Energy storage in carbon nanoparticles

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TECHNOLOGICAL
UNIVERSITY**

ENERGY STORAGE IN CARBON NANOPARTICLES

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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ENERGY STORAGE IN CARBON NANOPARTICLES

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Summary

Hydrogen (H_2) and methane (CH_4) are clean energy sources, and their storage in carbonaceous materials is a promising technology for safe and cost effective usage of the energy gases in transportation/power industries. In this thesis, high quality activated carbons (AC) prepared via template synthesis method (referred to as templated carbon or TC) were investigated for hydrogen and methane storage. TCs were synthesized using zeolite Y as the template and with different carbon sources. TC samples were characterized with various experimental techniques and evaluated for their performance as the adsorbents for hydrogen/methane storage.

The research work carried out in the dissertation mainly includes three parts. The first concentrates on TC preparation using different carbon sources, their characterization and H_2/CH_4 storage capacities at different conditions. TC prepared using sucrose as the carbon source (TC S1100) possesses a BET surface area of $\sim 1500\text{ m}^2/\text{g}$ -carbon, a total pore volume of $\sim 1.4\text{ cc/g}$. The sucrose-derived TC exhibits good methane storage capacity of $\sim 180\text{ cc-STP/g}$ at 300 K and 35 bar. To overcome the defect of low bulk density of the as-synthesized carbon flakes, carbon pellet was fabricated using a polymer binder on which the methane storage capacity was significantly improved to 93 on the volumetric basis (v/v) (The volume of gas stored per unit volume of adsorbent). TC S1100 presents a hydrogen uptake of 2.4% on the weight basis (wt%) at 77 K and 10 bar. The high value of the isosteric heat of hydrogen adsorption ($\sim 8000\text{ J/mol}$) reveals that TC possesses a portion of small micropores which was subsequently confirmed by CO_2 sorption at 273K.

TC derived from PFA (poly-furfuryl alcohol) (TC C1050) presents a BET surface area of $\sim 2500\text{ m}^2/\text{g}$ by argon adsorption and a total pore volume $\sim 1.5\text{ cc/g}$. A major micropore peak was found at the pore size of 1.3 nm. TC C1050 presented a methane storage capacity of $\sim 246\text{ cc-STP/g}$ at 35 bar and 298 K, and a gravimetric hydrogen storage capacity of 2.6 wt% at 10 bar and 77 K. At 303 K and 50 bar, TC C1050 exhibits a hydrogen storage capacity of $\sim 1.0\text{ wt\%}$, which is superior to the commercial single wall carbon nanotubes (SWCNT) and some commercial ACs. The isosteric heat of hydrogen adsorption was found about 7800 J/mol at the low surface loading. TC

C1050 was also found to possess excellent pelletisation properties. A simplified binderless hot-compression technique was developed to fabricate TC pellets. TC pellet C1050P presents a bulk density of ~ 0.98 g/cc, an ultimate tensile stress of 1 MPa, and a high volumetric methane capacity of 127 v/v.

Secondly, the development in the porous structure of TCs was investigated under various carbonization temperatures. It was found that a high carbonization temperature generally results in TCs with a higher surface area and more pore volume, but too high temperature will collapse micropores and reduce the microporosity. The carbonization temperature was found to significantly affect the degree of graphitization and the pore size distributions of TCs. Analysis shows that there exists an optimal temperature, which balances the pore size, surface area, and the pore volume of TCs.

Thirdly, the adsorption kinetics of methane was studied on C1050 and C1050P using the linear driving force (LDF) model and the Fickian diffusion (FD) model. It was found that the LDF model can adequately describe the batch adsorption kinetics on both TC C1050 and TC pellet C1050P.

In addition, for a comparison, a commercial AC and a commercial SWCNT were also investigated for their applications in H_2/CH_4 storage. However, the adsorption capacities were found low on these commercial products. It was concluded that these commercial products were unsuitable for energy storage unless their structures are modified for the specific applications.

In conclusion, this thesis studies have demonstrated that the template synthesized carbons possess good potential for the energy storage applications. TCs synthesized and the carbon pellets developed for methane storage are close to the practical target for ANG applications. The more effective hydrogen storage would require TCs with micropores predominantly in the size range of 0.6-0.9 nm. The future research efforts should be focused on the increase in the volume fraction of small micropores in TCs.

List of publications

Papers resulted from this thesis:

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2. Guan, C.; Su, F.; Zhao, X. S.; Wang, K., Methane storage in a template-synthesized carbon. *Sep. & Purif. Tech.* (2008) 64, 124-126.
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4. Guan, C.; Yang, C.; Wang, K., Methane storage in a commercial activated carbon. *Carbon – Sci. Tech.* (2008), 1, 16-17.
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List of Abbreviations

AC	activated carbon
ANG	adsorbed natural gas
CNG	compressed natural gas
CNF	carbon nanofiber
CNT	carbon nanotube
CVD	chemical vapor deposition
DOE	Department of Energy, USA
FD	Fickian diffusion model
IUPAC	International Union of Pure and Applied Chemistry
LDF	linear driving force model
LJ	Lennard-Jones' potential
MOF	metal organic framework
MWCNT	multi-walled carbon nanotube
NG	natural gas
NLDFT	non-local density functional theory
OMC	ordered microporous carbon
PFA	polyfurfuryl alcohol
PSA	pore and surface analyzer
PSD	pore size distribution
SEM	scanning electron microscopy
SSA	specific surface area
STP	standard temperature and pressure, T=273.15 K, P=760 torr
SWCNT	single-walled carbon nanotube
TC	templated carbon
TGA	thermal gravimetric analysis
TEM	transmission electron microscopy
XRD	X-ray diffraction

List of Symbols

A_{cs}	cross-sectional area A_{cs} for an adsorbate molecule (nm^2)
b	adsorption affinity
C_μ	adsorbed phase concentration (mmol/g)
$C_{\mu s}$	saturation capacity of the adsorbent
D/R^2	diffusion time constant (s^{-1} , for spherical particles with uniform radius R)
D/l^2	diffusion time constant (s^{-1} , for slab particle with the thickness of $2l$)
J_μ	adsorbed phase flux ($\text{mol/m}^2/\text{s}$)
k_L	rate constant of adsorption (s^{-1})
N_A	Avogadro number ($6.023 \times 10^{23} \text{ mol}^{-1}$)
q	amount adsorbed (mmol/g)
q_m	maximum monolayer capacity (mmol/g)
P	adsorbate pressure (bar)
p/p_0	relative pressure
Q_{iso}	isosteric heat of adsorption (kJ/mol)
R	gas constant (8.31 J/mol/K)
S_{BET}	BET-specific surface area (m^2/g)
t	heterogeneity parameter of the adsorbent
T	temperature (K)
V_t	total pore volume (cc/g)
V_{mic}	micropore volume (cc/g)
V_{me}	mesopore volume (cc/g)
W	the pore width (nm)
ε_{HC}^*	potential well depth (J/mol)
ε/k	Molecular property (K , k is Boltzman Constant, $1.3807 \times 10^{-23} \text{ J/K}$)
Δ	distance between two graphite lattice layers in the pore wall (0.335 nm)
ρ_s	number density of carbon molecules per unit volume of the pore wall (114 nm^{-3})
ρ_c	bulk density of carbon (g/cc)

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CHAPTER 1 INTRODUCTION

1.1 Energy gas storage applications

Sustainable energy supply is one of the most urgent issues facing the world today. The excessive consumption of fossil fuels in the past has caused quick depletion of natural resources and resulted in environmental problems such as atmospheric pollution and global warming. People are working hard to search for more energy reserves (or alternatives) and, meanwhile, to develop technologies with higher energy efficiency and lower emissions. Among these technologies, the utilization of natural gas (NG, with methane > 70%) and hydrogen as fuels represents promising short-term and long-term solutions, respectively. Hydrogen is largely considered as a potential solution of the energy issues in the future. However, there are some difficult technical barriers ahead of the so-called hydrogen economy [1]. On the other hand, methane-enriched nature gases can be utilized in large scale with current mature technologies

Hydrogen (H_2) is a “green” energy if it is derived from renewable sources. As a fuel, it has the highest energy content on the basis of per unit mass and it is “clean” because it produces only water upon oxidation. Methane (CH_4), the major component of NG, is also a clean energy next to hydrogen due to its high hydrogen content. Its large quantity in natural reserves, relatively cheap price and cleaning burning nature make it a very attractive fuel for the automobile/power industries. The use of NG as a vehicular fuel has grown considerably in recent years. More and more NG vehicles (buses and cars) are appearing in the streets of urban areas where air quality has become a major public concern.

However, safe and efficient storage of the energy gases still poses a major technical challenge for their large-scale use in automobile industries. The current storage technology is mainly by mechanical compression, in which H_2/CH_4 gases are compressed into metal cylinders at the pressure range of 200~300 bar. In addition to the safety concern, the compression process is energy intensive, and such kind of storage tanks is expensive. Therefore, new storage technologies are highly desirable. US

Department of Energy (DoE) has set the practical targets for energy gas storages technologies [2,3] to compete with the compression technology and the current liquid fuel tank. Table 1-1 lists the DoE targets while Table 1-2 shows the energy densities of a number of fuels.

