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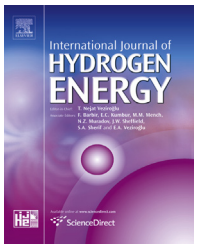

Experimental and simulation study on structural characterization and hydrogen storage of metal organic structured compounds

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ABSTRACT

One of the barrier for common usage of hydrogen energy system is storing hydrogen efficiently. Especially for mobile applications, it is very important to store hydrogen in small spaces reversibly. Metal-organic framework (MOF) structured materials step forward with the ability of reversible hydrogen storage which meet the storage targets. The MOF structured compounds were synthesized using Cu(II) and Zn(II) metals, trimesic acid (benzene 1,3,5 tricarboxylic acid) (TMA) and 1,10 phenantroline (Phen) building blocks. The compounds were activated thermally at 398 K for 4 days under a vacuum for sorption experiments. Then, DTA/TGA, FT-IR, powder-XRD, BET surface area and elemental analysis techniques were used to determine the molecular structures of the synthesized compound. Finally, the hydrogen storage properties were measured at 77 K and 1 bar of hydrogen pressure. In addition to experimental investigations, hydrogen adsorption characteristics and performances of the compounds were also determined with the molecular simulation calculations. It is found that the Cu(II) and Zn(II) compounds could uptake 2.652 wt. % (sim. 2.434 wt. %) and 1.383 wt. % (1.187 wt. %) respectively, at 77 K and 1 bar pressure. Consequently, hydrogen adsorption mechanism and capacities of the compounds clarified. And it is found out that the compounds have good storage performance in comparison to the previously reported MOFs.

Introduction

In recent years many adsorbents have been tested for hydrogen storage media. One of the most promising adsorbent families, Metal-Organic Framework (MOF) structured chemical compounds, have a high adsorption ability of hydrogen with their large and controllable pores [1]. Also, the MOFs have convenient accessible surfaces for hydrogen adsorption. It results with good adsorption kinetic and total hydrogen adsorption. Hydrogen could be stored in different conditions depending on the utilization in MOFs [2–4]. For instance, storing hydrogen at normal conditions (room temperature and 1 bar of pressure) could be wise for small sized

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storage systems which are used for small and non-detachable devices. On the contrary, for the bigger and settled systems, a larger hydrogen storage requirement causes extreme storage conditions, such as temperatures as low as 16,5 K and high pressures up to 150 bars [5,6].

Most known MOF are mainly mono ligand compounds which consist of benzene-carboxylate based building blocks. Because the carboxylate based benzene groups form large spaces inside the crystals that the hydrogen molecules could fill in. For instance, MOF-5 has good hydrogen storage performance as a result of a highly accessible surface area where the building blocks were Zn_4O as a metal cluster and 1,4-benzenedicarboxylic acid (BDC) as a linker [7]. Organic linker BDC consist benzene that have two carboxylic acids linked at para position. Khvostikova et al. [8] reported hydrogen storage capacity of tree carboxylic acid included linker BTC (1,3,5-benzenetrikarboxylic acid) based cupper compound. In another work Luebke et al. [9] reported new organic linker which was constructed with three TMA groups and s-heptazine and used it to form MOF for hydrogen storage. Other well-known metal-organic structured compounds, MOF-177 and MOF-199, are constructed with Zn_4O/benzene tri-benzoic acid and 1,3,5-benzene tri-carboxylic acid respectively [10]. Some other MOFs are formed with mixed ligands and metal/metal clusters. For example, various mixed ligand metal-organic compounds reported by using 4,4′-bipyridine, N,N′-di(4-pyridyl)-1,4,5,8-naphthalene tetracarboxydiimide and other di-carboxylic acids with zinc metal ions. In their work, Bae and co-workers [11] synthesized framework structured metal-organic compound by using DPNI and NDC organic linkers and zinc ions (dpni; N,N′-di-(4-pyridyl)-1,4,5,8-naphthalene tetracarboxydiimide, ndc; 2,6-naphthalene dicarboxylate). In another work Lee and co-workers [12] reported abtc (azobenzene-3,3′,5,5′-tetracarboxylate) and DMF (dimethyl formamide) based Cu (SNU-5) and Zn (SNU-4) mixed ligand complexes for hydrogen storage. Dabco (1,4-diazobicyclo [2.2.2] octane) and bdc (benzene-1,4-dicarboxylate) included mixed ligand complex of cupper also been reported by Guo et al. [13]. Chun et al. [14] also reported new mixed ligand zinc complexes which are including dabco and bdc. Also, the synthesis and activation process play an important role on the porosity, therefore the hydrogen storage property of MOF structured compounds differs. Framework structured HKUST-1 constructed with copper ion and benzene-1,3,5-tricarboxylic acid has 1482 m^2/g according to Liu et al. [15], 1239 m^2/g according to Krawiec et al. [16] and 1507 m^2/g according to Rowsell and Yaghi [17] BET surface areas as a result of different synthesize and activation conditions. Similarly, MOF-5 with the ingredients expressed above has 4746 m^2/g according to Rowsell and Yaghi [17] and 3100 m^2/g according to Li and Yang [18] BET surface areas. MOF structured compound that has the highest surface area was reported by Koh et al. [19] and the value was 5200 m^2/g. The following three MOFs which have the highest surface areas are MOF-5 with 4746 m^2/g [17], NOTT-116 with 4664 m^2/g [20] and MOF-200 with 4530 m^2/g [21].

