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Enhanced Room-Temperature Hydrogen Physisorption in Zeolitic Imidazolate Frameworks and Carbon Nanotube Hybrids

Syedvali Pinjari ^{1,2}, Tapan Bera ² and Erik Kjeang ^{1,*} 

¹ Fuel Cell Research Laboratory, Simon Fraser University, 250-13450 102 Avenue, Surrey, BC V3T 0A3, Canada; spinjari@sfu.ca

² Alternative Energy, Indian Oil R&D Centre, Sector-13, Faridabad 121002, India; berat@indianoil.in

* Correspondence: ekjeang@sfu.ca

Abstract: In this work, zeolitic imidazolate frameworks (ZIF-8, ZIF-67, and ZC-ZIF) and their hybrid composites with carboxylate-functionalized carbon nanotubes (fCNTs) are synthesized through low-cost synthesis methods for enhanced physisorption-based hydrogen storage at room temperature. While both base and hybrid structures are designed to improve hydrogen uptake, the base materials exhibit the most notable performance compared to their carbon hybrid counterparts. The structural analysis confirms that all samples maintain high crystallinity and exhibit well-defined rhombic dodecahedral morphologies. The hybrid composites, due to the intercalation of fCNTs, show slightly larger particle sizes than their base materials. X-ray photoelectron spectroscopy reveals strong nitrogen–metal coordination in the ZIF structures, contributing to a larger specific surface area (SSA) and optimal microporous properties. A linear fit of SSA and hydrogen uptake indicates improved hydrogen transport at low pressures due to fCNT addition. ZIF-8 achieves the highest SSA of 2023.6 m²/g and hydrogen uptake of 1.01 wt. % at 298 K and 100 bar, with 100% reversible adsorption. Additionally, ZIF-8 exhibits excellent cyclic repeatability, with only 10% capacity reduction after five adsorption/desorption cycles. Kinetic analysis reveals that hydrogen adsorption in the ZIF materials is governed by a combination of surface adsorption, intraparticle diffusion, and complex pore filling. These findings underscore the potential of ZIFs as superior materials for room-temperature hydrogen storage.



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Keywords: zeolitic imidazolate frameworks; hybrid materials; hydrogen storage; room temperature; physisorption

1. Introduction

Protecting the environment by reducing carbon dioxide emissions and replacing fossil fuels with alternative energy sources is a key motivation for many nations worldwide [1,2]. Among several energy vectors, hydrogen has emerged as a sustainable fuel for industrial processes, stationary power, and transportation, particularly for fuel cell electric vehicles [3–5]. However, hydrogen storage remains a challenge due to underdeveloped refueling infrastructure and high costs of high-pressure storage vessels [6]. Therefore, high-capacity hydrogen storage materials are essential for the cost-effective implementation of hydrogen fuel cell technologies. Physisorption-oriented solid-state materials, mostly porous crystalline, are one of the potential approaches to achieve a practical solution. These materials have the fundamental advantages of reversible hydrogen storage with fast kinetics at near-ambient conditions, potentially avoiding thermal management difficulties [7,8]. Among

several physisorption materials, metal–organic frameworks (MOFs) are known to be significant hydrogen carriers at cryogenic temperatures (77 K, up to 100 bar) [9–11]. Due to their large SSA, high pore volume, and structural uniformity created by three-dimensional frameworks, MOFs are capable of storing high hydrogen density at low temperatures. Zeolitic imidazolate frameworks (ZIFs), a subclass of MOFs, offer unique advantages for hydrogen storage due to their synthesis-controlled frameworks [12], varied micropore properties [13], and good stability. The crystalline structure of these compounds consists of metal ions (Zn^{2+} , Co^{2+} , or In^{3+}) coordinated with imidazolate ligands to form one-, two-, or three-dimensional periodic ordered structures that are porous and have significant voids that can be filled with hydrogen molecules [14–16]. This unique structure makes ZIFs ideal candidates for hydrogen adsorption.

Several theoretical research works concerning H_2 storage in ZIFs have been published. For instance, a fundamental study of adsorption sites on ZIF-8 was conducted through Fourier analysis of neutron powder diffraction data and first-principles calculations [17]. The strongest adsorption sites for hydrogen are associated with the organic linkers (imidazoles), where a maximum of 28 H_2 molecules (~4.2 wt. %) can be adsorbed in a symmetrical ZIF-8 framework. Additionally, Grand Canonical Monte Carlo (GCMC) simulations have shown that various structural forms of ZIFs, namely tetragonal, orthorhombic, and monoclinic, also contributed hydrogen adsorption, with the body-centred lattice being effective for high uptake [18]. These simulations describe a high hydrogen adsorption energy of 15 kJ/mol at 77 K in ZIF-11 due to strong van der Waals interactions at low temperatures [12]. Another study found that due to strong interaction energies, ZIF-8 achieved ~5 wt. % hydrogen storage at cryogenic temperatures [19]. Moreover, the substitution of electronegative functional groups ($-\text{NO}_2$, $-\text{Cl}$, $-\text{CN}$, and $-\text{CH}_3$) also influenced H_2 storage, with higher electronegativity leading to higher uptake amounts, as determined through GCMC simulations [20].

Compared to the extensive theoretical and experimental works reported for MOFs, only a few experimental works have been reported on ZIFs regarding hydrogen storage. For instance, Park et al. studied the thermal and chemical stability of twelve ZIF structures synthesized by varying the metal ions and organic ligands [21]. Among them, ZIF-8 achieved good textural properties ($1630 \text{ m}^2/\text{g}$, $0.636 \text{ cm}^3/\text{g}$) and a hydrogen uptake of ~3 wt. % at 77 K and 55 bar. Zhou et al. conducted a high-pressure volumetric study on the same material at a wide range of temperatures and pressures and obtained a maximum absolute adsorption of 4.6 wt. % at 30 K and 5 bar, while only 0.3 wt. % was recorded at 300 K and 65 bar [22]. Recently, under similar conditions, Bose et al. obtained 2.5 wt. % (at 77 K) and 0.22 wt. % (at room temperature) for ZIF-8 [23]. Additionally, Hayashi et al. collected the H_2 isotherms for ZIF-20 at 77 K, where the uptake showed 1.1 wt. % at 800 Torr [24].

Other works have synthesized or modelled various forms of chemically different ZIF frameworks for hydrogen storage applications, for instance, replacing Zn^{2+} with Co^{2+} (also known as ZIF-67), MOFs with mixed metals, core–shell frameworks, and hybrid composites. Firstly, ZIF-67, formed by coordinating cobalt ions with 2-methylimidazolate (HmIm), has been documented to have a high surface area ($\sim 1700 \text{ m}^2/\text{g}$) with numerous active sites that facilitate hydrogen storage [25,26]. Secondly, Kaur et al. synthesized Zn/Co-ZIF materials by tuning the metal concentrations, where $\text{Zn}_{25}\text{Co}_{75}$ -ZIF-8 showed 1.55 wt. % H_2 adsorption at 77 K and 1 bar [27]. Additionally, core–shell MOFs have shown captivating properties for gas storage applications, exhibiting a maximum hydrogen uptake of 2.03 wt. % (77 K and 1 bar) so far [28,29]. Synthesizing hybrid materials, i.e., the combination of MOF and carbon materials, is suggested as a means to form new pores at

the interface between host and carbon species [30]. Examples of such hybrid composites are ZIF-8/GO [31], Pt@ZIF-8/GO [32], and MOF-5@carbon compounds [33–36].

Although hydrogen adsorption in ZIFs has been extensively studied at cryogenic temperatures, detailed investigations of their performance under ambient conditions are still limited. Further evaluation and understanding of physisorption materials are needed for practical and economical hydrogen storage at room temperature and moderate pressure. Considering the beneficial features of high SSA and ordered porous structures of ZIFs, this work aims to further develop the ZIFs through enhanced synthesis techniques for effective physisorption-based hydrogen storage at 298 K and 100 bar. Our goal is to achieve efficient hydrogen storage at ambient temperature, hence the choice of room temperature. The selection of 100 bar pressure aligns with practical storage applications, as cost-effective tank configurations are feasible up to this pressure. In this direction, we first prepared three forms of ZIFs (ZIF-8, ZIF-67, and ZC-ZIF-8) and then used carboxylate-functionalized carbon nanotubes (fCNTs) to synthesize hybrid composites (ZIF-8-H, ZIF-67-H, and ZC-ZIF-H). The enhanced synthesis technique involves methanol media to provide suitable reaction conditions for creating the ordered porous structures. These porous structures facilitate the confinement of hydrogen molecules within the pores, enhancing their interaction with the framework and leading to increased adsorption density. Furthermore, the carboxylate groups on the fCNTs interact with the imidazolate linkers of the ZIFs through hydrogen bonding and π - π stacking interactions [37], which could facilitate favourable hydrogen transport within the structures. The obtained materials are subjected to a range of physico-chemical characterization techniques to investigate the fundamental material structures and metal–ligand coordination, corroborating enhanced changes in textural properties and hydrogen uptake capacities at room temperature. To further understand the underlying adsorption mechanisms, a kinetic analysis is conducted using pseudo-first-order (PFO) and Avrami models.

