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Hydrogen storage on highly porous novel corn grain-based carbon monoliths

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ABSTRACT

The hydrogen (H_2) adsorption capacity of the highly porous novel corn grain-based carbon monoliths (CG-CMs) was assessed. The obtained H_2 adsorption results at 77 K (up to 1 bar) and 298 K (50 up to bar) were presented in the mass basis as well as in the volume basis. In addition, the mass basis and volume basis H_2 adsorption capabilities of the prepared carbon monoliths were correlated with their corresponding physical properties. Particularly, the influence of piece density on the volumetric H_2 capacity was discussed in detail. It was found that the H_2 adsorption abilities of the prepared CG-CMs are similar or higher than the other superactivated carbons or carbon monoliths.

1. Introduction

Now-a-days, the severe energy demand, increasing crude oil price and various environmental pollution problems due to the combustion of various liquid fuels are the hot issues in our world. In addition, the international energy agency has also announced that the world's primary energy requirement is projected to grow by 55% between 2005 and 2030 along with increasing carbon dioxide and other greenhouse-gas emissions by 57% [1]. Hence, we are in the position to find out environmentally and economically satisfied alternative fuel.

Hydrogen (H_2) is a promising alternative and pollution free fuel, which can replace the crude oil-based fuels, mainly in the field of mobile application. At the same time, H_2 requires special storage technique because of its low energy density [2] and primarily low boiling point, 20.28 K. There have been several conventional methods (liquefaction, compression and metal hydride) used to solve the hydrogen storage problem. Nevertheless, these methods contained a lot of problems such as high energy for retrieval of the absorbed hydrogen from metal complex, large boil-off loss, safety and high capital cost etc. Thus, the recently developed adsorption-based H_2 gas storage (AHGS) system has been attracted much attention because of its convenient storage conditions compared to the conventional methods [2–5]. The successful design of the AHGS system mainly depends on the properties of the adsorbent [2–10]. The influence of the various physical properties of the adsorbent such as the surface area, micro pore volume, pore size and pore size distribution on a mass basis H_2 adsorption result has been investigated extensively [3–12]. On the other hand, the volumetric H_2 adsorption capacity [13], which is also one of the most important required properties for the feasible design of an AHGS system [3,14,15], has been investigated by the less number of researchers. Also, it has been suggested that the piece density of the adsorbent should be considered along with the other physical properties of the adsorbent for determining the adsorption capability of the adsorbent, more specifically for the estimation of the volumetric H_2 adsorption capacity [14]. However, the influence of piece density on the volumetric H_2 adsorption have been discussed in a very few works [3,14,15].

Activated carbons (ACs) have been used for the adsorption of H_2 due to their microporous surface nature, availability, low cost and most importantly their unique surface interaction with H_2 gas molecules [3–10]. In fact, the preparation of most highly microporous ACs without the mesopores is a difficult task [17]. However, these problems can be solved by preparing the monolith form of carbon materials, which not only reduce the mesopores but also reduce the excess void volume [16–18]. The volumetric adsorption capacity of the carbon monolith can be high because of its high piece density and larger amount of micropores compared to that of the powdered form of ACs. Apart from this, the monolith form of adsorbent is very convenient for on-board applications because of its compactness [14].

The aim of the present study is to investigate the possibility of using corn grained-based carbon monoliths (CG-CMs) such as MR-1/2, MR-1/3 and MR-1/4 for the storage of H_2. The physical

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properties of the prepared carbon monoliths were characterized by the nitrogen (77 K) and carbon dioxide (273 K) adsorption and desorption analyses. The mass basis and volume basis H_2 adsorption abilities of the prepared CG-CMs were studied at 77 K (up to 1 bar) and 298 K (up to 50 bar).

2. Experimental

2.1. Preparation and characterization of carbon monoliths

The carbon monoliths were prepared by compressing the mixture of corn grain-based activated carbons and sodium derived carboxymethylcellulose sodium salt. Consequently, corn grain-based carbon monoliths such as MR-1/2, MR-1/3 and MR-1/4 were made from the powdered form of R-series (R-1/2, R-1/3 and R-1/4) corn grain-based activated carbons. Here, R and M refer namely the used ratios of carbonized char and activating agent for the preparation of activated carbons, and their consecutive monolithic forms, respectively. The detailed procedures for the preparation of corn grain-based activated carbons [19] as well as carbon monoliths [17,18] are available in elsewhere. Although these CG-CMs were used for few other processes such as volatile organic compounds removal [17] and methane adsorption [18], this is the first report about the adsorption of hydrogen on CG-CMs.

