The Effect of Surface Area and Dopant Percentage on Hydrogen Storage of Pt@AC loaded Activated Carbon and Cu-BTC Composites

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Abstract-Hydrogen storage as part of a hydrogen energy system needs to be investigated deeply for a common usage of the system. Many alternative hydrogen storage media have been investigated in the last decade to solve efficient hydrogen storage problems. Storing hydrogen in adsorbents physically is a significant solution. Carbon based materials and framework structured metal-organic compounds also have intense attention for hydrogen storage by physical adsorption. In this work, the effect of surface area and dopant percentage on hydrogen storage have been emphasized. Different amounts of platinum loaded with activated carbon as the dopant is milled with the activated carbon and Cu-BTC as matrix materials. It was found that the increased amount of dopant caused more adsorption on the adsorbent surfaces. Thus, the hydrogen storage properties increased. But, the excess amount of additives decreases the micro-porosity by way of the hydrogen storage. At 4 wt. % of the additive, platinum loaded activated carbon, increases the hydrogen uptake approx. 10 and 15% in activated carbon and Cu-BTC respectively. On the contrary, 10 wt. % of the additive decreases the hydrogen uptake approx. 2 and 25% of adsorbents in the same order.

KeywordsHydrogen storage, Pore size distribution, Composites, MOF.

1. Introduction

Alternative energy systems gets more attention by the increased energy consumption as a result of the increased world population. Hydrogen energy system is one of the best candidates to the existing systems by its sustainability [1], [2], [3]. Hydrogen energy systems consist of three main parts which are hydrogen production by primary energy resources, energy conversion to other kinds of energy by using hydrogen, and hydrogen storage and delivery [4], [5]. Thus, the storing of hydrogen safely and efficiently is an important case that needed to be investigated.

Hydrogen could be stored in cylinders as pressured gas and in special tanks as a liquid form [6]. Over the last decade, there is great interest in the storing of hydrogen in advanced materials chemically or physically [7]. Hydrogen storage by physical adsorption, namely physisorption, are of great interest with respect to the life cycle, ability to store hydrogen at a standard temperature and pressure, low adsorption energy and light weight [8], [9], [10]. Some fundamentals of hydrogen adsorption by physisorption has also been reported by Ozturk et al. [11]. It is known that the adsorbents which have a high surface area could uptake more hydrogen. Yang et al. [12] reported that zeolite like carbon materials as adsorbents could uptake more hydrogen if they have a higher surface area. In another work, Cai et al. [13] investigated the hydrogen storage capacities of ordered porous carbons which have a large surface areas. The importance of surface area for hydrogen storage gets more attention especially for carbon based adsorbents. Because the electron density thereby van der Waals interactions are weaker in related materials in comparison to metal decorated and metal consisted adsorbents. Zhang et al. [14] investigated and have also explained the aforementioned situation at their place of work. They investigated the electron density of metal modified carbon based graphene sheets and found that the hydrogen adsorption energies increased, in other words, the hydrogen storage capabilities increased.

Some adsorbents such as metal-organic frameworks (MOF) which consist of metal centers or clusters, have better hydrogen storage capacity against dopant free carbon based adsorbents. Carbon based materials which were derived from natural and synthetic precursors have the hydrogen uptake capacity of about 2-3 wt. % at 77 K and 1 bar pressure [15] while one of most famous framework structured MOF-5 have up to approx. 7 wt. % hydrogen storage capacity at the same conditions [16]. Preparing the composite is an option to increase the hydrogen storage capacities of adsorbents. Additives in the matrix affect the hydrogen adsorption energy hence the hydrogen storage capacity increases. The phenomena called spillover which is described by Wang and Yang [17] in detail. The effect of spillover on the carbon based adsorbents for hydrogen storage was investigated by the same authors in another work [18]. The spillover effect on the MOF structured compounds has also been investigated by Liu et al. [19]. It is possible to prepare composites according to the bridged additive composites while the adsorbents being synthesized and mechanically mixed by using ball milling. Ardelan et al. [20] reported that there is not a meaningful difference between hydrogen storage capacities of bridged and mixed MOF structured composites. But the hydrogen storage capacities more often increases with the amount of additives. Falcaro et al. [21] investigated better hydrogen storage capacities in the metal oxide composites of a kind MOF structured compound, HKUST-1. Wang and Yang reported in another work [22], that the hydrogen storage capacities of template carbon could store more hydrogen with a metal nano-particle decoration. Sometimes, the additives could decrease the storage capacities of the matrix adsorbent. In our previous work, the platinum loaded activated carbon as an additive decreased the hydrogen storage capacities of Zn (II) based MOF structured compound [23]. The hydrogen storage capacity of the HKUST-1 decreased from 1.8 to 1 wt. % after the platinum loaded graphene oxide decoration according to the investigation of Zhou et al. [24]. In another work, Yang et al. [25] prepared composites by using MOF-5 as a matrix and platinum loaded multi-walled carbon nano-tube as an additive. And, they found that the hydrogen storage increased after the additive decoration while the surface area decreasing. Thus, the relation between the additive amount and the matrix porosity needs to be investigated.

