Mg$^{2+}$ Doped into Electro-synthesized HKUST-1 and Their Initial Hydrogen Sorption Properties

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Abstract. The hydrogen storage materials are essentially play important roles in supporting the utilization of hydrogen as a promising alternative energy. Several innovative materials have been proposed and intensively investigated in this regard, including Metal-Organic Framework (MOFs). MOFs type HKUST-1 [Cu$_3$(BTC)$_2$] (BTC = benzene-tri-carboxylate) is the most explored materials in hydrogen storage. In this research, HKUST-1 was electro-synthesized under 15 volt for 1.5 h. This material was ex-situ modified with magnesium(II) ion with variation: 3, 5 and 10 wt% to add attractive sites for hydrogen to form Mg$^{2+}$@HKUST-1. The final materials were characterized by XRD, FTIR, SEM-EDX, and SAA. Hydrogen sorption measurement was conducted using Sievert system at 30 and 80 °C with pressure from 0.2 to 1.5 bar in 10 minutes for each condition. According to XRD analysis, the basic structure of Mg$^{2+}$@HKUST-1 was remaining stable. In contrary, SEM analysis showed that HKUST-1 morphology was changed after modification with Mg$^{2+}$. In addition, the surface area of materials significantly increased from 372.112 to 757.617 m$^2$/g, based on SAA analysis. The presence of Mg$^{2+}$ in the HKUST-1 increased the hydrogen sorption capacity up to 0.475 wt% at 1.4 bar at 30 °C and 0.256 wt% at 80 °C (1.4 bar).

1. Introduction

Metal-organic frameworks (MOFs) have been more attractive to be investigated due to their interesting characteristics, such as highly flexible in structural design in producing various pores and coordination sites, high crystallinity, various chemical and physical properties. Metal ions or metal oxide clusters and organic ligands combination is a way to design the various type of framework [1]. The pore size and surface area of MOFs and the occupancy of unsaturated metal center in their structure, especially in the node part, provide its active site and ability to store gases with non-covalent interaction, like-Van Der Waals, electrostatic and dipol-dipol interactions [2]. HKUST-1 is a well-known type of MOFs consisting...
of Cu$^{2+}$ as nodes and trimesic acid [benzene-1, 3, 5-tricarboxylate] as linker in the cube lattice (Fm-3m) with paddle wheel structure of secondary building unit. HKUST-1 has two types of pore size 9 and 3.5 Å [3]. The hydrogen storage and capture is highly dependent on the inorganic and organic inherent structure molecules in three dimensional structure[4]. In the framework of HKUST-1, Cu$^{2+}$ metal ion forms dimers, each Cu$^{2+}$ coordinated with 4 oxygen atoms from water molecule and BTC ligand. The ability to bind water molecules of Cu$^{2+}$ ions coordination sphere indicates that there are still available coordination in Cu$^{2+}$ [5] which can be used to interact with hydrogen after the activation process[6].

So far, HKUST-1 for hydrogen storage is obtained from solvothermal synthesis [6, 7, 8]. This method is not efficient because the reaction requires high energy and longer reaction time with low yields and the process must be conditioned at high temperature and pressure. Furthermore, the use of metal salts containing nitrate or chloride in the solvothermal synthesis produces unsafe side reaction, therefore it is not environmentally friendly [9]. Electrochemical synthesis HKUST-1 pioneered by Mueller et al [10], is simple and safe because it is conducted at ambient temperature. In the electrochemical synthesis, electrode plates will be oxidized and the ligand will be deprotonated and reduction reaction take place to form hydrogen gas and MOF itself [11]. This method requires an electrolyte solution for ion transfer and voltage and electric current for energy source [12].

In order to enhance the hydrogen sorption capacity, HKUST-1 need to be modified with electropositive metal. The metal ions investigated for HKUST modification so far are Pd$^{2+}$ [13] Li$^+$ and Na$^+$ [14] and Pt$^{2+}$ [15]. The use of Pd$^{2+}$ can increase hydrogen storage capacity up almost twice than unmodified HKUST-1 [13]. In-situ Na$^+$ @HKUST-1 and Li$^+$@HKUST-1 did not change the basic structure, but Na$^+$ ion can block the HKUST-1 pores [14]. The loading of Pt$^{2+}$ ion nanoparticles also did not change HKUST-1 structure. However, the Pt$^{2+}$ nanoparticles can decrease the pore volume and surface area of HKUST-1 [15]. Meanwhile, Mg$^{2+}$ doping into HKUST-1 have never been studied. Based on previous literature, Mg$^{2+}$ is an electropositive metal and it can be modified into MOF due to its low binding energy with the material [16]. In this research, we have studied hydrogen storage capacity on HKUST-1 prepared under electrochemical method and ex-situ modified with Mg$^{2+}$.