The physical properties of the prepared monoliths were examined by conducting N_2 (77 K) and CO_2 (273 K) adsorption studies (Micrometrics ASAP 2020). Here, the Brunauer–Emmett–Teller (BET) theory was used to determine the specific surface area (S_{BET}) of carbon monoliths from the N_2 adsorption data in the relative pressure range of 0.01–0.05 [20,21]. The total pore volume (V_T) was estimated by converting the amount of N_2 adsorbed at a relative pressure range of 0.99 to the volume of liquid adsorbate. Based on the calculated S_{BET} and V_T values, the average pore width was evaluated by using the following expression, $4\,V_T/S_{BET}$. The N_2 and CO_2 adsorption isotherms were independently analyzed with the Dubinin–Radushkevich (DR) equation for determining total micropore volume ($V_{DR}(N_2)$) and narrow micropore volume ($V_{DR}(CO_2)$), respectively [14].

2.2. Hydrogen adsorption studies

The hydrogen adsorption capacities of the prepared CG-CMs were assessed at 77 K and 298 K, respectively. In the case of the hydrogen adsorption on CG–CMs at 77 K and up to 1 bar, a volumetric adsorption analyzer [22], where the carbon monolith was placed in the adsorption cell equipped with a vertical stopcock, was used. After loading the carbon monolith into the adsorption cell, the system was evacuated in order to remove the adsorbed impurities at 473 K until 1×10^{-3} kPa. Then, the adsorption cell was immersed in liquid nitrogen and certain level of the liquid nitrogen was maintained throughout the experiments. Each point in the isotherm was recorded after 5 min equilibrium.

The room temperature (298 K) hydrogen adsorption studies were done up to 50 bar by using a gravimetric adsorption analyzer, which