In this work, composite adsorbents prepared by using activated carbon and Cu-BTC (commercially called Basolite C 300) as a matrix, and platinum loaded activated carbon as an additive for the purpose of relations between the additive amount and surface area investigation. Five different weight percentages of additives were selected to investigate the relation for both matrix materials. Composites characterized with powder-XRD and EDS analysis. Then, nitrogen and hydrogen adsorption isotherms created with adsorption measurements. Also the pore size distribution and nitrogen adsorption energies were determined by using adsorption data. And, hydrogen uptake gravimetric percentages for the adsorbents was calculated and plotted. At last, hydrogen storage capacities plotted against surface areas of adsorbents.

2. Experimental Details

The chemicals which are used in the experiments are used and purchased without any purification. Platinum loaded activated carbon (10 wt. % platinum loaded activated carbon), Basolite C300 (0.35 g/cm3 bulk density, HKUST-1 or Cu-BTC) and activated carbon (100 mesh particle size, powder) was purchased from Sigma-Aldrich (St. Louis, MO). Platinum loaded activated carbon as an additive mixed with matrix materials, activated carbon (AC) and Cu-BTC (Basolite), in ball milling (Restsch, MM400, Düsseldorf, Germany) for 3 minutes in 20 Hz horizontal shaking frequency. After mixing 2, 4, 6, 8 and 10 weight percent additives to the matrix materials, collected composites degassed and activated at 200 ˚C for 3 days under 10-5 bar vacuum (Wiseven, Witeg, and Wertheim, Germany). EDS analysis of the composites realized in the SEM instrument equipped with EDS (Oxfordshire, Onca act, 51-add0013, UK) up to 20 kV. Then, the nitrogen and hydrogen adsorption data of composites measured at 77 K and different relative pressures (up to 1 bar) (Quantachrome, AutosorbIQ, Baytonbeach, FL). Pore size distribution is calculated according to the BJH method [26] based on the Kelvin equation (1) by using nitrogen adsorption data.

$$r_K = \frac{-2\gamma V_m}{RTln(P/P_0)} \quad (1)$$

Where, γ is surface tension of the nitrogen at its boiling point, V_m represents the molar volume of the liquid nitrogen and r_K is the Kelvin radius of the pore. Other symbols R, T and P/P_0 represent, gas constant, boiling point of the nitrogen and relative pressure respectively. The equation simplified for nitrogen as follows in Eq. (2).

$$r_K(\text{Å}) = \frac{4.15}{\log\left(\frac{P_0}{P}\right)} \quad (2)$$

Theactualporeradius (r_p) calculatedbymultiplyingr_K and the thickness of the adsorbed layer (t) which are described inequation (3) and (4).

$$r_p = r_k + t \quad (3)$$

$$t\ (\text{Å}) = \left[\frac{13.99}{\log\left({}^{P_0}/_{P}\right)+0.034}\right]^{1/2} \quad (4)$$

Additionally, the surface area of the adsorbents were calculated by using the BET method [27], that the following equation (5) represents a line.

$$\frac{1}{W\left(\left({}^{P_0}/_{P}\right)-1\right)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_0}\right) \quad (5)$$

W, W_m and C terms in the equation (5) represents the weight of gas adsorbed at a relative pressure, weight of adsorbate constituting a monolayer of surface coverage and the BET constant respectively. It needed to be pointed out that the multipoint BET should be linear in the P/P_0 range of 0.05 to

