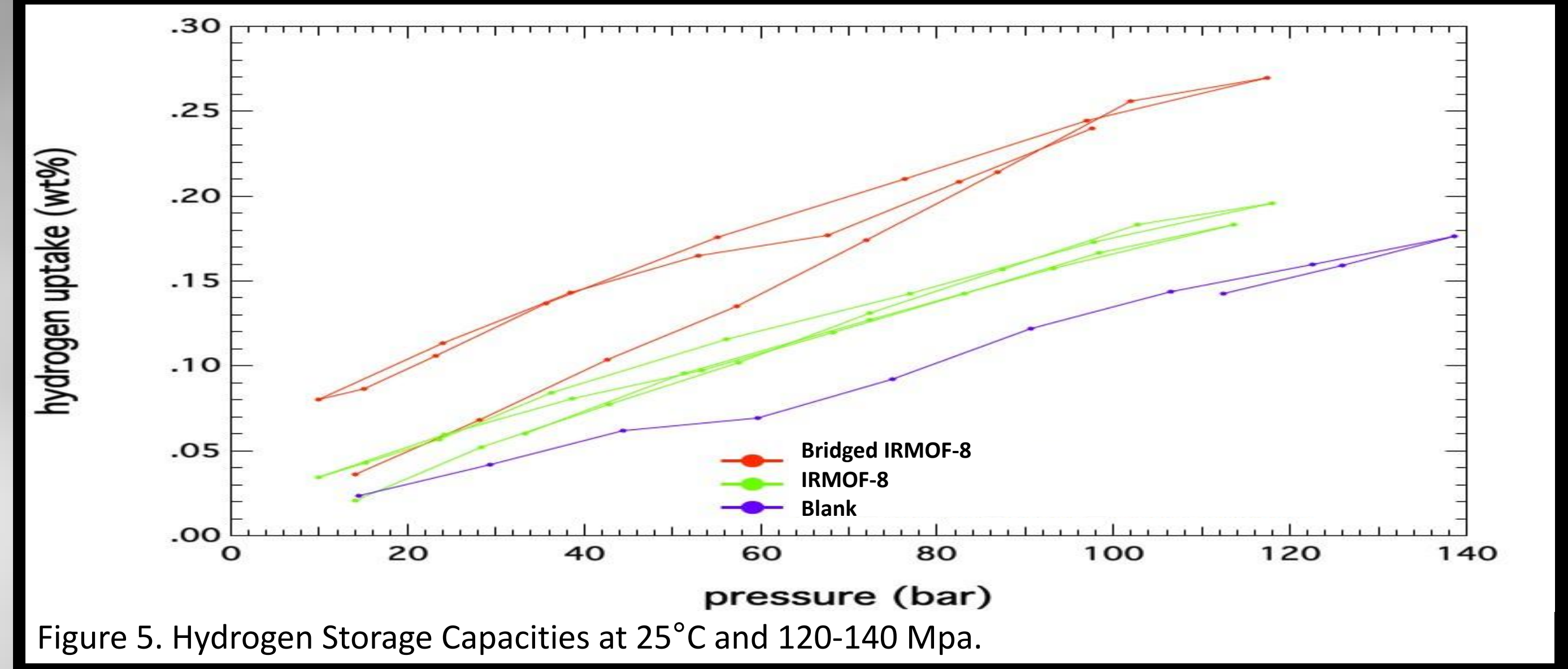

Figure 5. Hydrogen Storage Capacities at 25°C and 120-140 Mpa.

Discussion

The Experimental XRD of IRMOF-8 shows a peak at 002 that could be due to the solvent not being removed from the pores of the IRMOF-8. Close comparison with the literature XRD (Fig. 2) shows the experimental XRD (Fig. 3) to be in good agreement when done with same technique. The TGA data shows that the solvent can remain within the pores of IRMOF-8 (Fig. 4). Fig. 5 in comparison to the literature storage capacity (Fig. 1) does not show significant hydrogen storage capabilities. The maximum weight % achieved was .3. Fig. 5 shows that the IRMOF-8 combined with platinum on activated carbon bridged with sucrose fails to show spillover enhancement in hydrogen storage. Based on this experiment, MOFs when bridged with sucrose to platinum does not have an increased effect on uptake/release (reversibility).

References

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