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Enhanced hydrogen sorption properties over Mg^{2+} modified solvothermal synthesized HKUST-1 ($\text{Mg}^{2+}/\text{HKUST-1}$)

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Abstract. The development of high capacity materials for hydrogen storage such as MOFs to support the utilization of hydrogen as a renewable energy source is an attractive area for further investigation. In this research, a well-known type of MOF, specifically HKUST-1, was synthesized using the solvothermal method and ex-situ modified with magnesium(II) ions at 3, 5, and 10 wt% to serve as additional binding sites to form $\text{Mg}^{2+}/\text{HKUST-1}$. The resulting materials were analysed via XRD, FTIR, SEM-EDX, and a nitrogen sorption isotherm. Hydrogen sorption measurements were conducted using a Sievert system. The structure and morphology of HKUST-1 remained stable after it was embedded with Mg^{2+} according to X-ray diffraction, FTIR, and SEM analysis. Nitrogen sorption isotherm revealed that before and after modification with Mg^{2+} , the materials could be classified as microporous and the surface area increased significantly from 713.283 to 1200.211 m^2/g . The presence of Mg^{2+} in the HKUST-1 enhanced its hydrogen sorption capacity up to 0.292 wt% at 1.2 bar under an operational temperature of 30°C and 0.48 wt% at 80°C (1.4 bar).

Keywords: HKUST-1, magnesium(II), solvothermal, ex-situ modification, hydrogen storage

1. Introduction

In recent decades, inadequate energy supplies are a major global problem. This relates to the depletion of major fossil-based energy sources and a related increase in air pollution caused by emissions such as CO_x , NO_x , and SO_x . One promising alternative energy source is the utilization of hydrogen as an energy carrier due to its relatively cleaner combustion and higher energy content as well as its ease of manufacture [1]. However, using hydrogen as an alternative fuel poses a challenge regarding storage. In automobiles, hydrogen storage systems have not been effective and efficient because a heavy cryogenic tank is required [2]. Hydrogen storage systems based on chemisorption such as the use of metal hydrides and clathrate hydrogen hydrate have been investigated [3]. In chemisorption, hydrogen atoms contact a solid sorbent and form highly reactive chemical bonds. This method may reach high levels of hydrogen uptake. However, chemisorption requires high temperatures and causes kinetic and thermodynamic problems when measuring hydrogen charging and discharging [4].



The use of an adsorption storage method involving porous material is one solution to this problem. Nano-carbons and zeolite can be applied to hydrogen storage, however, nano-carbons have wide pore size distributions, and zeolite is hydrophilic and has a low micropore volume [5, 6]. As a new class of porous materials, metal-organic frameworks (MOFs) can also be used in storage systems [7]. Furthermore, MOFs are more flexible and can be designed according to specific requirements or applications. Compared to other porous material, MOFs can be constructed via self-assembly from various metal ions and ligands (i.e. organic linker) [8]. Structurally, MOFs are organic-inorganic hybrid porous materials, meaning a combination of metal ions or metal-oxide clusters as the nodes and organic ligands as the linkers forming infinite crystalline coordination polymers [9]. Therefore, MOFs can store gas due to not only their high porosity but also active sites on both their metal and ligand [10].

The capability of MOFs as hydrogen storage materials is based on physisorption [11]. In this case, the mechanism could be a trough Van der Waals or coulomb interaction. Moreover, hydrogen stored in MOFs can be compressed effectively to a high-volume density, compared to the same pressure and temperature with free gas [12]. The most frequently studied MOF for methane and hydrogen storage is HKUST-1 [13]. It was first synthesized by Chui *et al.* [14] in 1999 using Cu^{2+} as a node and trimesic acid (H_3BTC) as a linker. So far, HKUST-1 intended for hydrogen storage material is obtained via solvothermal synthesis [15-17]. Reactions in the solvothermal condition operating at high pressures and temperatures for long periods lead to high rates of crystal growth [13]. HKUST-1 has been prospected to adsorb hydrogen due to its coordinative vacancy of Cu^{2+} ion where it is shown by presence of water molecule connected with coordination sphere of Cu^{2+} ion [18].

