

A Kind of Energy Storage Technology: Metal Organic Frameworks

Z. Ozturk*, D. A. Kose**, A. Asan*, B. Ozturk**

*Department of Chemical Engineering, Faculty of Engineering, Hitit University, 19030, Corum, Turkey

**Department of Chemistry, Faculty of Arts and Sciences, Hitit University, 19030, Corum, Turkey

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Abstract- For last fifteen years energy has been transferred by using electricity. As an energy carrier electricity has some disadvantages like its wire need for transportation and its being non-storable for large amounts. To store more energy safely and to transport it easily, new storing medias and devices are needed. Metal hydrides, carbon nanotubes, metal organic frameworks (MOFs), compressed gas hydrogen and liquid hydrogen systems are being investigated to store and transport hydrogen safely and easily. To use hydrogen as renewable and sustainable energy source on board for transportation and many mobile applications economically and efficiently, USA Department Of Energy (DOE) had set targets for 2010 and 2015. System gravimetric and volumetric density should be 5.5 % wt and 40 g/L respectively according to DOE. To meet the DOE 2015 targets a novel organometallic valin-Cu(II) complex studied. After metal organic framework structured valin-Cu(II) complex synthesis, it is characterized by elemental analysis, X-Ray, FT-IR and thermo analytic TG-DTG techniques. And then hydrogen storage capacity of complex is determined by HPVA-100 adsorption analyser

Keywords- Metal Organic Frameworks, MOFs, Hydrogen Storage, Hydrogen Energy

1. Introduction

A potential solution to develop clean and low-carbon future, replacing fossil fuels with zero-carbon energy systems such as hydrogen energy system which uses sunlight, wind, geothermal heat [1]. Mostly these sources are environmentally favourable, but they are not supplemental enough on their own. It is strongly believed that as alternative renewable energy source hydrogen energy can help to address the growing demand for energy and slow down global climate because it is environmentally clean, abundant in nature and shows higher gravimetric energy capacity compare to other energy sources [2]. However due to gas storage in tanks is the most know technique in industry but has very low volumetric energy capacity [3]. Therefore efficient, safe and reversible storage of the sufficient amount of hydrogen is the main obstacle to application of hydrogen as a conventional fuel [4]. Although several applications such as compressed hydrogen gas and cryogenically stored liquid tanks for storing hydrogen are being pursued to overcome this storage problem, they are still far away from the targets which are declared by United States Department of Energy (US-DOE) for the development of hydrogen vehicles. For 2010 storage system performance targets are 6.0 wt % H₂ and 45 g H₂/L and these numbers increase to

9.0 wt% and 81 g/L by 2015 [5]. Materials-based approaches to store hydrogen, different alternatives uses such as ammonia borane, hydrides, amides, composite materials, high surface area materials etc. At this point Metal-organic frameworks (MOFs), are currently emerging as ideal candidates for hydrogen storage due to their goal directed structures, high thermal stabilities, adjustable chemical functionalities and ultrahigh surface areas [6]. They are basically built with rigid organic ligands linked to metal or metal containing clusters

2. Experimental

All used chemicals were analytical reagent products. Elemental analyses (C, H, N) were carried out by standard methods with LECO-CHN. IR spectras are collected with a Perkin Elmer 1000 FT-IR spectrophotometer using KBr pellets. A Rigaku TG 8110 thermal analyser combined with a TAS 100 thermogravimetric analyzer was used to record simultaneous TG, DTG and DTA curves. The thermal analysis experiments were performed in static air atmosphere with a heating rate of 10 Kmin⁻¹ from room temperature to 1000°C in platinum crucibles. The sample was weighted approximately 10 mg and highly sintered α -Al₂O₃ was used as a reference material. Chrystal structure of synthesized

complex was characterized by using Stoe IPDSII diffractometer. Hydrogen storage properties were detected by HPVA-100 high pressure volumetric analyzer at 77 K after degasification at 363K for 4 hours.