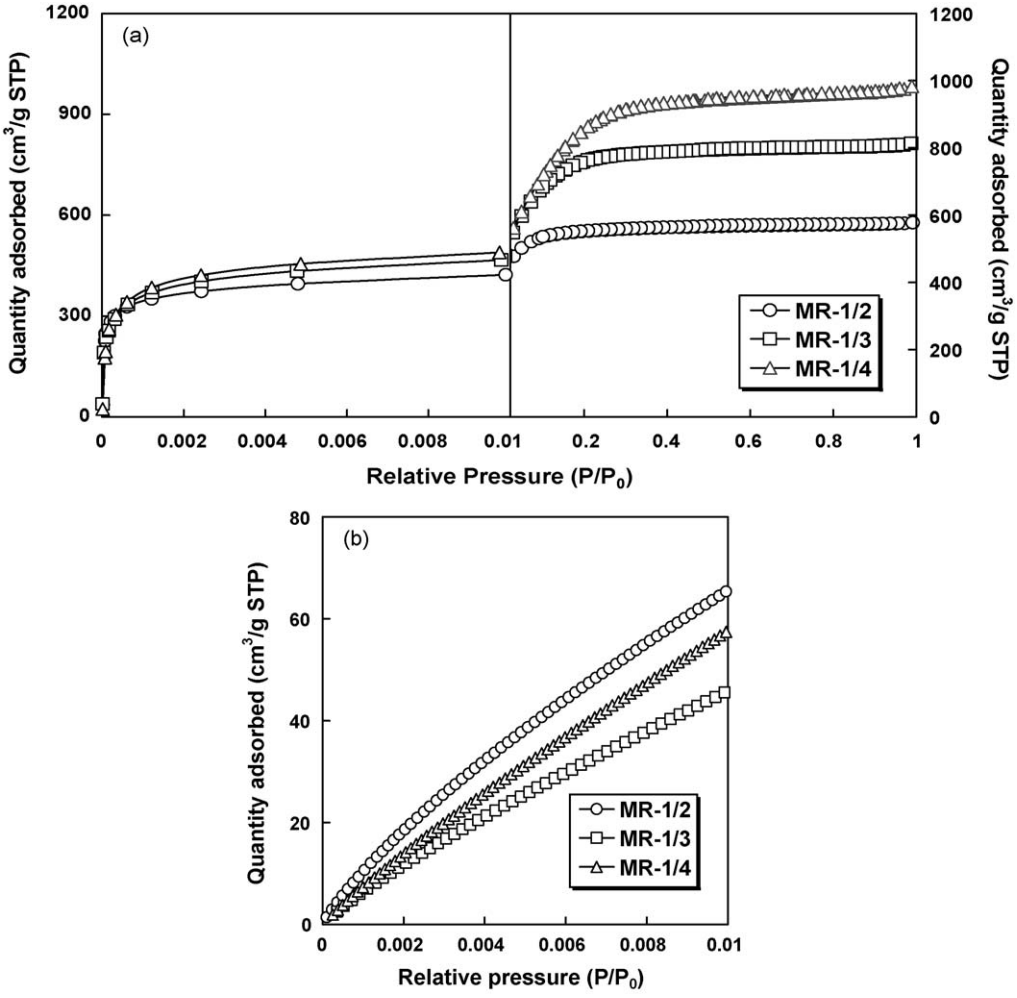

Fig. 1. The adsorption isotherms of N_2 (a) and CO_2 (b) on corn grain-based carbon monoliths at 77 K and 273 K, respectively.

consists of raw H_2 gas pre-treatment unit, H_2 dosing unit, magnetic suspension microbalance (Rubotherm), and data acquisition and control unit [23]. Here, the carbon monolith was used after degassing at 473 K for 12 h. During the adsorption studies, the pressure of the system was gradually increased and the temperature of the adsorption cell was controlled by using the water circulation unit. At each equilibrium step, the amount of adsorbed gas was calculated by measuring the weight change in the carbon monolith sample. After completing the adsorption step, the desorption of H_2 was also carried out at 298 K by reducing the pressure from 50 to 0 bar, to investigate the deliverability of the prepared carbon monoliths. Furthermore, the measured data were in the error range of ±0.0067 wt%.

3. Results and discussion

3.1. Carbon monoliths

The adsorption and desorption isotherms of N_2 on CG-CMs at 77 K [18], which are shown in Fig. 1a, represent the characteristic of type I isotherm according to the classification of International Union of Pure and Applied Chemistry [24]. The physical properties of the prepared carbon monoliths (MR-1/2, MR-1/3 and MR-1/4) such as the surface area, total pore volume, micropore volume, average pore width and piece density are listed in Table 1. In particular, the $V_{DR}(N_2)$ and $V_{DR}(CO_2)$ micropore volumes of carbon monoliths were determined from the low pressure ($P/P_0 \leq 0.01$) N_2 and CO_2 isotherm data, which are shown in Fig. 1a and 1b. Here, the order of N_2 and CO_2 adsorption capacities of carbon monoliths were noted as follows: MR-1/4 > MR-1/3 > MR-1/2 and MR-1/2 > MR-1/4 > MR-1/3, respectively. The observed dissimilarities in between the low pressure N_2 and CO_2 isotherm data clearly indicated the existence of ultramicrorpores (<0.7 nm) in the prepared carbon monoliths, especially in MR-1/2 and MR-1/4. In addition, the micropore size distribution (MPSD) trends in the prepared CG-CMs were estimated by comparing both $V_{DR}(N_2)$ and $V_{DR}(CO_2)$ values [3,18]. Because of the smaller difference between V_{DR} (N_2) and $V_{DR}(CO_2)$, the relatively narrow MPSD was found in MR-1/2, followed by MR-1/4 and MR-1/3 (see Table 1).

The surface energetic heterogeneity of the prepared CG-CMs were assessed from the adsorption energy distributions, using the Fowler–Guggenheim adsorption equation as a local adsorption isotherm model [17,20,25,26]. The adsorption energy distributions were calculated by using the low pressure N_2 adsorption data ($P/P_0 \leq 0.1$) and the corresponding results are shown in Fig. 2. In all the cases, the dual peaks, which are an indication of bimicroporous structures, were noticed [27]. The available peaks in the lower and higher energy parts were detected in the ranges between 3–7 and 7–11 kJ/mol, respectively. By considering the several characteristics of the adsorption energy distributions (the peak location, peak height and peak intensity), the order of energetic heterogeneity was identified as follows: MR-1/3 > MR-1/4 > MR-1/2.