0.35. In other words, the BET constant *C* should be positive, otherwise the results would be non-physical.

Nitrogen adsorption energies of the composites is calculated by using the Dubinin-Radushkevich (DR) method [28] that uses nitrogen adsorption in different relative pressures. Following the DR equation (6 and 7) was used to calculate fraction of the adsorption volume (*V*) occupied by the liquid adsorbate.

$$V = V_0 exp\left[-\left(\frac{RTln(P/P_0)}{\beta E_0}\right)^2\right] \quad (6)$$

$$E_0 = \sqrt{\frac{2.303}{m}}\frac{RT}{\beta} \quad (7)$$

In the equations, V_0,β *and* E_0represents the micropore volume, affinity coefficient and adsorption energy.

At last, the adsorbed amount of hydrogen that is collected in ml/g unit ad raw data, changed to weight percentage by using the real gas equation PV=nzRT that the compressibility factor (z) for different pressures from the NIST thermophysical properties of fluid systems database [28].

The methods used in this work could be outlined in three parts which are preparation of composite adsorbent by using ball milling technique, characterization of the adsorbents by using powder-XRD and EDS mapping, and gas adsorption measurement and related calculations.

3. Results and Discussion

Powder-XRD peaks in Figure 1 of ball milled composites shown that the additives placed in the matrix adsorbents. Because the characteristic diffractions detected in the powder-XRD spectrums which are marked in Figure 1. The characteristic platinum (1 1 1) peak is found in approx. 38-40 two tetha degree for both the activated carbon (AC) and Cu-BTC composites. According to Figure 1 it is clear that all final structures are amorphous and characteristic activated carbon peaks marked with the four corner star. In addition, the characteristic Basolite amorphous peaks found in the spectrums of the Cu-BTC composites and marked with pentagon in Figure 1.b.

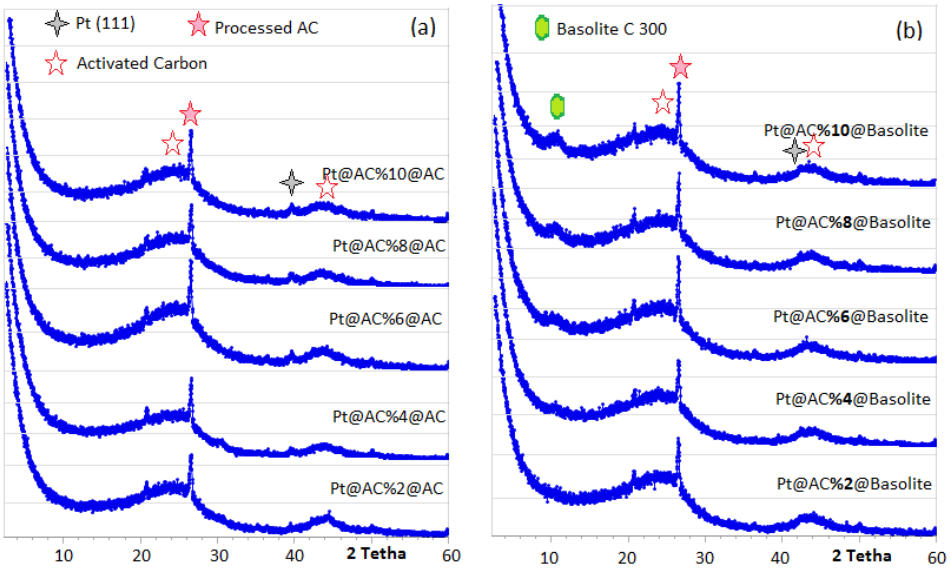

Figure 1. Powder-XRD peaks of composites.

The additive distribution in the matrix was analyzed by using the EDS (energy-dispersive spectroscopy) analysis and two of them are given in Figure 2. It is clear that the additives dispersed nicely inside the matrix. The green dots in Figure 2 represent platinum atoms and show a nice distribution. In addition, the green dot density in Figure 2.a is higher than 2.b because the composite represented in 2.a has a higher amount of platinum inside than the 2.b.

