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Hydrogen adsorption and storage on porous materials☆

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Abstract

The development of safe and efficient methods of hydrogen storage is a prerequisite for the use of hydrogen with fuel cells for transport applications. In this paper, results available for adsorption of hydrogen on porous materials, ranging from activated carbons to metal organic framework materials, are discussed. The results indicate that up to ~5 and ~7.5 wt% of hydrogen can be stored on porous carbon and metal organic framework materials, respectively, at 77 K. The amounts of hydrogen adsorbed on porous materials at ambient temperatures and high pressures are much lower ($\lesssim$0.5 wt%). The strong temperature dependence of hydrogen physisorption on porous materials is a limitation in the application of this method for hydrogen storage in addition to storage capacity requirements.

Keywords: Hydrogen; Adsorption; Storage; Carbons; Metal organic frameworks; Porous materials

1. Introduction

Recent years have seen a recognition of the future need for a hydrogen based economy. The benefits of using hydrogen as a fuel are both strategic and environmental arising from decreased reliance on oil and major reduction in air pollution. There are major scientific challenges to overcome before the technology necessary to change from petroleum to hydrogen as an energy carrier can be implemented [1,2]. Hydrogen storage is the main problem to be conquered for the successful implementation of fuel cell technology in transport applications and it represents a major materials science challenge. The methods of storage currently under consideration include high pressure gas, liquid hydrogen, adsorption on porous materials, complex hydrides and hydrogen intercalation in metals. None of these methods completely satisfy all the criteria for the amount of hydrogen that can be supplied from a given weight or volume of tank for transport purposes.

The use of hydrogen physisorption on porous materials is one of the main methods being considered for vehicle applications. The objective is storage of large amounts of hydrogen at near-ambient temperatures and 'safe' pressures. These materials would also need to satisfy the requirements of reasonable volume, weight and realistic kinetics for charging and discharging the hydrogen gas. The U.S. DOE has set targets to develop and verify on-board hydrogen storage systems achieving 6 and 9 wt% for 2010 and 2015, respectively [3].

The weak interaction of hydrogen physisorbed within pores needs to be understood in order to optimize porous materials for hydrogen adsorption. The important measurements for this application are

(1) amount adsorbed as a function of pressure;
(2) temperature dependence of adsorption;
(3) the enthalpies of adsorption;
(4) the adsorption/desorption characteristics.

Amounts adsorbed can be compared using adsorption isotherms while the temperature dependence can be evaluated using isotherms over a temperature range and also, isobars. Measurements of a series of hydrogen adsorption isotherms over a temperature range provide information for calculation of the enthalpies of adsorption. These characteristics are important in relation to the hydrogen charging and discharging characteristics. Adsorption/desorption kinetic measurements are required because of the need for fast charging and discharging of hydrogen. In this paper, the current status of studies of hydrogen adsorption on porous materials is reviewed.

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2. Experimental methods

Accurate hydrogen adsorption measurements on porous materials are difficult to obtain. Some of the early work on hydrogen adsorption on porous materials did not include enough information to confirm the validity of the measurements and some have been shown to be incorrect. Gravimetric measurements provide a direct measurement of adsorption whereas volumetric measurements give an indirect measurement. The problems encountered with the measurements have usually been associated with the adsorption of impurities from either the hydrogen used or within the vacuum system, and extremely small leaks in the instrument. The latter is very important for indirect volumetric measurements at high pressure. In our experience with gravimetric isotherm and isobar measurements, the following basic system requirements are needed:

(1) an ultra-clean high vacuum system with all metal seals with diaphragm and turbo pumps (i.e. oil free system) which can be out gassed to 10^{-10} bar;
(2) a purification system for hydrogen.

The latter is necessary even when ultra-pure hydrogen is used.

The isotherm resolution needs to be high enough to define the shape of the isotherm unambiguously. Verification of the experimental protocols for isotherm determination is essential and the following methods can be used:

(i) Impurity adsorption is often observed as a very slow adsorption on top of a fast equilibrium and a failure to reach a true equilibrium. Therefore, extensive repeatability and long term stability studies of adsorption equilibria are required to confirm the absence of significant amounts of impurity adsorption. The virtual complete desorption of the adsorbed H_2 needs to demonstrated in isotherm and isobar studies at low temperature to establish that impurities have not been adsorbed. Fig. 1 shows the adsorption/desorption isotherms for both H_2 and D_2 on a microporous carbon with virtually no hysteresis [4].

(ii) Thermodynamic requirements are that the isosteric enthalpy of adsorption at zero surface coverage should be constant and this needs to be confirmed for the experimental set up being used [4].

(iii) Comparison of H_2 and D_2 adsorption shows that the ratios of the amounts adsorbed under the same conditions are in the range 1.06–1.09 on a mole basis for porous carbons [4,5]. Fig. 1 shows a comparison of the H_2 and D_2 adsorption and desorption isotherms from which ratios are obtained. Similar ratios have been obtained for adsorption of H_2 and D_2 on metal organic framework materials [6,7].

(iv) The density of adsorbed hydrogen can be obtained by comparison of the maximum amount adsorbed obtained from isotherm studies with the total and micropore volumes determined for the materials. The density value for liquid H_2 probably represents an upper limit, so the observed adsorbate density is expected to be lower than this value when hydrogen adsorption takes place above the critical temperature.

(v) When adsorption is carried out at high pressure, the problem of impurity adsorption is far greater than at atmospheric pressure because of the much larger amount of hydrogen in the system.

(vi) Accurate buoyancy corrections for gravimetric instruments (or dead volume corrections for volumetric instruments) are essential for accurate high pressure adsorption data. The propagation of errors is a major source of uncertainty in determining the accuracy of high pressure measurements.

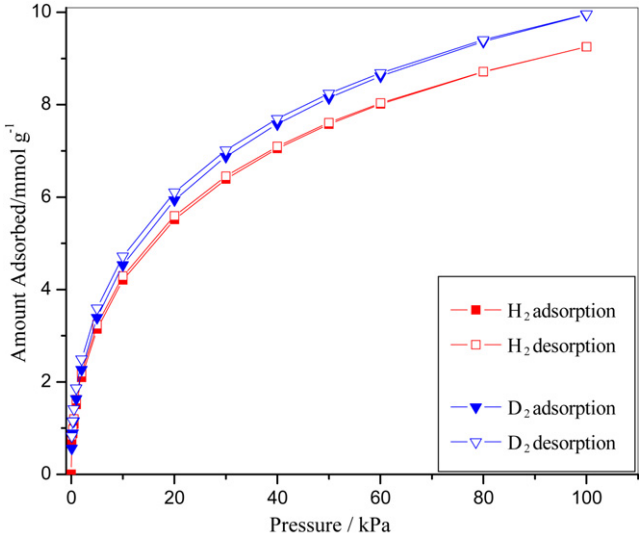

Fig. 1. Isotherms for hydrogen and deuterium adsorption and desorption on activated carbon at 77 K [4].