3. Conclusion

Thermogravimetric analysis of the compounds has been conducted in the 25-900°C temperature range under nitrogen and the TG/DTG and DTA curves are given in Figure 1. The observed mass losses for the dehydration and decomposition steps agree well with calculated values. The loss of coordinated water was observed at 122 and 174°C in DTA curve (found: 7.26%, calc.: 7.82%).

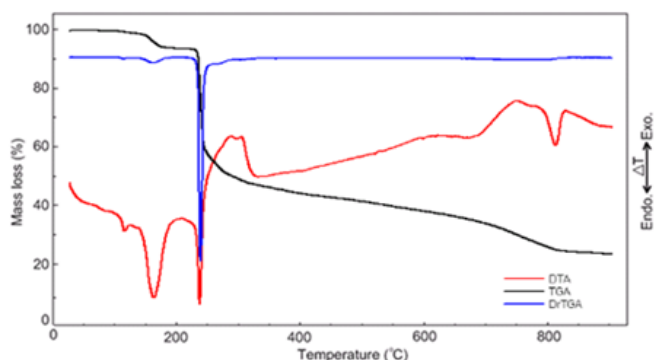


Fig. 1. TG/DTG and DTA curves of complex

The anhydrous form of the copper complex is relatively stable showing a plateau in the range 185-240°C while four decomposition immediately starts were recorded in the 400-1000°C region following the final dehydration step. The overall weight loss in the range 245-900°C corresponds to the loss of organic matter in the form of H₂O, CO/CO₂ and NO/NO₂ in several consecutive steps to give the metal oxide residue around 950°C (found: 62.22%, calc.: 64.35%). The final residue is CuO compound (found: 31.73%, calc.: 34.56%).

The important vibrations of Cu(II) complex are given Table 1. The strong and broad absorption band in the range of 3600-3000 cm⁻¹ corresponds to asymmetric and symmetric stretching vibrations of aqua molecules.

Table 1. Selected FT-IR vibrations of Cu(II) complex

Assignment	Cu(II) Complex (cm ⁻¹) ^a
v(OH) _{H₂O}	3600-3000 vs,b
v(NH) _{NH₂}	3334, 3264, 3159 s
v(CH) _{CH₂}	2953, 2925 m
v(C=O)	1676 s
v _{as} (COO ⁻)	1604 vs
δ(OH)	1580 s
v _s (COO ⁻)	1421 s
Δ(v _{as} -v _s) _{COO⁻}	183
v(C-O)	1382, 1320 vs
δ(OCO)	746 w
Cu-O, Cu-N	557, 476 w

Abbreviations: w, weak; m, medium; s, strong; vs, very strong; b, broad

The 3334 cm⁻¹, 3264 cm⁻¹ and 3159 cm⁻¹ bands are belong to N-H stretches of primary amides. The weak bands at the 2953 cm⁻¹ and 2925 cm⁻¹ are attributed to the -CH₂ vibrations of valin. The coordination carboxylate group exhibits strong bands in the region of 1676 cm⁻¹ and 1580 cm⁻¹. The vibrations Cu-O and Cu-N bands are seen at the 557 cm⁻¹ and 476 cm⁻¹, respectively [7].

A single crystal of the synthesized compound, C₅H₁₀CuNO₂, was mounted on a glass fiber for data collection performed on a STOE IPDS II diffractometer at 296 K. Details of crystal data are given in Table 2.