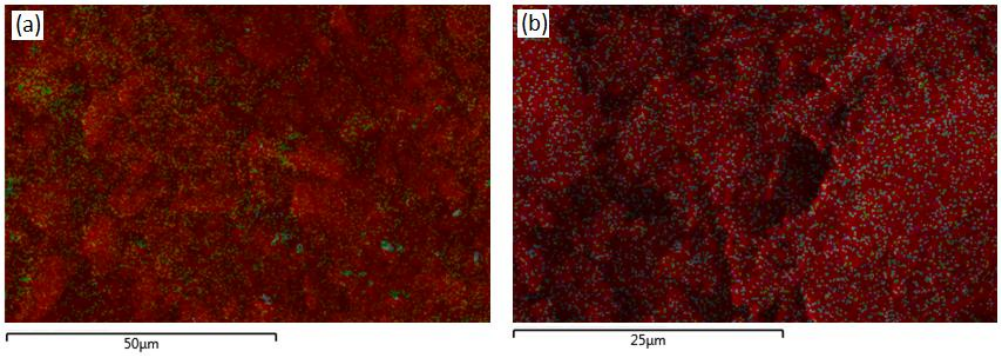

Figure 2.EDS analysis Pt dispersion maps of the AC and Basolite composites. (a) 10 wt. % additive included activated carbon composite and (b) 4 wt. % additive including Basolite composite**.**

The Nitrogen adsorption data is used to determine the surface area and pore characteristics of the adsorbents. The pore size distribution (PSD) curves and cumulative pore volumes are given in Figure 3.a and 3.b for activated carbon composites. The highest peak represents micro-pores which are found in 2 wt. % platinum loaded activated carbon composite in Figure 3.a. It is clear that the highest additive amount does not adress higher micro-pores. Interestingly, an increased amount of additive forms more meso-pores than the micro-pores. This is why the 4 wt. % additive included activated carbon composite has the highest meso-pore (bottom of Figure 3.a). 6 wt. % of additive including activated carbon composite have the highest total pore volume in spite of 2 and 4 wt. % additive included composites (Figure 3.b).

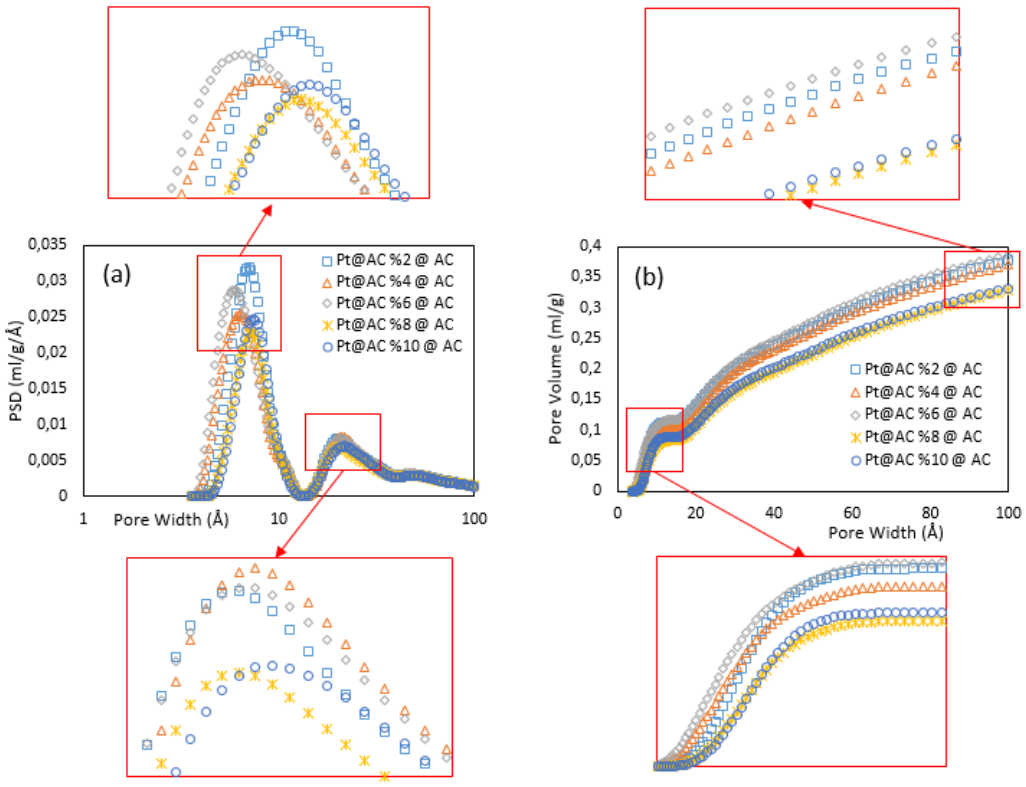

Figure 3. Pore size distribution (a) and cumulative pore volumes (b) of the AC composites.