3.2. Hydrogen adsorption on corn grain-based carbon monoliths at 77 K

The adsorption of H_2 on CG-CMs at 77 K and up to 1 bar was analyzed using a volumetric adsorption analyzer. The mass basis

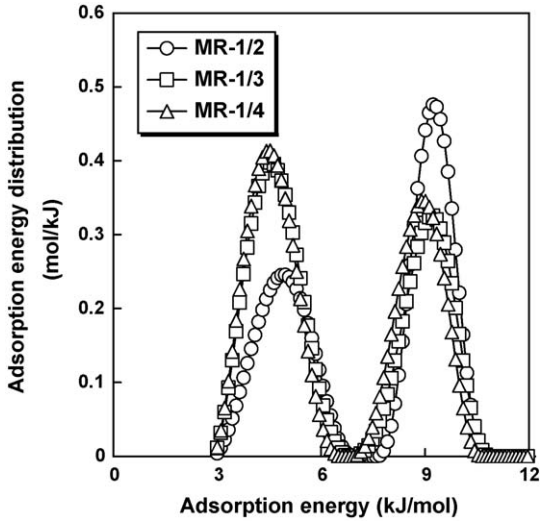

Fig. 2. The adsorption energy distribution of N_2 on corn grain-based carbon monoliths.

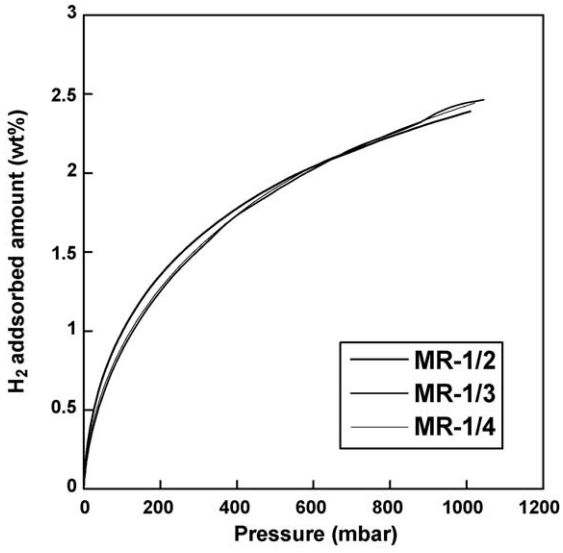

Fig. 3. Hydrogen adsorption on corn grain-based carbon monoliths at 77 K.

H_2 adsorption capacities of MR-1/2, MR-1/3 and MR-1/4 are shown in Fig. 3. In overall, the maximum hydrogen uptake on three different carbon monoliths was observed in between 2.39–2.45 wt% at 77 K and 1 bar. Although the samples MR-1/3 and MR-1/4 have high surface area in contrast to the sample MR-1/2, still they showed the same H_2 adsorption ability compared to the sample MR-1/2 due to the broad MPSD of MR-1/3 and large pore size of MR-1/4, respectively.

The obtained mass basis H_2 adsorption results of CG-CMs were compared with (coal [3,14], commercial [8,11,28,30] and biomass-based [29]) highly porous ACs and coal-based carbon monoliths

Table 1
Physical properties of corn grain-based carbon monoliths.

Adsorbent	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	V_{DR} (cm^3/g)		Average pore width (Å)	Piece density (g/cm^3)
			N_2	CO_2		
MR-1/2	2147	0.894	0.762	0.508	16.7	0.420
MR-1/3	2541	1.258	0.896	0.422	19.8	0.323
MR-1/4	2647	1.512	0.955	0.515	23.0	0.292

