Enhancing hydrogen uptake in uio-66 metal-organic frameworks: A comparative study of modified and pristine MOFS with tunable linker vacancies

M. Ledwaba[1, 2], L. Barbour[2], G. Ndlovu[1], and R. Hassanalizadeh[1]

[1]Mintek, South Africa
[2]University of Stellenbosch, South Africa

This study compares the hydrogen uptake capacity of pristine University of Oslo-66 (UiO-66) metal-organic frameworks (MOFs) to modified UiO-66 MOFs with missing linkers. By tuning the linker vacancies, the surface area of the MOFs can be significantly improved, leading to enhanced adsorption capacity and catalytic activity. Additionally, the pore size can be optimised to further enhance the MOF performance in hydrogen storage applications. The hydrogen uptake was studied at both high (up to 100 bar) and low pressures (up to 1 bar) at different temperatures. The surface area and pore sizes of the MOFs were measured using the Brunauer-Emmett-Teller method, while the hydrogen uptake at low pressures was assessed using a micrometric 2020 HD analyser. The Hiden Xemis intelligent gravimetric analyser was used to determine the hydrogen uptake at high pressures. According to our findings, the modified UiO-66 MOF had a larger pore size than the unmodified MOF, increasing its surface area from 1443 to 1698 $m^2.g^{-1}$, which led to a rise in hydrogen uptake at low pressures and low temperatures from 1.51 to 2.29 wt.%. The increase, however, still falls short of the 5.5 wt.% minimum hydrogen uptake required by the U.S. Department of Energy. At high pressures, the hydrogen uptake capacity increased from 7.4 to 10.3 wt.%. Our findings, in accordance with literature, suggest that low temperatures and high pressures are optimal conditions for efficient hydrogen uptake in these materials, which could lead to more cost-effective and efficient hydrogen storage. Furthermore, this research could pave the way for advancements in hydrogen fuel cell technology that relies on efficient hydrogen storage.

Keywords: Hydrogen uptake, storage, pristine MOFs, UiO-66, high pressures

INTRODUCTION

Hydrogen fuel cell technology has gained significant attention in recent years due to its potential to offer a cleaner and sustainable energy source. However, one of the major challenges facing the widespread adoption of this technology is the efficient and cost-effective storage of hydrogen gas. Currently, hydrogen storage technologies suffer from limitations such as low storage densities, high cost, and safety concerns. The U.S. Department of Energy (DOE) has established targets for hydrogen storage materials to promote the development of more efficient and cost-effective technologies. These targets include minimum requirements for storage capacity, release rate, and durability. The minimum requirement for usable hydrogen storage capacity is currently set at 5.5 wt.% for on-board storage in vehicles, but researchers are actively working to develop materials that can store hydrogen at higher capacities. These targets aim to increase the efficiency of these vehicles and reduce their greenhouse gas emissions (1). Various methods such as compression, liquefaction, and solid-state storage are being explored to develop effective hydrogen storage solutions (2).

Researchers have been working on developing new materials and technologies to address these challenges and improve the efficiency of hydrogen storage. For instance, nanoporous materials such as metal-organic frameworks (MOFs) and porous carbon have been shown to have high hydrogen storage capacities (3, 4). Additionally, advances in the development of hydrogen storage systems such as solid-state hydrogen storage tanks and chemical hydrides have shown promise in improving the storage density of hydrogen (5, 6). Therefore, it is important to continue exploring and improving upon hydrogen storage technologies to enable the widespread adoption of hydrogen fuel cell technology and its potential benefits for a sustainable future.

In recent years, MOFs have attracted significant attention as potential materials for gas storage and separation due to their tunable structures and high surface areas (7, 8). Among MOFs, UiO-66 has shown promise for hydrogen storage due to its high stability and large pore size (9). However, the low affinity of hydrogen for the MOF surface limits its storage capacity (10). To overcome this limitation, various methods have been developed to modify the MOF surface, such as linker functionalisation (11). The specific techniques used for linker functionalisation can significantly impact the performance of the MOFs for hydrogen storage.

The UiO-66 (Zr) MOF was founded in 2005 by a team of researchers from the University of Oslo and has since been extensively studied for its potential applications in gas storage, catalysis, and drug delivery (12). The UiO-66 (Zr) MOF is significant due to its high surface area, thermal stability, and ability to selectively adsorb gases (13). Tuning the UiO-66 (Zr) MOF involves modifying its structure and composition to enhance its properties and performance. This can be achieved through various methods such as doping, post-synthesis modification, and defect engineering (14).

Linker functionalisation has been shown to significantly impact MOF properties such as stability and gas adsorption capacity (15). Additionally, the optimisation of linker functionalisation has been reported to improve the performance of MOFs in various applications, including gas separation (16) and catalysis (17). The linkers used in UiO-66 (Zr) MOF are typically carboxylic acids, such as terephthalic acid or benzenedicarboxylic acid. They are responsible for connecting the metal nodes and creating the framework structure of the MOF. The length and flexibility of the linkers can also affect the porosity and gas adsorption properties of UiO-66 (Zr) (18). They are connected through six-membered rings of Zr-O-Zr, an example of which is shown in Figure 1 (19). These six-membered rings of Zr-O-Zr are known as zirconium oxide rings and they provide structural stability to the material. Additionally, the presence of these rings also contributes to the high thermal and chemical stability of zirconium-based MOFs (20).