2. Materials and Methods
2.1 Materials

Cu plate (99%), H$_3$BTC (95%), MgCl$_2$·6H$_2$O (95%), Tetrabutylammoniumtetrafluoroborate (TBATFB) (99%) were purchased from Sigma Aldrich Germany, Ethanol (96%) was commercially obtained from Merck, deionized water was obtained from Bratachem Indonesia.

2.2 Synthesis of Mg$^{2+}$@HKUST-1

HKUST-1 was synthesized via electrochemical method using Regulated DC (Power Supply) AT TEN TPR 3005T-3C according to reported procedures [17] then doped with Mg$^{2+}$ through ex-situ modification. MgCl$_2$·6H$_2$O was used as Mg$^{2+}$ source doped into HKUST-1 with variation of 3, 5 and 10 wt% Mg$^{2+}$ of 1 g of HKUST-1. The mixture of MgCl$_2$·6H$_2$O and HKUST-1 were stirred in 24 mL solvent (deionized water : ethanol, ratio 1:1) for 15 minutes then placed into Teflon vessels covered with stainless-steel autoclaves and heated to 393 K in an oven MEMMERT (type 67 UN30) for 12 h. The final product was cooled, filtered and dried for 24 h at ambient temperature.

2.3 Characterization

The X-ray powder diffraction (PXRD) data were obtained on Rigaku Miniflex 600 Benchop, using Cu-Kα radiation (λ = 1.5406 Å), with the current and voltage under 30 mA and 40 kV (20 = 5-50°) at a scan rate of 1°/min. The morphology of the final materials were performed using scanning electron microscopy (SEM) type: inspect S50-FEI. Infra-Red spectra were collected by using Shimadzu IR Prestige-21 in KBr
pellets in the range of 400-4500 cm$^{-1}$. The nitrogen sorption isotherm at 77 K were obtained from a Quadsasorp evo (Quantachrome instruments).

2.4 Hydrogen sorption measurement

General procedures: the material (0.5 g) was heated under vacuum condition at 473 K for 1 h. Hydrogen storage measurement was carried out using Sievert system as published by Suwarno et al [18] at 30 and 80 °C with pressure from 0.2-1.5 bar, in each pressure the measurement was conducted for 15 minutes.

3. Results and Discussion

Diffractogram of Mg$^{2+}$@HKUST-1 compared with HKUST-1 are presented in Figure 1. The diffraction pattern of the obtained materials have three main peaks at 2θ: 6.73° (2 0 0); 9.47° (2 2 0) and 11.65° (2 2 2) which are confirmed through similarities with the simulated pattern created from CCDC number 112954. Moreover, there are no peaks identified at 2θ: 36.43°; 35.5° and 38.7° indicating the absence of Cu$_2$O and CuO [19] and [20]. The XRD peaks of Mg$^{2+}$@HKUST-1 are similar with unmodified HKUST-1. It may be assigned that structure of HKUST-1 was remaining stable after being doped with Mg$^{2+}$. In addition, Mg$^{2+}$ ions are not chemically bonded with the HKUST-1 atoms, which can be inferred from the absence Mg$^{2+}$ peaks detected in the diffractogram. Based on previous report [14], the electropositive metals ion doped into HKUST-1 do not chemically change its main structure.

![Figure 1. Diffractogram of doped HKUST-1 with Mg$^{2+}$ and undoped HKUST-1 compared to simulated pattern #CCDC 112954](image)

IR spectra of the final products (Figure 2) revealed that Mg$^{2+}$ doped into HKUST-1 does not change the basic structure. The band identified at around 1715 cm$^{-1}$ shows C=O stretching vibration present in the H$_3$BTC. Ligand deprotonation after complexation with Cu$^{2+}$ causes C=O shift to 1665 cm$^{-1}$. As a result, the band at 714 cm$^{-1}$ can be assigned to stretching vibration of Cu-O revealed O$^{2-}$ ion is coordinated with Cu$^{2+}$ [12]. The broad absorption at 3100-3600 cm$^{-1}$ shows the existence of coordinated water molecules in the structure. The peak at 3000-3100 and 1452 cm$^{-1}$ indicates vibrational stretching of C-H aromatic and C=C aromatic of the ligand. In addition, the band at 714 cm$^{-1}$ can be assigned to stretching vibration of
Cu-O, revealed O$^{2-}$ ion is coordinated with Cu$^{2+}$ from the paddle wheel moiety in the secondary building unit in HKUST-1 [12].