3. Results and discussion

Hydrogen adsorption has been investigated on a wide range of carbon, silica, alumina, metal organic framework and polymer porous materials [4–44]. However, even within the same type of materials, comparisons are limited by the availability of hydrogen adsorption data over a wide pressure range sufficient to determine the maximum hydrogen adsorption accurately, characterization data for the porous materials and the use of different methods for calculating pore structure characteristics, such as surface area and pore volume parameters. In some ultra-microporous materials, activated diffusion effects may be observed for nitrogen adsorption at 77 K resulting in adsorption kinetic limitations and hence, nitrogen adsorption isotherm data are not available. In porous carbon materials, a pore size distribution is present, whereas in metal organic frameworks, the materials are often crystalline with well defined pore structures. However, some studies have overlap of characterization information which allows comparisons of hydrogen adsorption data with porous structure characteristics.

3.1. Carbon materials

Carbon materials have been studied extensively as potential hydrogen storage materials because of their low density, wide

variety of structural forms, extensive pore structure, good chemical stability and the ability to modify the structures using wide range of preparation, carbonization and activation conditions. Since the first account of hydrogen adsorption on carbon nanotubes, a wide range of uptake values have been reported, from negligible to extremely large. Recently, more consistent results have been achieved by research groups examining many varieties of carbon materials ranging from nanotubes, nanohorns, etc., to porous activated carbons [4,5,8–25]. Adsorption and desorption of hydrogen on carbon nanotubes, nanoporous materials and activated carbons usually have little or no hysteresis and are usually fast at 77 K [4,5]. The fast adsorption/desorption kinetics make it suitable for fast recharging and discharging of hydrogen although there is the enthalpy of adsorption to consider. Kinetic isotope quantum molecular sieving effects have also been observed in the adsorption of H_2 and D_2 on porous carbons [5].

Some consistent trends emerge from comparison of the porous structure characterization and the data for H_2 adsorbed at 1 bar and 77 K. The variation of hydrogen uptake (wt%) at 77 K and 1 bar pressure on a wide variety of porous and nanostructured carbon materials with total pore volume is shown in Fig. 2. It is evident that the results show a large degree of scatter. Some of the materials with very high total pore volumes do not adsorb hydrogen at 1 bar to a large extent. This is due to the much lower interaction energy of hydrogen in wide pores compared with smaller micropores (<0.7 nm). The variation of hydrogen uptake (wt%) at 77 K and 1 bar pressure on a wide variety of carbon materials with BET surface area is shown in Fig. 3. The correlation shows greater scatter in the data for surface areas >1000 $m^2\ g^{-1}$. The maximum surface area for adsorption on both sides of a graphene layer gives a surface area of 2630 $m^2\ g^{-1}$. Also, materials with larger surface areas may have wide pore size distributions. Some of the materials with higher apparent surface areas may have contributions from pore filling effects and the values quoted may not represent a true surface area. The variation of hydrogen uptake (wt%) at 77 K and 1 bar pressure on a wide variety of carbon materials with micropore volume is shown in Fig. 4. Micropore volumes have been obtained by several methods. The micropore volume obtained from extrapolation of the Dubinin–Radushkevich (DR) equation for carbon dioxide adsorption data at 273 K quantifies pores $\lesssim$0.7 nm. The micropore volume obtained from nitrogen adsorption data at 77 K refers to pores <2 nm [45–47]. Both micropore volumes

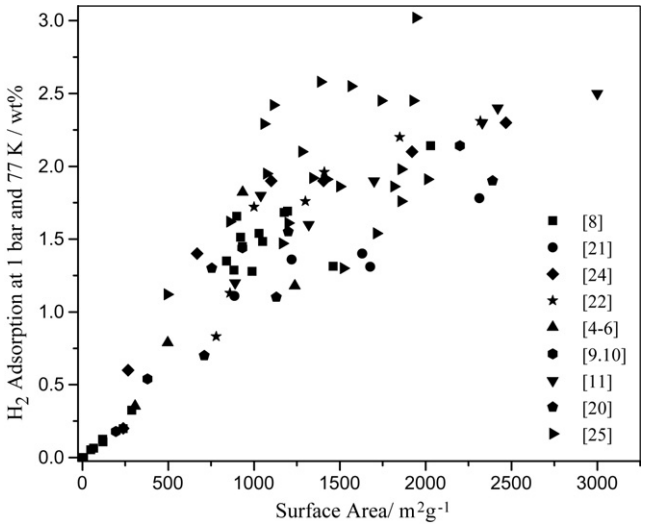

Fig. 3. The variation of H_2 adsorbed at 1 bar and 77 K with surface area for carbon adsorbents: (■) Nijkamp et al. [8], (●) Pang et al. [21], (◆) Parra et al. [24], (★) Takagi et al. [22], (▲) Zhao et al. [4–6], (⬢) Schimmel et al. [9,10], (▼) Texier-Mandoki et al. [11], (⬟) Gadiou et al. [20] and (▶) Gogotsi et al. [25]. Surface areas obtained from BET method except [22] where surface area is sum of micro and external surface area from *t*-method.