As demonstrated in the forthcoming sections, this work presents significant advancements over existing hydrogen storage materials. Compared to previous studies, the present ZIF materials demonstrate higher hydrogen uptake at ambient conditions, enhanced structural stability, and a more cost-effective synthesis method. The integration of carboxylate-functionalized CNTs with ZIFs provides new insights into hybrid material opportunities in hydrogen storage applications. Moreover, the present approach addresses scalability and economic feasibility challenges by utilizing simple and affordable raw materials. Nonetheless, the scientific value of this work lies in its potential to bridge the gap between laboratory-scale hydrogen storage and real-world applications, contributing to the development of sustainable energy solutions.

2. Experimental Section

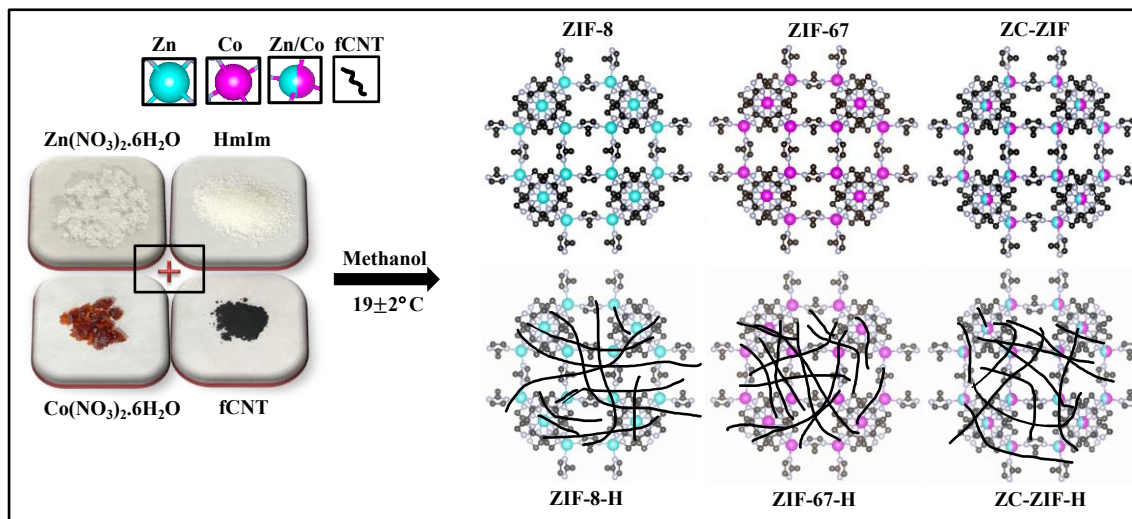
2.1. Materials

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, extra pure) and cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, extra pure) were purchased from Lobha Chemie Pvt. Ltd., Mumbai, India. 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 99%) was supplied by Spectrochem Pvt. Ltd., Mumbai, India. Methanol (CH_3OH , 99%) was acquired from Advent Chembio Pvt. Ltd., Navi Mumbai, India. Carboxylate-functionalized CNTs were purchased from Nanostructured & Amorphous Materials, Inc., Los Alamos, NM, USA. These chemicals were of laboratory reagent grade and were used without further purification.

2.2. Synthesis of Base Materials (ZIF-8, ZIF-67, and ZC-ZIF)

As depicted in Scheme 1, the samples were synthesized with slight modifications to the procedure reported by Zhang et al. [38], where specific reagent amounts used are detailed

in Table S1. In a typical procedure, firstly, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and/or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2-methylimidazole (HmIm) were dissolved in methanol separately. The HmIm solution was slowly poured into the metal precursor solution(s) and stirred at room temperature ($19 \pm 2^\circ\text{C}$) for 1 h. After the reaction, the ZIF-8 product was collected by centrifugation of the white suspension and washed three times with methanol ($3 \times 15\text{ mL}$) to remove any unreacted residue. Similarly, ZIF-67 and ZC-ZIF products were separated through filtration and washed with 15 mL of methanol. All products were then dried in a vacuum oven at 150°C and 50 mbar for 10 h to remove residual methanol and any volatile by-products. Finally, the samples were carefully ground in a mortar and pestle and transferred into glass vials, which were stored in a vacuum desiccator.



Scheme 1. Formation of ZIFs and their hybrid structures from the combination of metal precursors, organic ligands, and fCNTs.

2.3. Synthesis of Hybrid Materials (ZIF-8-H, ZIF-67-H, and ZC-ZIF-H)

The hybrid materials were prepared similarly to the base materials mentioned above, with the addition of 100 mg of fCNTs, which were sonicated for 30 min and added to the mixture of metal precursor and HmIm solution before stirring. The obtained hybrid materials are denoted as ZIF-8/fCNT (ZIF-8-H), ZIF-67/fCNT (ZIF-67-H), and Zn/Co-ZIF/fCNT (ZC-ZIF-H).

2.4. Analytical Techniques

The surface morphology and Energy-Dispersive X-ray spectroscopy (EDX) of ZIFs and their hybrid composites were performed using a JEOL JSM-6610 LV (JEOL, Tokyo, Japan). The scanning electron microscope (SEM) images were captured at 20 kV with a spot size of 42 nm. Energy-dispersive spectroscopy (EDX) was measured using an Ametek EDAX, model octane prime instrument. High resolution morphology (Transmission Electron Microscopy—TEM), and elemental mapping using bright-field imaging in scanning transmission electron microscopy (STEM BF) were carried out using JEOL JEM-2100 (JEOL, Tokyo, Japan). X-ray diffraction (XRD) tests were conducted on PANalytical X'pert3 (Malvern Panalytical, Worcestershire, UK) powder diffractometer with generator settings of 30 mA and 45 kV. The patterns were recorded using a $\text{CuK}\alpha$ source ($\lambda = 1.540\text{ \AA}$) over a 2θ range from 5° to 50° . The average crystallite size was calculated by the Scherrer equation. The chemical states and elemental composition of all samples were characterized by X-ray photoelectron spectroscopy (XPS) using a PHI 5000 Versa Probe II system (ULVAC-PHI Inc., Chigasaki, Japan). Thermogravimetric analysis (TGA) and differential

TGA (DTG) were carried out in an air atmosphere using a Mettler Toledo TGA/DSC 3+ instrument (Mettler-Toledo India Pvt. Ltd., Mumbai, India), with the samples combusted at a ramp rate of 10 °C/min from room temperature to 1000 °C.

2.5. Measurement of Physisorption Properties

The textural properties of the materials were determined by N₂-physisorption isotherms performed on a Belsorp Max automatic apparatus (MicrotracBEL Corp., Osaka, Japan). The samples were outgassed at 150 °C under fast vacuum mode at 50 Pa for 15 h. The surface area and pore size distribution were determined using in-built Brunauer–Emmett–Teller (BET) and Horvath–Kawazoe (HK) methods, respectively, and the micropore volume was obtained from the t-plots. Hydrogen storage isotherms were measured at 298 K and up to 100 bar pressure using an automated volumetric apparatus—Belsorp HP (MicrotracBEL Corp., Osaka, Japan). The samples were pretreated under vacuum (−30 kPa) at 150 °C for 15 h before hydrogen uptake measurements.

3. Results and Discussion

3.1. Morphology, Particle Size, and Crystal Structure

The morphology and particle size of the six adsorbent materials were characterized using SEM and TEM. The TEM images in Figure 1a–f show the isomorphous nature with clear rhombic dodecahedral shapes in 3D form for the ZIF-8, ZIF-67, and ZC-ZIF base materials. After the in-situ addition of fCNTs, the hybrid composites (ZIF-8-H, ZIF-67-H, and ZC-ZIF-H) inherited the structures of the base materials but exhibited an irregular surface. For instance, the apparent intercalation of fCNTs in the ZIF-8 framework and nanotube attachment on the surface and within a few pores inside ZIF-67 and ZC-ZIF can be seen. Furthermore, Figure 1c,f, along with elemental mapping (Figures 2 and S1 of ZC-ZIF and ZC-ZIF-H, confirm the core–shell frameworks (ZIF-67@ZIF-8) with Co distribution in the core and Zn at the shell, consistent with the literature reports [39,40]. It can be noted that, unlike ZIF-8-H, the uneven distribution of fCNTs in ZIF-67-H and ZC-ZIF-H can be attributed to the differences in crystallization and composition of these materials. These hybrids have a more complex structure, which can prevent effective intercalation of fCNTs into the ZIF frameworks. Moreover, the metal ions in the ZC-ZIF-H hybrid exhibit different coordination preferences and affinities towards the carboxylic groups present in fCNTs, which can further affect the distribution of nanotubes within the framework. In summary, the morphological and elemental analyses confirm successful synthesis of both base and hybrid materials while highlighting viable strategies to tune the resulting frameworks and fCNT distributions.