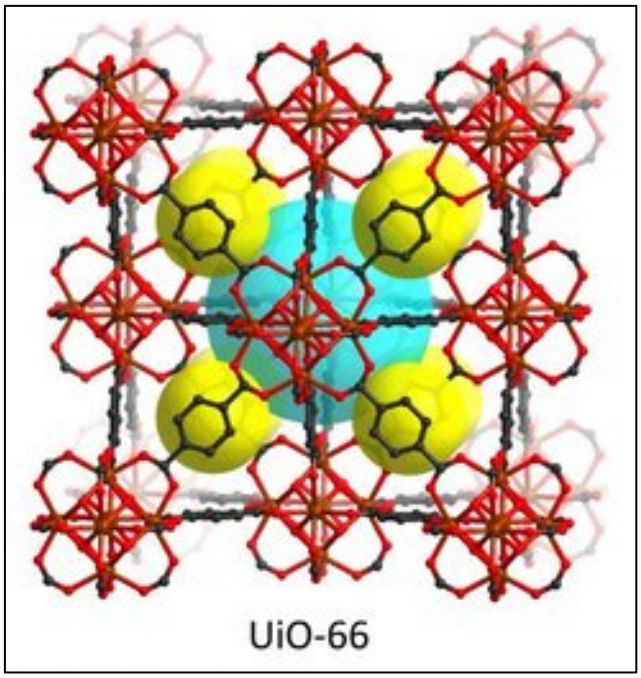

Figure 1. Structures of six-nodes in zirconium MOFs UiO-66. Red, white, and black spheres represent Zr, O and C atoms, respectively. The large yellow and turquoise spheres represent empty pores within the MOFs. (19).

Recent studies have shown the potential for MOFs to be effective in hydrogen storage, with some MOFs demonstrating high hydrogen uptake capacities and favourable desorption properties (21, 22). Modified UiO-66 MOFs, in particular, have been shown to have enhanced hydrogen storage properties due to their tuneable pore size and high thermal stability (23). However, there is still a need for further optimisation of these MOFs to achieve practical applications in hydrogen storage (24). Furthermore, the exploration of other types of MOFs as potential hydrogen storage materials, such as ZIFs and MILs, has also gained interest in recent years (25, 26).

Linker chemistry refers to the chemical reactions and interactions between the organic linkers and metal ions that form the MOF structure. Understanding and controlling linker chemistry is crucial for tailoring MOFs for specific applications. This paper aims to investigate the effect of linker functionalisation on the gas adsorption capacity of UiO-66 (Zr) MOFs. The results showed that tuning the linker chemistry can significantly impact the performance of UiO-66 (Zr) MOFs in hydrogen storage. The average surface area of UiO-66 (Zr) MOFs is approximately 1500 m^2/g. This makes UiO-66 (Zr) a promising material for the efficient adsorption of gases. We do however hypothesise that with the tuning of the linkers, we will introduce mesopores in the UiO-66 (Zr) structure and thus enhance its adsorption ability.

Materials and Experimental Methods

Chemicals and reagents

Zirconium tetrachloride ($ZrCl_4$, Sigma–Aldrich, 99.5+%, CAS no.: 10026-11-6), terephthalic acid (H_2BDC, Sigma–Aldrich, 98%, CAS no.: 100-21-0), hydrochloric acid (HCl, Sigma–Aldrich, 35%, CAS no.: 7647-01-0), formic acid (HCOOH, Sigma-Aldrich, >95%, CAS no.: 64-18-6), N,N-dimethylformamide (DMF, Sigma–Aldrich, 99.8%, CAS no.: 68-12-2), and methanol (CH_3OH, Sigma–Aldrich, 99+%, CAS no.: 67-56-1) were purchased and used without further purification.

Synthesis of unmodified/pristine UiO-66 (Zr) MOFs

The unmodified UiO-66 (Zr) sample was synthesised by adding sequentially 3.78 g $ZrCl_4$, 2.86 ml 35% HCl, and 5.38 g H_2BDC to a conical flask containing 97.4 ml DMF. The mixtures were stirred until transparent, transferred into Teflon liners, sealed in autoclaves, and heated for 20 hours at 493 K. The resulting microcrystalline powders were centrifuged and washed with 60 mL fresh DMF. The

microcrystalline powders were activated to remove DMF and remaining modulator molecules from pores.

Synthesis of modified UiO-66 (Zr) MOFs

Modified UiO-66 (Zr) MOFs were prepared by adding 0.7 g (3.00 mmol) of $ZrCl_4$, 45 mL of DMF (42.48 g, 580 mmol), and 0.52 mL (0.55 g, 9.09 mmol) of HCOOH to a 100 mL round bottom reaction flask. A magnetic stirrer bar and H_2BDC linker (0.05 g, 0.30 mmol) were added to the solution. The solution was heated on a hot plate at 473 K for five hours during which a visible change of colour from colourless to white was observed. The reaction was further heated for 18 hours, after which the solution was cooled to room temperature. The resultant solution was sonicated for 30 s and allowed to stir for 18 hours at 298 K at 200 rpm. The MOF was isolated from the supernatant by centrifugation and washed three times using DMF and the solvent was exchanged with CH_3OH. Samples were placed in a vacuum oven at 353 K overnight before analysis.