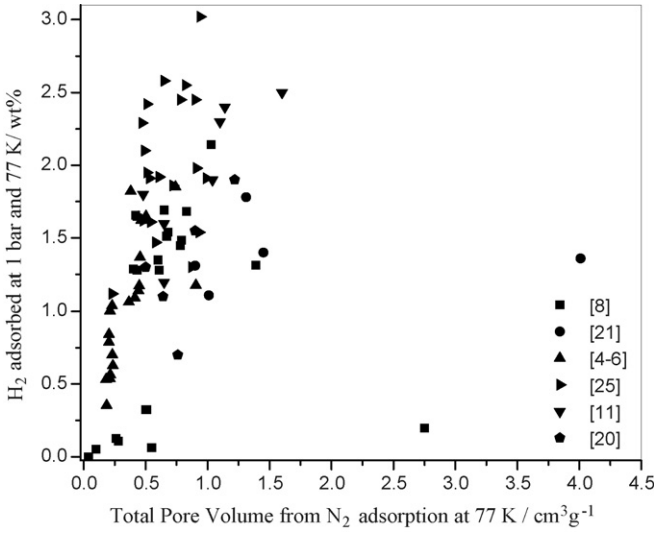

Fig. 2. The variation of H_2 adsorbed at 1 bar and 77 K with total pore volume obtained from nitrogen adsorption at 77 K for carbon adsorbents:(■) Nijkamp et al. [8], (▲) Zhao et al. [4–6], (●) Pang et al. [21], (▼) Texier-Mandoki et al. [11], (⬟) Gadiou et al. [20] and (▶) Gogotsi et al. [25].

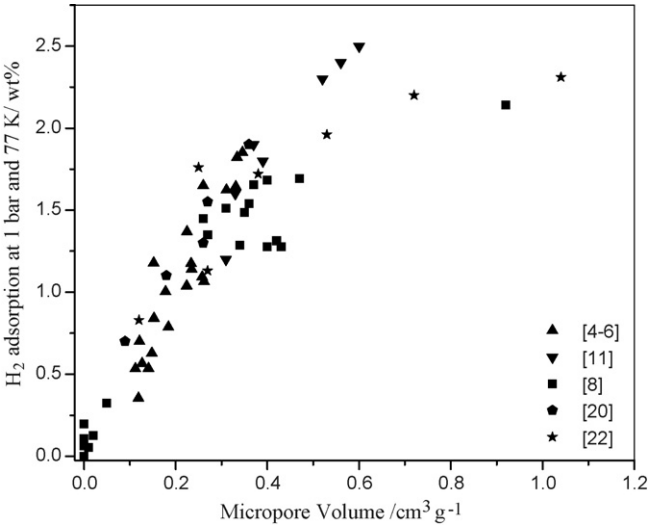

Fig. 4. The variation of H_2 adsorbed at 1 bar and 77 K with micropore volume for carbon adsorbents: (■) Nijkamp et al. [8], N_2 (77 K) micropore volume; (▲) Zhao et al. [4–6], CO_2 (273 K) micropore volume; (▼) Texier-Mandoki et al. [11], CO_2 (273 K) micropore volume; (⬟) Gadiou et al. [20], CO_2 (273 K) micropore volume; (★) Takagi et al. [22].

are used in the graph (see legend for details) and correlations are similar within the scatter in the data. It is apparent that there is an approximate linear relationship between H_2 adsorbed at 1 bar and micropore volumes $<0.6\ cm^3\ g^{-1}$. This illustrates the importance of the narrowest porosity in determining hydrogen adsorption at low pressure.

The amounts adsorbed at a specific pressure only give limited information since the shapes of isotherms vary with pore structure characteristics and it is better to compare the maximum amounts of hydrogen adsorbed obtained from either direct measurement of the hydrogen adsorption plateau or extrapolation of the isotherm data using isotherm models to give maximum capacity. The former requires accurate high pressure measurements free of impurity adsorption while the latter can be used provided the maximum isotherm uptake is close to a plateau and the isotherm can be fitted to a suitable model. The maximum adsorption capacity is directly related to the porous structure of the material. Fig. 5 shows the correlation between the H_2 adsorption capacity at 77 K and micropore volume. Details of the micropore volumes used are given in the legend for the figure. It is apparent that there is good agreement between the sets of data from various research groups. In adsorption studies, the density of the liquid is often used for the density of adsorbed phase and it is reasonable to regard this as the maximum density of the adsorbate. The density of liquid hydrogen is $0.0708\ g\ cm^{-3}$ at 20.28 K, while hydrogen at the triple point (13.8 K) a density of $0.077\ g\ cm^{-3}$ [48] and the line for the former density is also shown in the Fig. 5. The majority of these data are below these lines indicating a lower density than liquid hydrogen, which is reasonable considering that the adsorption temperature is above the critical temperature (33.18 K). This confirms the importance of the narrowest pores in determining hydrogen adsorption characteristics.

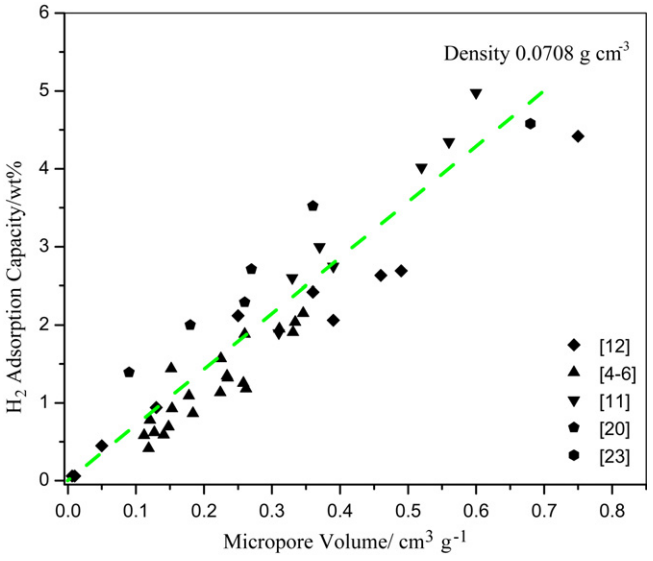

Fig. 5. The variation of H_2 adsorption capacity at 77 K with micropore volume for carbon adsorbents: (▲) Zhao et al. [4–6], DR CO_2 (273 K) micropore volume and H_2 capacity from Langmuir analysis; (▼) Texier-Mandoki et al. [11], DR CO_2 (273 K) micropore volume and H_2 capacity from Langmuir analysis; (⬟) Gadiou et al. [20], CO_2 (273 K) DR micropore volume; (◆) Panella et al. [12], (⬢) Zhou et al. [23].