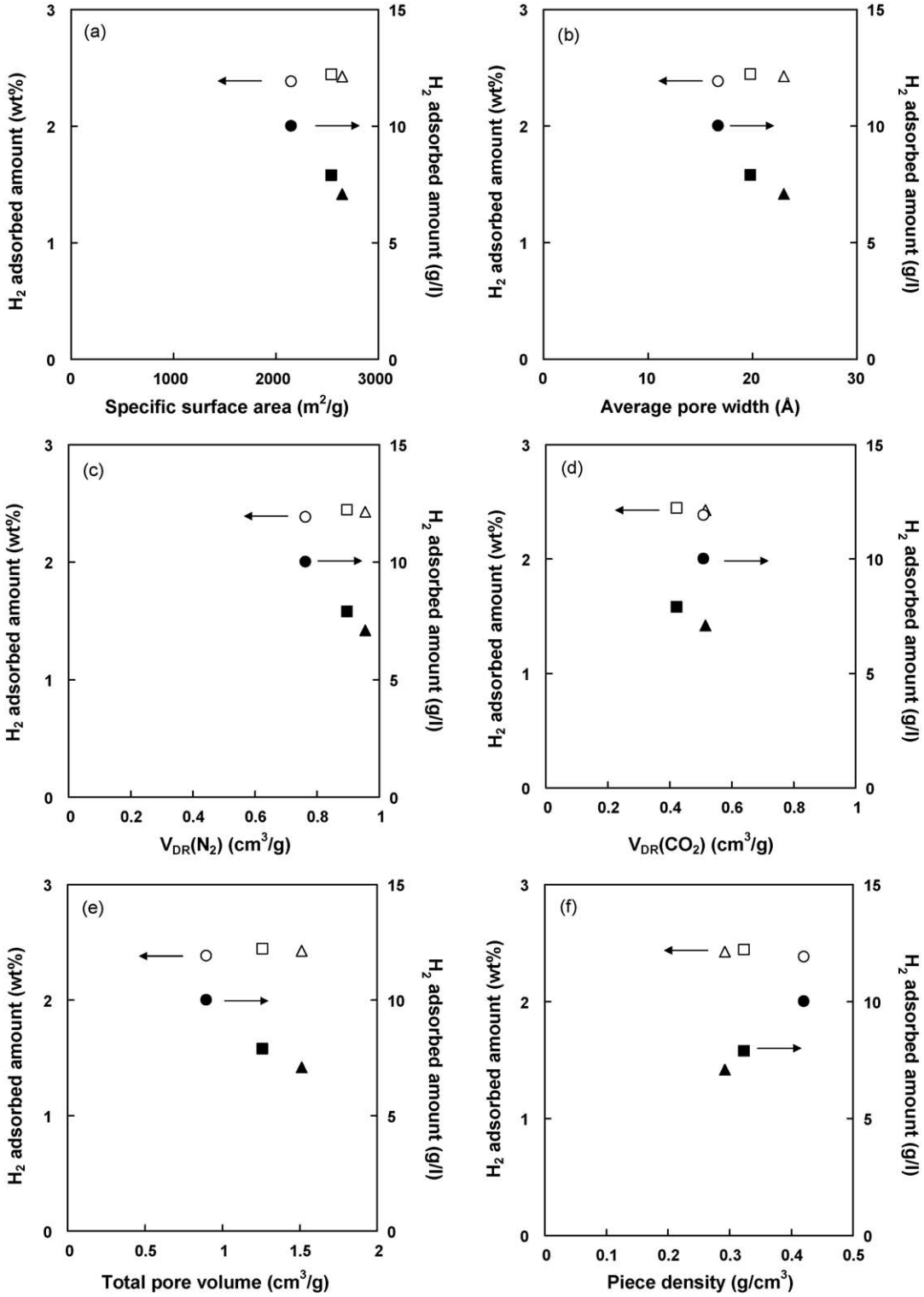

Fig. 4. Comparisons of mass basis (opened symbol) and volume basis (closed symbol) adsorption capacities corn grain-based carbon monoliths (MR-1/2 (○, ●) MR-1/3 (□, ■) MR-1/4 (△, ▲)) at 77 K with their corresponding physical properties (surface area, average pore width, micropore volumes ($V_{DR}(N_2)$, $V_{DR}(CO_2)$), total pore volume, and piece density).

[14], which were also used as adsorbents for H_2 adsorption. It was observed that the prepared CG-CMs showed the almost similar [3,8,14,28,29] or higher [3,8,11,29,30] H_2 adsorption capabilities compared to that of the reported ones. Most importantly, it should be noted that the prepared corn grain-based carbon monoliths showed similar or higher H_2 adsorption capacities contrast to the compared non-monolithic form of carbon materials [3,8,11,14,28–30], even they have more or less similar physical properties compared to those non-monolithic from of carbon materials. Furthermore, the maximum mass basis as well as the volume basis H_2 adsorption capacities of the prepared CG-CMs at 77 K and 1 bar are plotted against their physical properties such as the surface area, average pore width, $V_{DR}(N_2)$, $V_{DR}(CO_2)$, total pore volume and piece density to investigate the influence of those properties on