Table 1-1 DoE targets for CH₄/H₂ storage [2,4] and their property data [5]

	Gravimetric capacity (wt %)	Volumetric capacity	Time line (year)	Properties of CH ₄ /H ₂		
				T _C (K) ^b	T _B (K) ^c	H _C (kJ/g) ^d
CH ₄	35%	180 v/v ^a	-	191	112	50.0
H ₂	6%	5.4 GJ/m ³	2010	33.3	20.4	120
	9%	9.7 GJ/m ³	2015			

^aThe volume of gas delivered per volume of the storage container at 35 bar, 298 K;

^bCritical temperature; ^cBoiling point at 1 atm; ^dHeat of combustion.

Table 1-2 Energy densities of some fuels [6]

Type of Fuels		Volumetric energy density (GJ/m ³)
Diesel		35
Petrol		32
Methanol		16.5
LPG (Propane)		27
Natural Gas	liquid (111 K)	21
	gas (300 bar)	12.2
	gas (200 bar)	9
Hydrogen	metal hydride	12
	liquid (20 K)	8
	gas (300 bar)	2.5
	gas (248 bar)	2.4
	gas (200 bar)	2.3

1.1.1 Hydrogen storage

The development of safe and effective storage technology is a key issue for hydrogen economy ahead [6]. Hydrogen presents a high energy density on gravimetric basis with the heat of combustion of 120 kJ/g, which is about three times that of gasoline. However, its energy density on volumetric basis is low (See Table 1-2), due to the low density of the gas [5]. For mobile applications, such as fuel cell cars, the hydrogen storage tanks should be compact, safe (low in pressure) and not too expensive. What is more, the on-board storage system should allow a driving ~500 km with a single-charge. With these targets, DoE suggested that the on-board hydrogen storage system should reach a storage capacity of 6% by weight (or wt%) by 2010. This capacity has been revised and upgraded to 9 wt% for the year of 2015 (Table 1-1).

The current and potential hydrogen storage technologies are [7]:

1. *Fuel tank*: This option is simple and easy to install, but the storage of large amounts of hydrogen requires either liquefaction at ultra-low temperature or deep compression at high pressure. Both processes are energy intensive and with safety concerns [7,8].

2. *Metal hydride*: This technology, which is based on the chemical reaction between hydrogen and metals, has the merits of low storage pressure and good capacity. But it also has a number of disadvantages and unsolved issues such as reversibility, slow kinetics in charge-regeneration cycle, expensive, and some safety concerns, etc. [7].

3. *Physical adsorption in porous materials*: Nanoporous adsorbent materials such as zeolites [9], metal organic framework (MOF) [10], and activated carbons [11] can offer a high surface area and relatively strong adsorption affinity within their microporous networks. This technology presents the advantage of simplicity, safety, low cost, and with good reversibility. However, it has disadvantages such as difficult to achieve sufficiently high storage capacity especially at room temperature. The main challenge for this technology is to develop adsorbents with very high surface areas and pores of optimal/uniform sizes towards the adsorbate molecules [12].

1.1.2 Methane storage

Currently, compressed natural gas (CNG) is being used commercially worldwide (with the storage pressure > 200 bar), which is energy intensive and with safety concerns. The adsorbed natural gas (ANG) technology is under intensive research because it offers the prospect of low energy costs and better safety (at the storage pressure of ~ 35 bar).

The performance of an adsorbent in ANG storage systems is evaluated/compared with the parameter of ‘delivered v/v’, that is, the volume of gas delivered per volume of the storage container. To compete with CNG technology, the DoE target for ANG technology has been set at 180 v/v at 298 K and 35 bar [4] (Table 1-1). Currently, physical adsorption in nanoporous activated carbons is the predominant technology under research for ANG applications [3,13].

1.2 The objectives of the thesis research

It can be seen from the above introduction that energy gas adsorptive storage is a promising energy storage technique. However, it's necessary to obtain novel adsorbents with high energy gas storage (hydrogen/methane) capacity and relative fast rate of charge/discharge (kinetics). A reliable technology for adsorbent synthesis and the theories for structural characterization are urgently needed for the development/application of energy gas storage.

In this thesis research, high performance ACs will be prepared via template synthesis method, in which carbon sources (precursors) are introduced into the highly ordered microporous channels of zeolites (the template) where they are carbonized via the controlled pyrolysis. These novel carbons (termed as the templated carbons or TCs) will be tested for energy storage (H_2 and CH_4) and compared with the performance of some commercial carbonaceous adsorbents. The objectives of the research are to develop TCs with good capacity for the storage application of energy gases (H_2 and CH_4). Meanwhile, application of existing theories/techniques for structural development and characterization will be investigated and linked to the storage performance. The

adsorption kinetics, pelletisation technique, and the synthetic conditions for sample preparations such as the carbonization temperature and carbon precursors will also be investigated for TCs in the related energy storage applications.

1.3 Overview of the thesis

The thesis consists of 9 chapters:

Chapter 1 outlines the motivation and background of the study and provides the objectives of the thesis research.

Chapter 2 reviews the current research on technologies for hydrogen and methane storage, with the emphasis on template synthesized carbon adsorbents in energy storage applications.

Chapter 3 describes the experimental studies, including sample synthesis, structural characterization, storage test, and measurement of adsorption equilibrium and kinetics.

Chapter 4 presents the results of hydrogen and methane storage in some commercial ACs and commercial CNTs.

Chapter 5 presents studies of methane storage on the two TC samples, in which the structural characterization, methane storage and pelletisation technology are developed and discussed.

Chapter 6 presents investigation of hydrogen storage on two TC samples which are synthesized using zeolite Y as template while sucrose and PFA are used as the carbon sources.

Chapter 7 presents studies of the structural development in TCs prepared under different carbonization temperatures and the energy storage performances of a few TC samples for methane/hydrogen.

Chapter 8 presents the analyses/modeling of the adsorption kinetics of methane in TCs and TC pellets.

Chapter 9 gives the conclusion of this thesis and outlines the recommendations for the future studies.

CHAPTER 2 LITERATURE REVIEW

2.1 Carbonaceous adsorbents

Carbonaceous adsorbents include activated carbon (AC), activated carbon fiber (ACF) and carbon nano-structures such as carbon nanotube (CNT) and carbon nanofiber (CNF). These materials have been under intensive researches for the application of energy storage and are introduced here.

2.1.1 Activated Carbon (AC)

ACs are used in a wide range of applications [14], such as air/water purification, gas/liquid separation, and energy storage [15]. ACs are produced from a range of carbonaceous precursors such as: biomass, coal, and polymeric compounds [16]. The production methods generally includes: (1) physical activation; and (2) chemical activation [16]:

1. Physical activation: This is a two-step method involving pyrolysis of a carbonaceous material (carbon precursor) followed by the gasification reactions (activation) of the resulted char at elevated temperature. The most popular activation agents are carbon dioxide and steam. The pyrolysis temperature ranges from ~700 K to ~1100 K while the activation temperature ranges from ~850 K to ~1150 K.

2. Chemical activation: This method mixes the carbon precursor with the chemical activating agents (e.g. ZnCl_2 , KOH, NaOH, and H_3PO_4 , etc.) which functions as both the dehydrating agent and the oxidant. Chemical activation is single-step with relatively lower temperature (about ~770-1050 K). However, the use of chemical activation agents raises some concerns in environmental aspects.

Figure 2.1 shows the schematic diagram of the graphitization in carbon during the activation process [17]. In general, a portion of the isotropic units (amorphous carbon) gains a degree of anisotropy and transform to graphitic carbon. This graphitization

process depends on the properties of the carbon precursors, and is a function of the activation agent and the thermal treatment temperature etc.

Figure 2.1 Schematic diagram of the graphitization process at different activation temperatures [17].

The graphite domains in ACs accommodate slit-shaped micropores, mesopores, and macropores between graphite layers (intraparticle) and among the graphite crystals (interparticle) which provide high adsorption potential and capacities. For energy storage application, the adsorption capacity predominantly resides in micropores [18].

2.1.2 Carbon nanotube (CNT) and carbon nanofiber (CNF)

CNTs can be visualized as the hollow tubes made of graphite sheets with the diameters in the nanometer scale. Depending on the number of graphite layers in the tube-walls, CNTs can be classified into single-walled carbon nanotubes (SWCNTs) (See Figure 2.2) and multi-walled carbon nanotubes (MWCNTs) (See Figure 2.3b). CNTs provide graphite pores of cylindrical configuration which may present high adsorption potential, capacity, as well as selectivity for molecules with specific molecular structure and dimension. The interlayer distance of the MWNT is similar to the interlayer distance in graphite (0.34-0.36 nm). SWCNTs and MWCNTs are usually several micrometers in their length.

Figure 2.2 Schematic structural diagram of the SWCNT [11].