Porous structure is the major factor in determining hydrogen adsorption characteristics. However, functionalization of activated carbons is a possible method for optimization of hydrogen adsorption because the surface chemistry of the adsorbent can be modified by the electron withdrawing or donating effects of the functional groups on the graphene layers. Zhao et al. studied the effect of oxygen and nitrogen functionalization of porous carbons on hydrogen adsorption characteristics [4]. Two series of carbons were prepared where the porous structure characteristics were virtually constant across a given series but the oxygen contents varied up to ~21 wt%. This allowed the effect of changes in functional groups to be studied with minimal effects due to changes in porous structure. The G series of carbons had a very low nitrogen content whereas the PAN series has a high (~8 wt%) nitrogen content. The maximum hydrogen adsorption capacities for both series of functionalized carbons at 77 K were estimated from extrapolation of Langmuir isotherms. Maximum hydrogen adsorption capacity decreased with increasing O/C ratio for both series of carbons (see Fig. 6) [4]. The density of the adsorbate was calculated using the maximum amount of H_2 adsorbed determined from Langmuir analysis of the isotherm data at 77 K and the micropore volume obtained from analysis of the carbon dioxide adsorption data at 273 K using the Dubinin–Radushkevich equation. The hydrogen adsorbate density and maximum hydrogen adsorption capacity decreased with increasing oxygen functional group concentration. Analysis of the data using a virial equation method showed a linear relationship with the A_1 virial parameter becoming more negative with decreasing maximum hydrogen adsorption capacity, which corresponds to increasing oxygen content [4]. This shows that increased adsorbate–adsorbate interactions due to the presence of functional groups results in decreased density of the adsorbate and hydrogen capacity.

Measurements of hydrogen adsorption at high pressure and ambient temperatures are subject to greater errors. This is due to the much larger corrections for buoyancy for gravimetric systems and dead volumes for volumetric systems at high

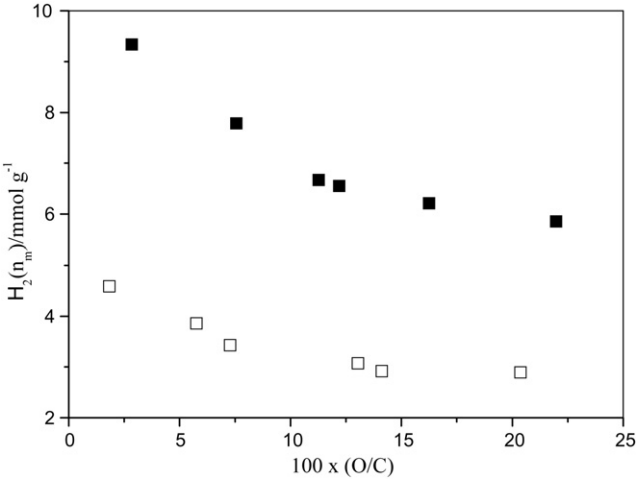

Fig. 6. The variation of maximum amount of hydrogen adsorbed (n_m) vs. O/C ratio: (■) G series; (□) PAN series [4].

pressure. Also, there is the greater availability of impurities in the hydrogen, in equilibrium with the adsorbent at high pressure and volumetric systems are more susceptible to the influence of very small leaks at high pressure. Panella et al. have shown that the maximum adsorption capacities for measurement pressures up to 65 bar at 77 K for a series of carbon were in the range <4.5 wt% but this was <0.5 wt% at 298 K [12]. They also showed a correlation between the adsorption capacities at 298 K and micropore volumes. Similar low hydrogen uptakes at ambient temperatures have been observed in other studies for a range of carbon materials. Zhou et al. observed 0.5 and 0.14 wt% H_2 adsorbed at 298 K and 6 MPa on activated carbon AX-21 and multi walled carbon nanotubes (MWCNT), respectively [23]. Similar low values for H_2 uptake of 0.3 wt% were observed at room temperature and 9 MPa on single walled carbon nanotubes (SWCNT) [17]. Takagi et al. reported H_2 uptakes <0.3 wt% at 303 K and 3.1 MPa for activated carbon fibers, SWCNTs and zeolites (H-YZ and H-ZSM-5) [22]. It is evident that H_2 uptakes are low at ambient temperatures even at high pressures (<9 MPa).

Zhao et al. investigated the temperature dependence of hydrogen adsorption using adsorption isobars for pressures up to 1 bar for several functionalized carbons and compared the results with isotherm measurements over the same temperature range [4]. Fig. 7 shows that virtually all the hydrogen was desorbed by 200 K. This demonstrates the marked temperature dependence of hydrogen adsorption on porous carbons. The low amounts adsorbed at ambient temperatures are related to the low enthalpy of adsorption. It is evident that the effect of temperature on hydrogen adsorption is very significant and there is increasing recognition that the temperature dependence of adsorption is critical because the very low amount of hydrogen adsorbed at ambient temperatures means that high pressures are required for storage of significant amounts of hydrogen. The current information available from ambient temperature and high pressure studies is limited but establishes the marked temperature dependence of hydrogen adsorption. It is not clear if very high pressures can increase the adsorption capacity at ambient temperatures up to levels approaching those obtained at 77 K.

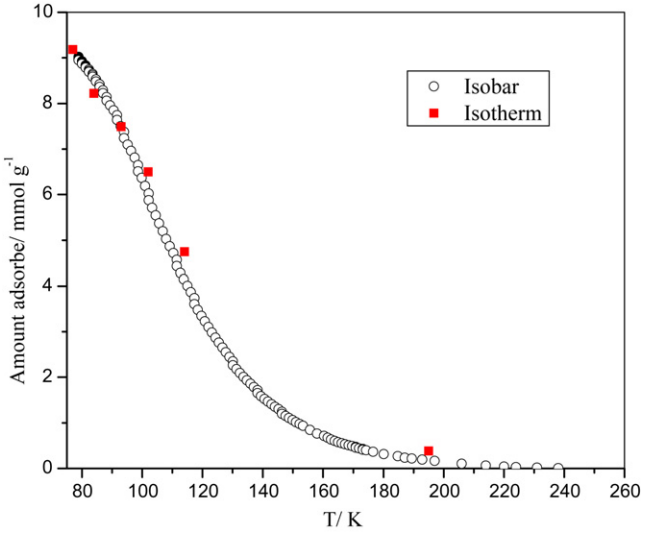

Fig. 7. Adsorption isobars for hydrogen desorption (only every 45th point included for clarity) from carbon G212 at 100 kPa: heating rate 0.3 K min^{-1} and (■) 100 kPa data from adsorption isotherms [4].