The real handicap of implementing MOF materials for hydrogen storage at near room temperature is fairly the low hydrogen interaction to the MOF framework-estimated by the isosteric heat of hydrogen adsorption- that only permits reaching high hydrogen adsorption capacities at cryogenic temperature. For this reason, one of the most effective approaches for enhancing this interaction is the inclusion of highly energetic binding sites like structural open metal sites and extra-framework metal species like alkaline, alkaline-earth or noble metals within the MOFs cavities [19, 20]. Moreover, modifications of MOFs have been performed by employing methods such as hydrogen spillover [21], catenation [22], and metal ion doping [23]. Doping of Li^+ and Na^+ ions into HKUST-1 increases surface area and enhances hydrogen sorption properties according to previous study. The presence of Li^+ and Na^+ ions can act as additional adsorption and hydrogen binding sites in HKUST-1 [19]. Alkali metal is an electropositive metal and has great potential to modify MOFs because of its low binding energy and thereby prevents agglomeration [24]. In line with this finding, in this research, HKUST-1 was synthesized under solvothermal conditions and modified by ex-situ embedding of an earth alkali metal ion; Mg^{2+} is embedded to form $\text{Mg}^{2+}/\text{HKUST-1}$. Mg^{2+} is a cation of light element which can produce low-density MOFs, so that it hopefully can increase the capacity of MOFs in adsorbing small-sized gases such as hydrogen [25]. The obtained materials were then characterized and analysed to determine their hydrogen storage capacity.

2. Materials and Methods

2.1. Materials

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (98%) and ethanol (96%) were commercially obtained from Merck Germany. H_3BTC (benzene 1,3,5-tricarboxylate 95%) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (95%) were purchased from Sigma Aldrich, Germany, and deionized water was supplied by Bratachem, Indonesia. Hydrogen gas with a purity of 99.99% was provided by PT Samator Gas, Indonesia. All chemicals were used as purchased without any further purification.

2.2. Synthesis of $\text{Mg}^{2+}/\text{HKUST-1}$

HKUST-1 was prepared under solvothermal conditions in a Teflon vessel covered with stainless-steel autoclaves and heated in a MEMMERT (type 67 UN30) controlled oven, based on procedures described by Schlichte *et al.* [26]. The obtained HKUST-1 was activated for 2 h prior to ex-situ modification with

Mg²⁺. MgCl₂.6H₂O (0.251; 0.418; 0.836 g) was dissolved in 24 mL of ethanol and water (1:1). Into this solution, (0.97; 0.95; 0.90) g of HKUST-1 was carefully added and stirred for 15 minutes. The mixture was placed into Teflon vessels and covered with stainless-steel autoclaves and heated to 393 K for 12 h. After they cooled, the resulting precipitate was filtered, washed with ethanol, and dried at ambient temperatures for 24 h.

2.3. Characterization

The X-ray powder diffraction (P-XRD) data were analysed on a Rigaku Miniflex 600 Benchtop, using Cu-K α radiation ($\lambda=1.5406$ Å), with the current and voltage under 30 mA and 40 kV ($2\theta=5-50^\circ$) at a scan rate of $1^\circ/\text{min}$. The synthesized materials' morphology and elemental composition was collected using Inspect S50-FEI, a type of scanning electron microscopy (SEM) equipped with energy dispersive x-ray (EDX) analysis. Infra-Red spectra were recorded by using KBr pellets in a Shimadzu IR Prestige-21. Nitrogen adsorption isotherms were performed with a Quadrasorb evo (Quantachrome Instruments) at 77 K. The samples were activated at 150°C for 12 h prior the measurement.

2.4. Hydrogen sorption measurement

Mg²⁺/HKUST-1 (0.5 g) was activated under vacuum conditions at 473 K for 1 h. Hydrogen sorption measurements were conducted using a Sievert system as reported by Dewa *et al.* [27] at 30 and 80°C with pressures ranging from 0.2 to 1.5 bar. Each pressure of 0.2-1.4 bars was tested for 10 minutes.