Figure 2.3 Schematic structure of CNTs and CNFs: (a) SWCNT; (b) MWCNT; (c) CNF, deck-cards; (d) CNF, hollow fish-bone; (e) CNF, solid fish-bone; and (f) CNF, ribbon-like. [11]

The adsorption sites in CNTs include: (1) inner tube; (2) outer surface; and (3) voids formed among tubes and bundles/ropes. The storage capacities depend on many

structural parameters such as: surface area, tube diameter, length, defects, voids, arrangement of the tubes and bundles, etc. [19].

CNF has graphite platelets, which can be formed via vapor deposition at elevated temperatures with the aid of a catalyst. The structure of CNF depends on the properties of the catalyst and the reaction conditions used (See Figure 2.3). The graphite platelets within a CNF accommodate capacity sites for gas storage.

2.1.3 Mechanisms of physical adsorption

Dispersive interaction is the main interaction between an adsorbate molecule (e.g. H₂) and carbon atom on the graphite sheet (basal plane). Such an interaction can be adequately described by the famous Lennard-Jones' 12-6 potential theory (LJ 12-6):

$$V(Z) = 4\varepsilon_{HC} \left[\left(\frac{\sigma_{HC}}{Z} \right)^{12} - \left(\frac{\sigma_{HC}}{Z} \right)^6 \right] \quad (2-1)$$

where V is the dispersive potential energy, Z is the distance between the carbon atom on the basal plane and the adsorbate molecule. σ_{HC} and ε_{HC} are the cross LJ parameters, which can be calculated using the Lorentz-Berthelot rule, respectively, as below:

$$\sigma_{HC} = \frac{\sigma_{HH} + \sigma_{CC}}{2}, \quad \varepsilon_{HC} = \sqrt{\varepsilon_{HH} \times \varepsilon_{CC}} \quad (2-2)$$

The dispersive interaction potential between an adsorbate molecule confined in a pore and all carbon atoms in pore walls is the summation of all the pair-wise interaction potential energies. At certain conditions, this summation can be expressed in the form of integrations. With the assumptions that the pores in ACs are slit-shaped while pore walls are made of many layers of parallel graphite sheets, this dispersive potential energy will take the popular form of LJ 10-4-3 potential:

$$V(r, z) = \frac{5}{3} \varepsilon_{HC}^* \left\{ \frac{2}{5} \left[\left(\frac{\sigma_{HC}}{r+z} \right)^{10} + \left(\frac{\sigma_{HC}}{r-z} \right)^{10} \right] - \left[\left(\frac{\sigma_{HC}}{r+z} \right)^4 + \left(\frac{\sigma_{HC}}{r-z} \right)^4 \right] - \left[\left(\frac{\sigma_{HC}^4}{3\Delta(0.61\Delta + r+z)^3} \right) + \left(\frac{\sigma_{HC}^4}{3\Delta(0.61\Delta + r-z)^3} \right) \right] \right\} \quad (2-3)$$

where r is pore half-width, $\varepsilon_{HC}^* = \frac{6}{5} \pi \rho_s \varepsilon_{HC} \sigma_{HC}^2 \Delta$ is the potential minimum (potential well depth) between an adsorbate molecule and a graphite lattice layer. The parameter, Δ , is the distance between two graphite lattice layers in the pore wall (generally taken as 0.335 nm). ρ_s is the number density of carbon molecules per unit volume of the pore wall (the normal value is 114 nm^{-3}) [18]. Table 2-1 lists the LJ parameters for carbon, hydrogen and methane, which are commonly used in molecular simulation studies.

Figure 2.4 The normalized adsorption potential minimum of methane and hydrogen in slit-shaped micropores (calculated with the LJ 10-4-3 potential).

Table 2-1 The LJ parameters for carbon, hydrogen and methane

	σ (nm)	ε/k (K)
Carbon	0.34	28
Hydrogen	0.283	59.7
Methane	0.376	148.6

Note: k is Boltzman Constant, $1.3807 \times 10^{-23} \text{ J/K}$

With the LJ 10-4-3 potential in Eq. (2-3), the normalized adsorption potential minimum of methane and hydrogen molecules sitting in the slit-shaped micropores are respectively calculated as a function of pore width (or diameter) and shown in Figure 2.4 [19,20]. It can be seen that, in the case of hydrogen/methane storage, the small micropores (in the size range of 0.6-0.9 nm) are desirable for maximizing the

physisorption potentials. For maximizing the adsorption capacities of H₂/CH₄ in ACs, however, such factors as pore size, pore volume and surface area should be optimized simultaneously.

2.2 Other storage materials and technologies

2.2.1 Metal hydrides

Many metal hydrides are reported in literature for hydrogen storage application, but they largely belong to a few major categories, such as: binary hydrides (e.g. MgH₂), complex hydrides (e.g. NaAlH₄), and intermetallic compounds (e.g. LaNi₅ compounds) [12]. The mechanism of hydrogen storage in metal hydrides is chemisorptions (H₂ adsorption accompanied with chemical reaction). For example, the reversible hydrogen capacity of up to 7.6 wt% was reported for Mg-based hydrides [12]. However, slow reaction kinetics, high regeneration temperatures (up to ~573 K) are major issues affecting the efficiency of this technology.

Since the operation at (or near) the ambient temperature is highly desirable for hydrogen storage technology, the major challenge for this technology is to lower the operational temperature [12]. Other issues of metal hydride technology include the reversibility, slow kinetics, cost, and safety.

2.2.2 Metal–organic frameworks (MOFs)

MOFs are crystalline solids with organic ligands connecting metal ions or other small cluster. Its 3D structure is somehow similar to that of zeolites. MOFs may consist of relatively uniform pores with the pore sizes ranging from 0.4 to 2.9 nm, surface area of 500 to 5000 m²/g, and densities from 0.21 to 1 g/cm³ [21]. Because of their high surface area and relatively uniform pore size in the micropore range, MOF is another good candidate for hydrogen storage. However, compared with activated carbons, MOFs has the unsolved problem of mechanical and thermal stability, due to the high organic content. As MOFs are a new class of adsorbents, other issues such as cost and safety are also topics under the studies.

2.2.3 Zeolite

Zeolites are crystalline frameworks of aluminum-silicates of alkali and alkaline earth metals (e.g. Na, K, Ca, and Mg) with 3-D porous structures. There are many types of natural zeolites and synthetic zeolites and they are popularly used in ion-exchange, adsorption/purification processes, and as catalysts/catalyst supports [22]. The pore geometry, window size, and volume of zeolites are dictated by their framework structure. However, the pore volume (which is largely related to the adsorption capacity) of microporous zeolites is generally less than those of microporous carbons or MOFs.

2.3 Energy storage in carbonaceous adsorbents

Because physisorption is the dominant mechanism for CH_4/H_2 uptake in carbonaceous adsorbents (ACs, CNTs, graphite, etc.), the key parameters for maximizing storage capacity are: 1) high surface area; 2) optimal pore sizes, and 3) high microporosity [23], although the three factors are interconnected. As supercritical gases at room temperature, CH_4/H_2 adsorption reside predominantly in pores with the dimension less than two to three times of their respective molecular dimensions (diameters) [24]. When pore size further increases, the adsorption potential decreases rapidly (please see Figure 2.4) and so is the uptake capacity. Thus, pores larger than 2 nm (meso- and macropores) are not useful for the CH_4/H_2 storage purpose, although some mesopore volumes are necessary for the efficient transport of the adsorbates into and out of the micropores.

2.3.1 Methane storage in ACs

A number of simulation/experimental studies indicate that the CH_4 capacity should mainly come from pores with a width of ~ 0.8 nm (approximately equal or larger than two methane molecules) while the volumes of meso- and macro- pores should be minimized [25,26,27,28]. Parkyns and Quinn [29] proposed that a linear relationship can be drawn between the methane uptake at 298 K, 3.4 MPa and the Dubinin-Radushkevitch (DR) micropore volume of the carbon sample. The DR volume is derived from nitrogen adsorption at 77 K. This correlation is:

$$\text{Methane Uptake (298 K, 3.4 MPa)} = 0.120 \times \text{Micropore Volume (cc/g)} + 0.021 \quad (2-4)$$

where the unit of the methane uptake is g-CH₄/g-carbon.

Moreover, it has been demonstrated by Menon and Komarneni [23] that there exists a linear relationship between the surface area of the carbon sample and the methane uptake capacity (unit: mg/g), as shown in Figure 2.5.

Figure 2.5 The derived linear relationship between surface area and methane storage capacity on some ACs [23].

Among various types of porous adsorbents (such as zeolite, silica gels, etc.), ACs were confirmed to be the most suitable materials for methane storage by many researchers [23]. Table 2-2 generalizes some experimental results of methane adsorption capacities on a number of commercial ACs at ambient temperature and 35 bar. It can be seen that the best carbon, Maxsorb (super AC with the surface area of 3,100 m²/g), had high methane adsorption capacity on weight basis (211 mg/g-AC). However, because of the low packing/bulk densities of the carbon sample (~0.37 g/cc), its methane volumetric storage capacity was 120 v/v, which is still below the DoE target of 180 v/v (See Table 1-1, Chapter 1). This shows there is no obvious advantage of the adsorbent over the current CNG technology.