Figure 3 presents the particle size distribution (PSD) in half violin graphs, with corresponding SEM images and PSD parameters provided in Figures S2–S7 and Table S2, respectively, in the Supplementary Material. The hybrid materials exhibited a slightly larger mean particle size, and a broader distribution range compared to the base materials. This can be attributed to the partial or complete infiltration of fCNTs into the base structures, which results in the enlargement of the particles. ZIF-8 showed the smallest mean particle size of 454 nm, while ZIF-67 had a larger mean size of 709 nm. This increase in size for ZIF-67 may be due to lower reagent concentrations used in this research (as noted in Table S1), which can influence particle growth kinetics, leading to larger particles [25]. The elemental composition analysis via SEM-EDX (Table S3) supports these observations, showing an increase in carbon and oxygen concentrations and a reduction in nitrogen, zinc, and cobalt in the hybrid materials. These changes are consistent with the addition of fCNTs, which are rich in carbon and oxygen. The larger reduction in nitrogen in the hybrids suggests possible disruption of metal–nitrogen bonds due to fCNT incorporation [41].

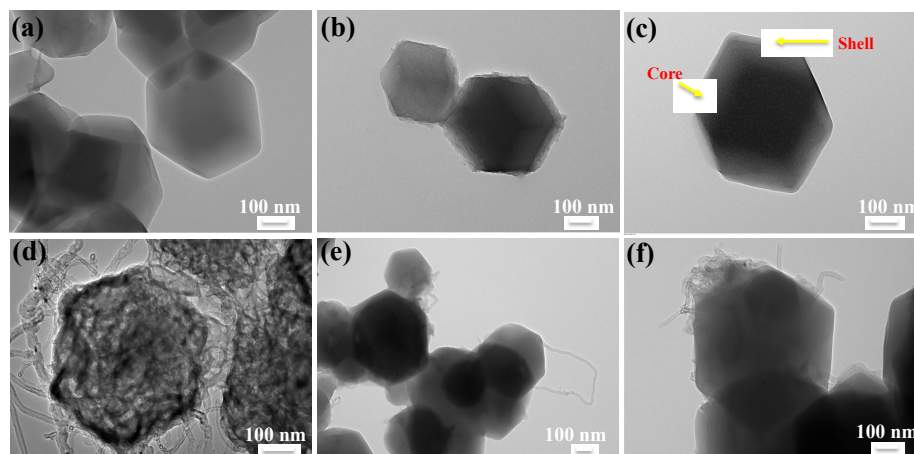


Figure 1. TEM images of base and hybrid materials. (a) ZIF-8, (b) ZIF-67, (c) ZC-ZIF, (d) ZIF-8-H, (e) ZIF-67-H, and (f) ZC-ZIF-H.

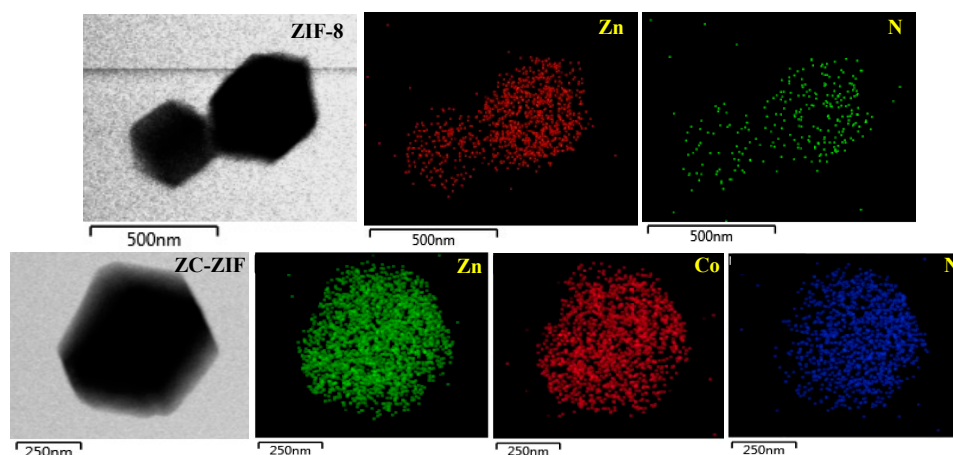


Figure 2. Selected STEM BF images with elemental mapping of ZIF-8 (top) and ZC-ZIF (bottom).

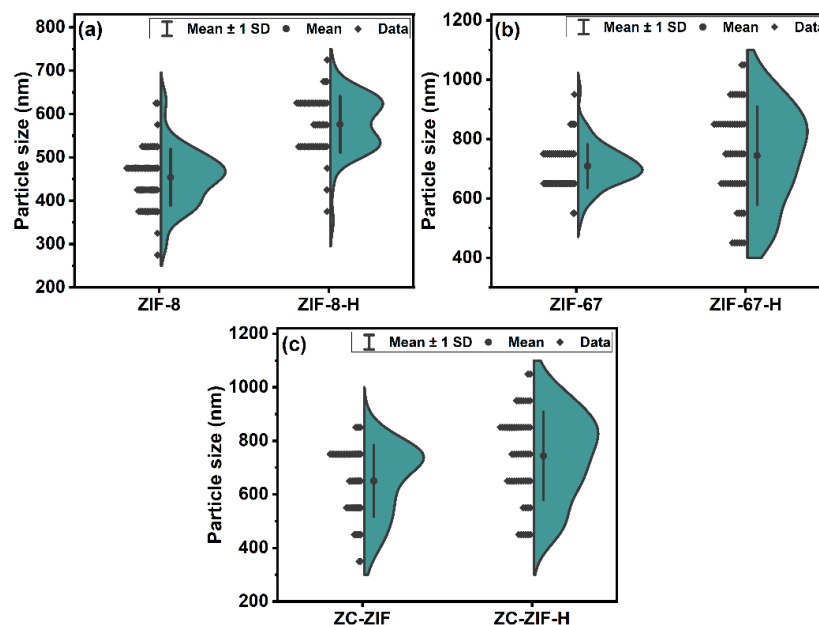


Figure 3. Half violin graphs representing the particle size distribution of (a) ZIF-8 and ZIF-8-H, (b) ZIF-67 and ZIF-67-H, and (c) ZC-ZIF and ZC-ZIF-H.

Figure 4 illustrates the XRD patterns of the ZIFs and their hybrid materials to determine the crystalline phase. The prominent reflections of all samples are identical and indexed at 2θ : 7.3° (011), 10.4° (002), 12.7° (112), 14.7° (022), 16.4° (013), 18° (222), 22.1° (114), 24.5° (233), 26.7° (134), 29.7° (044), 30.6° (334), 31.5° (224), 32.5° (235), 35° (226), and 36.6° (444), which are in good agreement with the simulated single crystal XRD results and confirm the sodalite topology of zeolites [42–44]. This indicates that the base ZIFs contain a tetrahedron structure where Zn and/or Co coordinates with four nitrogen atoms of HmIm, as depicted in Scheme 1. In addition, XRD peaks of both ZIF-8 and ZIF-67 are present in ZC-ZIF due to isomorphism and nearly similar lattice parameters. Since the ionic radii of Zn and Co are nearly equal, the location of these metals is arbitrary in ZC-ZIF and ZC-ZIF-H and depends on the order of mixing the metal(s) with the imidazolate solution. Hence, both metals interact easily and form a core-shell framework.