The correlations outlined above indicate that strategies for improving the adsorption capacity must involve increasing the BET surface areas and micropore volumes of the porous material. The narrower micropores have the major influence on hydrogen adsorption characteristics while larger pores are less significant. Oxygen and nitrogen functionalization of porous carbons has a detrimental effect on hydrogen adsorption characteristics. The marked decrease in hydrogen adsorption with increasing temperature is a factor which needs to be considered. Recent literature indicates that hydrogen adsorption of approximately ~5 wt% at 77 K and ≲0.5 wt% at room temperature can be achieved under high pressure conditions for a wide variety of carbon materials.

3.2. Silica and alumina materials

Nijkamp et al. studied the hydrogen storage capacities of an extensive series of silicas, aluminas and zeolites and compared them with carbon materials [8]. The results showed a correlation between the amount of hydrogen at 1 bar and 77 K and BET surface (see Fig. 8.). However, the amounts adsorbed at 1 bar pressure were slightly lower than corresponding carbons for a specific surface area. They concluded that storage of hydrogen was only possible when the adsorbents contained a large amount of micropores with appropriate size. The limited micropore volumes present in zeolite materials

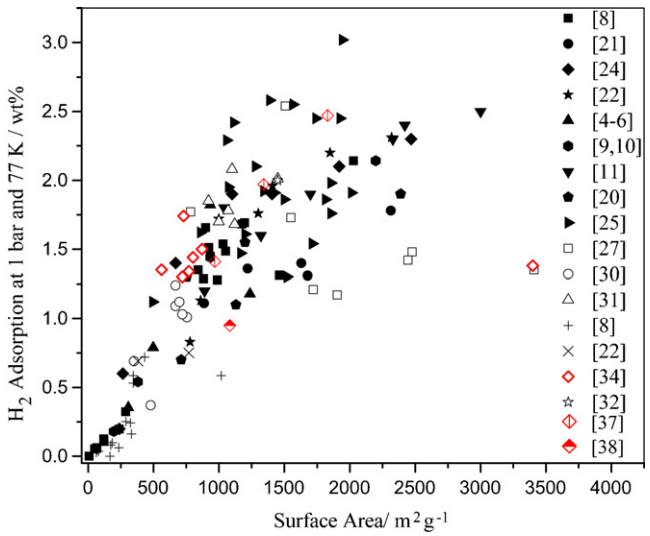

Fig. 8. The variation of H_2 adsorbed at 1 bar and 77 K with BET surface area for porous adsorbents. Carbon materials (solid symbols): (■) Nijkamp et al. [8], (●) Pang et al. [21], (◆) Parra et al. [24], (★) Takagi et al. [18,22], (▲) Zhao et al. [4–6], (⬢) Schimmel et al. [9,10], (▼) Texier-Mandoki et al. [11], (⬟) Gadiou et al. [20], (▶) Gogotsi et al. [25]. Silicas, alumina, zeolites (cross symbols): (+) Nijkamp et al. [8], (×) Takagi et al. [22]; MOFs (open symbols): (□) Rowsell and Yaghi [27], (○) Chapman et al. [30], (△) Chun et al. [31], (◇) Kaye and Long [34], (☆) Dybtsev et al. [32], (◈) Chen et al. [37], (◆) Dietzel et al. [38]. Surface areas obtained from BET method except ref. [22] where surface area is sum of micro and external surface area from *t*-method.

makes these materials less suitable for obtaining high hydrogen adsorption capacities than carbon materials where greater scope for optimization of the porous structure is available [8]. Takagi et al. obtained similar results for two zeolites to those obtained for carbons [22].

3.3. Metal organic framework materials (MOFs)

A wide variety of porous MOFs have been synthesized [7,26–40] and these differ from porous carbons, etc., in that systematic design strategies can be used for developing new materials. In some cases, the frameworks are flexible and some structures have windows which need to open in order to allow guest access to the porous structure [29,49–51]. The aim is to optimize the design of the pore structure and surface chemistry of the framework for hydrogen adsorption. The crystalline structure of many MOFs allows a detailed study of hydrogen adsorbed in the pores. Takamizawa and Nakata used X-ray diffraction studies for the direct observation of the H_2 dense aggregates in the adsorbed state in metal organic framework $[Rh(II)(bza)_4(pyz)]_n$, where bza = benzoate, pyz = pyrazine; at 90 K [52]. This clearly shows aggregates of hydrogen molecules, which form the adsorbate phase in pores. Spencer et al. have reported variable temperature single crystal Laue neutron diffraction studies of hydrogen loaded Zn_4O(1,4-benzenedicarboxylate)$_3$ [53]. The nodal regions appear to be the sites for hydrogen adsorption. Two sites were identified; one located over the shared vertex of the ZnO_4 units at the center of the node and the other over the face of ZnO_4 tetrahedra.

Recent studies have reported hydrogen adsorption isotherms for over 30 MOFs at pressures up to ~1 bar with porous structure characterization data derived from both crystallographic and gas adsorption data for the materials [7,26–40]. The data for hydrogen adsorption capacities for MOFs at 1 bar are plotted against surface area and compared with those obtained for porous carbons, silicas, aluminas and zeolites in Fig. 8. It is apparent that there are marked similarities with the data for hydrogen adsorption on MOFs overlapping with the data for other porous materials. As mentioned earlier, the use of a hydrogen capacity measurement at 1 bar and 77 K is limited because the shapes of isotherms differ and it is more appropriate to compare the maximum hydrogen capacity with pore structure characteristics. This requires hydrogen adsorption measurements at high pressure where experimental difficulties are greater and only limited information is available.

Zhao et al. found that $Ni_3(btc)_2(3\text{-pic})_6(pd)_3$ {btc = benzene 1,3,5-tricarboxylic acid; 3-pic = 3-picoline; pd = 1,2-propandiol} adsorbed ~2.6 wt% of hydrogen at 2 MPa and 77 K [29]. Ferey et al. synthesized a MOF MIL-101 with stoichiometry $Cr_3F(H_2O)_2[O_2C)C_6H_4(CO_2)]_3{\cdot}nH_2O$ [26]. This material has a zeotype cubic structure with a very large cell volume (~702,000 Å^3), and hierarchy of very large pore sizes (approximately 30–34 Å). The material had a nitrogen pore volume 2.0(1) cm^3 g^{-1} and Langmuir surface area of ~5900 m^2 g^{-1}. Hydrogen adsorption studies showed that the material adsorbed 4.5 wt% at 77 K and 3 MPa.