Table 2-2 CH₄ adsorption capacity of some commercial ACs at 298 K and 35 bar [23]

Carbon	Surface area	Packing density	Methane capacity	Methane uptake
	(m ² /g)	(g/cc)	(mg/g)	(V/V)
Saran (B)	900	0.32	87	43
BPL	1030	0.44	75	51
Norit R1	1240	0.39	82	49
Amoco GX-32	2500	0.3	175	81
Maxsorb	3100	0.37	211	120
Norit WX6	445	0.71	48	52
Calgon SGL	900	0.49	65	49
Calgol BPL	1030	0.44	75	51
Darco vapure 184-01	1095	0.58	84	75
AC carbon CNS196	1190	0.44	80	54
Norit R3	1270	0.42	92	59
Kureha BAC	1350	0.59	99	90
California GMS-70	1502	0.41	108	68
Barnebey MI	1730	0.46	109	77
Sutcliffe GS/60	1860	0.34	129	67
Osaka M-30	2415	0.34	144	75
Kansai Maxsorb	2671	0.27	164	68

Most of the commercial ACs listed in Table 2-2 are in the form of granular carbons and their bulk densities are generally low. Their storage performance can be possibly improved by the following two strategies: 1) optimizing the porous structure of the ACs (via activation processes) [30,31,32], and 2) improving the packing density of the carbon (by making carbon pellets or monolith) [30,33,34]. The reduction in production cost is another concern for the practical ANG applications [35]. The commercial ACs have advantage in this aspect so that their possible upgrades are discussed below:

(1) Optimizing porous structure

The texture and the microporosity of the AC are mainly controlled/developed by the activation process. Many researches focus on the advanced techniques of controlled pyrolysis and activation processes. For example: Linares-Solano's research group [30] prepared a series of ACs using coals as carbon precursor and KOH as the activation agents. The best carbon (with the code of KUA-41701) presents the surface area of $\sim 3300 \text{ m}^2/\text{g}$ and micropore volume of $\sim 1.50 \text{ ml/g}$, and has a methane storage capacity of $\sim 160 \text{ v/v}$ (after the compaction in a vessel with the pressure of 54 MPa). Table 2-3 lists the texture properties and methane uptakes for some of their AC samples and are compared with a commercial AC (Maxsorb-A). It can be seen that KUA-41701 presents better performance in methane storage application than the commercial Maxsorb-A AC.

Marcos et al. [34] utilized biomass coconut shell (particle size: 2.00-2.83 mm) as carbon precursor to prepare granular AC via the combination of chemical activation by H_3PO_4 (and ZnCl_2) and the subsequent CO_2 physical activation processes. They found that chemical activation using low proportion of chemical activation agents allowed the development of a narrow microporosity while causing no significant reduction in bulk density of the derived carbon sample. The physical activation that followed then would further fine-tune the micropore sizes of the sample. As the results, their granular activated carbons achieved a reasonably high methane adsorption capacity of $\sim 95 \text{ v/v}$.

Table 2-3 The porous texture properties and methane uptake values at 303 K and 35 bar for the AC samples [30]

Carbon	Surface area (m^2/g)	Packing density (g/cc)	Methane capacity (mg/g)	Methane uptake (v/v)
KUA-21801	2085	0.63	164	160
KUA-41651	2523	0.59	166	153
KUA-41701	3290	0.56	191	166
KUB-41701	2123	0.64	166	165
Maxsorb-A	3100	0.5	197	152

(2) Activated carbon monoliths (ACMs)

In addition to the high gravimetric methane capacity, an AC is also expected to possess relatively high density to present high volumetric storage capacity. This can be

achieved by fabricating carbon monoliths (ACM) out of the powdered AC by using a binder. For example, Lozano-Castello et al. [30] prepared ACMs with various binders (Teflon, Phenolic resin, PVA, a proprietary binder named WSC, etc.). The ACM made of WSC gave a deliverable capacity of 126 V/V.

Although a binder can effectively increase the bulk density of an AC, it decreases the microporosity as well. In some cases, activation is needed to re-develop the microporosity of the ACM [36]. This additional step is costly. Two types of binderless methods were also reported for ACM fabrication. The first method employs a pre-treatment step, that is, the carbon precursor is first compressed into pellets and then undergoes the activation process. Inomata et al. [37] prepared carbon pellets using compressed cellulose microcrystals (compressed at a pressure of ~98 MPa) and activated by CO₂. Nakagawa et al. [38] fabricated carbon discs by activating the compressed olive stones (at a pressure of 150 MPa) with chemical agents (ZnCl₂ and H₃PO₄). Depending on the pre-compression and the activation parameters, the density of those ACMs ranged from 0.4 to 0.9 g/cm³, while the methane capacity reached as high as 160 v/v [37].

The second type of binderless densification method applies a post-treatment (e.g. hot-pressing) of the synthesized AC powders. Celzard et al. [39] loaded AC powder into a steel piston-cylinder container and subjected the AC to an axial pressure of up to 20 MPa. It was found that the carbon attained a density of ~0.8 g/cm³ and a methane capacity of 193 v/v (at 3.5 MPa methane pressure and 293 K) when the axial pressure was 10 MPa. Hou et al. [40] reported an ACM made of ordered microporous carbons via hot-pressing under vacuum with a temperature of 300 °C and a pressure of 147 MPa. The ACM had significantly improved density, surface area, and micropore volume on a volumetric basis. The post-treatment method with hot pressing is more flexible as the pelletisation process only employs the mechanical compression and is in more control of the products derived.

2.3.2 Hydrogen storage in carbonaceous adsorbents

2.3.2.1 Activated carbon (AC)

Hydrogen storage in ACs was reported in some early studies. For example, Carpetis and Peschka [41] reported in 1980 that hydrogen could be effectively stored in high surface area ACs at deep cryogenic temperature (77 K) with the pressure up to 40 MPa. Agarwal et al. [42] showed that hydrogen adsorbed roughly increases with the specific surface area of the carbon samples, and a capacity of ~4.2 wt % was attained at 87 K and 5.9 MPa. Nijkamp et al. [43] carried out hydrogen adsorption measurements on a few AC samples at 77 K and 1 bar, the maximum storage capacity achieved was 2.13 wt %. The experimental results showed that hydrogen capacity generally increases with the specific surface area (SSA) [44,45,46,47,48]. Hirscher et al. [49] showed that for various types of carbon adsorbent materials, the hydrogen capacity at 77 K correlates well with their SSA. Zuttel et al. [19] gave the correlation of SSA with hydrogen uptake at 77 K and 1 bar as 1.5 wt % per 1,000 m²/g-AC. Based on extrapolation of the correlation, Strobel et al. [11] suggested that a hydrogen storage capacity of ~6 wt % would be possibly obtained at 77 K on an AC with SSA > 4,000 m²/g.

Besides the high SSA, the pore size also exerts a strong influence on hydrogen adsorption in ACs. Bhatia and Myers [50] studied the optimal pore size of carbon for hydrogen adsorption based on the LJ interaction model and proposed that the optimal pores should be ~0.92 nm so that the “ideal” carbon will have the deliverable capacity of >6 wt% at a cryogenic temperature. Wang and Johnson [51] carried out theoretical computation and pointed out that ACs with small micropore (with the size ~0.56 nm) are the optimal structure for the application. Other recent studies [48,52] showed that the surface area associated with the optimal pores with the size of about 0.7 nm dictates hydrogen storage in porous carbons at ambient conditions. According to the various proposed mechanisms of hydrogen adsorption on carbons, it is believed that the optimal pore size for hydrogen sorption is in the range of 0.6-0.9 nm. From this point of view, conventional ACs, which normally have a wide span of pore size distribution, are not viable options for hydrogen storage.

An important parameter for the characterization of hydrogen adsorption storage is the adsorption energy. Bhatia and Myers [50] conducted Monte Carlo (MC) simulations and showed that, for hydrogen storage at ambient temperature and the delivery pressure between 30 and 1.5 bar, the adsorption enthalpy should be ~ 15 kJ/mol. For carbon adsorbents, of which the average enthalpy change is typically ~ 5.8 kJ/mol, an optimum operating temperature of about 115 K is predicted. Recently, the adsorption energy of 11 kJ/mol was reported on some Carbide-Derived Carbons (CDCs) [52]. Noticeably, the pores in CDC may deviate significantly from the slit-geometry commonly found in ACs.

However, at room temperature and moderate pressure, only small quantities of hydrogen could be stored in the conventional commercial ACs [47,53], although they have very high surface area. For example, the carbon KUA-6, made by Jorda 'Beneyto et al. [54], with a surface area of $3,808 \text{ m}^2/\text{g}$, could store 0.4 wt% hydrogen only at 298 K and 50 bar. This pointed out the importance of small micropores for the application.