Basolite composites have similar pore characteristics but the highest values change with the amount of additives that the PSD and cumulative pore volumes are given in Figure 4.a and 4.b. 4 wt. % additive included composites of Basolite both have the highest miro-pores and meso pores unlike activated carbon composites (Figure 4.a). The same composite also has the largest pore volume among other Basolite composites (Figure 4.b).

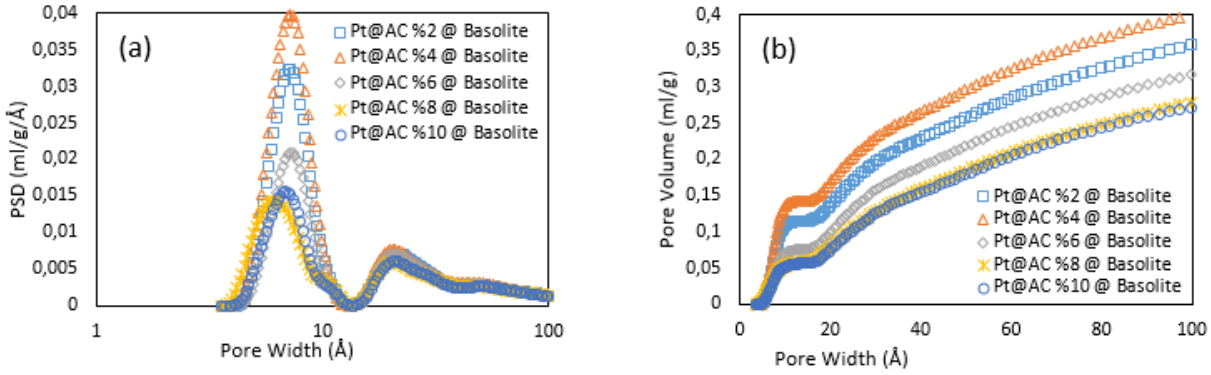

Figure 4. PSD and cumulative pore volumes of Basolite composites**.**

The nitrogen adsorption data is used to calculate surface areas. Accordingly, the BET surface areas of the AC composites are 519.97, 489.40, 528.72, 416.89 and 429.21 m^2/g for the increased amount of additives from 2 to 10 weight percent. The BET surface areas of the same amount of additive included Basolite composites are 507.86, 596.30, 392.86, 325.56 and 318.15 m^2/g. Also the BET surface areas are plotted in Figure 6.

Hydrogen storage capacities of the activated carbon and Basolite composites plotted against relative pressure in Figure 5. The continuous lines in Figure 5 represents hydrogen storage curves of additive free matrix materials. It is clear that the increased amount of additives increased the hydrogen uptakes, but more additives effect the adsorption and decreases the hydrogen storage. Hydrogen storage has a maximum for both adsorbents in a similar manner with surface areas of adsorbents, shown in Figure 4. Maximum hydrogen storage capacities of the AC composites are 3.187, 3.434, 3.401, 3.124 and 3.045 wt. % at 77 K and 1 bar pressure while the additive free AC could store 3.109 wt. % hydrogen at the same conditions. Hydrogen storage percentages of the Basolite composites also have similar distribution with the AC composites but the highest and lowest hydrogen uptakes differ. So, hydrogen storage capacities of the Basolite composites which have increased amount of additives are 3.424, 3.620, 2.967, 2.321 and 2.275 wt. % while the Basolite has 3.150 wt. %. Hydrogen storage capacity results also matching with the previous works that platinum loaded Cu-BTC composites investigated [29], [30].