Results and discussion

Physical characterisation of the MOFs synthesised

The crystal size remained fairly constant even when the linker concentration was reduced, but the resulting crystals were less well-defined than the original material and showed heterogeneous agglomerates, as observed in Figure 2. This suggests that the linker concentration plays a crucial role in determining the crystal growth of UiO-66s. The nucleation rate was a little slower under these low linker concentration conditions, taking five hours to produce precipitates as opposed to three hours during the synthesis of the pristine material. According to the coordination modulation mechanism, this tendency toward crystal growth indicates that the concentration of the linker had an impact on UiO-66's growth during frame formation.

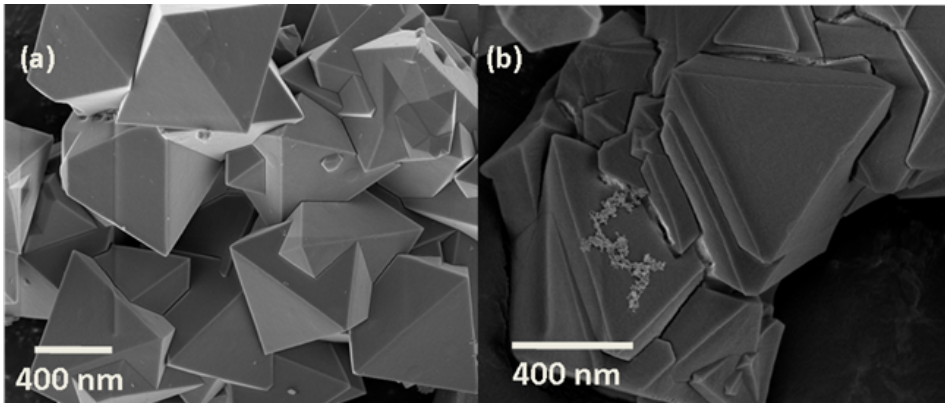

Figure 2. SEM images of (a) unmodified and (b) modified UiO-66 (Zr) MOF.

XRD images of unmodified and modified UiO-66 (Zr) MOF are depicted in Figure 2. UiO-66 MOF XRD peaks are found at 2θ angles of approximately 7.6°, 9.6°, 12.4°, 16.7°, 18.6°, 19.8°, and 22.0°, which correspond to the (100), (110), (200), (220), (222), (310), and (320) planes of the UiO-66 crystal structure, respectively. These peaks can be used to confirm the identity and purity of the unmodified UiO-66 MOF samples. Terephthalic XRD peaks found at 2θ angles of approximately 7.8°, 9.0°, 12.7°, 13.6°, and 26.8°, corresponding to the (001), (100), (101), (110), and (200) planes of the crystal structure, are shifted, some are absent, and others have decreased intensity in the modified UiO-66 samples. The shift in the XRD peaks confirms that the MOF has undergone a phase transformation, indicating that its crystal structure has changed. This phase transformation is caused by the removal of some of the organic linkers, which changes the coordination environment of the metal centres and alters the overall crystal symmetry.

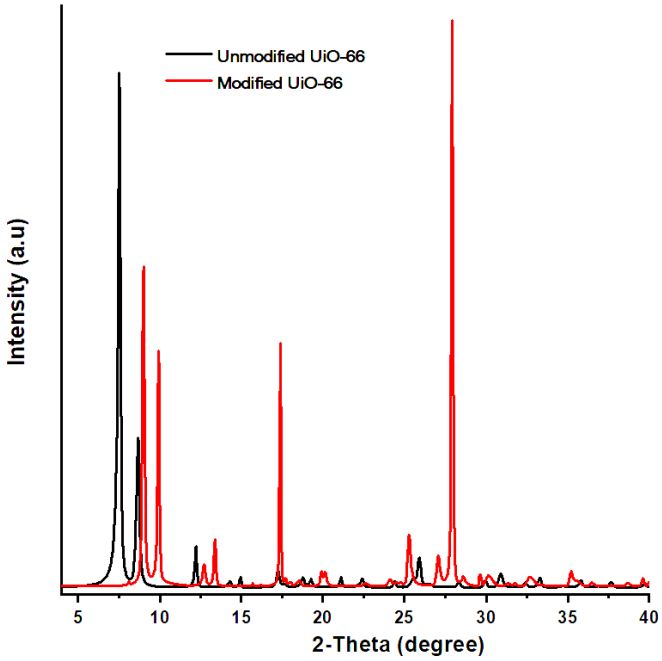

Figure 3. XRD images of unmodified and modified UiO-66 (Zr) MOF.

It has been reported that the pore size of pristine UiO-66 MOF is approximately 1.2 nm in diameter. In Figure 4 these pore sizes distribution in both the pristine and unmodified MOFs are provided. These pores have a volume of less than 0.3 cm^3/g which is below the minimum required pore volume of 0.5 cm^3/g for efficient hydrogen adsorption. We also observe pore sizes smaller than 1.2 nm in UiO-66 MOF due to the presence of coordinatively unsaturated metal sites in the MOF structure, which can act as nucleation sites for the formation of small pores (27). Moreover, the modified MOFs also have mesopores in the range of 2-2.5 nm. Mesopores are cavities or channels in the MOF structure that have a diameter between 2 and 50 nanometers, which allows for the adsorption of larger gas molecules and enhances the overall efficiency of the material. The mesopores allow for increased surface area and improved accessibility to the active sites hence we see an increase in the hydrogen uptake (28). Studies have shown that the optimal pore size range for efficient hydrogen adsorption is in the range of 0.5-2 nanometers. However, the specific pore size required can vary depending on the type of material being used for adsorption (29).