Table 2. Crystallographic data and refinement parameters for complex

Empirical Formula	C ₅ H ₁₀ CuNO ₂
Formula weight	179,55
Temperature(K)	296
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions a (Å)	5.2133(3)
b (Å)	10.8115(6)
c (Å)	13.4941(10)
Volume (Å ³)	760.58(8)
Z	4
Calculated density	2.006 Mg m ⁻³

At the end of the hydrogen storage measurements, it is determined that the complex has the maximum value of hydrogen 2,9502 % wt adsorption at nearly 100 bars hydrogen pressure and PCT diagram shown in Figure 2. Hydrogen storage capacity of this complex is better than some other MOFs for instance MOF-74 has approximately wt%2 and IRMOF-20 (Izoreticular MOF) has approximately wt%3,2 hydrogen uptake at 77K and nearly 90 bars hydrogen pressure while MOF-177 uptakes wt%7,5 hydrogen at same conditions [8]. At low hydrogen pressure and temperatures higher than 77 K, almost all widely known MOFs don't store sufficient hydrogen. For instance most powerful storage complex MOF-177 stores wt%1,25 hydrogen at 77 K and 1 bar hydrogen pressure [9].

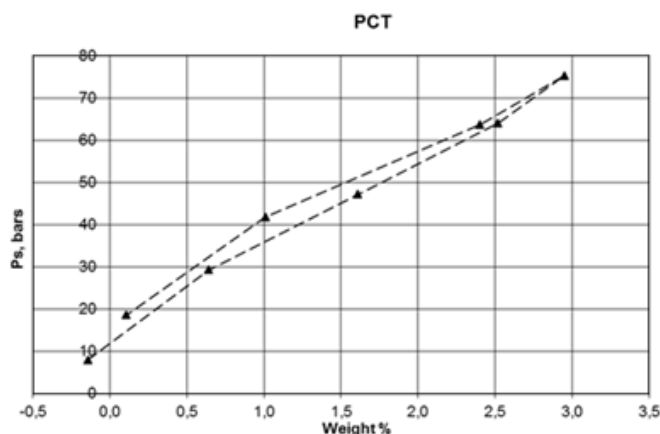


Fig. 2. PCT diagram of Cu(II)-Valin Complex.

DOE 2010 energy density targets for the hydrogen storage system (including container and necessary components) are 7.2 MJkg^{-1} and 5.4 MJL^{-1} , which is equal to $\text{wt}\%6$ and $45 \text{ kg H}_2 \text{ per m}^3$ [10]. The goals for 2015 are even more onerous as $\text{wt}\%9$ and $81 \text{ kg H}_2 \text{ per m}^3$ for using hydrogen in mobile applications like automobile [11]. If we compare hydrogen uptake values of MOFs with DOE 2015 goals almost all MOFs fails as our complex does (Figure 3). To solve this problem more novel MOFs should be synthesized, characterized and tested for hydrogen storage.

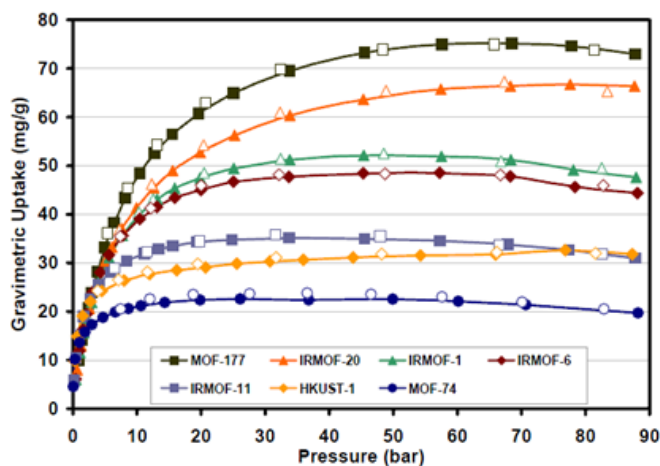


Fig. 3. Gravimetric Uptake for some MOFs at 77K.

Nomenclature

MOF	: Metal Organic Framework
DOE	: Department of Energy
HPVA	:High Pressure Volumetric Analyser
TG	:Thermo Gravimetry
DTG	: Differential Thermo Gravimetry
DTA	: Differential Thermic Analysis
PCT	:Pressure-Concentration-Temperature
IRMOF	:Iso Reticular Metal Organic Frameworks

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