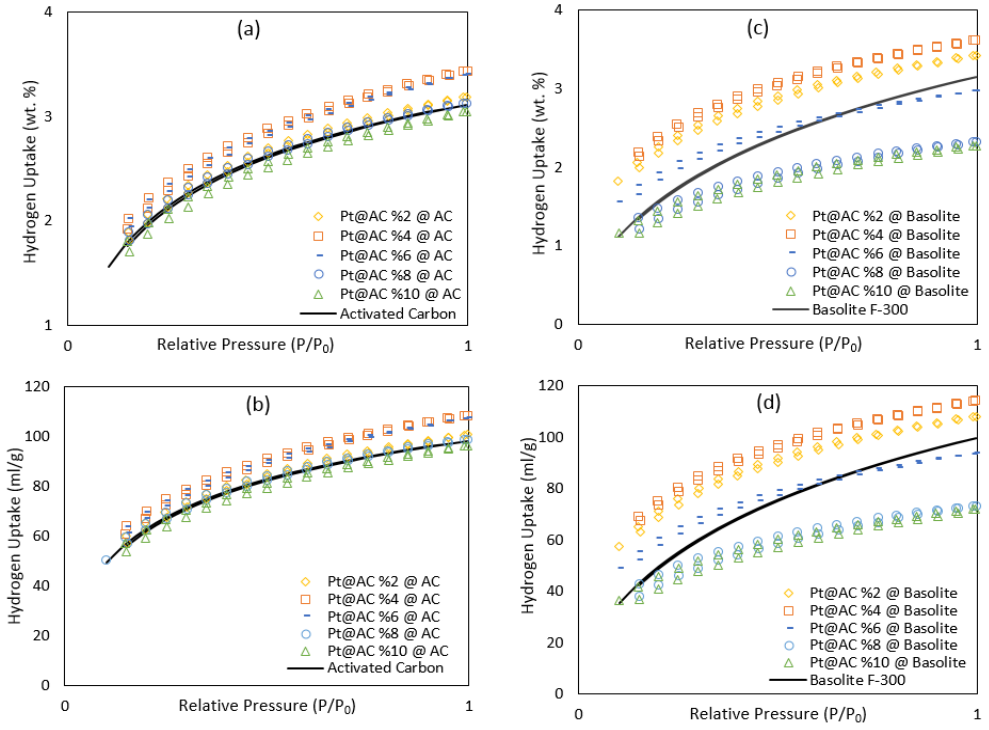

Figure 5. Hydrogen storage capacities of adsorbents by weight percent (a) and volume adsorbed (b).

In case of differences between the additive included composites, describing the increase or decrease percentages on the hydrogen storage capacities in comparison to the additive free adsorbents become meaningful. The percentages which represent the difference between the matrix and composites are 2.44, 9.46, 8.58, 0.48 and -2.11 for the AC composites and 8.00, 12.98, -6.16, -35.71 and -38.46 for the Basolite composites. Hydrogen storage capacity changes by additive amount show that the Basolite composites have more differences in comparison to the AC composites. In the other word, the additive amount in the Basolite composites effect the hydrogen storage more than the AC composites. The difference could be explained by the existing metal ion or centers placed in the matrix material. Because, the Basolite structures have cupper metals inside.

An additive which is platinum loaded activated carbon (Pt@AC), percentages affect the BET surface area, cumulative pore volume, nitrogen adsorption energies and gravimetric hydrogen storage capacities that changes are given in Figure 6. It is found that the 4 wt. % additive included composites of activated carbon and Basolite have the maximum total hydrogen uptake. The Uptake capacity of the mentioned composites are 3.434 and 3.620 wt. % hydrogen at 77 K and 1 bar pressure.

Interestingly, the 4 wt. % additive included activated carbon composite does not have the biggest surface area, but has the highest hydrogen uptake capacity. The phenomena could be explained with the adsorption energies. So, the 4 wt. % additive included AC composites have the maximum adsorption energy according to Figure 6.c. Similar results for adsorption energies which were calculated in the same way was reported by Blanco et al. [31].

