

Hydrogen Sorption Behaviors on Lithium Doped MIL@53-Al at Non-Cryogenic Temperatures.

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Research Article

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Abstract

The current research work reports the methods that have been developed to dope the Lithium nanoparticles to the MIL@53-Al surface frameworks without inducing the structures. The prepared MIL@53-Al MOFs and Li/MIL/53-Al were characterized by XRD, TEM, SEM, BET, and TGA. The developed Lithium doped MIL@53-Al and MIL@53-Al were measured for the hydrogen sorption capacities at 298 and 253 K under a pressure of 75 bar. The study reports revealed that sorption capacities of MIL@53-Al enhanced significantly due to the doping of lithium ions; however, doping of these ions should be controlled for obtaining good uptake capacities as the higher concentrations of lithium might damage the frameworks of the synthesized materials. The lithium doping enhances the hydrogen uptake from 1.37 to 1.75 wt % at 253 K and 75 bar pressure.

1. Introduction

The metal ions clusters and organic multidentate ligands form Metal-organic frameworks (MOFs), and these materials are highly crystalline and porous [1, 2]. MOFs emerged as potential materials for application in science like catalysis [3], storage [4], biomedical, and sensors [5, 6] from the past decade. MOFs can be changed into many varieties by altering the ligands or metal ions, as their structures can be tuned by changing the pore sizes. Additionally, MOFs consist of substantial surface areas and volumes, making them attractive hydrogen storage candidates [7–9]. Hydrogen storage might be crucial to achieving a hydrogen economy that can be used as a fuel carrier for the fuel cells. Even though many researchers study several materials for the storage application of hydrogen, to date, no material was achieved "DOE" ("US Department of Energy") targets, i.e., volumetric capacities (40 g/L) and gravimetric capacities (5.5 wt%) at the ambient temperatures [10]. MOFs and COFs (Covalent organic frameworks) are considered suitable sorption materials for hydrogen as they have significant surface areas and porosities. MOFs and COFs utilize weak Vander Waals interactions to enable reversible/fast discharge, which might store hydrogen.

Nevertheless, due to these interactions at ambient temperatures, significant amounts of hydrogen cannot be stored. According to the literature available, several researchers have been that at cryogenic temperatures, the hydrogen storage capacities have reached above 5.5 wt %; however, none of the studies said that hydrogen uptake capacities reached around two wt % at room temperature conditions [11–17]. Insertion of cations with alkaline nature to the MOFs Nano space has gained many researchers' attention to overcome the common storage problems associated with hydrogen storage. Specifically, cations like lithium are promising materials as these compounds have a lower molecular weight and provide an affinity for the molecules of hydrogen as they induce dipole interactions[18]. According to the literature available, the researchers have proposed several theoretical theories by doping lithium to COFs and MOFs to achieve a hydrogen storage wt % of 6 at ambient temperatures [19, 20]. Many research groups have been demonstrated the experiments by doping lithium with MOFs and revealed that these ions' doping enhanced the storage capacities of hydrogen at non-cryogenic temperatures [21–29]. These studies used MOFs consisting of specific functionalized groups such as hydroxyls to form lithium alkoxides by

removing the protons with lithium cations [24, 26]. MOFs with specific functionalized groups are limited; thus, new methods like doping of lithium might be adopted to develop wide varieties of MOFs.