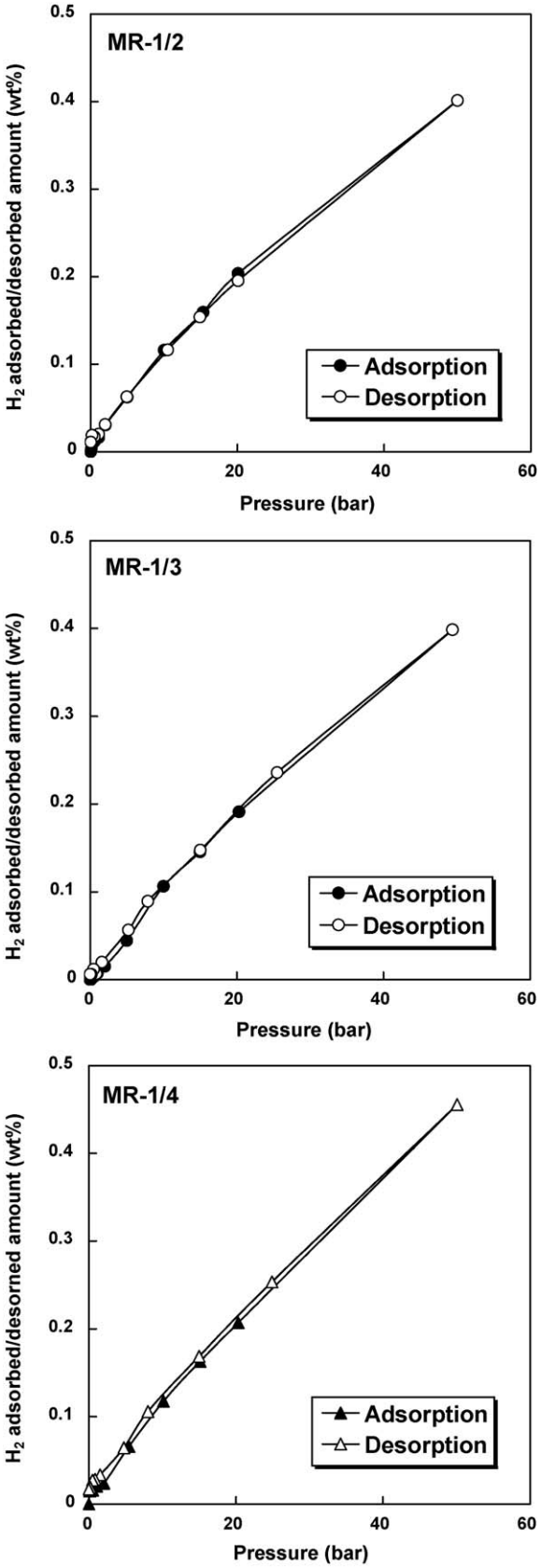

Fig. 5. H_2 adsorption and desorption on corn grain-based carbon monoliths at 298 K.

hydrogen adsorption, as shown in Fig. 4. From the results, it was found that there are no straight forward relationships between the mass basis H_2 adsorption results and the physical properties. Most importantly, the increase in $V_{DR}(N_2)$ and $V_{DR}(CO_2)$ also could not improve the H_2 adsorption on a mass basis, which clearly indicated the existence of very small micropores in the prepared carbon monoliths that even not possible for the penetration of CO_2 molecules [4,5]. However, the reason for the almost same mass basis H_2 adsorption capabilities of CG-CMs might be explained as follows, the narrow MPSD [10], useful pore size [7] and higher micropore volume ($V_{DR}(CO_2)$) [8] in MR-1/2 and the undetected micropores [4,5] as well as the higher surface areas [9] in both MR-1/3 and MR-1/4.