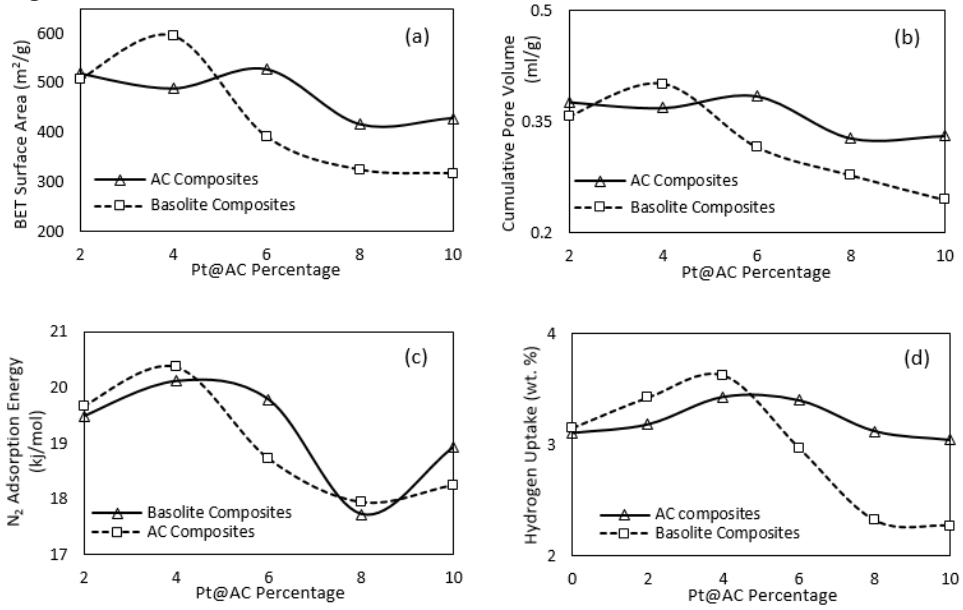

Figure 6. BET surface areas (a), cumulative pore volumes (b), nitrogen adsorption energies at 77K (c) and hydrogen adsorption percentages (d) of adsorbents versus additive percentages.

Gravimetric hydrogen uptake capacity changes by surface area for the composites which are prepared in this work and some previous results [23], [32] set in Figure 7. It was found that the hydrogen storage capacity changes with surface area shows approximate linear increment for the composites. In other word, the composites which have high surface areas also have better hydrogen storage capacities. If some examples are ignored, it is possible to make the generalization that the hydrogen storage capacity increases with the increased surface areas.

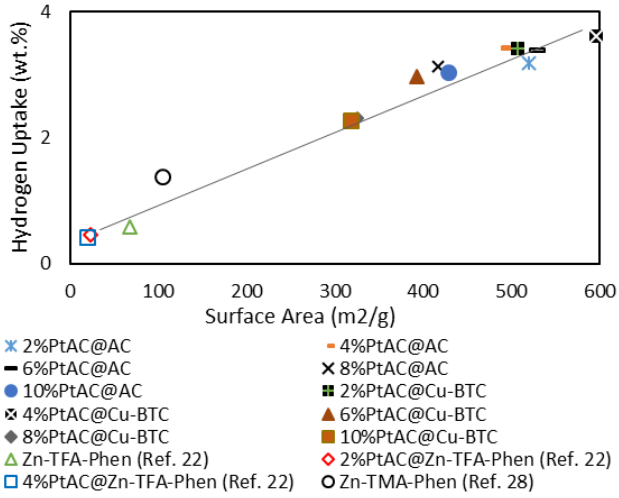

Figure 7. Hydrogen uptake capacity changes by surface area for composites.

4. Conclusion

In conclusion, platinum loaded activated carbon as an additive affect the hydrogen storage capacities in relation to surface areas of the composites. It is clearly understood that the additive percentages have limits for the highest hydrogen storage capacity, in parallel to previously published works. Zhou et al. reported that the hydrogen storage capacity of platinum loaded graphene oxide composite of the Cu-BTC increases for 5 wt. % additive while the storage capacity decreases lower value for 10 wt. % additive in comparison to the additive free adsorbent [24]. But the relation between the surface area and hydrogen capacity is more comprehensible. Because the results showed many times that the increased surface area result increased hydrogen storage capacities. At last, hydrogen storage investigations needed more attention to clarify unspecified points. After that it would be possible to mount the storage units to microgrid energy systems [34].

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