Composite MOFs are prepared to enhance hydrogen uptake capacities by doping carbonaceous materials[30]. The developed composite materials have significant mechanical properties and moisture stabilization; It was also observed that doping of carbonaceous materials with transition metals enhanced hydrogen uptake capacities at room temperature. The enhancements in uptake capacities are attributed to the spillover mechanism - the MOFs act as secondary receptors consisting of a larger surface area for hydrogen atoms [30, 31]. Theoretical investigations have also been reported in the literature on the cation alkali metals doped to the MOFs consisting of organic linkers to the fullerenes and carbon nanotubes to enhance uptake capacities [32]. Lithium cations are the most common materials doped to the MOFs as they can effectively donate the electrons to the linkers of MOF and these ions are easy to dope as they have low molar masses[33]. Some computational studies on the MOFs doped with lithium revealed that Li donates the electrons to MOFs' linkers and leads to the high binding energy of hydrogen, which exhibited a solid affinity for MOFs nearer to Li[34]. Meng et al. reported that hydrogen sorption capacities in computational studies achieved at 298 K with a 100 bar pressure attained a weight of 4 wt% with a simulation doping lithium with IRMOF9. In the theoretical studies at ambient temperatures, MOFs and COFs doped with lithium also achieved a weight of 6 % hydrogen[35]. Klontzas et al. conducted theoretical calculations and reported that utilization of functionalized organic linkers consisting of lithium atoms showed enhanced MOFs' performance to store hydrogen. It was also found that enhanced hydrogen uptake capacities were observed in the experimental approaches. In his empirical studies[36], Li et al. revealed that hydrogen uptake capacities in conjugated polymers (microporous) with lithium over 1 bar pressure at 77 K were a weight percent of 6.1; adopting these mechanisms to real-time applications are not possible due to inconsistent repeatability[37]. Mulfort et al. reported enhanced uptake capacities of hydrogen over 1 bar pressure at 77 K, i.e., up to 75 % in the MOFs doped with lithium than the pristine MOFs; further reported that the organic linkers might increase these capacities with functionalized groups[38]. Himsl et al. revealed that lowering the pressures enhanced the uptake capacities of hydrogen from a weight of 0.5 to 0.7 % by the post-synthesis formation of lithium alkoxides in MIL-53 (Al) hydroxyl functionalized groups[39]. By immersing MOF with lithium chloride solutions, Yang et al. prepared NOTT 200 and further doped it with the lithium, showing enhanced efficiency in hydrogen uptake[40].

Further, experimental and theoretical studies confirmed that doping lithium is the most effective method for enhancing MOFs' H₂ sorption capacities. Even though many studies are available in the literature on uptake capacities of hydrogen at lower pressures (up to 1 bar) in the MOFs doped with the lithium; however it is challenging to find the Li doped MOFs' studies at high pressures. Thus, paucity in the literature about the sorption capacities of hydrogen at high pressures motivated us to perform the current research, mainly focused on the uptake capacities of hydrogen at cryogenic temperature and room temperatures up to a pressure of 70 bar inside MOFs doped with the lithium. For the present study, MIL-53 (Al) was selected; as these materials consist of high thermal stabilities, exhibits stability to moisture, and

high surface area/volume, which helps in the dispersal of ions doped with the MOFs. MIL-53 (Al) is a MOF doped with aluminum consists of trans chains where the corners are shared with the octahedra of $\text{AlO}_4(\text{OH})_2$, which are interconnected by the BDC (benzene dicarboxylate) linkers. These frameworks consist of 1-D channels (one dimensional) removed by the solvents and benzene dicarboxylate. In the present study, MIL-53 (Al) was synthesized by doping the ions of lithium. Adsorption isotherms of hydrogen at high pressure were performed at 253 and 298 K up to 70 bar pressure to determine doped lithium's effect on hydrogen storage at high-pressure capacity in these materials [41–45].

2. Materials And Methods

2.1 Materials and synthesis

The reagents utilized in the current study are analytic grade and further used in the experiments without purification. Aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), 1,4- benzene dicarboxylic acid were procured from the sigma Aldrich. Lithium nitrate ($\text{Li}(\text{NO}_3)$), Dimethylformamide, and ethanol were purchased from Merck chemicals.

2.2 MIL-53 (Al) Synthesis

Loiseau et al. [41] methods are adopted for the materials synthesis under hydrothermal conditions using the aluminum nitrate nonahydrate, BDC, DMF, and double-distilled water; these materials' composition is in the ratio of aluminum nitrate nonahydrate: $\frac{1}{2}$ BDC: 80 (H_2O). The solution prepared was placed in the Teflon coated steel autoclave for three days at 493 K and further allowed to react hydrothermally. The solution obtained after the reaction was filtered and washed with the deionized water; the product obtained consist of synthesized MIL@53-Al along with unreacted BDC compounds; to remove the unreacted BDC, 1 gram of synthesized MIL@53-Al consisting of unreacted BDC was dispersed with DMF of 25 ml, and this solution was autoclaved at 423 K for 15 hours. The final product obtained was cooled, filtered, and further calcinated at 553 K over a night.

2.3 Li/MIL/53-Al preparation

To activate the MIL@53-Al, these compounds are subjected to 473K for 4 hours in the vacuum. The combination that is activated was immersed in the lithium nitrate/ethanol of 0.5 M solution by continuous stirring for 24 hours at room temperatures; by further filtration, lithium nitrate was added to the MIL@53-Al and formed a compound, i.e., LiNO_3 @MIL@53-Al was attained through intended aeration for one day at 333K. The nitrates in the LiNO_3 @MIL@53-Al are removed by heating in a vacuum at 573 K for two hours to obtain lithium ion-doped with MIL/53(Al)(Li/MIL/53-Al).

