Hittite Journal of Science and Engineering, 2014, 1 (1) 01-05
ISSN NUMBER: 2149-2123
DOI: 10.17350/HJSE19030000001

Porous Metal-Organic Cu(II) Complex of L-Arginine; Synthesis, Characterization, Hydrogen Storage Properties and Molecular Simulation Calculations

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ABSTRACT

Cu(II)-arginine coordination compound was synthesized and characterized by using DSC, DTA, EA, FT-IR, XRD, SEM and EDX analysis techniques and then the hydrogen storage properties were investigated. Hydrogen storage performance of synthesized compound was determined both experimental and theoretically by using Materials Studio which is one of the Molecular simulation software and adsorption measurement equipment. It is found out that the arginine compound uptakes approximately 1.2 wt. % experimentally and 0.8 wt. % theoretically hydrogen in 77K and 100 bars pressure. Also the surface characteristics was calculated and also the possible cites which could uptake hydrogen in a single lattice cell were determined. At the end of this research, in addition to drug and other applications of L-arginine, it is proved that could be used as a part of adsorbent for hydrogen storage application.

Article History:
Received: 2014/08/07
Accepted: 2014/12/25
Online: 2014/12/31

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Key Words:
Hydrogen Storage; Cu-II compound; L-Arginine; Coordination Compound; Molecular Simulation.

INTRODUCTION

Most known alternative to fossil fuel energy system is widely researched hydrogen economy in the other name hydrogen energy system [1]. The main obstacle to use hydrogen economy in daily life is to store hydrogen as an energy carrier, safely and economically [2-3]. In order to store hydrogen, compressed and liquid gas systems [4] have been being used but for safely and more profitable storage there are many choices such as, metal hydrides [5], carbon nanotubes [6-7], metal organic frameworks (MOFs) [8] which are needed to be improved. Some target values are set for storing acceptable amount of hydrogen to use in portable systems by US DOE (4.5 wt. % by 2007, 6 wt. % by 2010 and 9 wt. % by 2015) [9] and these target are being cited widely by international community. In order to reach the targets, researchers have been working on alternative storage medias and systems which are safe and widely useful for mobile applications like automobile and portable power systems. Weak forces act a great role in physical sorption (also called as physisorption) in solid hydrogen storage medias and reaches great numbers within low temperatures down to 77K. With common usage areas such like gas sorption [8], gas separation [10], catalyst [11-12]; MOFs have a great sorption ability for hydrogen. For instance, Yaghi and co-workers reported that IRMOF-1, IRMOF-8, IRMOF-11, IRMOF-18 and MOF-177 uptakes hydrogen wt.% 1.32, 1.5, 1.62, 0.89 and 1.25 respectively at 77K and 1 bar [13]. With reticular structure, Cu(II)-arginine complex could be called as a MOF structured complex. Too many MOF structured complex are synthesized by using metal or metal clusters with benzene di-, tri- (or more) carboxylic acids widely but amino acids are not used as building block. Amino acids are used for biological or pharmaceutical applications in general such as vascular effects of dietary of arginine or effects for immunity [14-15]. In addition to other applications, in this work a novel Cu(II)-arginine coordination

compound is synthesized and characterized to use for hydrogen storage which is not used before, then the storage properties are calculated. To calculate hydrogen storage performances and surface area of synthesized materials molecular simulation calculation was employed which was previously performed by Han et al. and Cao et al. [16-17].

The main aim of the research was to investigate hydrogen storage capability of Cu(II) compound of arginine. And also to have feedbacks from the simulations to improve experimental set up.

EXPERIMENTAL

Throughout the experiments, all chemicals used for the synthesis were of reagent grade and $Cu(NO_3)_2.6H_2O$ and L-arginine (Sigma-Aldrich) were used as received. For the synthesis of Cu (II)-arginato complex firstly sodium-arginate salt was prepared by using arginine and $NaHCO_3$. After that $Cu(NO_3)_2.6H_2O$ solution was mixed with sodium-arginate solution and stirred for two hours. The dark blue complex was obtained after four weeks and then was filtered off and dried in air. A view of molecular structure of reagents and synthesized complex with the crystal reticular form is shown in Figure 1.