Wong-Foy et al. have studied hydrogen adsorption on seven MOFs at high pressure and 77 K [36], with four of these materials having been included in a previous low pressure study [27]. The variation of uptake at saturation with Langmuir surface area is shown in Fig. 9. It is evident that there is an approximate linear correlation between hydrogen saturation uptake and surface area. The pressures at which saturation occurs varies quite markedly between samples and the highest saturation uptake was 7.5 wt% at ~70 bar for MOF-177. The hydrogen adsorption data were also compared on a volumetric basis since this is also a practical limitation for hydrogen storage for use in transportation applications. The volumetric uptakes were quite similar (±20% range) despite the wide range on a gravimetric basis. Structures with high surface area and moderate density provide the highest storage density on a volumetric basis. IRMOF-20 had the highest capacity on a volumetric basis. The results showed volumetric capacities up to 34 g L^{-1} which compares with the DOE target of 45 g L^{-1} for a practical system for 2010.

Lin et al. synthesised three copper co-ordination framework materials based on biphenyl, terphenyl and quaterphenyl tetracarboxylic acids with formulas, $[Cu_2((OOC)_2C_6H_3{\cdot}C_6H_3\ (COO)_2)(H_2O)_2]$, $[Cu_2((OOC)_2C_6H_3{\cdot}C_6H_4{\cdot}C_6H_3(COO)_2)(H_2O)_2]$ and $[Cu_2((OOC)_2C_6H_3{\cdot}C_6H_4{\cdot}C_6H_4C_6H_3(COO)_2)(H_2O)_2]$ [7]. The variation in length of the organic backbone of these ligands gave a series of structural analogues in terms of framework structure and topology which showed a correlation of pore size with gas adsorption behaviour. In this series of materials, the density of the adsorbed hydrogen decreased with increasing pore size while the amount adsorbed increased. This suggests that there is an optimum pore size for hydrogen adsorption. There are now four reported metal organic co-ordination frameworks $[Cu_2((OOC)_2C_6H_3{\cdot}C_6H_4{\cdot}C_6H_3(COO)_2)(H_2O)_2]$ [7], $[Cu_2((OOC)_2C_6H_3{\cdot}C_6H_4{\cdot}C_6H_4C_6H_3(COO)_2)(H_2O)_2]$ [7], MOF-177 [36] and IRMOF-20 [36] which have >6 wt% H_2 storage capacity at 77 K and moderate

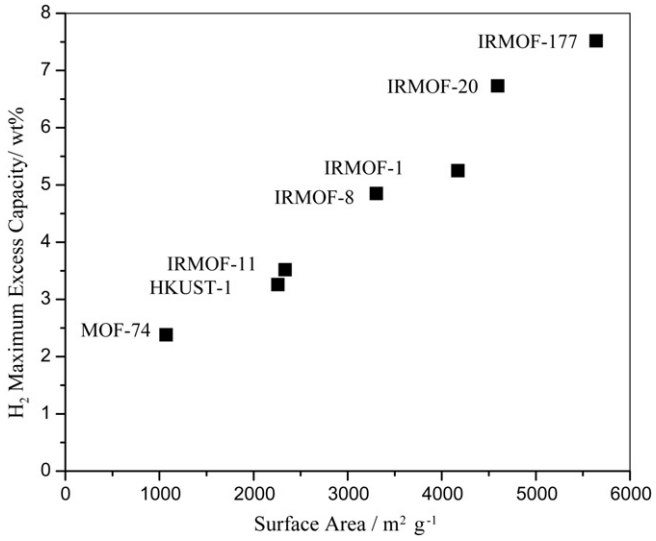

Fig. 9. The variation of H_2 adsorbed at saturation with Langmuir surface area for porous metal organic framework materials at 77 K [36].

pressures (<80 bar), the H_2 storage capacity target of the 2010 DOE guideline. The volumetric capacity of $[Cu_2((OOC)_2C_6H_3{\cdot}C_6H_4{\cdot}C_6H_3(COO)_2)(H_2O)_2]$ was 43.6 g L^{-1} and this is very also close to the U.S. DOE 2010 target of 45 g L^{-1}.

Panella and Hirscher have reported hydrogen adsorption studies of IRMOF-1 at room temperature and 77 K for pressures in the range 1–67 bar [28]. The agreement with previous work was good for adsorption at 77 K but the material only had an uptake of 0.2 wt% at room temperature and 67 bar. Similar results were obtained for H_2 adsorption on $Ni_2(dhtp)(H_2O)_2{\cdot}8H_2O$, where dhtp is the anion of 2,5-dihydroxyterephthalic acid. This MOF has one-dimensional cylindrical pores [38]. Ferey et al. reported similar values 0.45 wt% at 293 K and 2 MPa for hydrogen adsorption on MOF MIL-101 [26]. The low adsorption hydrogen uptake on MOFs at room temperature and high pressure is in agreement with similar studies for carbon materials [4,12,14,17,22,23]. Therefore, currently there is little evidence for very marked differences in hydrogen adsorption capacity characteristics for porous carbons, aluminas, silicas, zeolites and MOFs.

Some differences are observed for hydrogen adsorption on 'rigid' adsorbents, such as activated carbons and flexible porous framework materials. These differences are related to the presence of narrow windows and pore cavities in some MOFs where the windows influence the adsorption/desorption kinetics [29,49–51]. In the case of MOFs, the pore structures are well defined and there is need for systematic studies in order to link porous structure with adsorption characteristics. Porous metal organic framework materials with the formula $Ni_2(bipy)_3(NO_3)_4$ templated with methanol (**M**) and ethanol (**E**) have subtly different structures [29,49–51]. Both have narrow windows, pore cavities and structural flexibility is required to allow the adsorption of the templates. **E** has a total pore volume of 0.149 $cm^3\ g^{-1}$ and windows 2.32 Å × 2.75 Å whereas **M** has window of 2.5 Å × 4.9 Å and a total pore volume of 0.181 $cm^3\ g^{-1}$. The kinetic trapping effect involves hysteretic adsorption. In these materials, hydrogen loaded at higher pressures does not desorb due to the presence of windows in the structure and stiffening of the flexible framework when filled with hydrogen. The hydrogen adsorption and desorption isotherms for **E** and **M** at 77 K are compared with those of an activated carbon (**AC**) and chiral framework (**C**: $(Ni_3(btc)_2(3\text{-pic})_6(pd)_3$ {btc = benzene 1,3,5-tricarboxylic acid; 3-pic = 3-picoline; pd = 1,2-propandiol})) in Fig. 10. This shows the isotherm adsorption/desorption hysteresis for **E** and **M** and virtually no hysteresis for **AC** and **C**. Fig. 11 compares the desorption isobars for **E** and **M** with **AC** and **C**. These measurements show that hydrogen desorption from **E** and **M** is restricted until 110 K. This is a proof of principle and the challenge is to increase the temperature when desorption starts as well as the hydrogen capacity of the materials, since both aspects are essential for a viable hydrogen storage system.