2.4 Characterization of samples

Philips CM@200 (TEM) was used for the examination of the synthesized compounds' morphology. TG-DTA (thermogravimetric analysis) was done by using Shimadzu DTG-60. XRD patterns were determined

by using ANalytical X'Pert PRO. The surface areas of these compounds are determined by using the BET analyzer method.

2.5 Hydrogen uptake studies

BEL japan (BELSORP-HP) instrument is used to determine the samples' hydrogen uptake capacities; all the samples after activation are heated for longer durations underneath a vacuum for removing solvent molecules from the pores. The uptake capacities of hydrogen were measured at 298 K and 253K up to a pressure of 70 bar. Extreme pristine gases of H₂ were used in these measurements.

3. Results And Discussion

3.1 Structures and Morphology

High-resolution transmission electron microscopy was used to examine MIL@53-Al morphology illustrated in Fig. 1a. According to Fig. 1b, the crystal size distribution is not uniform and ranging from 50-100nm. The TEM image's further magnification revealed that microscopic pseudo-spherical-like particles are closely attached to these MIL-53 composites.

SEM images of the MIL@53-Al produced by the synthesis depicted in Fig. 2a. The compound was crystalline, with size ranges from 1–20 μm in the contract. Small crystal size was observed in the Li/MIL/53-Al; analogous spherical particles with a size of 50 nm overhung above the surfaces of MIL@53-Al can be seen in Fig. 1b. The MIL-53 (Al) was found to be faceted, and it is evident that the MOF frameworks are not altered even after loading with nanoparticles of lithium. The spherical points on the EDS confirmed lithium's presence, which is not shown in the image.

Figure 3 depicts the patterns (XRD) of MIL@53-Al, Lithium nitrate @MIL-53-Al, and Li@MIL. These compound patterns suggested a mixture of empty channels with a high temperature and low temperature. The water molecules present the channel's center; the small peak at 12.2° is allocated to the high temperature. MIL-53 (Al) appears as intrinsic for commercialization as two forms are stated in the literature. From pattern (a), it can be observed that the diffraction of peaks at 18.2°, 19.8°, 25.5°, 8.8°, 9.6°, and 27.5° might be similar to the peak positions of Loiseau et al., 2004 reported, indicating that MIL-53 (Al) crystals are synthesized successfully. In contrast, different patterns are exhibited by the "LiNO₃@MIL@53-Al". The MIL@53-Al shows breathing effects due to the structure's shrinkage due to the guest molecules of water. The pattern changes in the XRD might be attributed to the ethanol remnant in "LiNO₃@MIL@53-Al"; to remove the ethanol residuals from pores surface in a vacuum at 573 K heat treatment was used, the patterns of Li-MIL@53-Al are analogous to the MIL@53-Al, which represents MIL@53-Al crystal structures are not affected by the heat treatment. It is to be noted that peaks attributed to the lithium nitrate are not observed in other compounds.

3.2 Surface area

"Brunauer Emmett Teller (BET)" method is used for the measurement using Quantachrome NOVA 1200e model machines to determine the specific surface area for the physisorption of nitrogen at 77K. Before the physisorption, the MIL@53-Al samples are degassed for two hours at 493K. The BET-surface area was estimated to be 1254 m² g⁻¹ (Table 1).

Table 1
presents the surface area and storage capacities of MIL@53-Al and Li/MIL/53-Al

Sample code	s_{BET} (m ² /g)	H ₂ storage in wt % (70 bar, v)	H ₂ storage in wt % (70 bar, 298 K)
MIL-53 (Al)	1254	1.37	1.10
Li@MIL-53-Al	948	1.75	1.19

3.3 TGA Analysis

The synthesized Li-MIL@53-Al was performed for the Thermogravimetric analysis (TGA) using Shimadzu DTG/60 instruments with a heating rate of five degrees per minute under nitrogen flow from 30⁰C to 800⁰C. The temperature ramping from 150–850 K with a rate of heating 5 K/min, and the measurements are taken under nitrogen atmosphere. The initial loss of weight was observed at 173 K, which might be attributed to the removal of water molecules from the samples, and further, no loss of weight loss was observed up to 423 K. Further weight loss above the 423 K might be due to the destruction of MIL@53-Al structures which might be owing to the BDC linkers of the frameworks