The volumetric H_2 adsorption capacities were calculated by considering both mass basis H_2 adsorption result and piece density of the prepared carbon monoliths [14]. It was observed that the prepared CG-CMs showed relatively moderate volumetric H_2 adsorption capacities due to their lower piece densities, even though they have very high surface areas as well as micropore volumes. In overall, the sample MR-1/2, which has relatively higher piece density than the other CG-CMs, showed the maximum volumetric H_2 adsorption capacity as 10.01 g/L at 77 K and 1 bar. Also, the good correlations between the volumetric results and the physical properties (except $V_{DR}(CO_2)$) were found, in contrast to the mass basis comparison results. However, these linear relationships between several physical properties and volumetric H_2 adsorption abilities of CG-CMs were found only after considering the piece density for the calculation of the volume basis adsorption capability. Hence, the piece density should be considered along with the other physical properties for the design of the AHGS system. Also, the relatively lower energetic heterogeneity surface having the sample MR-1/2 was beneficial to obtain the higher volumetric H_2 adsorption capabilities, even though there is some non-linear relationship between the energetic surface heterogeneities and volumetric H_2 adsorption results of CG-CMs.

3.3. Hydrogen adsorption on corn grain-based carbon monoliths at 298 K

The H_2 adsorption and desorption on CG-CMs at 298 K were done using a gravimetric adsorption instrument and the obtained mass basis results are presented in the Fig. 5a–c. A very small or no hysteresis was detected in the Fig. 5, which markedly suggested the reversible adsorption-desorption of H_2 on carbon monoliths. At 298 K and 50 bar, the maximum mass basis H_2 adsorption capacities of the samples MR-1/2, MR-1/3 and MR-1/4 were found as follows 0.40, 0.41 and 0.46 wt%. In addition, it was observed that the mass basis H_2 adsorption abilities of CG-CMs (298 K and 50 bar) are higher than the highly porous coal-based ACs [3], coconut-based ACs [4], several commercial ACs and carbon cloths [10], activated carbon fibers [12] Maxsorb [3,9], and AX-21 [3].

As discussed in the low temperature H_2 adsorption studies, the effect of various physical properties on the mass basis as well as the volume basis H_2 adsorption capabilities of CG-CMs were examined, as shown in Fig. 6. Here, the little correlations were noted between the room temperature mass basis H_2 adsorption capabilities and the physical properties of carbon monoliths under the given experimental conditions. The observed little (298 K) as well as no straight forward correlation (77 K) between the physical properties of CG-CMs and their corresponding mass basis H_2 adsorption capacities indicated the unclear relationships, which quite possibly due to the unbalanced proportions of the required physical properties in each CG-CM.

In the case of volume basis results, the comparatively higher piece density having the sample MR-1/2 showed the larger volumetric H_2 adsorption capacity in contrast to the other CG-CMs,