Figure 2. FTIR spectra of doped HKUST-1 with Mg$^{2+}$ and undoped HKUST-1 compared to H$_3$BTC ligand

Nitrogen sorption isotherm (Figure 3) indicates that the materials could be classified as microporous materials, before and after they modified with Mg$^{2+}$. It was concluded from IUPAC that the sorption type-1 with small hysteresis loop. Doping of Mg$^{2+}$ decreases pore volume and surface area of HKUST-1 (Table 1). This phenomenon is probably due to blocking of Mg$^{2+}$ into HKUST-1 pores. After doped with Mg$^{2+}$, the pore volume changed with inhomogeneous pore distribution. It is assumed that distribution of Mg$^{2+}$ particles in the HKUST-1 is not well spread.

| Material               | Pore Volume (cc STP g$^{-1}$) | Langmuir Surface Area (m$^2$/g) |
|------------------------|-------------------------------|---------------------------------|
| HKUST-1                | 0.066                         | 372.112                         |
| Mg$^{2+}$ 3 wt%@ HKUST-1 | 0.042                         | 111.271                         |
| Mg$^{2+}$ 5 wt%@ HKUST-1 | 0.036                         | 33.255                          |
| Mg$^{2+}$ 10 wt%@ HKUST-1 | 0.057                         | 757.617                         |

Table 1. Pore Volume and Surface Area of doped HKUST-1 with Mg$^{2+}$ and undoped HKUST-1
Figure 3. N\textsubscript{2} adsorption-desorption isotherm at 77 K of doped HKUST-1 with Mg\textsuperscript{2+} and undoped HKUST-1

Based on SEM-EDX analysis (Figure 4), HKUST-1 morphology was changed after doped with Mg\textsuperscript{2+}. Based on Table 2, it is observed that the content of Mg elements were not exactly detected according to theoretical calculation. It may because Mg\textsuperscript{2+} lost during stirring or filtering and it was not measured at the well spread particles position. Moreover, identified Cl\textsuperscript{−} ions show that doping method was not optimum. Mg\textsuperscript{2+} and Cl\textsuperscript{−} ions size are too small, 0.072 nm [21] and 0.18 nm [22] which may diffused into HKUST-1 pores.

Figure 4. SEM-EDX images of doped HKUST-1 with Mg\textsuperscript{2+} and undoped HKUST-1
Table 2. Elements Composition of doped HKUST-1 with Mg\(^{2+}\) and undoped HKUST-1

| The material | C     | O     | Cu    | Mg    | Cl    |
|--------------|-------|-------|-------|-------|-------|
| HKUST-1      | 34.43 | 27.26 | 38.31 | -     | -     |
| Mg\(^{2+}\) 3 wt%@HKUST-1 | 30.84 | 21.47 | 41.94 | 1.69  | 4.05  |
| Mg\(^{2+}\) 5 wt%@HKUST-1 | 35.03 | 13.43 | 49.43 | 2.12  | -     |
| Mg\(^{2+}\) 10 wt%@HKUST-1 | 37.48 | 13.05 | 38.06 | 3.52  | 7.89  |

Figure 5. Hydrogen adsorption capacity of Mg\(^{2+}\)@HKUST-1 under conditional temperature (top) 30 °C (bottom) 80 °C
Figure 5 shows the hydrogen storage capacity of Mg\(^{2+}\)@HKUST-1 compared with HKUST-1 under operational temperature 30 and 80 °C. The optimum storage capacity of Mg\(^{2+}\)@HKUST-1 is up to 0.475 wt% (measured at 30 °C, 1.4 bar, obtained from Mg\(^{2+}\) 5 wt%@HKUST-1. Additionally, the optimum storage capacity under operational temperature 80 °C is up to 0.256 wt% at 1.4 bar, obtained from undoped HKUST-1 with Mg\(^{2+}\). The result shows that at ambient temperature, the hydrogen storage capacity was higher than at high temperature [6]. Agglomeration of HKUST-1 particles causes doped Mg\(^{2+}\) to be spread unevenly and blocking in the pores. Finally, doping Mg\(^{2+}\) can’t increase the hydrogen storage capacity of HKUST-1. This study is in line with previous research conducted by Lim et al [23].

4. Conclusion
Ex-situ modification of Mg\(^{2+}\) into electro-synthesized HKUST-1 was successfully carried out and applied for hydrogen sorption. The result indicates that presence of Mg\(^{2+}\) ions do not change the HKUST-1 structure but increases HKUST-1 surface area. After doped with Mg\(^{2+}\), hydrogen storage capacity was increased up to 0.475 wt% at temperature 30 °C (1.4 bar). Further investigation on hydrogen gas interactions with HKUST-1 and Mg\(^{2+}\) doped into HKUST-1 should be studied by Inelastic Neutron Scattering (INS). TG-DTA study could also be performed in order to assess the adsorption enthalpy, so that interaction strength of the hydrogen with the materials at low and high temperature can be discussed intensively.

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