3.4 Hydrogen sorption properties

BELSORP-HP instrument is used for measuring volumetric measurements at 253 and 298 K (non-cryogenic temperatures) at 75 bar pressure. Hydrogen sorption capacities at high pressures were performed in the same experimental settings in the MIL@53-Al and Li@MIL53-Al. H₂ adsorption capacities are found to be high in all the concentrations MIL-53 (Al) doped with lithium, i.e., Li/MIL/53-Al, in comparison to the pristine MIL@53-Al; This might be attributed to the destruction of frameworks by the lithium ions at higher concentrations, which is further proved by the PXRD and BET surface area measurements. Thus, it is evident that controlling the lithium ions during doping is necessary to retain the MOFs framework to achieve more sorption capacities. Henceforth, the increase in hydrogen uptake capacities in the Li/MIL/53-Al is due to lithium ions' interactions during doping with the pores of MIL@53-Al.

4. Conclusions

The synthesized MIL@53-Al MOFs were doped with the Li ions and analyzed the sorption the hydrogen sorption behaviors at 298 and 253 K up to 75 bar pressure. The Li doped MOFs enhanced the sorption capacities of hydrogen at both temperatures at these experimental settings. It was observed that

excessive further doping of Li ions deformed the structures leading to the loss of the crystalline structure and decreased the sorption capacities of hydrogen. Thus, it is evident that the optimum usage of Li ions for the doping of MOFs is to be maintained to enhance the surface areas and disperse the metal ions for hydrogen sorption. The same was observed in our study by using the MIL@53-Al, and the current research concludes that doping of Li-ions enhances the sorption capacities of hydrogen in MOF

5. Declarations

Conflict of interest:

none

Acknowledgments:

none

6. References

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Figures

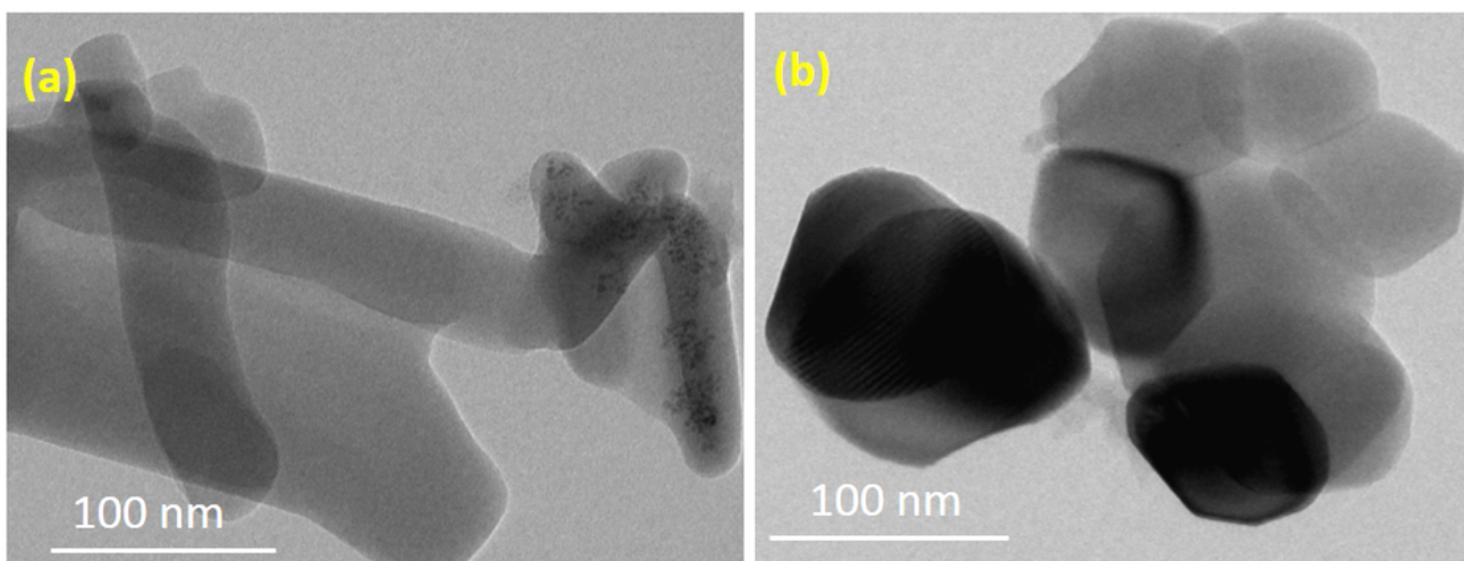


Figure 1

TEM image of (a) MIL@53-Al (b) Magnified TEM image of MIL@53-Al

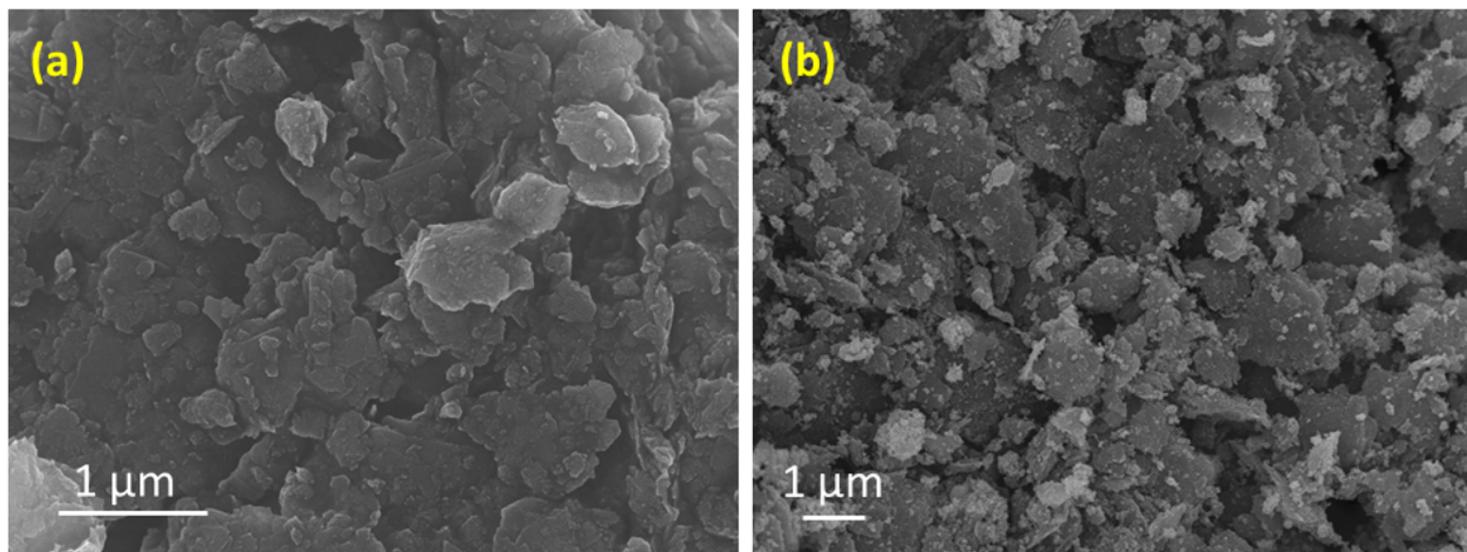


Figure 2

SEM images of (a) MIL@53-Al (b) Li@MIL-53 (Al)