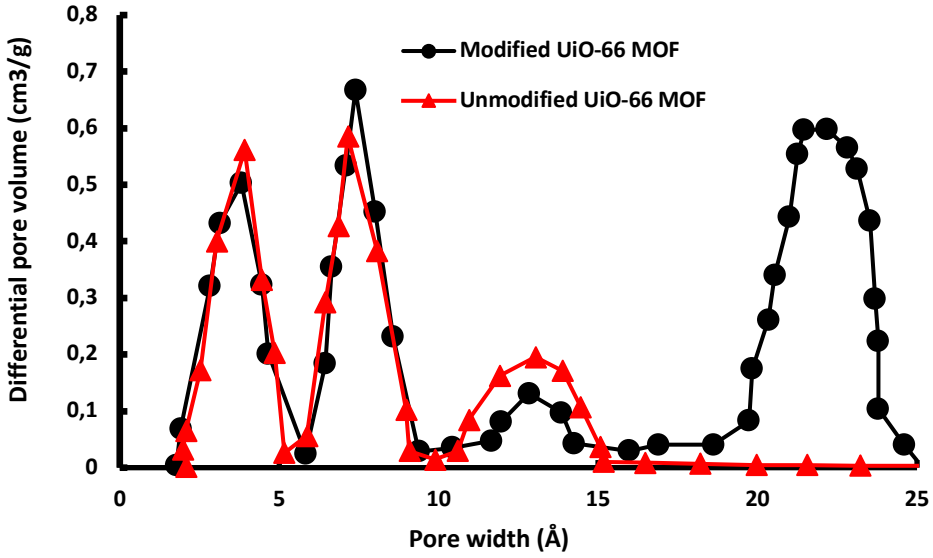

Figure 4. Pore size distribution of the unmodified and modified UiO-66 (Zr) MOF.

Adsorption performance of the MOFs synthesised

As shown in Figure 5, both isotherms reveal a type I isotherm indicating that the UiO-66 (Zr) adsorbent is microporous, furthermore the modified material has a type 3 hysteresis. An increase in surface area is observed from 1443 $m^2.g^{-1}$ to 1698 $m^2.g^{-1}$. The type I isotherm suggests that the adsorption occurs on a surface with low affinity, while the type H3 hysteresis indicates the presence of mesopores in the modified UiO-66 (Zr) adsorbent. This increase in surface area can be attributed to the modification process, which may have increased the accessibility of existing surface functionalities or active sites. The presence of mesopores in the modified UiO-66 (Zr) adsorbent could enhance its adsorption capacity and selectivity for hydrogen molecules. Although hydrogen requires pores with diameters ranging from 0.5 to 2nm for efficient adsorption, mesopores with larger diameters may allow hydrogen molecules to diffuse more quickly, making the modified UiO-66 (Zr) adsorbent a promising candidate for hydrogen storage applications (30).

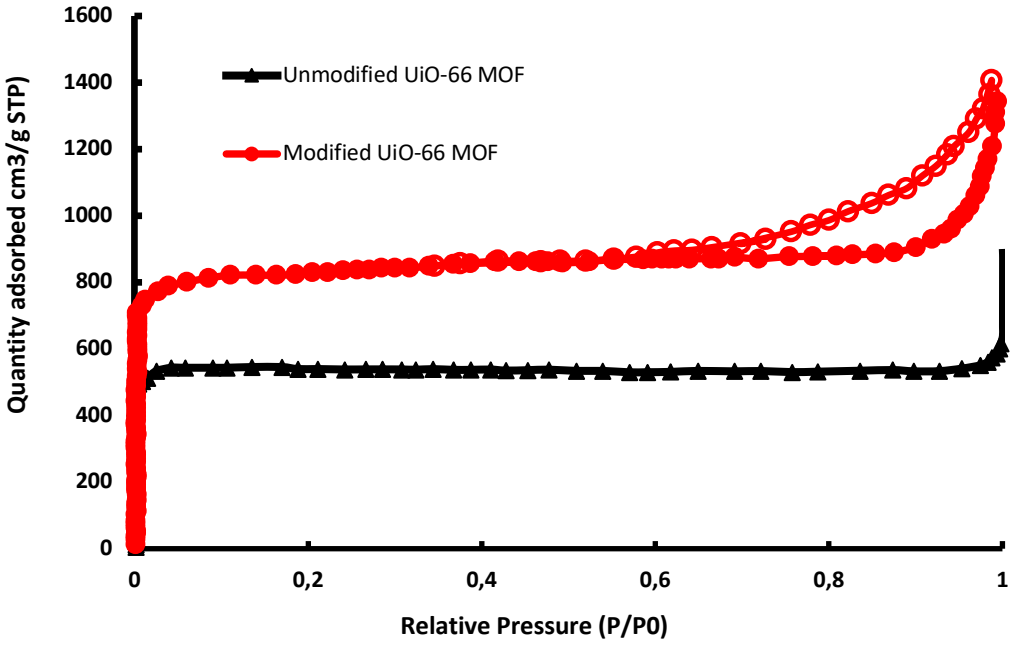

Figure 5. N_2 isotherm for unmodified and modified UiO-66 (Zr) MOF at 77K.