3. Results and Discussion

3.1. Materials Characterizations

A diffractogram of Mg²⁺/HKUST-1 with Mg²⁺ loadings of 3, 5, and 10 wt% is presented in Fig. 1. The diffraction pattern of the synthesized materials is confirmed through similarities with a simulated pattern generated from CCDC number.112954 at 2θ : 6.73° (2 0 0), 9.47° (2 2 0), and 11.65° (2 2 2). The structure of HKUST-1 remained stable after being embedded with Mg²⁺, as indicated by similarities in the XRD peaks of HKUST-1 embedded with Mg²⁺ with those of unembedded HKUST-1. This result demonstrates that the presence of electropositive metal ions embedded in HKUST-1 does not change its structure chemically, which is consistent with a previous study conducted by Anbia and Faryadras [23]. Furthermore, a lack of peaks at 2θ : 36.43° , 35.5° , and 38.7° indicates the absence of Cu₂O and CuO [21, 28]. The relative crystallinities of the materials were calculated according to the sum of the areas of the seven strong peaks between 2θ of 6 and 25° , assuming that the relative crystallinity of the HKUST-1 was 100%. The comparison of the 102% and 103% relative crystallinities of Mg²⁺ 3 wt%/HKUST-1 and Mg²⁺ 5 wt%/HKUST-1 with the 100% relative crystallinity of HKUST-1 indicated that the two materials exhibit a slightly higher crystallinity state after embedded with Mg²⁺, but the 95% relative crystallinity of Mg²⁺ 10 wt%/HKUST-1 showed decreased crystallinity as the Mg²⁺ content increased (table 1).

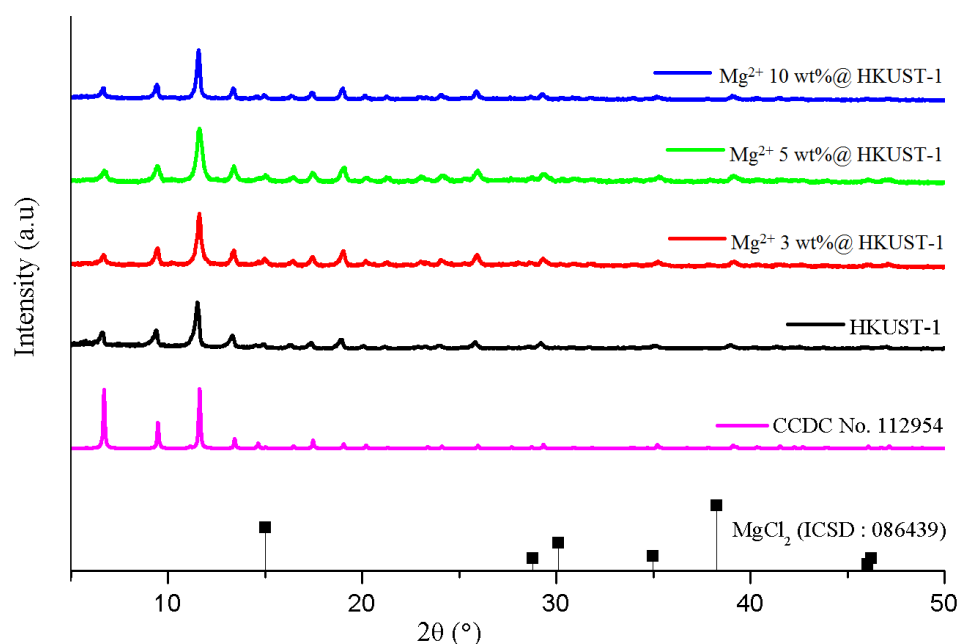


Figure 1. X-Ray diffractogram of solvothermal synthesized HKUST-1 and Mg^{2+} modified HKUST-1 at different loading.

Table 1. Relative crystallinities and different Mg content of the HKUST-1 samples.

Materials	Relative crystallinity	Mg content, wt% (EDX)
HKUST-1	100%	0
Mg^{2+} 3 wt%/HKUST-1	102%	1.04
Mg^{2+} 5 wt%/HKUST-1	103%	1.35
Mg^{2+} 10 wt%/HKUST-1	95%	1.67

FTIR spectra of the obtained materials (Fig. 2) also confirmed that the presence of Mg^{2+} does not change HKUST-1's structure. The band found at 1715 cm^{-1} revealed C=O stretching vibration was present in the H_3BTC ligand. Complexation with Cu^{2+} was indicated by the band shift to 1665 cm^{-1} . The broad band in the range of $3100\text{--}3600\text{ cm}^{-1}$ reflects the existence of coordinated water molecules in the structure. The peak at $3000\text{--}3100$ and 1452 cm^{-1} indicates aromatic C-H and C=C vibrational stretching. The sharp peaks at 1665 and 1372 cm^{-1} show asymmetric vibrational (COO^-) and symmetric vibrational (COO^-) forming a *syn-syn* bidentate bridge [28]. Moreover, the band at 714 cm^{-1} can be assigned a stretching vibration of Cu-O, revealing the O^{2-} ion is coordinated with Cu^{2+} [28, 29].