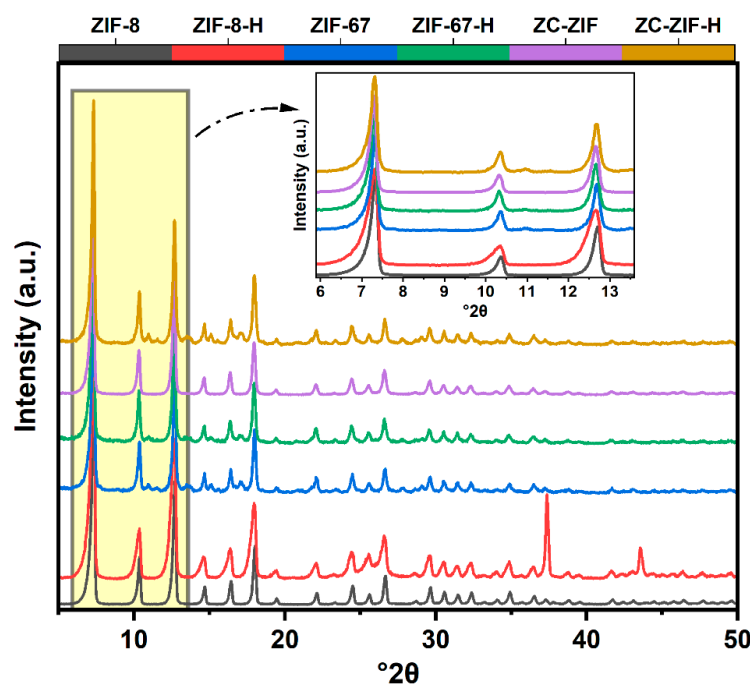


Figure 4. XRD profiles of the base ZIFs and hybrid materials (inset: magnified view between 6° and 14°).

The XRD peak positions of the hybrid composites closely match those of the base materials. However, the peaks are slightly broader with reduced intensity, indicative of minor structural changes due to fCNT intercalation. For example, the two peaks of ZIF-8-H at $2\theta \sim 37^\circ$ and $\sim 48^\circ$ show a slight deviation from those of the ZIF-8 base material. This deviation is attributed to structural changes induced by the intercalation of fCNTs, which can introduce local distortions or stresses within the ZIF framework. The quantified data in Table 1 show that the relative intensity and average crystallite size of the base ZIFs are significantly higher than the hybrid composites. The reduction in crystallite size and intensity in the hybrid materials, compared to the base materials, is indicative of the functionalization impact of fCNTs [34]. This reduction correlates with the structural flexibility introduced by fCNT intercalation, which alters the mesoporosity while preserving the microporous framework of the ZIFs. This is critical, as the fine balance between microporosity and mesoporosity directly influences the hydrogen storage capacity. Overall, the major structures of the base ZIFs were well preserved in their hybrid composites, and the XRD patterns are in good agreement with the literature [41].

Table 1. Crystalline metrics for XRD reflections of the base ZIFs and hybrid composites.

Samples	$^{\circ}2\theta$	Relative Intensity (%)	Avg. Crystallite Size (nm)
ZIF-8	7.46	100.0	36.42
ZIF-8-H	7.90	70.7	22.48
ZIF-67	7.32	15.69	29.94
ZIF-67-H	7.30	15.54	27.92
ZC-ZIF	7.30	49.78	30.14
ZC-ZIF-H	7.32	20.51	29.64

3.2. X-Ray Photoelectron Spectroscopy

XPS characterization was applied to the material samples to gain insights into the chemical states of elements. The survey spectra (Figure 5a) confirm the presence of C, N, O, Zn, and Co elements in the base ZIFs and hybrid composites. The elemental compositions from XPS are tabulated in Table S4, and are generally consistent with the SEM-EDX results in Table S3. From the wide scans of ZC-ZIF and ZC-ZIF-H, it can be inferred that the Co2p intensity is low compared to the Zn2p peaks, suggesting that ZIF-67 is encapsulated within the ZIF-8 shell (see Figure 5c). Because of the low intensity and lesser Co content in these two samples, deconvolution of Co2p could not be processed, which aligns with the literature [28]. The C1s peak was fitted with two main peaks corresponding to C–C (284.6 eV) and C–N (285.2 eV), as shown in Figure 5b. However, ZIF-8-H (Figure S8a) shows additional hydroxyl (C–OH at 286.2 eV) and carboxylic groups (COOH at 288.6 eV), attributed to the intercalation of fCNTs. In addition, satellite peaks of $\pi - \pi^*$ evolved at ~290 eV due to changes in structure formation in ZC-ZIF, ZIF-67, ZIF-67-H, and ZC-ZIF-H (Figures 5c, S9a–S11a) [45]. These changes can be related to the additional peak recorded between 405.1 eV and 407.2 eV under high-resolution N1s spectra, along with pyridinic (N–C), pyrrolic (N–H), and graphitic (N–Zn) groups (Figure 5d,e) [46]. Mallineni et al. reported that the additional peak may be attributed to various nitrogenated substances in the product [47]. In our study, we believe that unreacted imidazoles were the main contributors to this extra nitrogen peak. While unreacted imidazoles do not directly contribute to hydrogen adsorption, their presence may slightly alter the surface properties and chemical composition of the materials. This is supported by the variation in peak areas of Zn–N and N–H (Table S5), implying uncoordinated N with Zn during the framework formation [48].

The high-resolution O1s spectra of ZIF-8 can be deconvoluted into three peaks at 531.7 eV, 532.8 eV, and 533.6 eV, corresponding to C=C, Zn–OH, and physically adsorbed H₂O, respectively (Figure 6a). In addition to these groups, a COOH group at 533.9 eV is also observed in Figure 6b for ZIF-8-H, which indeed confirms the presence of carboxylic functionalized CNTs. Moreover, hydroxyl and carboxylic groups were also recorded in the C1s spectra of the same sample (Figure S8a), whereas they were not observed in the other materials (Figures S9a, S10a, and S11a). Despite having three main peaks under O1s, ZC-ZIF and ZC-ZIF-H were fitted with C–O and COOH species in both samples (Figures S11c and S12a), consistent with existing reports [49]. The deconvolution of the Zn2p peak consistently maintained Zn2p_{3/2} and Zn2p_{1/2} at ~1020 eV and ~1043 eV, respectively, as shown in Figures S8c,d, S11d and S12b. The Co2p in ZIF-67 and ZIF-67-H, having two significant peaks at ~779 eV (Co2p_{3/2}) and ~794 eV (Co2p_{1/2}), was deconvoluted into Co³⁺ and Co²⁺, accompanied by a satellite peak (Figures S9d and S10d, and Table S6) [50].

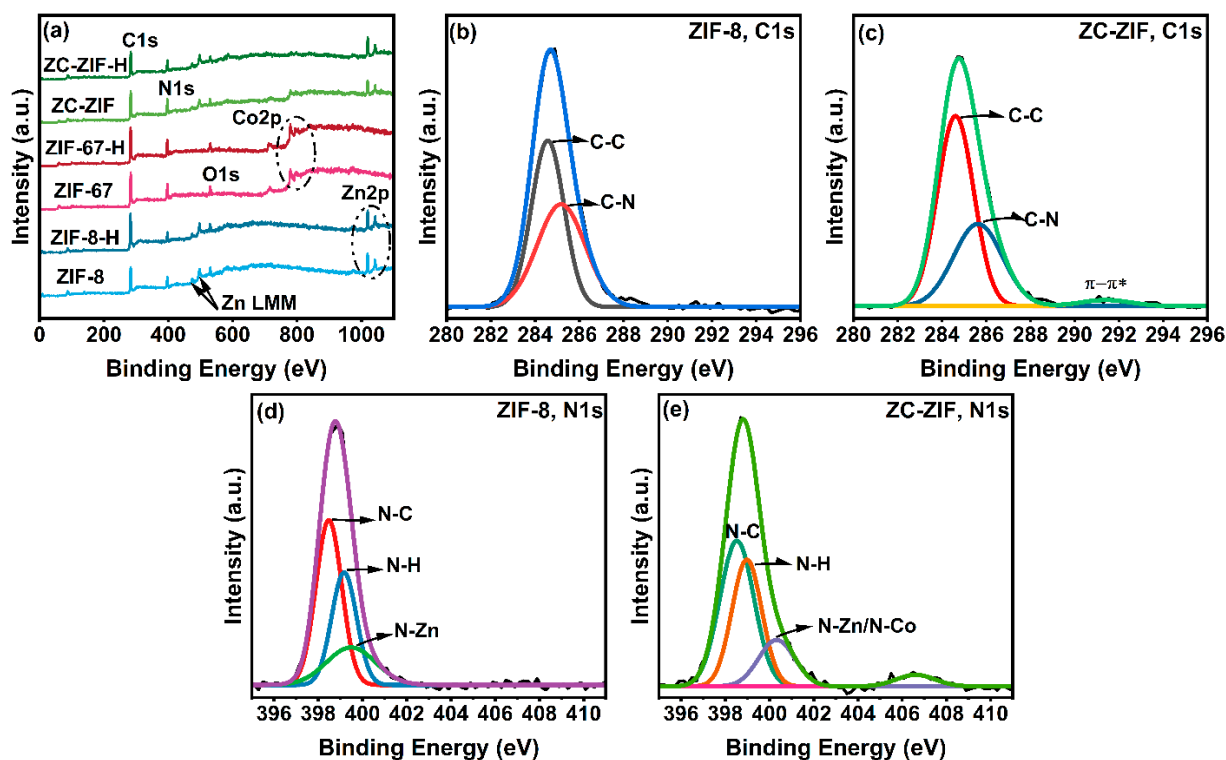


Figure 5. (a) XPS wide spectra for all six samples, high resolution C1s XPS spectra of (b) ZIF-8 and (c) ZC-ZIF, and N1s XPS spectra of (d) ZIF-8 and (e) ZC-ZIF-8.