Hydrogen adsorption performance at low pressure

Figure 6 shows the hydrogen adsorption isotherm at 3 distinct temperatures and pressure of up to 1 bar; the highest hydrogen uptake for Zr-MOF occurs at 77 K and is 1.51 wt.%. This result indicates that UiO-66 (Zr) MOF has a high potential for hydrogen storage at low temperatures, which is important for the development of efficient and safe hydrogen fuel cell technologies. According to the DOE, the minimum hydrogen storage capacity for any material should be at least 5.5 wt.%, which is the minimum amount required for practical use in fuel cell vehicles and other hydrogen-powered devices. The hydrogen uptake capacity of Zr-MOF is 1.51 wt.%, which is lower than the minimum hydrogen storage capacity required for practical use in fuel cell vehicles and other hydrogen-powered devices (28). The highest hydrogen uptake for Zr-MOF occurs at 77 K, indicating that this material has a high potential for hydrogen storage at low temperatures.

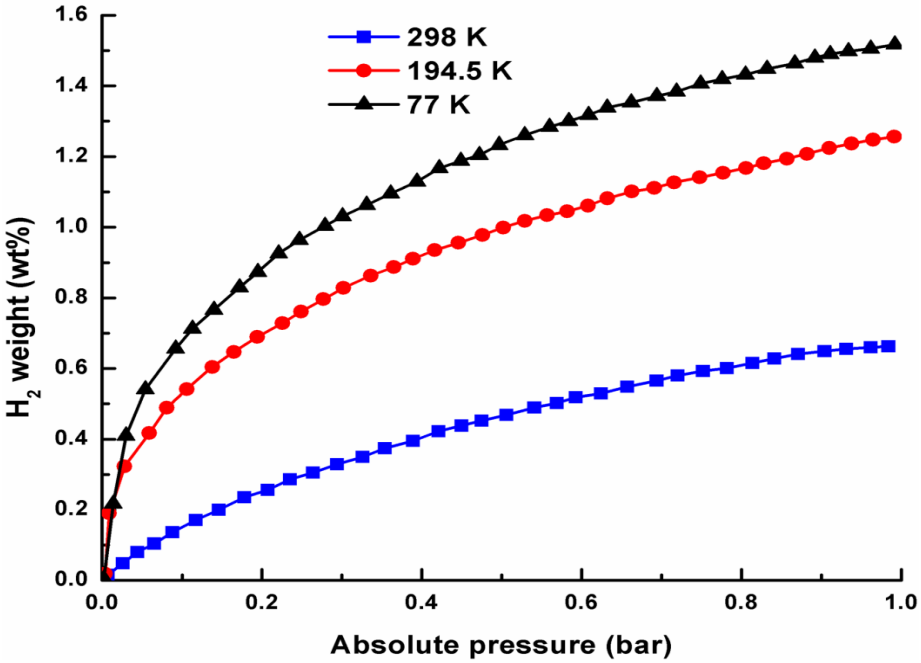

Figure 6. Low-pressure gravimetric H_2 adsorption isotherms on unmodified UiO-66 (Zr) MOF at 77 K, 194.5 K, and 298 K.

The low-pressure hydrogen adsorption by modified UiO-66 (Zr) MOF is reported in Figure 5. At 77 K, 194.5 K and 298 K, the hydrogen uptake measured was 2.29, 2.09 and 1.92 wt.%, respectively. It was observed that the adsorption falls below the required standard set by the DOE for materials that can be employed for hydrogen storage applications. However, it is worth noting that the modified UiO-66 (Zr) MOF may still have the potential for other gas storage applications or could be further optimised for hydrogen storage at higher pressures. At higher pressure, the hydrogen uptake may increase due to the greater number of available sites for adsorption, enhancing the storage capacity. However, this increase in pressure may also lead to a decrease in the kinetics of hydrogen uptake, and require more energy to adsorb and desorb the hydrogen (31).