Some novel ACs have been developed for hydrogen storage. For example, the carbide derived carbons (CDC) [52], with a specific surface area of up to $2,000 \text{ m}^2/\text{g}$ showed some promising aspects for hydrogen storage. CDCs are produced by the selective thermo-chemical etching of metal atoms from carbides (e.g. ZrC, TiC, SiC, etc.). At the temperature of 77 K, hydrogen storage capacities of CDCs can reach ~ 3 wt% at room pressure.

2.3.2.2 Carbon nanotube/nanofiber (CNT/CNF)

Hydrogen storage in CNT/CNF has also been studied intensively [55,56,57,58,59,60,61]. However, recent research results do not confirm any advantage of CNT/CNFs over ACs for hydrogen storage [50,62,63]. According to the past research results, hydrogen storage capacity in such carbon nanoparticles were reported to vary significantly from as low as 0.05 wt % to as high as 21 wt % [11]. But the high capacity values have not been verified independently. Such high storage capacities were attributed to different sorption mechanisms which have not been independently confirmed up to now. In some cases, experimental pitfalls such as moisture contamination were found to be responsible [16]. Currently, the maximum uptake by

CNT/CNF seems to be of the order of ~4 wt % at 77 K, and less than 1 wt % at room temperature [49,64].

Bhatia and Myers [50] examined hydrogen storage in CNTs and ACs using Monte Carlo simulations and demonstrated that CNTs provide little advantage over ACs in terms of enhanced delivery capacity. Ansón et al. [65] measured hydrogen uptake on SWCNTs at two temperatures (77 K and 298 K) and the pressure up to 1 bar. The hydrogen storage capacity was only ~0.01 wt % at 298 K and ~1 wt % at 77 K. The heat of hydrogen adsorption obtained from the isotherms at three different temperatures for the SWCNT samples were 7.42~7.75 kJ/mol. In their later work in 2005, Ansón et al. [66] measured the storage capacity of SWCNTs using three different techniques, such as volumetric, gravimetric and electrochemical, etc., respectively. Very low capacities were reported, e.g., 0.01 wt % at room temperature and atmospheric pressure and the 0.1 wt % at room temperature and ~19.0 bar.

In order to improve hydrogen storage capacity of CNT/CNFs, many research attempts have been made to carry out further activation [67] or use additives to the carbon materials [68]. These measures can effectively increase the hydrogen uptake capacity, but the overall storage performance is still below that of ACs.

2.4 ACs prepared from template synthesis

Template synthesis is a novel approach for the preparation of quality ACs. This technique presents a number of advantages over the conventional pyrolysis/activation methods in the fabrication of ACs for specific applications. In some cases, the derived ACs present highly ordered (microporous or mesoporous) structures (replicas) on nm/sub-nm scale and were referred to as the ordered microporous carbons (OMCs). The technique makes use of the highly ordered microporous (or mesoporous) channels in zeolites or silicas as the “template”, in which carbon resources are incorporated (via impregnation or vapour deposition or a combination of both) and then pyrolyzed into carbons with thermal treatments [69,70]. Therefore, the porous structure of the template-derived AC (termed as TC) can be largely manipulated via the selection of template, carbon source, or the pyrolytic conditions, etc., for the designated applications.

Template synthesis generally involves three steps: (1) incorporation of a carbon precursor into the pores and channels of the microporous template; (2) carbonization in an inert media (e.g. N₂); and (3) removal of the template by acid washing (HF is popularly used). Figure 2.6 shows the schematic diagram of the above procedures in template synthesis process.

Figure 2.6 Schematic diagram of template synthesis. [(a) template, (b) the impregnation, and (c) the resulted TC.]

Inorganic, ordered porous solids are good candidates as the template, such as zeolite and ordered mesoporous silica (MCM-48, SBA-1, and SBA-15 etc.) [69]. A suitable template for the energy storage application is expected to possess the following characteristics:

- 1) With uniform pores of sub-nanometer sizes;
- 2) The walls (framework) thickness should be less than 1 nm;
- 3) Stable structures at the elevated temperature (>1273K);

Zeolite Y has been popularly used as the template to prepare microporous carbons [71,72,73,74] because of its structure has better compatibility with the above criteria. A number of carbon precursors have been used in literature, such as: sucrose, furfuryl

alcohol (FA), phenol resin, mesophase pitch, polydivinylbenzene, acrylonitrile, propylene, acetonitrile (AN), etc. [75,76,77]. Table 2-4 lists synthetic conditions for TCs and their surface properties.

Table 2-4 The reported template carbons (TCs) using zeolites

Carbon precursor	Template Zeolite	Carbonization condition	S_{BET} (m ² /g)	Ref.
poly(AN)	NaY	973K, 3h	580	[15]
poly(FA)	NaY	973K, 3h	590	[15]
propylene	USY	973K~1073K, 12~18h	1600-2200	[15]
PFA+propylene	Y	973K~1173K, 4h	2200-3600	[15]
acetylene	Y	873K~973K, 4h	3170-3370	[78]
AN	13X	1073K~1273K, 3h	500-1600	[79]
AN	Y	1073K~1273K, 3h	430-1900	[79]
AN	BETA	1073K~1123K, 3h	2100-3200	[80]
PFA+AN	Y	1073K~1173K, 2h	3310	[81]
propylene	NaY	993K~1033K, 4h	2117	[82]
propylene	CaY	993K~1033K, 4h	2470	[82]
butylene	NaY	993K~1033K, 4h	2456	[82]
butylene	CaY	993K~1033K, 4h	2061	[82]
sucrose	NaY	1073~1273K, 4h	1062-1752	[83]
FA	NH4Y	873K~1373K, 4h	700-3600	[84]

The main challenge of the template synthesis technique is the complete infiltration of the carbon precursor within the narrow channels of the microporous template. There are three major infiltration methods, that is, (1) impregnation/polymerization, (2) carbon vapour deposition or CVD, and (3) the combination of polymerization and CVD (a two-step method).

Zhao's group [83,84] developed TCs using the polymerization method: Powder zeolite Y was impregnated with furfuryl alcohol (FA), which was polymerized inside the zeolite channels. The resulted polyfurfuryl alcohol (PFA)/zeolite composite was heated in N₂ under different carbonization temperatures (873~1373 K). The

carbonization temperature greatly influences the BET surface areas (from 708 to 3683 m²/g) and micropore volume (from 0.32 to 1.59 cm³/g) of the porous carbons. The best carbon has a BET surface area of 3,683 m²/g and micropore volume of 1.59 cm³/g, which was prepared under 1373 K.

Chen et al. [82,85] prepared TCs using different cation-exchanged (Ca, K, H and Na) forms of zeolite-Y as the templates. Propylene and butylene were used as carbon sources in a single-step CVD process. Argon gas was used as the inert blanket while the reactor temperature reached ~1000 K. Thereafter, propylene/butylene were introduced for 4 hours. Results show that the cation of the template zeolite and the gas type significantly alter the structure of the derived TCs. With the simple CVD method, the carbons derived better resemble the structural regularity (patterns) of the zeolite.

Kyotani's research group [81] synthesized a template carbon using two-step method (polymerization followed by CVD): FA was introduced into the micro-channels of zeolite Y (Na-form, SiO₂/Al₂O₃ = 5.6) and polymerized. The resulted composite was then heated to ~973 K in N₂ stream for few hours and then propylene was introduced to deposit more carbon sources into the unsaturated template channels. After that, the temperature was further increased to ~1100 K under the N₂ flow stream for a period of time. The reported surface area of the prepared TC is ~3600 m²/g-AC. This method, however, does not work well for other template materials such as zeolite beta, ZSM-5, and mordenite [74], indicating more research efforts are needed in this aspect.

In the third step of template synthesis process, the infiltrated and thermally treated template composites are subject to acid washing to obtain the carbon powders (e.g., the composite was treated with HF (46%) at room temperature for ~12 hours to remove the template. The remaining carbons were washed with an excess of deionized water. In the literature, thermogravimetric analysis (TGA) has confirmed that the HF acid washing process is complete) [69].

2.5 Templated carbons (TCs) for energy storage

2.5.1 TCs for hydrogen storage

Because of their large surface area and relatively homogeneous pore size, TCs show marked advantages for energy storage application [86,87]. Table 2-5 generalizes a number of experimental results on hydrogen adsorption in some TCs.

For example, Yang et al. [80] fabricated a TC (or OMC) by using β -zeolite as the template and acetonitrile as carbon source. The zeolite-derived TC had a surface area of $\sim 3150 \text{ m}^2/\text{g}$. The OMC exhibited enhanced hydrogen storage capacity up to 6.9 wt % at 77 K and 20 bar. The isosteric heat of adsorption was calculated to be 8.2 kJ/mol. The microporosity of the as synthesized TC is dominated by pores of size 0.6-0.8 nm. Thus, the surface area associated with “optimal pores” is also high, which leads to the enhanced hydrogen uptake capacity. Hu et al. [90] measured the hydrogen adsorption isotherms of a TC derived from sucrose/silica aerosols. Hydrogen adsorption of >4.0 wt % at 77 K and >20 bar was found. However, at room temperature, hydrogen adsorption could only reach 0.25 wt % at 50 bar.