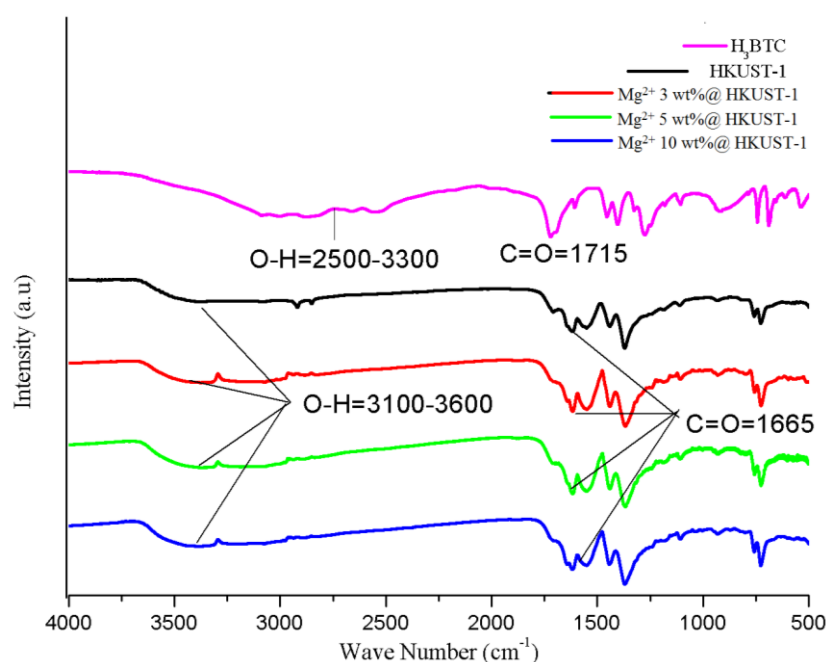


Figure 2. FTIR spectra of solvothermal synthesized HKUST-1 and Mg^{2+} modified HKUST-1 at different loading.

A nitrogen sorption isotherm (Fig. 3, table 2) revealed that before and after modification with Mg^{2+} , the materials fit type I and II of the IUPAC adsorption isotherm and could be classified as micro-meso porous materials. HKUST-1 modified with Mg^{2+} 3 and 5 wt% showed the highest pore volume and largest surface area, respectively, however after modification with higher Mg^{2+} content (Mg^{2+} 10 wt%) both pore volume and surface area dramatically decreased. This data correlated with relative crystallinity data of the materials as presented in table 1. Moreover, based on this phenomenon, we can assume the HKUST-1's pores were blocked by Mg^{2+} . The pore volume changed with inhomogeneous pore distribution (Fig. 4) after being embedded with Mg^{2+} . It is assumed that the Mg^{2+} particles in the HKUST-1 are not evenly distributed. The presence of embedded Mg^{2+} increases HKUST-1's pore volume and surface area, and 10 wt% Mg^{2+} /HKUST-1 has a smaller surface area and pore volume than 3 wt% and 5 wt% Mg^{2+} /HKUST-1. This results implied in the nitrogen sorption capacity, the higher the surface are, the higher the nitrogen adsorbed.

Table 2. Pore volume and surface area of embedded HKUST-1 with Mg^{2+} and unembedded HKUST-1.

Sample	Langmuir surface area (m^2/g)	Pore volume (cc STP g^{-1})	Average pore size (\AA)
HKUST-1	713.283	0.068	10.196
Mg^{2+} 3 wt%/HKUST-1	1101.632	0.097	10.006
Mg^{2+} 5 wt%/HKUST-1	1200.211	0.091	9.717
Mg^{2+} 10 wt%/HKUST-1	973.515	0.073	9.630