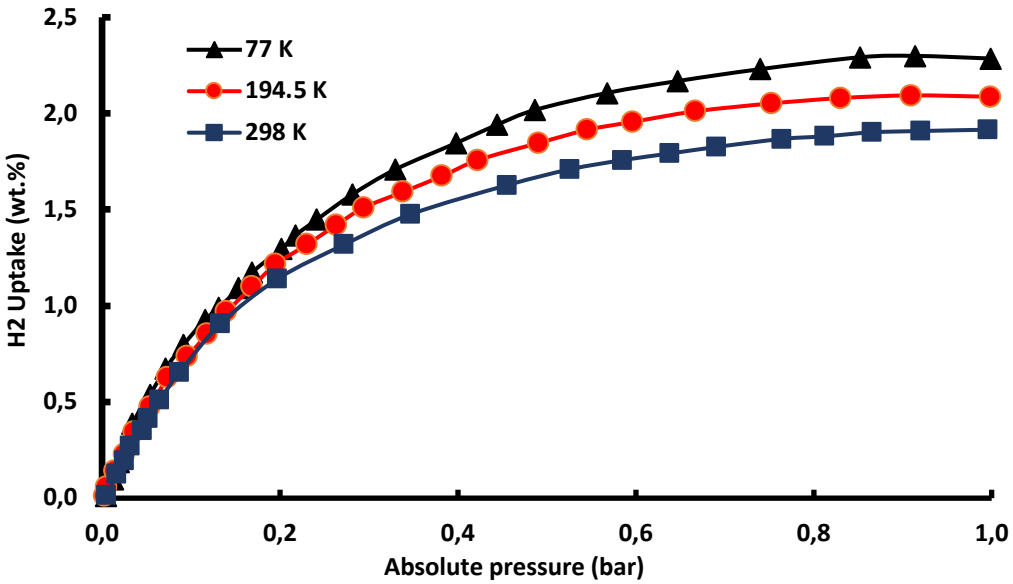

Figure 6. Low-pressure gravimetric H_2 adsorption isotherms on modified UiO-66 (Zr) MOF at 77 K, 194.5 K, and 298 K.

In Figure 7, a comparison of the low pressure hydrogen uptake of modified and unmodified MOFs at 298K, in line with the DOE's minimum operating temperature requirement of -40oC (233K) for hydrogen storage, is presented. The modified MOFs exhibited a higher capacity for low pressure hydrogen uptake compared to the unmodified MOFs, indicating that the modification process has enhanced the MOFs' ability to store hydrogen. However, despite the improvement, the storage capacity remains insufficient. Further modifications are necessary for the MOFs to achieve the required hydrogen storage capacity at the minimum operating temperature.

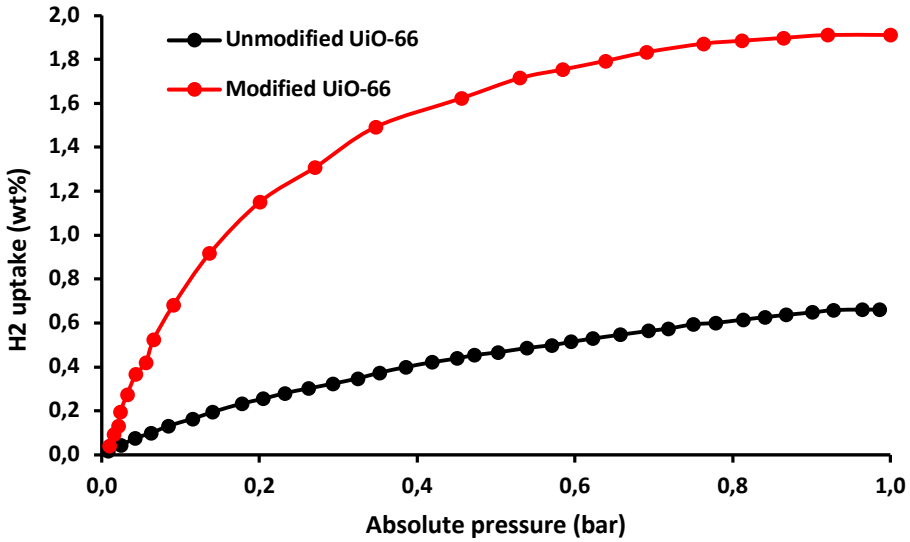

Figure 7. Low-pressure gravimetric H_2 adsorption isotherms on modified and unmodified UiO-66 (Zr) MOF at 298 K.

Hydrogen adsorption performance at high pressure

The hydrogen uptake measurements were tested at high pressures and we noticed a significant increase in hydrogen uptake compared to the low-pressure results as depicted in Figure 8. It is clear that the unmodified UiO-66 MOF reaches saturation at 100 bar at 194.5 K, and that the material then satisfies the DOE standard of ~6.0 wt.% at this temperature. Furthermore, at 60 bar the material meets the DOE standard at temperature 77 K, making it a good candidate for use in cryogenic procedures like low-temperature storage. This finding also suggests that the material tested may have the potential for use in high-pressure hydrogen storage applications, which could be important for the development of alternative energy sources. Hydrogen uptake increases at elevated pressures due to the exertion of further forces to capacitate more hydrogen molecules uptake into the material's pores, and improving the storage performance. The amount of pressure that can be applied before the material becomes unstable or the hydrogen molecules start interacting with one another is, however, limited.