For characterization, FT-IR data was collected in the 400-4000 cm^{-1} wave number ranges. Thermal decomposition data was collected in the temperature range of 298-1173K under nitrogen atmosphere to investigate thermal stability. For the investigation of thermal stability TGA analysis was performed and also DTG and DTA data were collected simultaneously with TG data. In order to check the accuracy of suggested molecular structure elemental analysis for C, H and N was realized. To determine crystal structure of complex, single crystal sample was mounted on a glass fiber and XRD data collected with graphite-monochromated MoKα radiation at 296K by using STOE IPDSII diffractometer. SEM images captured by using Zeiss EVO 60 Scanning Electron Microscopy (SEM) and also electron dispersive spectroscopy (EDX) analysis actualized that the details are given in supplementary file. HPVA-100 (Micromeritics Instrument), volumetric hydrogen storage performance test station was used to determine hydrogen uptake value of complex experimentally. After 12 hours degas under vacuum and 373K temperature, sample was transferred to hydrogen storage test aperture. In eight different pressures which reaches up to 92 bars were the adsorption and desorption measurement steps. Molecular simulation software Materials Studio (MS) was used to calculate surface area and hydrogen storage performances. Sorption module with force fields gives almost the exact values when compared with the experimental measurements [18]. In this work, hydrogen uptake values are calculated for 77, 273 and 298K temperatures and 0-100 bar pressure range by using modified universal force field (UFF). The modification enables temperature dependent quantum effect on physical adsorption which was described by Dimitrakakis et al. [19] also the Lennard Jonnes parameters

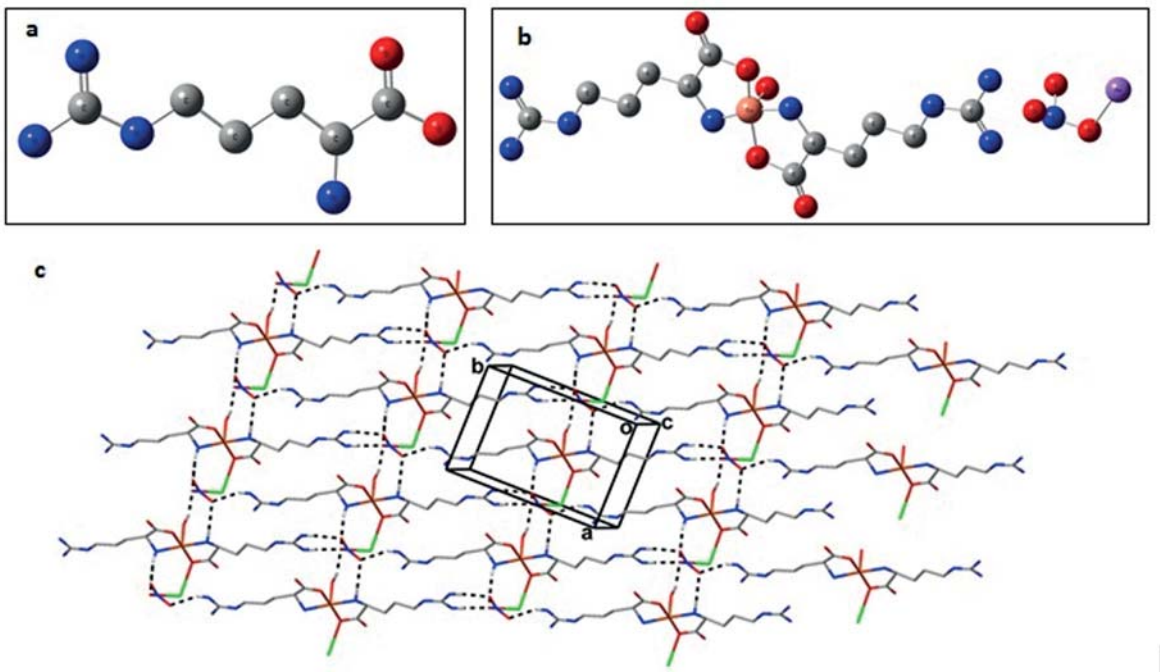

Figure 1. a) Molecular structure of arginate, b) general view of unit, c) crystal packing arrangement of complex.