Table 2-5 Hydrogen adsorption capacity in some TCs

Sample	T (K)	P (bar)	H ₂ capacity (wt %)	Ref.
SBA-15 replica After activation	77	0.9	1.0-2.0	[88]
Zeolite Y replica	77	1	1.2-2.0	[82]
Zeolite beta replica	77	1	2.6	[80]
Zeolite beta replica	77	20	6.9	[80]
Monolith of SBA-15 replica	77	20	3.4	[89]
Zeolite Y replica, N-doped	77	20	4.5	[79]
Carbon from sucrose/silica aerosols	77	1.1	1.2-2.0	[90]
Carbon from sucrose/silica aerosols	77	50	4.3	[90]
Carbon from sucrose/silica aerosols	298	50	0.25	[90]
MCM-48 replica after CO ₂ activation	77	1	2.19	[91,92]

Gadiou et al. [93,94] fabricated the other type of OMC (ordered mesoporous carbon) material by using the mesoporous silicas as the template. They found that the hydrogen storage capacity on their TC could be correlated to the microporous volume (V_{DR, CO_2}) determined by CO_2 adsorption using Dubinin-Radushkevich (DR) equation. This indicates that ultramicropores (pores with the sizes smaller than 0.7 nm) play a very important role in hydrogen storage. They also found that, for a given microporous volume, the hydrogen adsorption capacity is higher for TCs than that for the commercial ACs.

2.5.2 TCs for methane storage

Unlike hydrogen storage, there is little work [95,96] on methane storage on TCs. Ohkubo et al. [95] measured adsorption isotherm (at 303 K) of methane uptake on CMK-1, a TC prepared using MCM-48 as the template. The surface area of the CMK-1 is $\sim 950 \text{ m}^2/\text{g}$, and pores are uniform with a size of 3.90 nm. The amount of adsorbed methane gas is 81.35 mg/g [$\sim 114 \text{ cc(STP)/g}$] at 35 bar and 298 K.

Although TCs have a very high specific surface area and relatively narrow pore size distribution, the apparent bulk density is very low (about 0.2-0.3 g/cc) which is not optimum for methane storage. Some researches tried to increase the bulk density of TC by pelletisation. For example, Hou et al. [40] carried out hot-pressing process at 573 K up to 147 MPa at under high vacuum for a carbon synthesized by using zeolite Y as template. The bulk density of the derived pellet reached $\sim 0.89 \text{ g/cc}$. However, there was no measurement of methane uptake on the carbon or carbon pellet.

2.6 Summary

H_2/CH_4 adsorptive storage capacity on carbonaceous adsorbents is strongly dictated by the nanostructure of the adsorbents. Most studies have shown that increasing the surface area of the carbons with optimal uniform micropores is the target for improving H_2/CH_4 storage capacity. Simulation studies have pointed out the feasibility of energy storage in the carbonaceous adsorbents, with the optimal structure (mainly pore sizes) and the desired adsorption energies. Template synthesis is a promising technology to

achieve these targets because of its capability and flexibility in preparing microporous carbon (templated carbon or TC) adsorbents with the large surface area and relatively uniform small pores. The structure of TCs can also be largely manipulated via the selection of template, carbon precursor, as well as the controlled pyrolytic conditions. This technology has the potential to fabricate the optimal AC adsorbents with designated porous structure for H₂/CH₄ storage applications.

CHAPTER 3 EXPERIMENTAL METHODS

This chapter describes the experimental theories and methods involved in this project, including the experimental rigs, standard analytical instruments, sample preparation/purification methods, structural characterization methods, and energy gas storage measurement, etc.

3.1 Sample preparation

3.1.1 The materials

TCs were fabricated using NH₄-Y zeolite as the template and with two carbon sources, sucrose and furfuryl alcohol (FA). Table 3-1 lists the properties of the zeolite, FA and sucrose.

Table 3-1 The properties of furfuryl alcohol (FA), sucrose and zeolite Y

	FA	Sucrose	Zeolite Y
Supplier	Aldrich	Fisher Scientific	Zeolyst Int., USA
Molecular formula	C ₅ H ₆ O ₂	C ₁₂ H ₂₂ O ₁₁	(SiO ₂ /Al ₂ O ₃ , 5.1)
Molar mass	98.1 g/mol	342.3 g/mol	-
Density	1.130 g/cm ³ , liquid	1.587 g/cm ³ , solid	-
melting point	-29 °C	186 °C	-
Boiling point	170 °C	-	-
Solubility in water	-	211.5 g/100 ml (20 °C)	-
Surface area	-	-	925 m ² /g
Window size*	-	-	0.74 nm

* Window size is the size of aperture of zeolite Y, which is formed by a 12-membered ring.

Figure 3.1 shows the XRD pattern of the zeolite sample. Several major peaks present at the XRD pattern, which include 6 °(2θ), 10 °(2θ) etc. The distinctive diffraction peak at 6° (2θ) is corresponding to the {111} plane of zeolite Y. The 10 °(2θ) is related to {220} plane of the zeolite Y.

Figure 3.1 The XRD pattern of the template zeolite Y.

3.1.2 Synthesis routes

The process of sample TC preparation mainly includes three steps:

(1) Impregnation of zeolite Y with the carbon source (FA or sucrose)

Before the impregnation, the zeolite Y powder was cleaned at 200°C for 24 hours in a flask under vacuum ($\sim 10\text{--}15\text{ Pa}$) and cooled down to the room temperature. Then, FA (purity $> 99\%$) was added to the flask ($\sim 4\text{ ml}$ of FA to every gram of zeolite template). After stirring at room temperature for 72 hours, the solid was filtrated off, washed with mesitylene to remove residual FA on the external surface of the template particles, and then air-dried.

For the impregnation of zeolite with sucrose, before adding into a solution (containing 10 g of sucrose ($> 98\%$) and 0.001 L sulfuric acid (98%) in 0.050 L deionized water.), the zeolite template powder was dried at 200°C for ~ 4 hours. The mixture was then stirred at room temperature for another 4 hours, and followed by drying at 100°C for 15 hours and at 160°C for 6 hours to form a zeolite/sucrose composite mixture.

(2) Carbonization of the FA/zeolite or sucrose/zeolite composite mixture at elevated temperatures

The mixture composite from Step (1) was heated at different temperatures (900, 1050, 1100, and 1150 °C, respectively) in a quartz tube under N₂ (99.999%) flow at the rate of ~100 cc(STP)/min. After 4 hours, the system was cooled down to room temperature under N₂ flow. The solid obtained is the zeolite/carbon composite.

(3) Removal of the zeolite template

The zeolite/carbon composites from Step (2) were treated in a large amount of HF solution (~45%) at room temperature for 24 hours. The black solid was filtered, washed with hot deionized water (at ~60 °C) for five times, and dried at 60 °C overnight. The solid obtained in this step was named C900, C1050 and C1150, respectively. For example, C900 means that this carbon sample was carbonized at 900 °C. Similarly, the carbon derived from sucrose was named S1100 because the carbonization temperature was 1100 °C.

Figure 3.2 Schematic diagram of the experimental setup for TCs synthesis. (1 = N₂ gas cylinder with regulator; 2 = N₂ flow-meter; 3 = tube furnace; 4 = programmable temperature controller; 5 = sample boat; 6 = quartz tube; 7 = lab fume hood)

Figure 3.2 shows the schematic diagram of the experimental rig used in the carbonization step. The rig comprises a horizontal quartz tube reactor (length: 900 mm;

OD: 50 mm), a tube furnace with programmable temperature controller, an adjustable N₂ flow-meter and pure N₂ supply station. The solid from the step (1) was placed in a quartz boat inside the quartz tube. Pure N₂ gas was used as the inert gas. The flow of N₂ was stopped once the temperature of the furnace reached less than 50 °C. The sample was then removed from the tube furnace.

3.1.3 Synthesizing TC pellets

Two kinds of pelletisation technologies (binder and binderless) were used in this project to fabricate carbon pellets out of TCs.

Binder method: To improve the volumetric capacity of TC S1100, carbon pellets (or ACM) were fabricated, which has been known as an effective way to increase the volumetric adsorption capacity. The procedures are as following:

- (1) TC flakes were ground into fine powders in a ball miller and sieved with 63µm mesh tray in a sieve-shaker;
- (2) ~7wt% of binder (polyvinyl alcohol or PVA, hydrolyzed, Sigma-Aldrich®) was mixed with the fine TC powder and added with DI water;
- (3) The mixture was put into a small metal mold made of aluminium foil;
- (4) The mold was put in a hydraulic press with heating function and subject to 30 bar and 180 °C overnight.

Binderless method: For C1050, a simplified hot-pressing method was proposed for the synthesis of TC pellet (referred to as C1050P). The procedures are:

- (1) TC powder was dried and put in a metal bag made of commercial aluminium foils;
- (2) The system was put under the heated press;
- (3) The temperature was raised to 200 °C and the pressure is increased to 50 MPa for 4 hours;

(4) The system was cooled down under natural cooling.