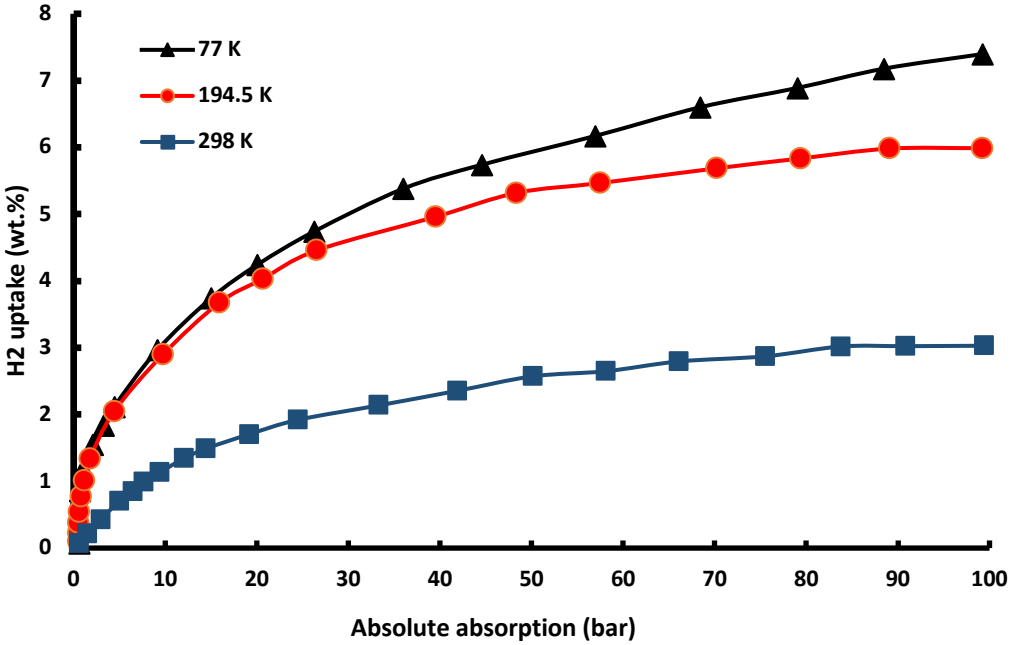

Figure 8. High-pressure gravimetric H_2 adsorption isotherms on unmodified UiO-66 (Zr) MOF at 77 K, 194.5 K, and 298 K.

A significant increase in hydrogen uptake was observed for the modified MOF when repeating the high-pressure hydrogen uptake test, as depicted in Figure 9. At temperatures of 77 K, 194.5 K, and 298 K, the recorded hydrogen uptake values were 10.3, 9.28, and 8.45, respectively. It is noteworthy that the hydrogen uptake decreased with increasing temperature. This phenomenon can be attributed to the thermal expansion-induced reduction in surface area of the material, which has a direct correlation with hydrogen uptake (32). Moreover, the lower affinity of the MOF structure for hydrogen molecules due to weakened host-guest interactions at higher temperatures may also lead to decreased hydrogen uptake. Therefore, considering the temperature dependence of MOFs is crucial when designing and utilising them in various applications (33).

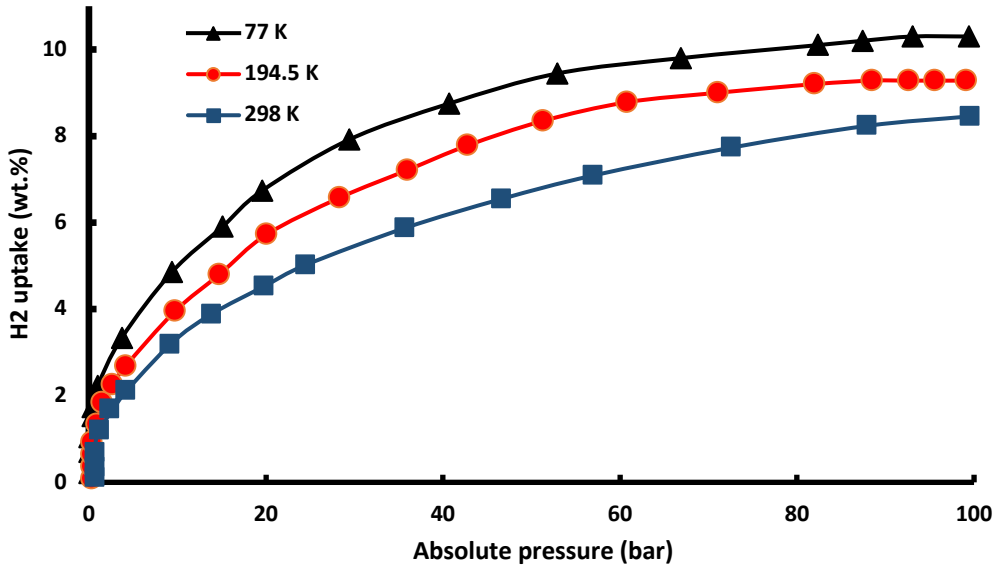

Figure 9. High-pressure gravimetric H_2 adsorption isotherms on modified UiO-66 (Zr) MOF at 77 K, 194.5 K, and 298 K.

The hydrogen uptake of modified and unmodified MOFs at high pressures and 298 K was compared once again. The modified MOFs exhibited a remarkable improvement in hydrogen uptake compared to the unmodified MOFs, indicating successful modifications to enhance their hydrogen storage capacity. The progress made in this study suggests that hydrogen could become a more feasible option as a clean and renewable energy source through this novel storage development. The modification process has shown some success in reducing the temperature dependence of hydrogen uptake, resulting in smaller differences in uptake at varying temperatures. This finding has important implications for hydrogen storage and transportation applications, as it could improve the stability and consistency of hydrogen uptake over a wider temperature range, which is a desirable property for hydrogen storage materials. However, further research is needed to confirm these results.