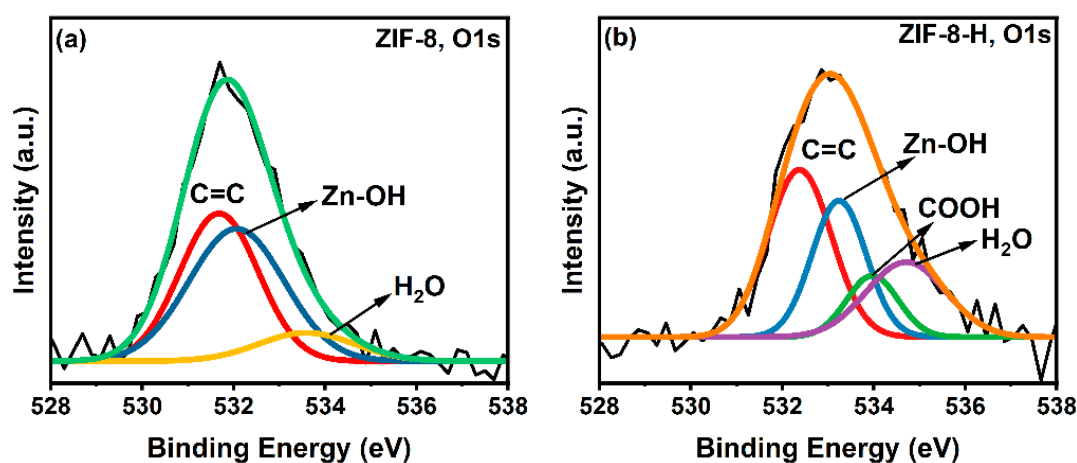


Figure 6. XPS O1s deconvolution spectra of (a) ZIF-8 and (b) ZIF-8-H.

3.3. Thermal Stability

The thermal stability of all ZIFs was characterized using TGA to analyze their weight loss and differential curves. The analysis curves and extracted parameters are shown in Figure 7 and Table 2, respectively. A minor weight loss below 120 °C is attributed to the evaporation of adsorbed moisture on the sample surfaces. Additionally, a gradual weight decrement between 200 and 300 °C was observed for ZIF-67, ZIF-67-H, ZC-ZIF, and ZC-ZIF-H, mainly due to the removal of solvent molecules and carbonization of unreacted HmIm (Figure 7c–f). This phenomenon did not occur in the ZIF-8 and ZIF-8-H materials, indicating complete consumption of reactants during the synthesis reaction. These temperatures could be considered as the limits for pre-treatment temperatures for N₂-physisorption and hydrogen storage measurements to remove the moisture and impurities

from the particles prior to testing [51]. Furthermore, the organic linker in the ZIF particles starts to decompose at the onset temperature (Table 2), which leads to structural collapse at the endpoint, followed by residue formation from zinc/cobalt and oxygen from the air. The multiple degradation steps of ZIF-8-H (Figure 7b) may be attributed to the oxidation of fCNTs intercalated in the ZIF-8 structure. The inflection point, which explains the maximum rate of weight loss at a particular temperature, is higher for ZIF-8, indicating good thermal stability compared to the other samples [52].

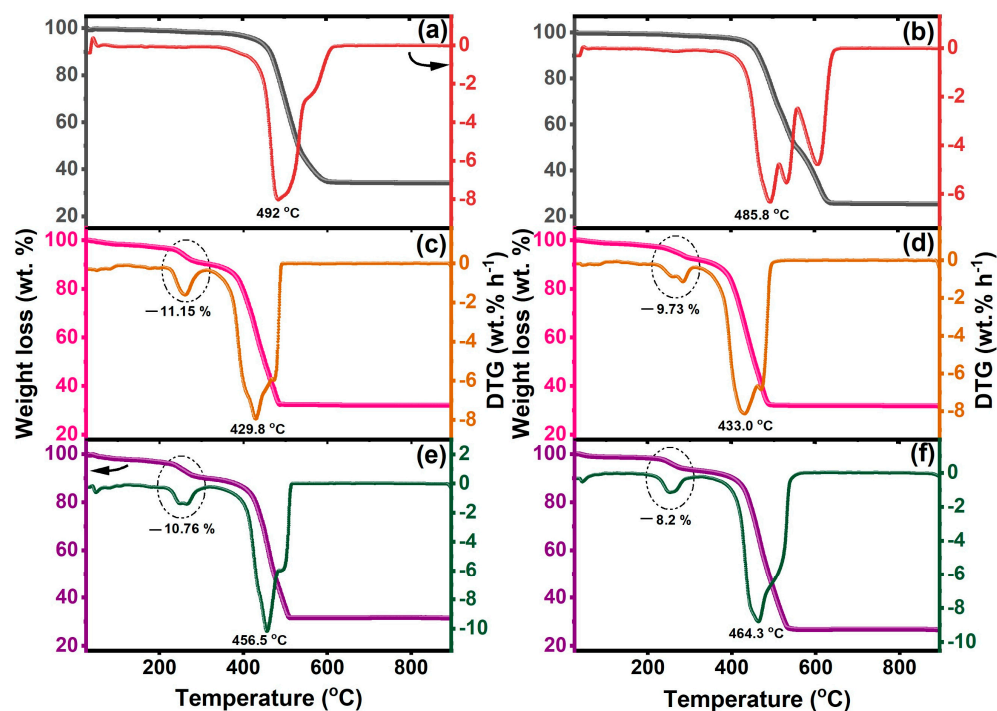


Figure 7. TGA and DTG analysis of (a) ZIF-8, (b) ZIF-8-H, (c) ZIF-67, (d) ZIF-67-H, (e) ZC-ZIF, and (f) ZC-ZIF-H. The arrows in (a,e) indicate the y-axis belonging to the respective curve in each plot (a–f).

Table 2. Thermogravimetric parameters of all ZIF samples with three DTG temperatures and yields.

Samples	Temperature (°C)			Yield (wt. %)
	Onset	Inflection	End Point	
ZIF-8	451.4	492.0	558.6	33.8
ZIF-8-H	446.2	485.8	637.6	25.3
ZIF-67	371.5	429.8	507.2	29.7
ZIF-67-H	380.8	433.0	452.1	29.6
ZC-ZIF	408.4	456.5	511.8	29.9
ZC-ZIF-H	428.4	464.3	540.0	31.1

3.4. Physisorption Properties

3.4.1. Textural Analysis

The N₂-adsorption/desorption isotherms of the base materials and hybrid composites shown in Figure 8a–c display reversible Type I isotherms, which are inevitable for microporous adsorbents and are a characteristic of typical ZIF structure present in all six samples. The microporous nature of the samples is indicated by the initial sharp rise in the isotherms corresponding to the filling of nitrogen into micropores, whereas the flat region of the isotherm appears when the micropores are saturated by the adsorbate [53,54]. However, a subtle hysteresis loop arises for the hybrid materials near $P/P_0 = 0.9$ and, eventually, for

the base ZIFs, indicating the presence of mesoporosity inherited from the mesoporous nature of the fCNTs and the space between ZIF particles, as observed in the TEM images [55]. The pore size distribution determined by the HK method is shown in Figure 8d–f. All six samples exhibited a similar trend of micropore sizes with three prominent peaks near 0.62, 0.87, and 1.01 nm, related to the common ZIF structure with little or no influence from fCNT hybridization. ZIF-8 possessed the highest specific micropore volume amongst the samples, which aligns with the t-plots given in Figure S13, followed by the ZIF-67 and ZC-ZIF samples, whereas the hybrid materials had reduced specific micropore volume due to the addition of fCNTs.