3.1.4 Commercial carbon samples

Two commercial carbons (Norit AC and SWCNT from CheapTube) were also studied for their applications in energy storage, which are listed in Table 3-2, together with TC samples prepared by us.

Table 3-2 Carbon samples used in the study

Sample	Supplier	General Properties
Norit AC	ESSCO Singapore	1. Cylindrical extruders with ~ 6mm OD. 2. BET surface area: 860 m ² /g
SWCNT	CheapTube Inc., USA	1. Purity>90%, Ash <1.5% 2. Outer diameter: 1~2 nm 3. Length: 5~30 um
S1100	CBE*	Powder
C1050	CBE	Powder
C1150	CBE	Powder
C900	CBE	Powder
C1050P	CBE	Pellet

**CBE is the name of the school building where the study was carried out.*

3.2 Sample characterization

3.2.1 Electron microscope (SEM, TEM)

Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM) were used to characterize the morphology characteristics of the derived carbon samples and the commercial samples. The sample preparations for the TEM/SEM analysis are described below:

TEM: At room temperature, ~5 mg of TC samples was dispersed into 2 ml of ethanol and ultrasonicated in a water bath for about 40 minutes. After the treatment, a few drops of the liquid mixture were spread on a copper grid for the TEM study in a JEOL 2010 microscope and was then analysed at 200 kV.

SEM: The carbon samples were firstly coated with gold for 60 seconds before the SEM characterization. The sample SEM images were collected in a JEOL environmental field-emission (FESEM) and an accelerating voltage of 5 kV was used.

3.2.2 X-RAY Diffraction (XRD)

In this project, the XRD study was performed using a SIEMENS BRUKER powder XRD. The samples were prepared in the form of fine powder. The XRD patterns with diffraction intensity versus 2θ were recorded from 4 to 50 degree at a scanning speed of 1 degree/min.

3.2.3 Raman spectroscopy

Raman spectroscopy is popularly used to study vibrational, rotational, and other low-frequency modes in a sample. In this project, a Raman spectrometer (Renishaw inVia Reflex, HeNe Laser, 633 nm) was used to analyze the degree of graphitization of TCs and TC pellet.

3.2.4 Thermogravimetical analysis (TGA)

TGA is a technique whereby the weight of a sample can be followed over a period of time while its temperature is being raised linearly under certain environment. In this project, TGA was conducted with a thermogravimetric analyzer (Thermal Analysis Instruments, USA). The TGA analysis was recorded with the temperature of up to 1073 K in air stream.

3.2.5 Density measurement

The bulk density of TC powder was measured according to the American Society for Testing and Materials method (ASTM D 2854-89). The basic procedures are:

- (1) The sample (e.g. TC powders) was dried at 150°C for 4 hours under vacuum;
- (2) The sample was added into a measuring cylinder, the volume of TC sample was obtained by slightly shaking and patting TC powders;
- (3) The weight of the sample was measured using a balance to the nearest 0.001g;

(4) The bulk density was calculated via the weight and the volume of the sample.

The helium density of TC sample was measured with a pycnometer (Ultrapycnometer 1000, Quantachrome, USA).

The bulk density of TC pellet was determined by the weight of the dried TC pellet divided by its geometrical volume (The geometric volume was calculated with its dimensions).

3.2.6 Gas adsorption

The pore structure of carbon samples can be characterized with the analysis of the physical adsorption of various ‘standard’ gases. Nitrogen adsorption at liquid nitrogen temperature, 77 K, has been popularly used in the literature. Ar adsorption at 77 K and CO₂ adsorption at 273 K were also used in this project to study the structure of TCs. The adsorption isotherms were subject to the analysis of various adsorption theories, from which the surface and structural properties of TC can be obtained, such as specific surface area, micropore volume, and total pore volume, pore size distribution etc.

Adsorption isotherm refers to the amount adsorbed at the fixed system temperature. With a given gas adsorbate and a porous adsorbent, there exists a specific equation:

$$q = f(P)_T \quad (3-1)$$

where q is the amount adsorbed (cm³-STP/g, or cc-STP/g), P is pressure, and T is temperature of the measurement. Eq. (3-1) represents the adsorption isotherm. Sometimes, an isotherm is represented in graphical form of q against P or P/P_0 , where P_0 is the saturation vapour pressure of the adsorbate at the experimental temperature.

3.2.6.1 Instrumentation for gas adsorption measurement

A commercial pore and surface analyzer (PSA, Quantachrome Inc., Autosorb-1) was used to measure the adsorption isotherms (See Figure 3.3) at 77 K, 195 K, and 273 K, respectively, with the adsorption pressure up to 1 bar. The system uses the volumetric

technology for adsorption isotherm measurement. The operation of the rig is available in its operation manual [97]. The major parts of the rig are described in Figure 3.3.

The isotherm measurement is carried out automatically and controlled by a computer. Autosorb-1 has the ability to measure gas adsorption at very low relative pressure, starting from 1×10^{-7} bar. The PSA can measure a number of adsorbates such as: N_2 , Ar, CO_2 , H_2 , and vapors of water, alcohols, etc.

Figure 3.3 The photo of the Autosorb-1 and its parts/functions.

3.2.6.2 Sample degassing

Before the measurement, the sample should be free from such contaminations as water, CO_2 , hydrocarbons, etc. These contaminations are removed in the outgassing station shown in Figure 3.3. Prior to adsorption isotherm measurements, samples are outgassed overnight under vacuum at a given temperature. Normally, outgassing temperature is >473 K and the vacuum below 1.0×10^{-5} Torr.

3.2.6.3 Determination of specific surface area (SSA)

Currently, the major method used to determine sample SSA from gas adsorption isotherm data is the Brunauer-Emmett-Teller (BET) method, which is based on the BET equation listed below [98]:

$$q = \frac{q_m c \frac{p}{p_0}}{\left(1 - \frac{p}{p_0}\right) \left[1 + (c-1) \frac{p}{p_0}\right]} \quad (3-2)$$

where q is the amount adsorbed, q_m is maximum monolayer capacity, p/p_0 is the relative pressure and c is the isotherm constant. Eq. (3-2) can be expressed in the linear form of:

$$\frac{\frac{p}{p_0}}{q \left(1 - \frac{p}{p_0}\right)} = \frac{1}{q_m c} + \frac{c-1}{q_m c} \frac{p}{p_0} \quad (3-3)$$

Eq. (3-3) is used to determine the monolayer capacity q_m , which is subsequently used to evaluate the BET-specific surface area, S_{BET} . With the cross-sectional area A_{cs} for an adsorbate molecule is known (e.g. the A_{cs} of nitrogen molecule is 0.162 nm^2 at 77 K), the S_{BET} can be calculated from:

$$S_{BET} = q_m A_{cs} N_A \quad (3-4)$$

where N_A is the Avogadro number ($6.023 \times 10^{23} \text{ mol}^{-1}$). The implicated assumptions of the BET equation (Eq.3-3) are that the surface is homogeneous and without lateral interaction between the adsorbed molecules. The BET surface area is generally taken from the traditional pressure range of $P/P_0 = 0.05 - 0.3$.

3.2.6.4 Micropore analysis

(1) Dubinin-Radushkevich (DR) method

DR equation [16,99] is used to calculate the micropore volume of adsorbents from the adsorption isotherm, that is:

$$V = V_0 \exp \left[- \left(C \ln \frac{P_0}{P} \right)^2 \right] \quad (3-5)$$

where $C = \frac{RT}{\beta E_0}$, V represents the adsorbed amount (volume), V_0 is the limiting volume of the adsorbed space equal to micropore volume, β is the affinity coefficient characterizing the polarizability of the adsorbate, and E_0 is the characteristic energy of adsorption of a standard vapor (usually benzene).

(2) Dubinin-Astakhov (DA) method

The DR equation can be generalized by DA equation [99] as:

$$V = V_0 \exp \left[- \left(C \ln \frac{P_0}{P} \right)^n \right] \quad (3-6)$$

where n is the so-called DA parameter. The value of the parameter n , which can be related to heterogeneity, empirically ranges from below 1 to ~14 [16]. The case where $n=2$ corresponds to DR equation. The pore size distribution from DA can be calculated by non-linear fitting to the isotherm with an assumption of a pore distribution function (Eq. 3-7), using the software embedded in Autosorb-1c [97].

3.2.6.5 Determination of pore size distribution (PSD)

The PSD of a porous sample is frequently derived from a standard adsorption isotherm using the nonlocal density functional theory (NLDFT) method. This function is provided by Quantachrome's built-in software (version 1.27) developed by Neimark and his co-workers [100]. The NLDFT method is based on statistical mechanics with the assumed adsorbate-adsorbate interaction potential (e.g. LJ 12-6) and adsorbate-adsorbent interaction potential (e.g. LJ 10-4-3). The observed isotherm is the summation/integration of the adsorption which took place in individual pores of assumed geometry over the complete pore size range. That is:

$$q(p/p_0) = \int_{W_{\min}}^{W_{\max}} q_K(p/p_0, W) f(W) dW \quad (3-7)$$

where $q(p/p_0)$ is the experimentally obtained adsorption isotherm, W is the pore width, $q_K(p/p_0, W)$ is the kernel of the theoretical isotherm of pores of width w , and $f(W)$ is pore size distribution function. Classical thermodynamic theories like Barrett-Joyner-Halenda (BJH) [101], Dubinin-Radushkevich (DR) [99] and Horvath and Kawazoe (HK) [102] are also equipped in the software of the PSA rig and some of these theories were also used to derive the PSD of the carbon samples for the comparison purpose.