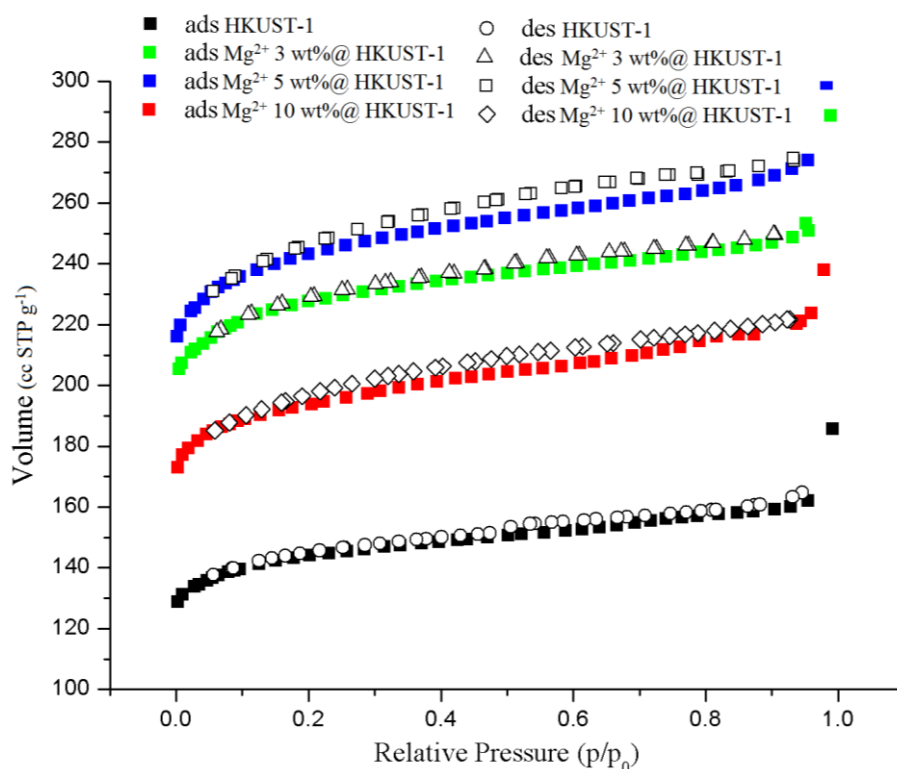


Figure 3. N_2 adsorption-desorption isotherm at 77 K of embedded HKUST-1 with Mg^{2+} and unembedded HKUST-1.

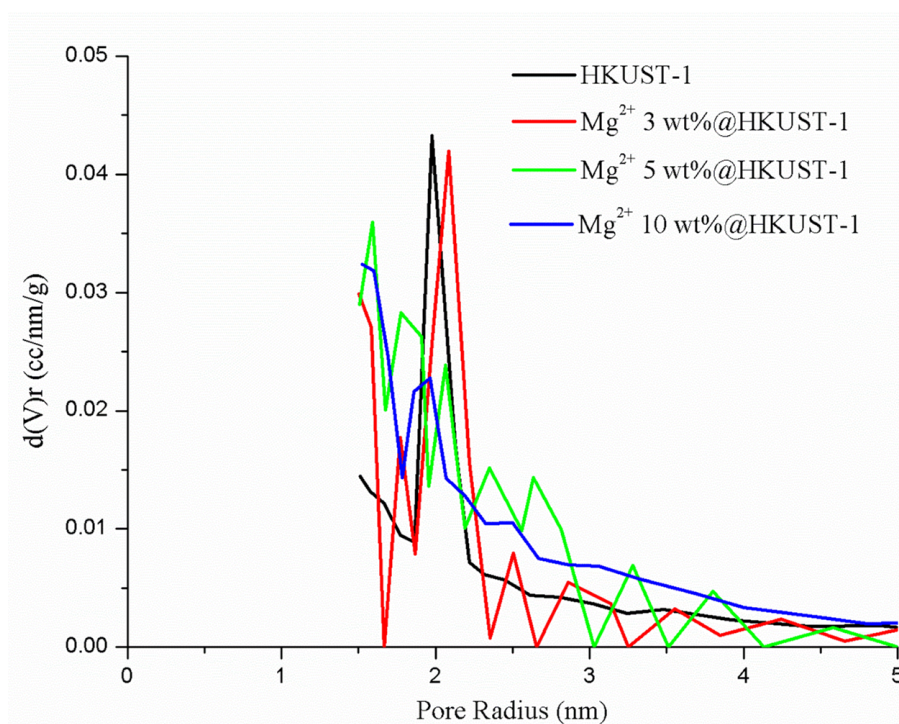


Figure 4. Pore size distribution of solvothermal synthesized HKUST-1 and Mg^{2+} modified HKUST-1.