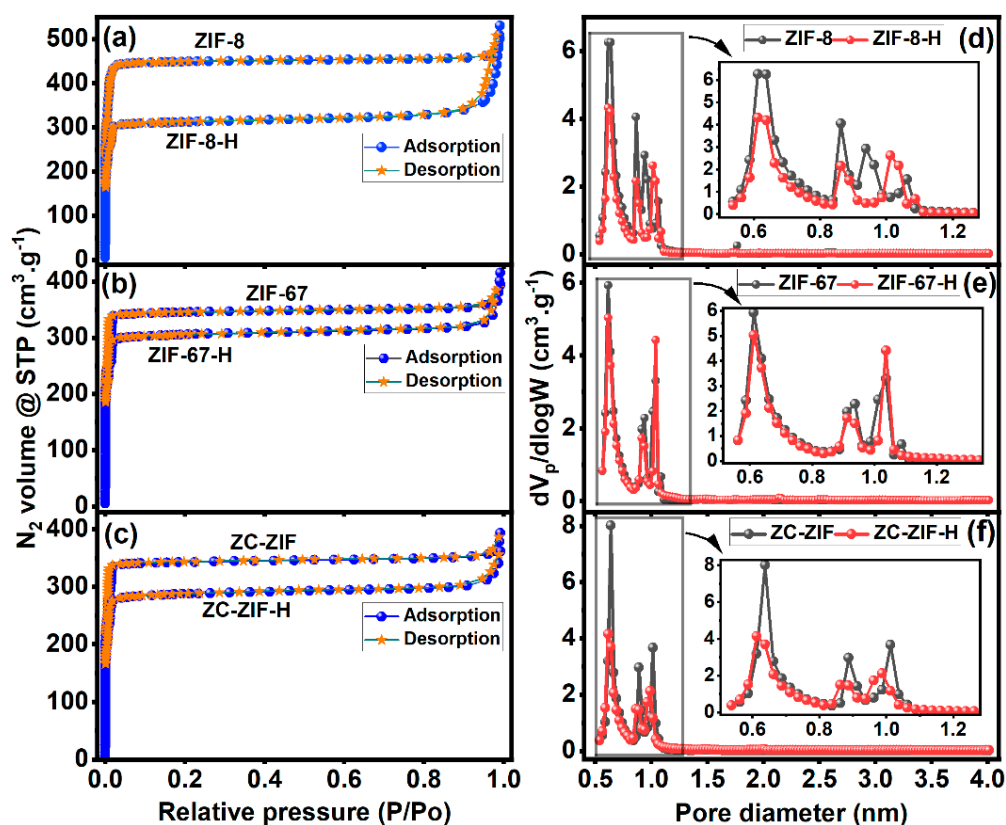


Figure 8. (a–c) N₂-adsorption/desorption isotherms and (d–f) HK pore size distributions of base materials and their respective hybrids.

Figure 9 summarizes the SSA from BET, total and micropore volumes, and average pore diameters of the six as-synthesized materials. The maximum SSA of 2023.6 m²/g (avg. pore size 1.18 nm) was observed for ZIF-8, followed by 1614.1 m²/g (1.52 nm) for ZC-ZIF and 1576.9 m²/g (2.07 nm) for ZIF-8-H. Although all materials exhibited similar sodalite topology and rhombic dodecahedral morphology, unintended crystallite formation and impurities may, in some cases, reduce the measured SSA [56]. In this work, the high SSA for ZIF-8 is attributed to its greater micropore volume and smaller pore diameter, which maximize N₂-adsorption properties. As shown in Table S7, the division of micropore volume into ultramicropore and supermicropore volumes reveals that for all materials, the ultramicropore volume is notably larger than the supermicropore volume. This indicates that microporosity is primarily dominated by pores smaller than 0.7 nm, which contributes significantly to the overall BET surface area and total pore volume. Furthermore, the obtained textural properties of the base materials are higher than the analogous literature reports due to the enhanced synthesis practice used to form appropriate materials [24,25,27,28,38,50]. In addition, it is interesting to see that all the hybrid materials experi-

enced lower SSA compared to their base materials due to the addition of fCNTs (added mass) that did not contribute new micropores [37]. The higher mesoporous volume and large characteristic pore diameters caused by nanotube intercalation are also typical factors for hybrid materials recording minimal textural properties, comparable with MOF/carbon composites [31].

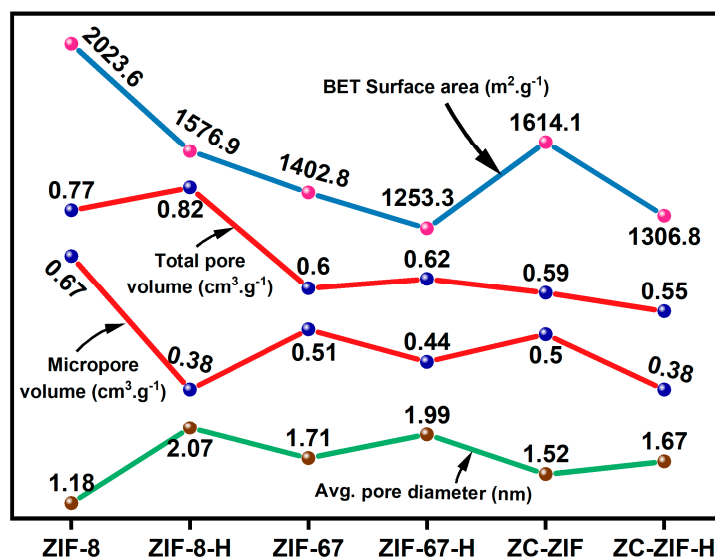


Figure 9. Textural properties of the six as-synthesized material samples.

3.4.2. Hydrogen Storage Tests

The hydrogen storage measurements were performed using a volumetric apparatus, where isotherms were recorded at 25 °C and up to 100 bar equilibrium pressure. As shown in Figure 10, ZIF-8 achieved the highest H₂ uptake of 1.01 wt. % (0.012 g.H₂/L) at 100 bar, followed by ZC-ZIF (0.68 wt. %) and ZIF-67 (0.545 wt. %). Although this uptake capacity may appear modest in comparison to some cryogenic studies, it is among the highest values reported for ZIF-based materials operating at 298 K and 100 bar. These results compare favourably with the theoretical and experimental values in the literature, attributed to the appropriate framework configuration that creates significant chemical structure, suitable crystalline parameters (high intensity and average crystallite size), larger SSA, and enhanced micropore properties [12,19,22,23,32]. To the best of our knowledge, this is the first time ZIF-8 material has been experimentally demonstrated at room temperature, showing promising high hydrogen capacity and complete reversibility compared to other porous materials [57–59]. On the other hand, all three hybrid material samples exhibited less hydrogen storage than their corresponding base materials; however, ZC-ZIF-H showed improved hydrogen uptake at low pressure (10 bar) due to the addition of fCNTs. Our previous study also showed similar results when fCNTs were separately tested for hydrogen storage measurements [37]. The superior performance of ZIF-8 is directly tied to its high SSA (2023.6 m²/g), microporous volume, and optimized pore structure. Notably, it can be seen from Table S7 that materials with higher ultramicropore volume tend to exhibit improved hydrogen storage capacity, suggesting that ultramicropores provide enhanced adsorption potential due to overlapping adsorption fields, while supermicropores improve gas accessibility and diffusion. The strong Zn-N coordination in ZIF-8, as well as the distribution of hydrogen adsorption sites, provides an ideal environment for reversible hydrogen physisorption. Indeed, the adsorbed hydrogen was fully reversible (100%) in all six samples, proving the physisorption-dominated storage process without kinetic

impediments and verifying equilibrium conditions for each data point recorded at room temperature.

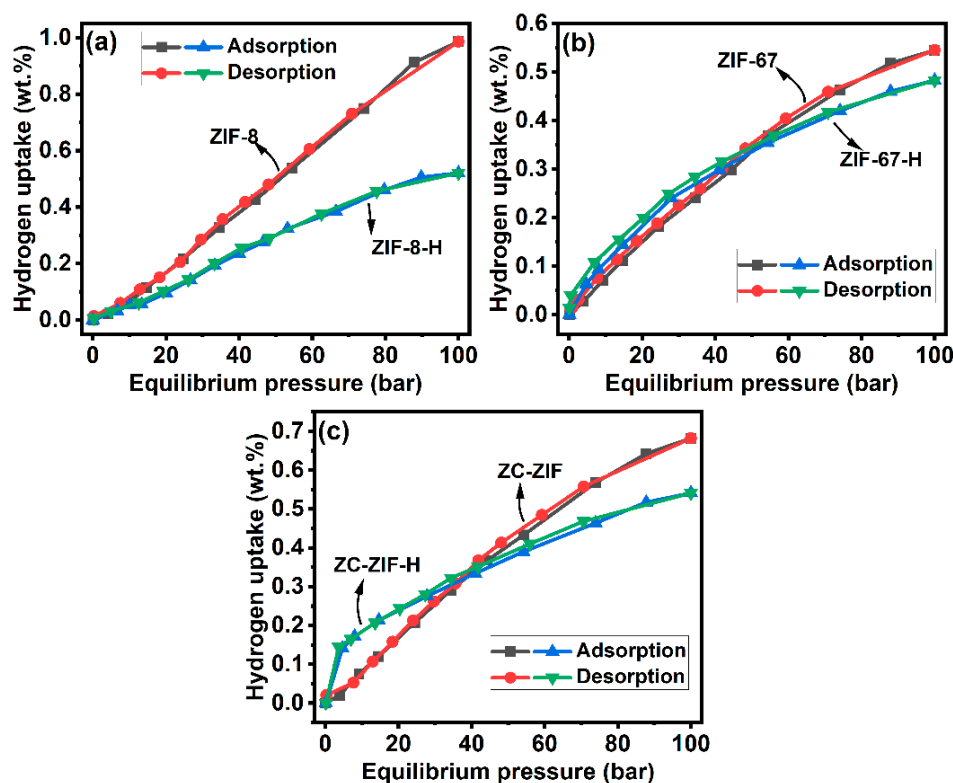


Figure 10. Hydrogen storage isotherms at 25 °C and up to 100 bar for (a) ZIF-8 and ZIF-8-H, (b) ZIF-67 and ZIF-67-H, and (c) ZC-ZIF and ZC-ZIF-H.