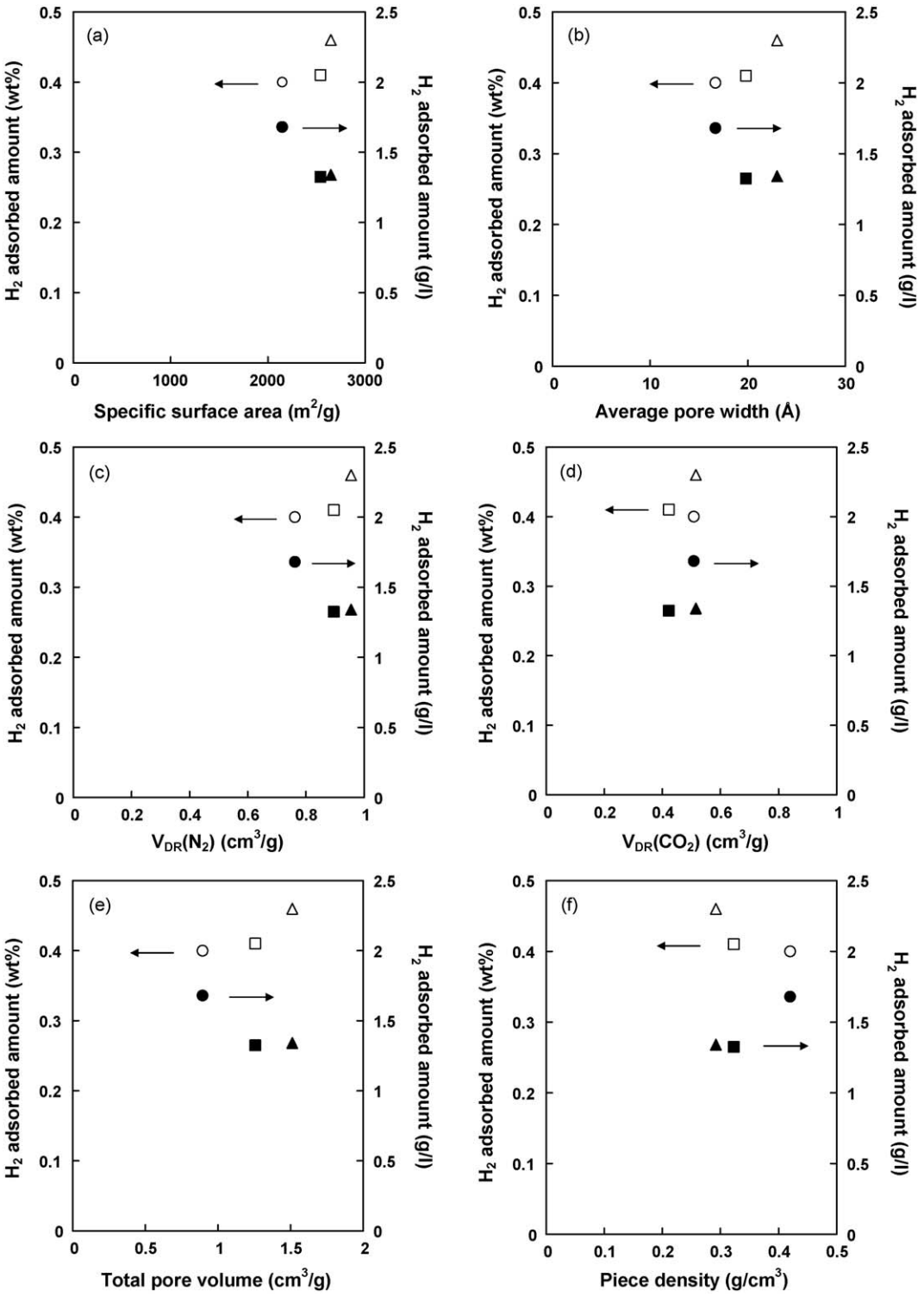

Fig. 6. Comparisons of mass basis (opened symbol) and volume basis (closed symbol) adsorption capacities corn grain-based carbon monoliths (MR-1/2 (○, ●) MR-1/3 (□, ■) MR-1/4 (△, ▲)) at 298 K with their corresponding physical properties (surface area, average pore width, micropore volumes ($V_{DR}(N_2)$, $V_{DR}(CO_2)$), total pore volume, and piece density).

as in the case of the low temperature volumetric H_2 adsorption results. Therefore, it can be suggested that the piece density of the carbon materials is one of the important key factors for the achievement of higher volumetric H_2 adsorption capacity. Besides, the moderate volumetric H_2 adsorption capacities of CG-CMs at 77K and 298 K clearly suggested the necessary in increasing piece density of CG-CMs, while keeping the high surface area as well as micropore volume, and also this corresponding study is in progress to achieve the higher volumetric H_2 adsorption capacities. Thus, the piece density must be taken into account along with the surface area, total pore volume, MPSD, pore size and micropore volume for the rational design of the on-board AHGS system, since the available volume for the storage system in the vehicle is limited.

Furthermore, a linear relationship between the surface energetic heterogeneities results and the room temperature (298 K) volumetric H_2 adsorption abilities of CG-CMs were observed in contrast

to the low temperature (77 K) volumetric H_2 adsorption results, which also once again confirmed the advantage of the lower energetic heterogeneity surface nature for H_2 adsorption.

4. Conclusion

The higher H_2 adsorption capacities of the highly porous novel corn grain-based carbon monoliths were confirmed from the low temperature as well as the room temperature adsorption analyses. It was observed that the difference between the mass basis H_2 adsorption capabilities of the prepared carbon monoliths at low temperature (2.39–2.45 wt%) and at room temperature (0.40–0.46 wt%) was not high because of the unbalanced proportions of the required physical properties in each carbon monolith. In addition, there were little correlations between the mass basis H_2 adsorption results of CG-CMs and their corresponding physical properties. On the other hand, the influence of the piece density of the prepared corn grain-based carbon monoliths was evidently confirmed from the low temperature as well as the room temperature volumetric H_2 adsorption results. Therefore, the piece density also has to be considered for the effective design of the adsorption-based H_2 gas storage system.

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