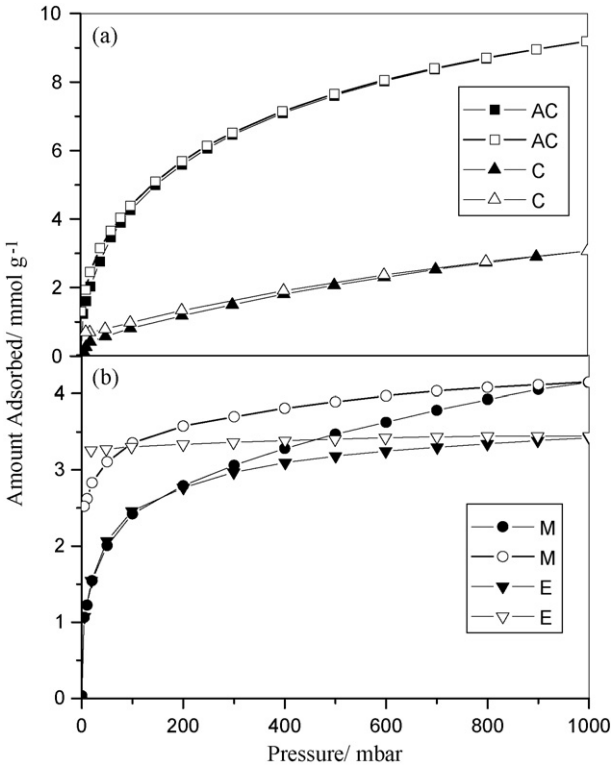

Fig. 10. Adsorption–desorption isotherms for H_2 adsorption (filled symbols) and desorption (open symbols) isotherms on adsorbents at 77 K [29]: (a) **AC** (■, □); **C**(▲, △); (b) **M** (●, ○); **E** (▼, ▽).

3.4. Porous polymers

Polymers usually have conformational and rotational freedom so that they pack efficiently and do not have high surface areas. However, recent developments included rigid structures that provide porous materials with higher surface areas (500–1600 $m^2\ g^{-1}$). The low intrinsic density due to being composed of only light elements is an advantage and they

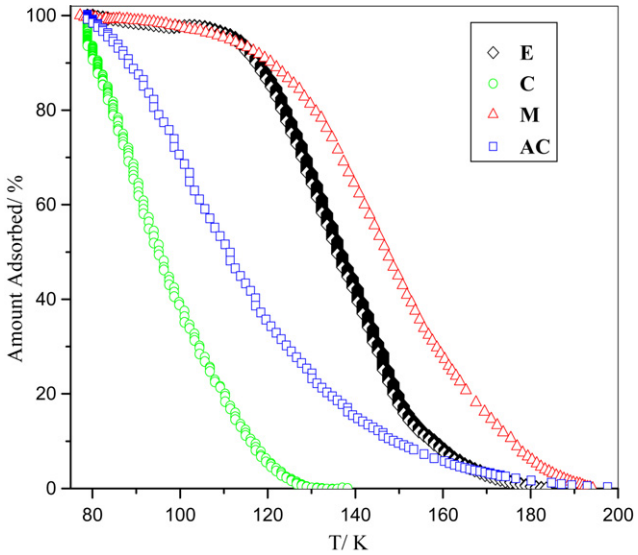

Fig. 11. Isobars for desorption of hydrogen from **AC** activated carbon G209 (□), **E** polymorph of $Ni_2(4,4'\text{-bipyridine})_3(NO_3)_4$ (◇), **M** polymorph of $Ni_2(4,4'\text{-bipyridine})_3(NO_3)_4$ (△), C Ni3(btc)2(3-pic)6(pd)3(○) {btc = benzene 1,3,5-tricarboxylic acid; 3-pic = 3-picoline, pd = 1,2-propandiol} at 1 bar hydrogen pressure [29].

also have good thermal and chemical stability. These porous materials, which include hyper crosslinked organic polymers have been considered as materials for hydrogen storage [41–44]. H_2 adsorption of 1–1.4 wt% at 1 bar and 77 K was observed on organic polymers with surface areas of 760–830 $m^2\ g^{-1}$ and this is within the range of values obtained for activated carbons and metal organic framework materials (see Fig. 8) [43]. A similar value of 1.5 wt% uptake of H_2 at 0.12 MPa and 77 K for a polymer with a surface area of 1930 $m^2\ g^{-1}$ has been reported [42]. The corresponding H_2 uptakes at 10 bar were in the range 1.4–1.7 wt% at 77 K. Higher pressure studies have shown a ~3 wt% H_2 adsorption at 15 bar on a material prepared by the polymerization of vinyl benzyl chloride by a Friedel-Crafts post-crosslinking reaction in dichloroethane at 353 K using $FeCl_3$ as the catalyst and this is the highest hydrogen uptake value obtained so far for a polymer [41]. This value is lower than the maximum uptakes observed for MOFs (7–7.5 wt%) [7,36] and activated carbons (~5 wt%) at 77 K [12] but further developments may be anticipated.