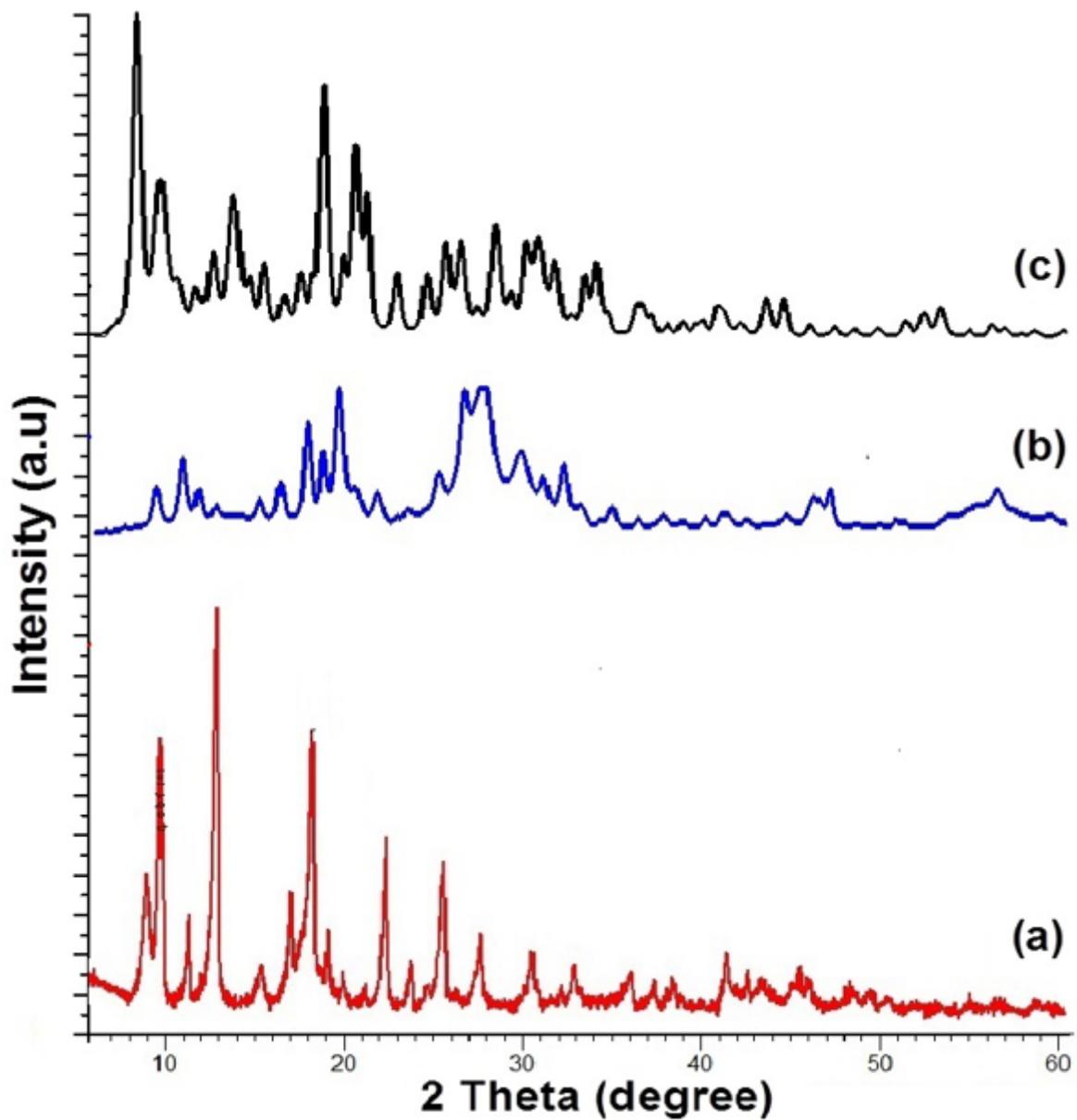


Figure 3

Depicts "(a) MIL@53-Al (b) Lithium nitrate@MIL@53-Al, and (c) Li/MIL/53-Al" of powdered XRD