According to results of the SEM-EDX analysis (Fig. 5, table 3), Mg^{2+} was successfully embedded in HKUST-1 and confirmed that the addition of Mg^{2+} up to 5 wt% did not change so much the morphology of the HKUST-1 correlated with crystallinity of the materials as shown in XRD data (Fig. 1, table 1). However, after the addition of Mg^{2+} 10 wt% changed their morphology and decrease the crystallinity. In addition, embedded Mg^{2+} ion quantities were not detected exactly as calculated theoretically. It may be because Mg^{2+} was lost during the filtration step. Furthermore, the identified Cl^- ion indicates the embedding method was not optimum. Mg^{2+} and Cl^- ions' sizes are very small, 0.072 nm [30] and 0.18 nm [31], which may occupy to the HKUST-1 pores.

Table 3. Elements composition of embedded HKUST-1 with Mg^{2+} and unembedded HKUST-1 analysed by SEM-EDX.

The material	Element (% wt)				
	C	O	Cu	Mg	Cl
HKUST-1	29.19	20.03	50.78		
Mg^{2+} 3 wt%/HKUST-1	20.72	24.94	53.30	1.04	-
Mg^{2+} 5 wt%/HKUST-1	32.10	20.62	45.20	1.35	0.72
Mg^{2+} 10 wt%/HKUST-1	32.35	24.93	39.63	1.67	1.42

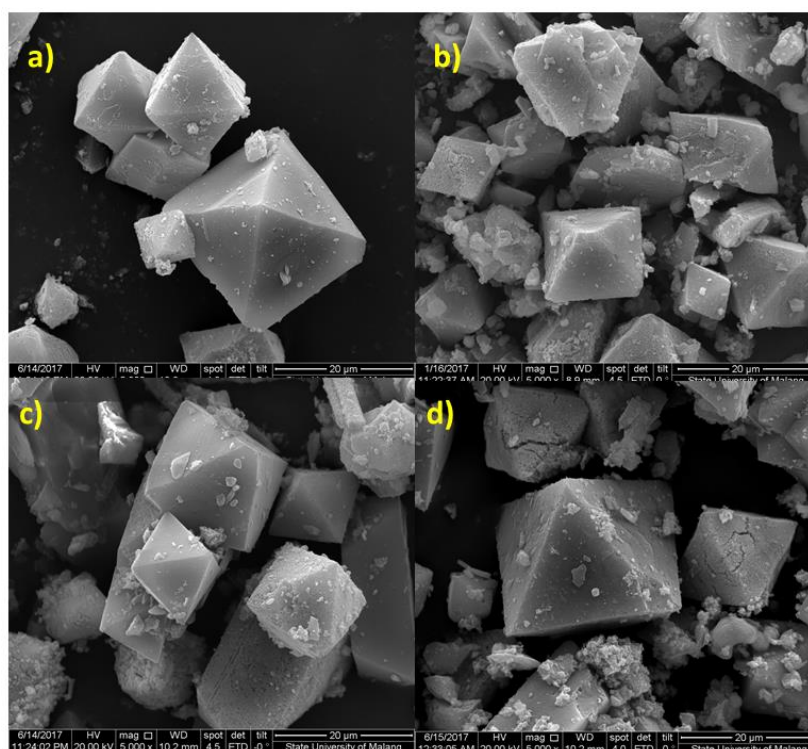


Figure 5. SEM image of solvothermal synthesized HKUST-1 (a) and Mg^{2+} modified HKUST-1 with loading of 3, 5, 10 wt% (b, c, d) and show morphology and crystallinity change after addition of 10 wt%.

3.2. Hydrogen Sorption Properties

Fig. 6.1 and 6.2 present HKUST-1's hydrogen adsorption capacity at 30 and 80°C which shows increase trend after being embedded with Mg^{2+} . Under an operational temperature of 30°C, the maximum

adsorption capacity is up to 0.292 wt% at 1.2 bar, obtained from Mg^{2+} 10 wt%/HKUST-1. Furthermore, its maximum adsorption capacity under an operational temperature of 80°C is up to 0.48 wt% at 1.4 bar, obtained from Mg^{2+} 3 wt%/HKUST-1. The result could be correlated to the nitrogen sorption isotherm analysis that Mg^{2+} 10 wt%/HKUST-1 has low pore volume with up to $0.073 \text{ cc STP g}^{-1}$ while Mg^{2+} 3 wt%/HKUST-1 has higher surface area which is $1101.632 \text{ m}^2 \text{ g}^{-1}$. It proves that the presence of Mg^{2+} as an electropositive metal ion embedded in HKUST-1 increases hydrogen uptake, and results from the additional binding sites and increased surface area of modified HKUST-1 [12]. This study is also in line with previous research conducted by Lim *et al.* [32].