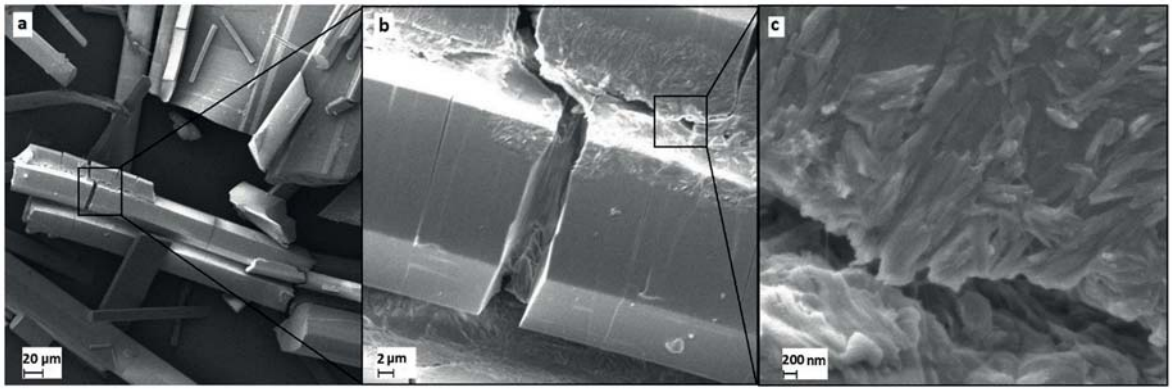

Figure 2. SEM images of complex a) in 500X, b) in 4000X and c) 20000X

are changed to 0.074 kcal/mol potential at 3.31 Å distance which was set previously by Fischer et al [20].

RESULTS AND DISCUSSION

It can be inferred from the IR spectra that the strong and broad absorption band in 3600-3000 cm^{-1} corresponds to asymmetric and symmetric stretching vibrations of aqua molecules. In the region of 1676 cm^{-1} and 1580 cm^{-1} strong coordination carboxylate group bands exhibit. The aim of thermal analysis study was not describing decomposition steps because of only stable temperature range was determined. According to TGA data approximately up to 473K, Cu complex of arginine was stable. Molecular formula was predicted as $[Cu(Arg)_2(H_2O)]NaNO_3$ and then confirmed by elemental analysis with 26.13(27.96), 5.12(5.83), 24.38(24.47) data for C, H and N contents found (calculated) % according to elemental analysis. According to crystallographic data, which is given in supplementary information in detail, $NaNO_3$ existence in crystal structure and the interactions via this molecule enables reticular form of crystal Perfect crystals are shown in Figure 2 which were captured and it is shown that the crystal packing or in the other word nanoparticles are not spherical or cubical geometry as like IRMOF-8 crystal or MIL-101TM crystals but poly crystalline [21-23].

The PCT diagram (Figure 3b) which seems like type 4 adsorption isotherm according to IUPAC classification [24]. According to experimental measurements, maximal uptake measured at the highest pressure which was 92 bars, 1.74 wt. % hydrogen at 77K (Figure 3a). The amount is also comparable to the common MOF structured materials for instance Li et al. [25] reported 3.42 and 2.05 wt. % hydrogen adsorption for Ni(II) and Co(II) based metal-organic coordination compounds at the same conditions. In another work, Yang et al. [26] reported that FMOF1 coded metal-organic structure constructed with Ag cluster was uptake 2.33 wt. % hydrogen at similar conditions.

Results for the molecular simulation calculations are shown in Figure 3b. As it is expected, the arginine compound