Many investigators have emphasized the link between the hydrogen uptake capacity and the building blocks of MOFs. But in nature, this was not easy because each building block changes its position to form crystals at low energy distribution. Thus the adsorption properties of MOFs are being used for classification. This is why MOFs are classified as ultrahigh porous and porous [21]. Adsorption and surface area expressions are important in explaining the performance of adsorbents. Thus the hydrogen storage performances of materials could be classified according to the surface areas, but this could be insufficient in some cases. The procedure for measuring surface area is crucial. Changing BET adsorption points affects the slope that is used for BET surface area calculation of adsorbent according to the BET theory. In addition, micro/nano pores could not be measured using nitrogen gas, as this results in non-linearity between surface area and hydrogen storage performance. Additionally, hydrogen storage characteristics of the adsorbents could be changed in different pressure regions. This is why the IUPAC classified adsorption isotherms for different types [22]. The best option to compare adsorbents is to use their hydrogen storage capacities under the same conditions. According to Liu et al. [15], HKUST-1 could uptake 2.9 wt. % hydrogen at 77 K and 1 bar while the value was 2.18 wt. % according to Krawiec et al. [16]. The hydrogen uptake value increases to 4.1 and 5.1 wt. % at 77 K and 10 bars of pressure for the same adsorbents according to a different synthesis procedure [23]. Frukawa and co-workers [21] reported MOF-210 coded compound constructed with BTE, Zn_4O and BPDC building blocks which has the highest hydrogen storage capacity with 15.0 wt. % uptake at 80 bars and 77 K temperature (BTE = 4,4′,4″-[benzene-1,3,5-triyl-tris(ethyne-2,1-diyl)]tribenzoate; BPDC = 4,4′-biphenyldicarboxylate). The following three adsorbents which have high hydrogen storage capacities are NU-100 with 14.09 wt. % uptake at 70 bars/77 K reported by Fahra et al. [24], MOF-200 with 14.0 wt. % uptake at 80 bars/77 K and SNU-77H with 11.0 wt. % uptake at 90 bars/77 K reported by Park et al. [25].

It is clear that hydrogen storage capacities decrease with decreased pressure. The situation could be described with the inter-molecular potentials which also called adsorption potentials. Hydrogen molecules could be placed closer to the adsorbent surfaces by increased pressure thus the hydrogen could be adsorbed to the host molecules easily with the effect of increased pressures. In our previous work [26], it was found that Zn(II) based metal-organic compound could uptake 0.5 wt. % hydrogen at 77 K and 1 bar hydrogen pressure conditions. Hydrogen storage capacities of MOF-74 and MOF-505 were reported that they could uptake 1.80 and 2.47 wt. % hydrogen at 77 K and 1 bar pressure [17,27]. Lee and co-workers [12] reported SNU-4 and SNU-5′ coded mixed ligand MOF structured compounds that could uptake 2.07 and 1.83 wt. % hydrogen at the same conditions. In another work Zhao et al. [28] reported that UiO-66 which consist bdc (benzene-1,4-dicarboxlate) and zirconium building blocks, could uptake 3.35 wt. % hydrogen at 77 K and 1.8 MPa pressure. In addition cromium and bdc based MIL-101 synthesized and hydrogen storage capacity measured as 1.92 wt. % at 77 K and 1 bar pressure by Ren et al. [29].

Hydrogen storage properties of the MOF structured compounds have also been explained using molecular simulation calculations. The simulations could be used for different purposes, for instance, to explain adsorption mechanisms and characteristics [30], to determine storage properties of some