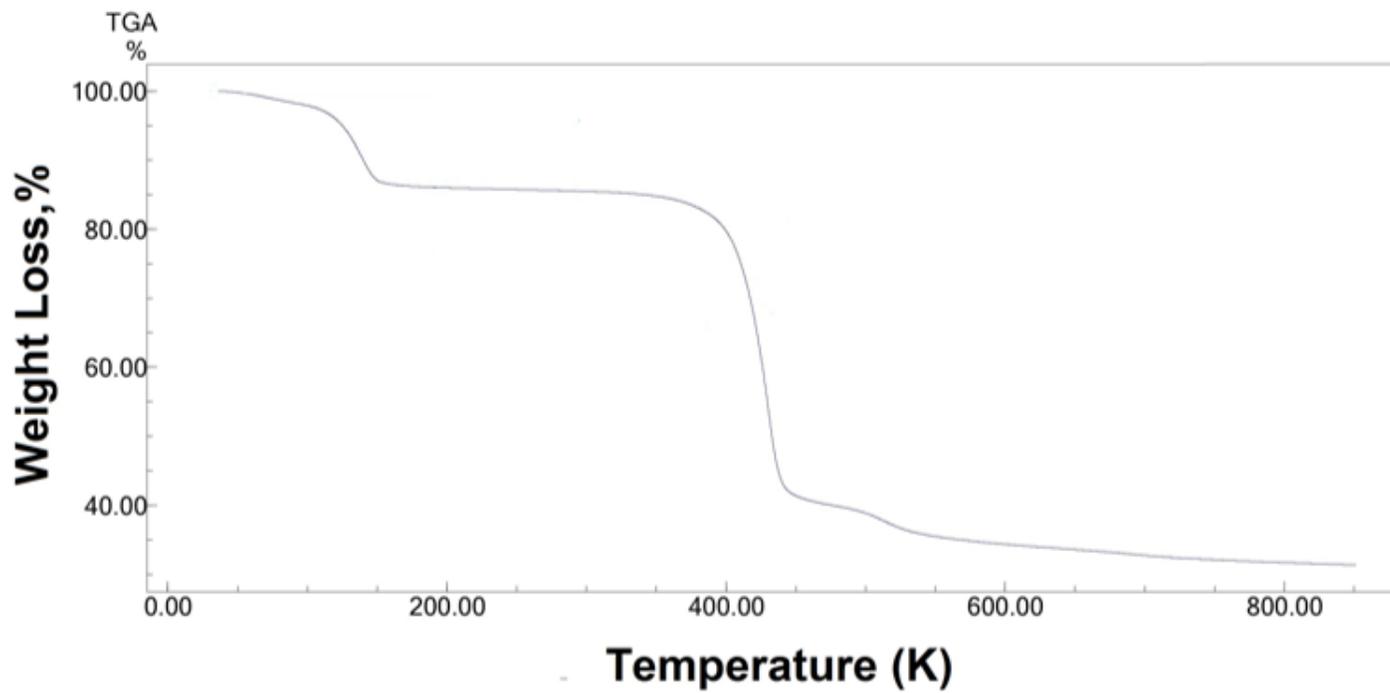


Figure 4

TGA plot of MIL-53 (Al)

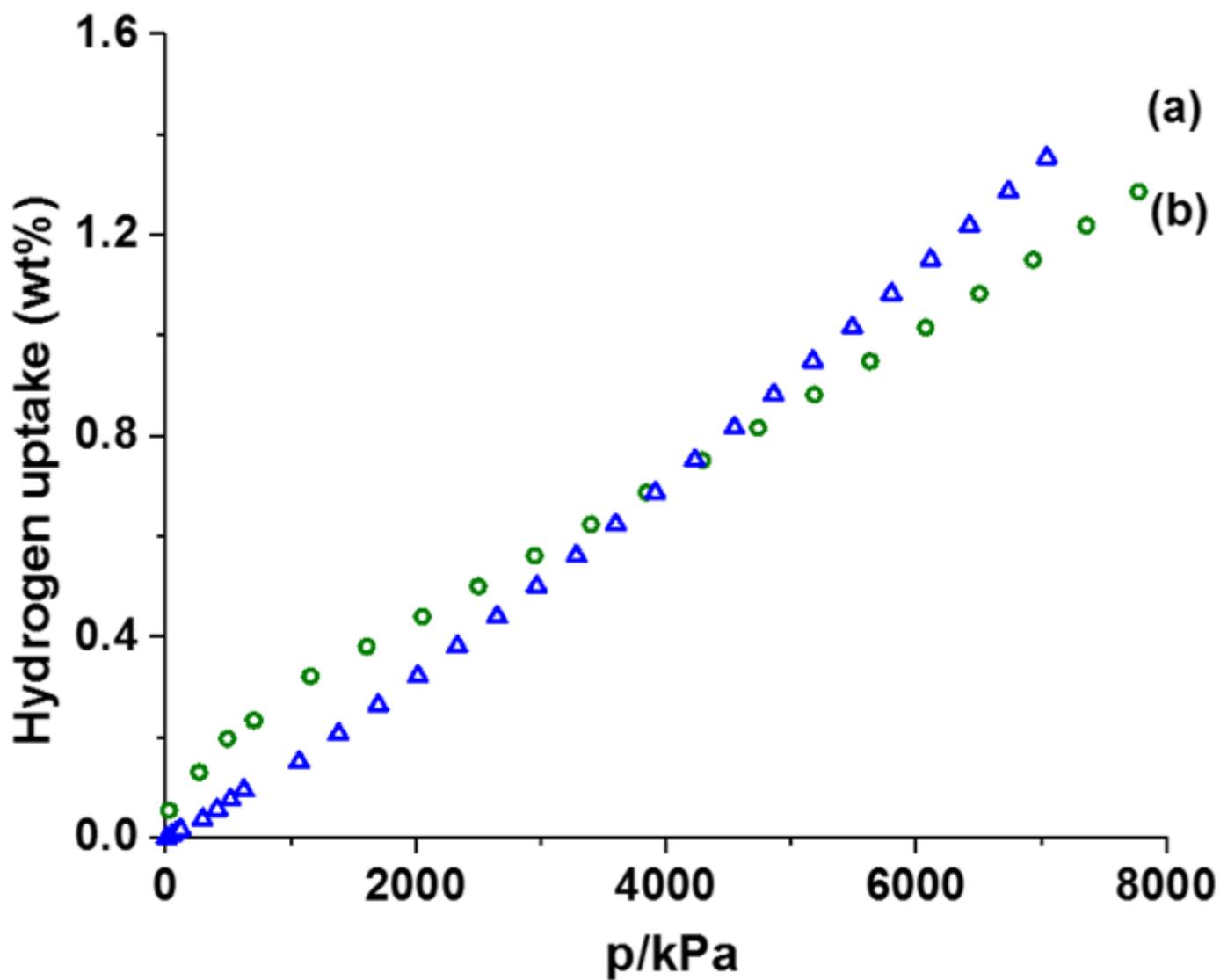


Figure 5

Hydrogen uptake capacities of (a)MIL@53-Al and (b)Li/MIL/53-Al at 298 K.