Generally, for physisorption materials, the H₂ storage capacity is expected to increase with increasing SSA of a given adsorbent material, typically in a proportional trend. We observed the same phenomenon in this work, as ZIF-8 possesses the highest SSA and hydrogen capacity. However, the decreased percentages (relative to ZIF-8) in hydrogen storage and SSA of the other materials are disproportionate (Table S8). The current analysis in Figure 11 focuses on the correlation between SSA and hydrogen uptake, which is a fundamental parameter for physisorption-based materials. As shown, ZIF-8 exhibits the highest SSA and hydrogen uptake, following a linear trend between surface area and storage capacity. The hybrid materials deviate from this trend, indicating the influence of other factors such as the chemical composition and pore structure. This observation for the hybrid materials indicates favourable and unfavourable interactions between ZIFs and fCNTs in each case. Favourable interactions in hybrid materials (ZIF-67-H and ZC-ZIF-H) arise from the enhanced hydrogen dynamics due to the mesoporosity introduced by fCNTs, which facilitates faster diffusion at lower pressures. Unfavourable interactions, such as those in ZIF-8-H, are attributed to changes in surface chemistry, pore structure, and the disruption of the microporous framework, which leads to reduced hydrogen uptake compared to the base materials [21]. It is reported that the significant hydrogen adsorption sites in ZIF-8 are organic ligands [60,61], whereas HmIm is the imperative source for zinc–nitrogen (Zn–N) coordination. Along this line, the present XPS results evidenced the highest Zn–N concentration in ZIF-8 (Table S5), hence possessing a maximum number of ligands that created a strong interaction between hydrogen and the ZIF-8 framework across the complete volume of adsorption sites. Thus, while SSA is a key driver of hydrogen storage performance, the adsorption and desorption sites within the channels and nanocages, along with the chemical composition (Zn, Co, and N), are also contributing factors.

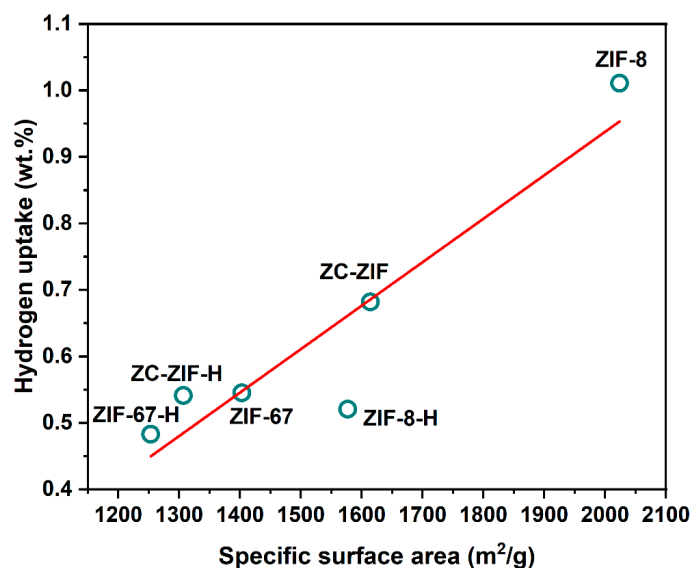


Figure 11. Linear trendline of H₂ uptake versus SSA for all samples.

To understand the hydrogen storage repeatability of ZIF-8, we conducted five complete cycling tests at room temperature and 100 bar equilibrium pressure (Figure 12). Remarkably, there was only a 10% reduction in hydrogen capacity after five cycles, indicating good repeatability and cycling stability for the hydrogen storage performance of this material. The first-cycle H₂ capacity of 1.07 wt. % was even higher than the data shown in Figure 10, and all five cycles showed completely reversible behaviour with 100% hydrogen desorption. Therefore, the above results indicate that the excellent hydrogen storage properties of ZIF-8 are highly appropriate for practical applications.

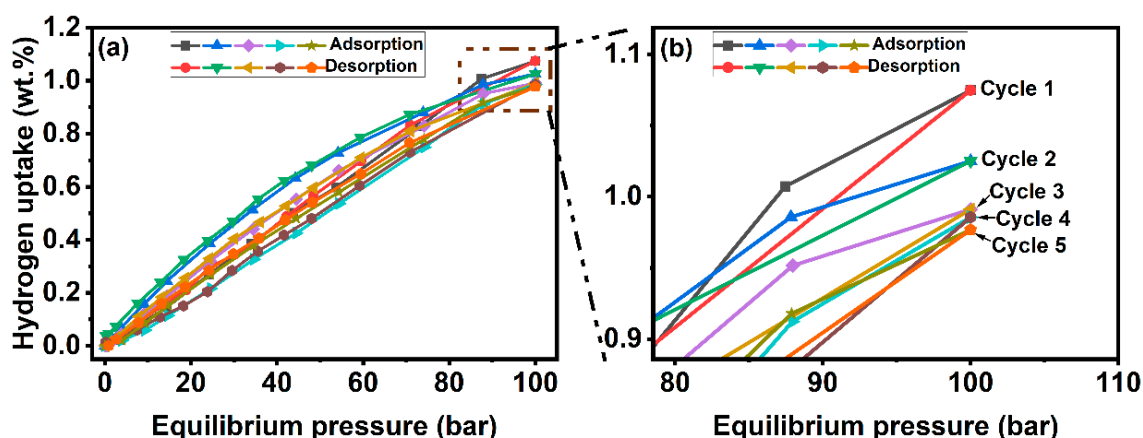


Figure 12. Cycling tests of hydrogen isotherms of ZIF-8: (a) five complete isotherm cycles and (b) magnified view at high pressures.

3.4.3. Hydrogen Adsorption Kinetics

To investigate the kinetics of the hydrogen adsorption process(es) of the base ZIF and corresponding fCNT hybrid materials, we applied both the PFO and Avrami kinetic models to elucidate the hydrogen adsorption mechanisms as follows [62,63]:

$$\text{Pseudo - first - order model : } \ln\left(\frac{q_e}{q_e - q_t}\right) = kt + \text{Intercept} \quad (1)$$

$$\text{Avrami model : } q_t = q_e [1 - \exp(-k_{av} \times t^n)] \quad (2)$$

where q_e is the equilibrium adsorption capacity, q_t is the amount of hydrogen sorbed at time t , k and k_{av} are the PFO and Avrami rate constants, respectively, and n is the Avrami exponent. The PFO and Avrami kinetic plots and associated model fits of ZIF-8 are illustrated in Figure 13, whereas kinetic plots for the rest of the materials are given in Figures S14 and S15. The fitting parameters are summarized in Table 3. Based on the PFO parameters given in this table, the relatively similar rate constants imply that the intrinsic adsorption kinetics are consistent among all ZIF samples. However, slight deviations in intercept suggest that the adsorption kinetics might not be governed solely by a simple first-order process. Similarly, the R^2 values (ranging from 83.61% to 96.06%) indicate that the PFO model captures the overall trend of the adsorption kinetics but does not account for all complexities, as is also evident from the data in Figure 13a.