3.5. Porous structure characteristics for H_2 adsorption

The interaction between a poorly polarizable H_2 molecule and pore surfaces is weak but this interaction is enhanced in narrow pores ($\lesssim$0.7 nm). The enthalpies for adsorption of hydrogen on carbons are in the range 4–8 kJ mol^{-1} [4,13,54–56]. In comparison, recent adsorption studies of porous metal organic framework materials IRMOF-1, IRMOF-11, MOF-74 and HKUST-1 indicate that the corresponding enthalpies for hydrogen adsorption at low temperature are in the range 5–9 kJ mol^{-1} and decrease with amount adsorbed [27]. Kaye et al. measured the enthalpies of adsorption for $M_3[Co(CN)_6]_2$ (M = Mn, Fe, Co, Ni, Cu and Zn) and $Zn_4O(BDC)_3$ (BDC = 1,4-benzenedicarboxylate) [34]. The enthalpies of adsorption decreased slightly with increasing surface coverage and were in a relatively narrow range of 5.3–7.4 kJ mol^{-1} for the $M_3[Co(CN)_6]_2$ series compared with 4.7–5.2 kJ mol^{-1} for $Zn_4O(BDC)_3$. The higher values for the former were attributed to the presence of co-ordinatively unsaturated metal centers and the order of the enthalpies followed the Irving Williams stability order with the exception of the Ni systems. Studies of hydrogen adsorption on silica gels gave heats of adsorption in the range 5.4–7.3 kJ mol^{-1} and for zeolites (4 Å, 5 Å and 13×) 5.9–7.9 kJ mol^{-1} [57]. Slightly larger values for the isosteric heat of adsorption in the range 6.2–10.7 kJ mol^{-1} were obtained for zeolite Na-A over the temperature range 40–120 K [57]. Germain et al. reported that the initial heat of adsorption of H_2 on a nanoporous hyper-crosslinked polymer was 6.6 kJ mol^{-1} [42]. Hence, there is similarity between the heats of adsorption of hydrogen on a wide range of porous materials.

Recently, the synthesis of MOFs with unsaturated metal sites has been proposed as a method for increasing the H_2 adsorption enthalpies so that the amounts and temperature dependence of H_2 adsorption are improved [33,37,39]. Foster et al. [39] studied hydrogen adsorption on nanoporous nickel (II) phosphates VSB-1 and VSB-5 [39]. VSB-5 adsorbed substantially more hydrogen at low pressure and temperature programmed desorption studies showed that hydrogen had a strong interaction with VSB-5 with the main desorption peak at 109 K and a small shoulder at 149 K. The strong interaction was confirmed by inelastic neutron scattering studies. VSB-1 did not show a similar interaction. It was proposed that co-ordinatively unsaturated Ni^{2+} sites accessible to H_2 molecules existed in VSB-5 which gave unique surface chemistry.

When the data H_2 adsorption at 1 bar and surface area for MOFs with unsaturated metal sites [33,37,38] are plotted in Fig. 8, it is evident that they also fit the correlation very well. Yang and Zhong carried out a combined grand canonical Monte Carlo simulation and density functional theory calculation of H_2 adsorption on MOF-505, which has co-ordinatively unsaturated metal sites [58]. They concluded that metal oxygen clusters were preferential adsorption sites for hydrogen, while the strongest adsorption was in the directions of co-ordinatively unsaturated open metal sites. The open metal sites had an increased adsorption at low pressure but at high pressure, the primary controlling factors were the pore volume and available surface area. The disadvantage of open metal sites is that they only represent a small proportion of the available surface area in MOFs and in real situations, trace impurities in H_2, such as water, may be adsorbed on these sites.

The relationships between hydrogen adsorption and porous structure characteristics are complex. Maximum hydrogen adsorption capacity and surface area have an approximate linear correlation for MOFs (see Fig. 9). A correlation between maximum hydrogen adsorption capacity and micropore volume has also been observed to be close to linearity for carbons with a wide range of functionalities and porous structures (see Fig. 5). These correlations indicate the primary importance of porous structure characteristics and secondary significance of surface interactions. Materials with large total pore volumes do not necessarily have correspondingly high hydrogen adsorption capacities. It is evident that narrow pores, where the adsorption potential is increased, are required for adsorption at low pressure. Large pores provide increased adsorption capacity at high pressures. Therefore, when synthesizing porous structures for hydrogen adsorption, there is a compromise which has to be made between adsorption capacity and adsorption at low pressure. There is also some evidence that the density of adsorbed hydrogen decreases with increasing pore size [7]. The results available indicate that at ambient temperatures and pressures up to 6 MPa, the amounts of H_2 adsorbed are <0.5 w% for carbon, zeolite and MOF materials. In the case of flexible porous MOFs, possible future directions for research include enhancing interactions between hydrogen and pore walls by functionalization to modify the surface interactions, the inclusion of unsaturated metal sites and enhancing the temperature dependence of storage capacity by kinetic trapping of hydrogen.

4. Conclusions

Hydrogen adsorption on porous materials is still in the early stages of development as a method of storage with the major

effort focused on developing materials with improved hydrogen storage capacities to meet U.S. DOE targets to develop and verify on-board hydrogen storage systems achieving 6 wt% and 45 g L^{-1} for 2010. Currently, a maximum of ~5 wt% of hydrogen can be adsorbed at 77 K and high pressure on rigid porous carbons while adsorption of ~7.5 wt% of hydrogen has been observed for porous metal organic framework materials under similar conditions. The discovery of new materials with enhanced H_2 storage performance at 77 K may be anticipated. The maximum amount adsorbed is limited by the H_2 adsorbate density, adsorbent pore structure and pore volume available in the narrowest pores. Adsorption of hydrogen at ambient temperatures and high pressures has produced inconsistent reports of uptakes. This is due to major experimental difficulties with the adsorption of impurities, isotherm corrections at high pressure, etc. However, recent results suggest that the amounts of hydrogen adsorbed are very small under high pressure and ambient temperature conditions. Fast adsorption/desorption kinetics and relatively small ($\lesssim$10 kJ mol^{-1}) adsorption enthalpies are observed for hydrogen adsorption on many porous materials which indicates that physisorption on porous materials is suitable for fast recharging with hydrogen. The narrowest pores make the biggest contribution to hydrogen adsorption capacity whereas mesopores contribute to total pore volume, but little to hydrogen capacity, and are detrimental for volumetric capacity. Porous materials with very narrow pores or pore size distributions are required for enhanced hydrogen capacity at low pressures.

The temperature dependence of hydrogen adsorption is a major consideration for storage applications. It is not clear from the results available to date that increasing the pressure will be sufficient to increase the adsorption capacity at ambient temperatures to a similar level to that achieved at 77 K. Kinetic trapping of hydrogen occurs in some metal organic framework materials and this is a method where there are possibilities for improving the temperature dependence of hydrogen adsorption. Design strategies are necessary for synthesis of metal organic framework materials with improved adsorption capacity, enhanced H_2 surface site interactions with higher enthalpies of adsorption and improved kinetic trapping characteristics. Improvements in hydrogen adsorption capacity of MOFs require an improved understanding of optimization of adsorption sites, while secondary interactions, which allow framework flexibility and window opening in MOFs are important in kinetic trapping characteristics.

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