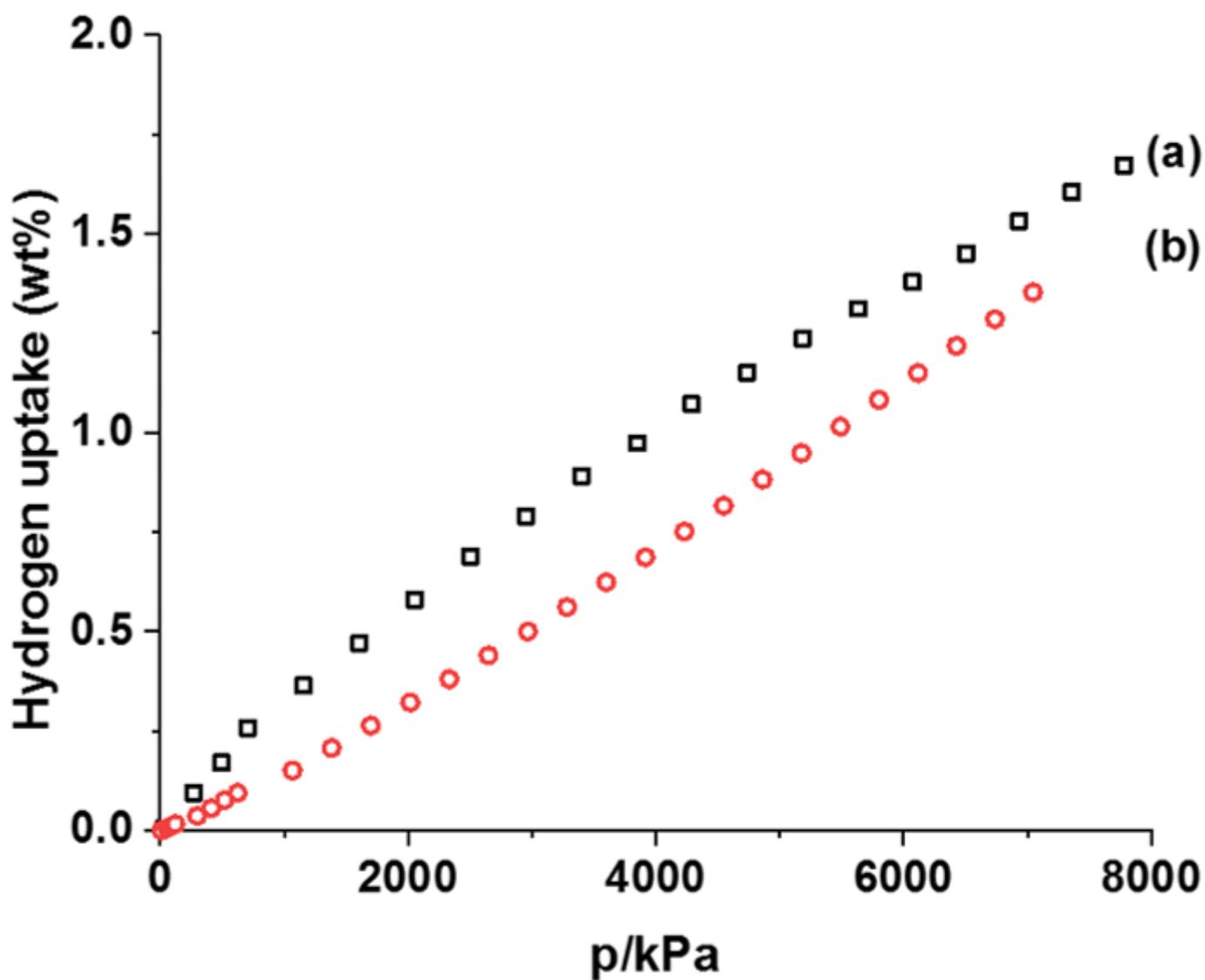


Figure 6

Hydrogen uptake capacities of (a) Li/MIL/53-Al and (b) MIL@53-Al at 253 K.

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