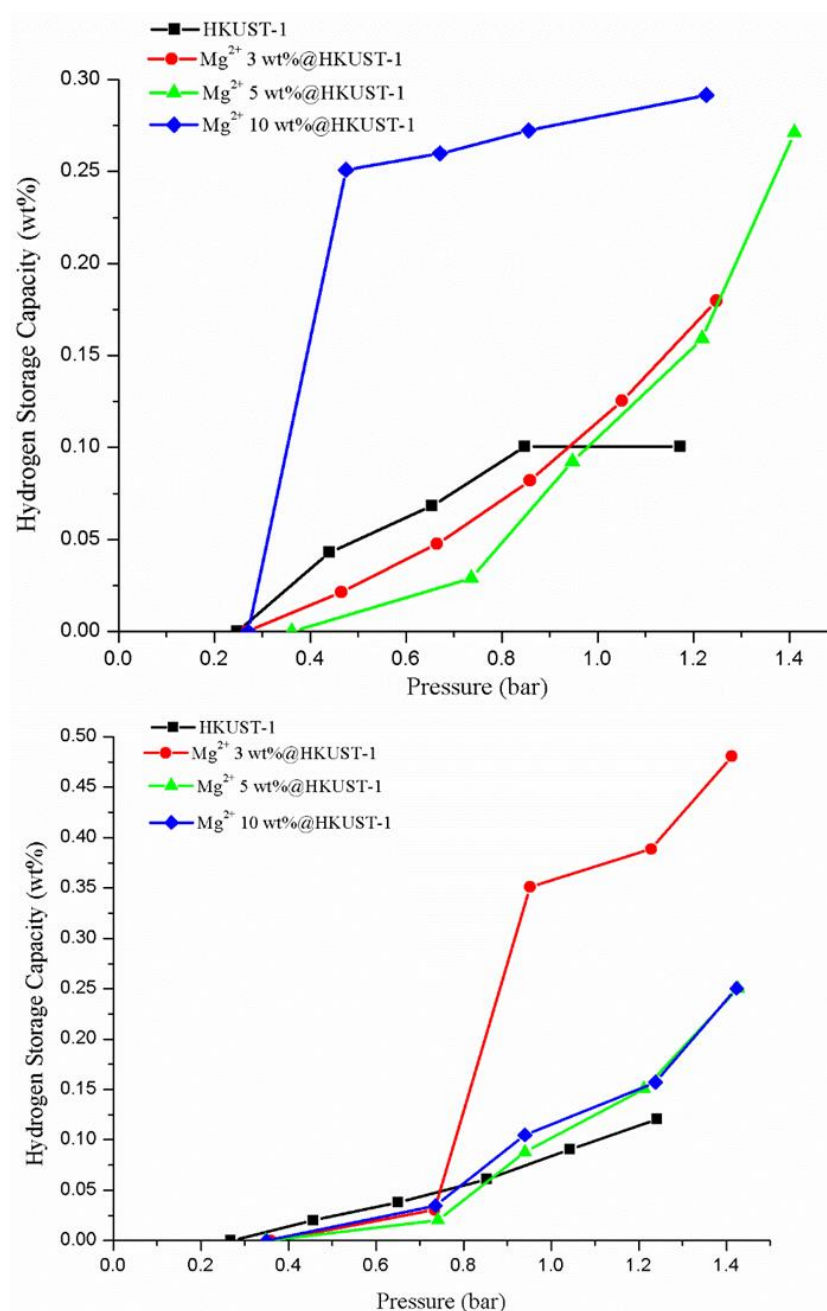


Figure 6. Hydrogen adsorption capacity of unembedded HKUST-1 (Mg) and embedded HKUST-1 with Mg^{2+} under conditional temperature (top) 30°C (bottom) 80°C .

4. Conclusions

Ex-situ modification of HKUST-1 with Mg^{2+} was successfully prepared and tested for hydrogen sorption. After it was embedded with Mg^{2+} , HKUST-1's structure did not change, but its surface area was increased. Additionally, the presence of Mg^{2+} enhanced its hydrogen sorption capacity at 30°C (1.2 bar) up to 0.292 wt% and 0.48 wt% at 80°C (1.4 bar). For the next study, the strength of the interaction between the materials and hydrogen molecules should be investigated via inelastic neutron scattering (INS). Moreover, adsorption enthalpy could be analysed by TG-DTA to discuss the effects of temperature on hydrogen sorption.

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