Synthesis Of Nickel (Ni) Doped HKUST-1 using Solvotermal Method with Addition of Acetic Acid as Modulator

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***Abstract* – Hong Kong University of Science and Technology-1 (HKUST-1) is metal organic framework (MOF) that composed from ligand BTC (1,3,5-benzene tricarboxylic) and copper ions. The method used in this study is solvotermal with variations nickel ion doping and additions acetic acid as modulator. The purpose of this study is to increase the hydrogen storage capacity. The results obtained were characterized by XRD showed that the HKUST-1 and Ni-HKUST-1 has formed, showed by peaks at 2 theta = 6.7, 9.5, 11.6, 13.4, and 19.0.**

***Index Terms* – Doping nickel, HKUST-1, MOF.**

INTRODUCTION

Metal Organic Framework (MOF) is porous crystalline material composed by coordination bonds between metal ion and multi dentate organic ligand forming a three-dimensional extended network with cavities [1]. MOF have large surface area (500-6500 m^2/ g), low density (0.17 to 1.7 g/cm^3) and controllable pores, and have been applied as gas storage, in particular hydrogen gas [2]. Hydrogen storage in MOF is performed by physisorption which influenced by the interaction of molecular hydrogen with MOF surface, surface area and pore volume [3].

Among other MOFs, HKUST-1 is capable of storage H_2 effectively. HKUST-1 (Hong Kong University of Science and Technology-1) is composed of a ligand BTC (1, 3, 5-benzene tricarboxylic) and copper ions in the lattice cube (Fm-3m). Cu^{2+} ions form a dimer in which each copper atom coordinated with four oxygen sources from the linker 1, 3, 5-benzene tricarboxylic and water molecules. The existence of water molecules in the first coordination copper ions directs the possibility of the presence of a coordinative vacancy on the species Cu^{2+}, so HKUST-1 has the potential for interaction with hydrogen and can be applied as a hydrogen storage material [4].

HKUST-1 has been reported [4-5] as a hydrogen storage material and has a hydrogen storage capacity 0.47 and 0.02% at temperature of 30 °C. Hydrogen storage capacity in the HKUST-1 has been reported to be lower than that of MIL-101 which has hydrogen storage capacity 1.14 wt.% [6], therefore it is necessary to increase the hydrogen storage capacity in the HKUST-1. Increasing the surface area and pore volume with doping metal ions and the addition of a modulator during the synthesis is one of method to increase the hydrogen storage capacity as reported [7-8]. This study reports the synthesis of nickel doping in HKUST-1 ($Cu_3(BTC)_2$) with solvotermal method and the addition of acetic acid as a modulator.

MATERIAL AND METHOD

A. *Material*

Cupric nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) (Merck 99,0%), nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) (Merck 99,0%), acetic acid (Merck 99,0%), Benzene-1,3,5-tricarboxylic acid (H_3BTC) (Sigma-Aldrich, 99,0%), N'N-dimethylformamide (DMF) (Merck, 99.8%), ethanol, methanol and aquades.

B. *Procedure*

Synthesis of HKUST-1. Cupric nitrate trihydrate (4,19 g) was dissolved in 33 mL of aquades. Benzene-1,3,5-tricarboxylic acid (2,10 g) was dissolved in 67 mL of solvent consisted by DMF : etanol (1:1 v/v). Cupric nitrat and benzene-1, 3, 5-tricarboxylic acid solutions are mixed and stirred. The mixture was transferred into teflon-lined stainless steel autoclave. It was kept in oven at temperature of 120 ℃ for 12 hours. After 12 hours, the autoclave was cooled down naturally into room temperature. Products were separated by filtration and washed by DMF and methanol. Then it was dried at room temperature. The procedure above was repeated with the addition of acetic acid as a modulator.

Synthesis of Ni-HKUST-1. synthesis of Ni-HKUST-1 was performed by similar procedure of HKUST-1 as described above with some modification of nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$) addition. The weight ratio of ($Cu(NO_3)_2\cdot 2.5H_2O$) and $Ni(NO_3)_2\cdot 6H_2O$) are 95:5; 90:10; 80:20 and 70:30%. The result will be characterized by XRD, FTIR, SEM, Nitrogen Adsorption-Desorption, TGA.

RESULT AND DISCUSSION

Blue colored was obtained from the synthesis. Solids synthetic results adding with acetic acid as the modulator has a smaller mass than the solids synthesized without added acetic acid. XRD characterization of all samples show in Figure 1.

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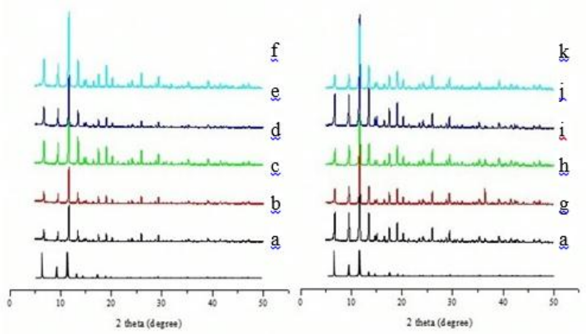

Figure 1. XRD pattern of HKUST-1 and Ni-HKUST-1 a) simulated, b)100% Cu, c)5% Ni, d) 10% Ni, e) 20% Ni, f)30% Ni, g)100% Cu + Mod, h)5% Ni + Mod, i)10% Ni + Mod, j)20% Ni + Mod, k)30% Ni + Mod

According to Figure 1, synthesized materials show peaks at 2 theta = 6.7, 9.5, 11.6, 13.4, and 19.0. Those characteristic peaks correspond to peaks of simulation and material HKUST-1, which has been reported [9]. This indicates that HKUST-1 has been formed. Ni ion doping in HKUST-1 does not change the pattern of diffractogram of Ni-HKUST-1 for all concentration studied. This shows that the doping metal ions Ni does not affect the structure of HKUST-1. To observe the morphology of the HKUST-1 and Ni-HKUST-1 materials the SEM analysis was performed and shown in Figure 2.

As seen in Figure 2, that the HKUST-1 and Ni-HKUST-1 have the shape of octahedral morphology. The doped HKUST-1 looks octahedral more regular than that of without doping, which is not doped and added with a modulator.

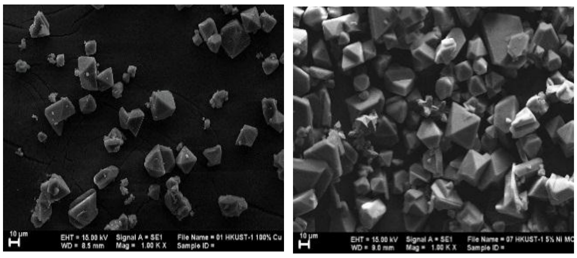

Figure 2. Photo sem of HKUST-1 and Ni-HKUST-1

CONCLUSION

In this study HKUST-1 and Ni-HKUST-1 has been successfully synthesized. Ni doping does not affect to the morphology of HKUST-1.

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