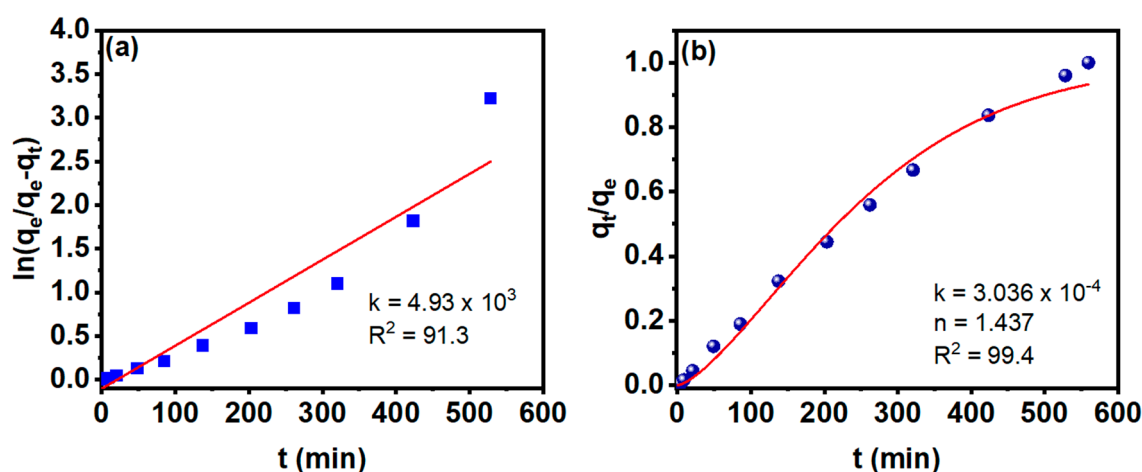


Figure 13. Kinetic analysis of hydrogen adsorption on ZIF-8: (a) pseudo-first-order plot and corresponding linear fit and (b) Avrami plot with the non-linear Avrami model fit.

Table 3. Kinetic fitting parameters for the six tested materials using pseudo-first-order (PFO) and Avrami models.

Material	PFO Model			Avrami Model		
	$k \times 10^{-3} \text{ (min}^{-1}\text{)}$	Intercept	$R^2 \text{ (%)}$	k_{av}	n	$R^2 \text{ (%)}$
ZIF-8	4.93	−0.105252	91.32	3.03×10^{-4}	1.43	99.42
ZIF-8-H	3.46	−0.071934	83.61	0.0086	0.91	95.27
ZIF-67	3.92	−0.107561	91.38	1.14×10^{-4}	1.55	99.23
ZIF-67-H	3.79	0.044047	96.06	0.0077	0.89	97.54
ZC-ZIF	4.18	−0.12691	92.81	1.79×10^{-4}	1.49	99.31
ZC-ZIF-H	5.37	0.056535	93.87	0.0296	0.68	95.52

The Avrami kinetic fitting parameters provide more detailed information on the adsorption mechanisms. This model yields two key parameters: the rate constant (k_{av}) and the Avrami exponent (n), as given in Table 3. For the base materials (ZIF-8, ZIF-67, and ZC-ZIF), the very low rate constant values on the order of 10^{-4} min^{-1} combined with n values greater than 1.0 (1.43–1.55) indicate a multi-step hydrogen adsorption process, involving complex pore filling and diffusion mechanisms in the ZIF frameworks [64]. In contrast, the higher k_{av} values (ranging from 7.7×10^{-3} to $2.96 \times 10^{-2} \text{ min}^{-1}$) along with lower n values (0.68–0.91) for the hybrid materials lead to a kinetic regime with two competing effects: enhanced initial kinetics and altered adsorption mechanisms. The increase in k_{av} indicates more rapid hydrogen adsorption in the early stages, which can be interpreted as an initial enhancement in mass transport at lower pressures, potentially

due to faster diffusion or additional pathways provided by the fCNT intercalation. On the other hand, the decrease in n (close to 1.0) implies a simple surface-dominated adsorption process, which may reflect a reduction in the complexity of pore filling. However, the fCNT intercalation may also disrupt the ZIF framework architecture, meaning the presence of carbon nanotubes can lead to partial pore blockage, thereby reducing the effective pore volume and hindering deeper diffusion. In other words, while the fCNTs enhanced the overall mass transport in the porous material, their alteration of the ZIF structure could introduce additional resistances that slow down the complete equilibration of hydrogen uptake. The higher R^2 values ($>95\%$) in all six materials indicate superior fit for the data and suggest that the adsorption process involves more than single-step kinetics. Overall, the base ZIFs displayed complex multi-step adsorption kinetics, whereas the hybrids exhibited faster initial uptakes, simpler surface adsorption kinetics, and partial pore blockage that ultimately limit complete hydrogen diffusion.

4. Conclusions

In this work, we synthesized three base zeolitic imidazolate frameworks (ZIF-8, ZIF-67, and ZC-ZIF) and their respective hybrid composites with carboxylate-functionalized carbon nanotubes (fCNTs) using a novel, low-cost synthesis method at ambient temperature ($19 \pm 2^\circ\text{C}$). This scalable approach offers economic feasibility for large-scale hydrogen storage material production. The integration of fCNTs with ZIF frameworks aimed to enhance hydrogen diffusion by introducing mesoporosity. Structural analyses confirmed that the base ZIFs exhibit highly ordered porous structures, suitable crystallinity, and large specific surface areas (SSAs), which contribute to excellent hydrogen storage properties at room temperature. ZIF-8 demonstrated the highest hydrogen uptake of 1.01 wt. % at 25°C and 100 bar, attributed to efficient Zn-N coordination and optimal crystallite alignment. The favourable physisorption properties of this material also showed full hydrogen storage reversibility and good cycling stability. While hybridization with fCNTs enhanced the mesoporosity, it led to reduced SSA and lower hydrogen capacity compared to base ZIFs. However, ZC-ZIF-H showed improved hydrogen uptake at lower pressures (e.g., 10 bar), highlighting potential applications for rapid hydrogen diffusion. The kinetic analysis supported this inference where fCNT intercalation improved overall mass transport and rate of initial adsorption, but also introduced a diffusion hindrance towards complete uptake. The superior fit of the Avrami model, especially in the fCNT hybrid systems, underscores the multi-step nature of the adsorption process, providing critical insights for the design of more efficient hydrogen storage materials.

Our findings emphasize the importance of highly crystalline, microporous ZIF structures, especially ZIF-8, for hydrogen storage at ambient conditions. The cost-effective synthesis method and excellent hydrogen uptake position ZIF-8 as a promising candidate for practical hydrogen storage applications. Future research will focus on further modification of ZIF-8 and optimized hybrid composites to enhance storage capacity and diffusion kinetics, contributing to the development of scalable, low-cost hydrogen storage materials for sustainable energy systems.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nanoenergyadv5020005/s1>. Figure S1: TEM images with elemental mapping of ZIF-8-H, ZIF-67, ZIF-67-H, and ZC-ZIF-H. Figure S2: (a) SEM image and (b) EDX spectra of ZIF-8. Figure S3: (a) SEM image and (b) EDX spectra of ZIF-8-H. Figure S4: (a) SEM image and (b) EDX spectra of ZIF-67. Figure S5: (a) SEM image and (b) EDX spectra of ZIF-67-H. Figure S6: (a) SEM image and (b) EDX spectra of ZC-ZIF. Figure S7: (a) SEM image and (b) EDX spectra of ZC-ZIF-H. Figure S8: High-resolution XPS spectra of (a-c) ZIF-8-H and (d) Zn2p of ZIF-8. Figure S9: High-resolution XPS spectra of ZIF-67. Figure S10: High-resolution XPS spectra of ZIF-67-H. Figure

S11: High-resolution XPS spectra of ZC-ZIF-H. Figure S12: High-resolution XPS spectra of ZC-ZIF. Figure S13: t-plots obtained from N₂-physisorption isotherms. Figure S14: Pseudo-first-order (PFO) kinetic plots with linear fitting for the six material samples. Figure S15: Avrami model kinetic plots with non-linear fitting for the six material samples. Table S1: Concentrations of zinc and cobalt precursors and 2-methylimidazolate ligand. Table S2: Particle size distribution parameters (all in nanometer units). Table S3: SEM EDX elemental concentrations of ZIFs and their hybrid composites. Table S4: XPS elemental composition in at. % (C, N, O, Zn, and Co). Table S5: Deconvoluted fitting results of XPS C1s, N1s, and O1s for all samples. Values are given in at. %, with binding energy (eV) in the parenthesis. Table S6: Deconvoluted fitting results of XPS Zn2p and Co2p. Values are given in at. %, with binding energy (eV) in the parenthesis. Table S7: Detailed textural properties. Table S8: Hydrogen storage parameters, percentage decrease, and cycling test data.

Author Contributions: Conceptualization, S.P. and E.K.; data curation, S.P.; investigation, S.P.; methodology, S.P.; writing—original draft, S.P.; supervision, T.B. and E.K.; resources management, T.B. and E.K.; project administration, T.B. and E.K.; funding acquisition, E.K.; writing—review and editing, E.K. All authors have read and agreed to the published version of the manuscript.

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