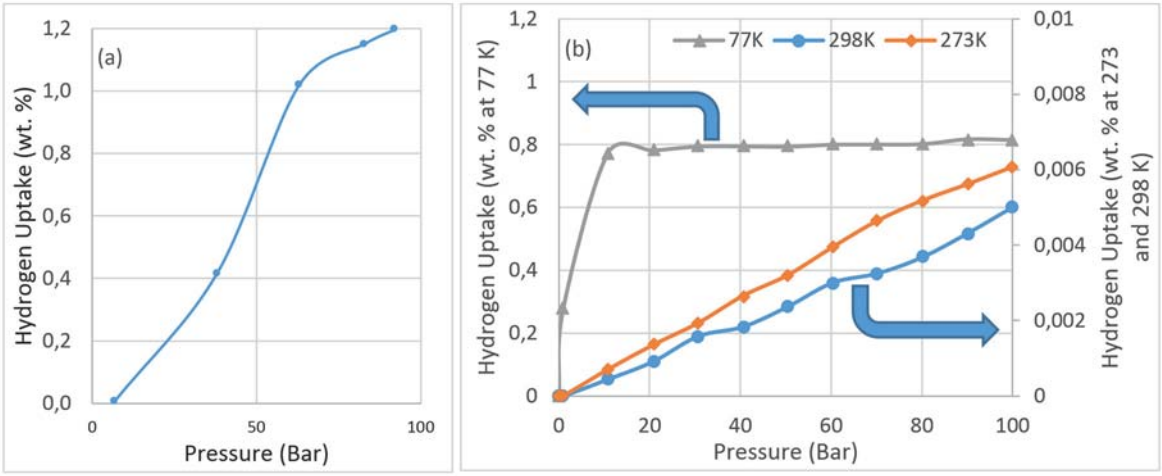

Figure 3. Hydrogen uptake isotherms, a) experimental data, b) simulated data

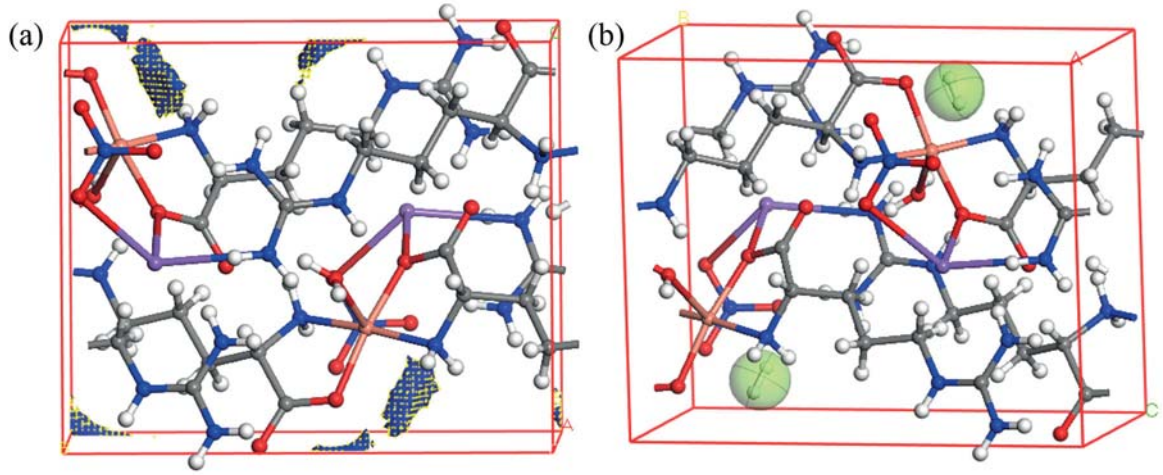

Figure 4. Possible places for hydrogen storage a) blue shells represent accessible solvent surface and b) green ellipsoids are the hydrogen molecules inside the unit cell.

uptakes maximum hydrogen at 77 K and 100 bars pressure, the amount was approximately 0.8 wt. % hydrogen. This value decreases with increasing temperatures which was 0.006 wt. % and 0.005 wt. % for 100 bars pressure, 273K and 373K respectively.

Surface area was calculated according to Solvent surface method with 0,15Å grid interval. By the way, the solvent surface area of single lattice was 16.68Å^2, in the common unit 97.47 m^2/g for nitrogen gas which has 1.097 Å van der Waals radii. Also the possible places for hydrogen storage in a single cell are simulated by using software and the places are almost similar which are given in Figure 4. Small surfaces in Figure 4.b are the places that could not store hydrogen because the radius of hydrogen is not convenient for those places.

CONCLUSIONS

Cu(II)-arginine complex as hydrogen storage material, was synthesized and characterized. Then its storage performance was determined. It is found out that the arginine which is an amino acid, uptakes acceptable amount of hydrogen when used as ligand in compound. In addition to its other applications hydrogen storage application of L-arginine amino acid shows average performance with 0.75wt.% in 77K-100 bars pressure theoretically and 1.7461 wt.% in 77K-92.02 bars experimentally. In such performances for meso-porous materials, it is possible to face differences between experimental measurements and theoretical calculations depends on force fields for simulations and spillover effect for experiments [27].

In conclusion, using an amino acid to synthesize coordination compound that is used for hydrogen storage in special conditions maybe is not the best application but if it is compared to other MOF structured coordination compound amino acids shows acceptable performance.

[CCDC 796731 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.]

ACKNOWLEDGEMENTS

We acknowledge to UNIDO-ICHET for their support and Hitit University Scientific Research Project Fund with the project number of MUH19001.14.003.

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