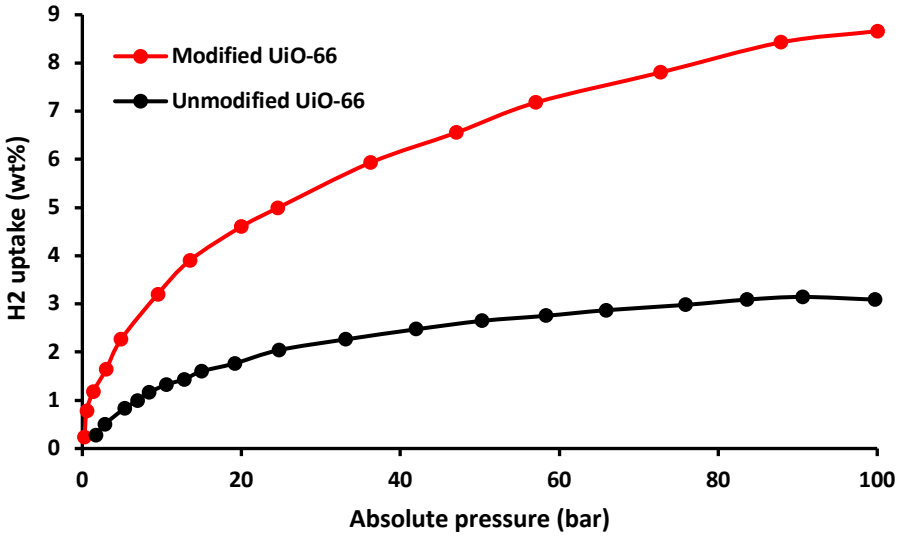

Figure 10. High-pressure gravimetric H_2 adsorption isotherms on modified and unmodified UiO-66 (Zr) MOF at 298 K.

As expected, the hydrogen uptake was significantly higher for the modified UiO-66 (Zr) MOF at high pressure as we had already seen that they performed better than the unmodified UiO-66 (Zr) MOF at low pressures. This is a great improvement as the results exceed the set DOE standard at all temperature levels tested. A summary of the results for both MOFs at various experimental conditions is listed in Table I. These findings suggest that the modified UiO-66 (Zr) MOF has the potential for use in hydrogen storage applications, particularly in high-pressure environments. In comparison to the pristine UiO-66 (Zr), the modified UiO-66 (Zr) reveals substantial differences in the adsorption and capacity of hydrogen uptake, revealing that the pore size is greatly increased due to missing linker and due to the creation of mesopores in the structure.

Table I. Summary of results for unmodified and modified UiO-66 (Zr) MOFs

Material	Temperature (K)	BET surface area ($m^2.g^{-1}$)	H_2 uptake at 1 bar (wt. %)	H_2 uptake at 100 bar (wt. %)	Ref
Modified UiO-66	77	1443	1.51	7.4	Present work
	194.5		1.2	5.99	
	298		0.63	3.03	
Modified UiO-66	77	1698	2.29	10.3	Present work
	194.5		2.09	9.28	
	298		1.92	8.45	
UiO-66	77	1434	1.6	4.2	[34]
	298			0.5	
UiO-68	77			6.3	[35]
	298			0.45	
MOF-5	77			4.7	[36]
DUT-5 (Pd NP)	298			5.0	[36]

CONCLUSION

In conclusion, this study compared the hydrogen uptake capacity of pristine UiO-66 MOFs to modified UiO-66 MOFs with missing linkers. By tuning the linker vacancies, the surface area and pore size of the MOFs were significantly improved, resulting in enhanced adsorption capacity. The surface area was observed to have increased from 1443 $m^2.g^{-1}$ to 1698 $m^2.g^{-1}$, and the modified samples exhibited mesopores which also enhanced the H adsorption and diffusion within the pores. The hydrogen uptake was studied at both high and low pressures and different temperatures, and the MOF performance was measured using various methods such as the Brunauer-Emmett-Teller method, a micrometric 2020 HD analyser, and the Hiden Xemis intelligent gravimetric analyser for N_2 and H_2 adsorption respectively. The results showed that the modified UiO-66 MOF had a higher surface area and larger pore sizes, leading to significant hydrogen uptake at low pressures and further increased capacity at high pressures.

The findings of this study suggest that low temperatures and high pressures are optimal conditions for efficient hydrogen uptake in these materials, which could lead to more cost-effective and efficient hydrogen storage. Additionally, the study highlights the importance of linker functionalisation in modifying MOF properties and performance. The modified UiO-66 MOFs demonstrated great potential for practical hydrogen storage applications due to their high hydrogen uptake capacity of 8.45 wt% at 298 K under pressure of up to 100 bar. These findings contribute to the ongoing efforts to improve hydrogen storage technologies and pave the way for advancements in hydrogen fuel cell technology. Further research is necessary to fully understand the mechanisms behind the observed enhancements and to explore additional methods for MOF modification and optimisation for hydrogen storage applications.

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Mpho Ledwaba

Post – Doc Fellow
Mintek

Born and raised in Gauteng, South Africa. Completed under graduate studies and up to masters degree in chemistry at Rhodes university, Grahamstown. Continued with doctoral degree at Stellenbosch university under a studentship offered by the Council of Scientific and Industrial Research (CSIR). Worked as a lab analyst at Modderfontein laboratory services. Currently working at Mintek as a Post Doc – Fellow.