3.3 Hydrogen adsorption isotherm measurement

Low pressure adsorption isotherm: hydrogen adsorption isotherms at 77 K were measured on the Autosorb-1 with an absolute pressure of ~0.5 mmHg to ~800 mmHg. The measurement procedures are similar to the one used in measuring N₂ adsorption isotherm at 77 K. The measurement is carried out automatically and controlled by the pre-set computer program.

3.3.1 High pressure adsorption rig

High pressure adsorption isotherm: A high pressure adsorption rig was designed and fabricated in this project for the measurement of adsorption isotherms at the pressure from 0.1 bar to above 50 bar. The rig was self-fabricated and shown schematically in Figure 3.4.

The rig consists of (1) sample cell with pressure gauge; (2) dose cell with pressure gauge; (3) gas supply system and (4) a turbo vacuum pump. The temperature of the sample cell and dose cell can be measured and controlled using a thermal bath (Model 9112, PolyScience, USA) with the accuracy of 0.01 °C. The pressure of the sample cell and dose cell were monitored by two high accuracy pressure transmitters with indicator (Druck DPI 104, GE. Accuracy: when ≥ 2 bar, 0.5% full scale). The gas supply system is equipped with a high pressure regulator (Model 4921362-67-000, Controls operation of American, USA) which can control and adjust the gas supply with the pressure up to 70 bar. A two-stage turbo vacuum pump station (Model EXT 255H 24V, BOC Edward, UK) was used for the evacuation of the rig and outgassing of the samples. The pump can

achieve a vacuum of 10^{-5} Torr in the rig. All components in the rig were constructed using 316 stainless steel materials. All fittings joining components of the rig were Swagelok stainless steel tube fittings with advanced geometry back ferrule design and excellent gas-tight sealing. A $0.5\ \mu\text{m}$ VCR filter gasket was used at the sample cell outlet to eliminate the possibility of sample intrusion into the other components of the rig. The dose cell volume, V_2 , was carefully calibrated using a standard reference cell.

3.3.2 Isotherm measurement with the high pressure rig

About 500 mg of the sample was loaded into the sample cell. The sample cell was put in a vacuum oven. The sample was then outgassed at $200\ ^\circ\text{C}$ overnight. After the sample cleaning process, the sample cell was measured again to obtain the accurate sample weight. The sample cell was then connected to the rig and helium was charged to the entire rig for performing a pressure leak test under 50 bar about 6 hours. After ensuring that the leakage rate was low enough ($<0.005\ \text{bar/hr}$), the rig was assumed to be leak-free. The sample cell volume (V_1) was calibrated using He gas and the known volume (V_2) of the dose cell. Helium was vented and the sample cell was degassed under $180\ ^\circ\text{C}$ overnight by using the high performance turbo vacuum pump before carrying out adsorption isotherm measurement test.

Figure 3.4 Schematic diagram of the high pressure volumetric adsorption rig.

The data collection for hydrogen adsorption measurement commenced after isolating the sample cell and charging the dose cell with hydrogen gas to the desired pressure. When the dose pressure data was stable, the isolating valve was opened for the purpose

of reaching adsorption equilibrium. This equilibrium typically occurred within half an hour. After the equilibrium was reached, the new dose pressure could be adjusted using the high pressure regulator for the next adsorption point.

3.3.3 Measurement of adsorption kinetics

The adsorption kinetics was measured on the powdered TC/TC pellets with the high pressure volumetric rig. The procedures are similar to the isotherm measurement described in Section 3.3.2. However, it is necessary to record the bulk pressure in the sample cell versus the time for each dosing. The pressure decay of the system is then related to the adsorption kinetics on the carbon samples. The adsorption kinetics of methane was measured in the following way: (1) the carbon sample is loaded into the sample cell and cleaned (free of adsorbates); (2) a certain amount of adsorbates with pressure, P_{01} , was dosed into the sample cell. As the adsorption proceeds, the pressure decay in the sample cell was recorded with respect to the time; (3) when adsorption equilibrium was reached in the sample cell, more adsorbates were dosed into the samples cell (the total pressure in sample cell was instantly increased to P_{02}). The adsorption would proceed again and the pressure decay in the sample cell was again recorded versus the time, and so on.

CHAPTER 4 METHANE/HYDROGEN STORAGE ON COMMERCIAL AC AND SWCNT

4.1 Methane storage in a commercial AC

Activated carbons (ACs) are excellent adsorbents for numerous applications [15]. The main factor that makes ACs excellent adsorbents is their porous structure. The pores can be classified generally as: macropores, mesopores and micropores. The schematic structure of ACs and the International Union of Pure and Applied Chemistry (IUPAC) classification for pores are listed in Figure 4.1. The different pore sizes allow the accesses for molecules with different dimensions. For example, the kinetic diameter of methane molecule is 0.38 nm. At room temperature, methane gas is supercritical gas and its adsorption takes place predominantly in pores which are less than four times molecular diameters in width. So these pores must be micropores. It should be noted that the micropores in ACs were generally idealized/hypothesised to be slit-shaped, which was supported by the structure of graphite and TEM studies [103].

Figure 4.1 Schematic diagram of pores in AC and the IUPAC classification of pores [103].

The surface of AC is generally nonpolar or only slightly polar, depending on the surface chemistry (functional groups) of the surface. Many investigations have been conducted to study commercial ACs for NG storage [13,104]. As indicated in Chapter 2 (Section 2.3.1), the deliverable storage capacities achieved are high on gravimetric basis but low on volumetric basis [105]. For the optimal storage of NG, an AC should possess large surface area and uniform micropores with the size ranging approximately from 0.8 to 1 nm [106]. Large pores, although not efficient for the storage capacity, are necessary for the charging and discharge kinetics.

In addition to the storage capacity requirement for the ACs used in ANG application, economical production of the adsorbents for NG storage is another important issue, which is greatly in favor of commercial ACs. From this point of view, a commercial AC, Norit AC, which was produced via steam activation of coconut shells, was examined for possible ANG application.

4.1.1 Structure characterization of AC

The structure of Norit AC sample was analysed with the PSA (Quantachrome, Autosorb-1). Nitrogen adsorption isotherms were measured on the sample at 77 K. Prior to the measurements, the sample was degassed at 250 °C overnight under high vacuum.

Figure 4.2a shows N₂ isotherms on the AC sample at 77 K. It can be seen that the AC is primarily microporous with a very small hysteresis in the desorption isotherm. The BET surface area of this carbon is found to be 860 m²/g, which suggests that the carbon is a reasonably good adsorbent for NG storage.

Table 4-1 Surface properties of Norit AC

BET area (m ² /g)	V _t (cc/g)	V _{mic} (cc/g)	V _{me} (cc/g)
860	0.55	0.48	0.07

Figure 4.2 (a) N_2 isotherm on Norit AC at 77 K; (b) the PSD and (c) cumulative pore volume of the Norit AC derived from N_2 isotherm at 77 K using NLDFT.

Figure 4.2b and Figure 4.2c show the pore size distribution (PSD) and the cumulative pore volume of the Norit AC derived from N₂ isotherm using the non-local density functional theory (NLDFT). It is seen that the Norit AC presents a narrow micropore peak around 1.1 nm with little mesoporosity. This PSD further suggests that the AC is a good candidate for NG storage, as the pore size is close to the optimal pore size of 0.8 – 1.0 nm for NG storage. The surface properties of the AC sample are listed in Table 4-1.

4.1.2 CH₄ sorption in AC

Methane adsorption isotherms were measured on the AC sample at 273 K and 303 K, respectively with the pressure up to 50 bar. Figure 4.3 presents the adsorption isotherms of methane as symbols. To better fit the isotherm data, Toth's model, which is a three-parameter isotherm model taking into account of the surface heterogeneity [107], was employed to fit the isotherm data. Toth isotherm takes the form of:

$$C_{\mu} = C_{\mu s} \frac{b \times P}{\left[1 + (b \times P)^t\right]^{1/t}} \quad (4-1)$$

where C_{μ} is the adsorbed phase concentration (mmol/g), $C_{\mu s}$ is the saturation capacity of the adsorbent, b is the adsorption affinity, and t is the heterogeneity parameter of the adsorbent. The fitting results are shown in Figure 4.3 as lines while the optimally obtained fitting parameters are listed in Table 4-2. It is seen that the Toth equation fits the isotherm data very well. The heterogeneous parameter $t = 0.33$ means that the carbon surface is very heterogeneous towards methane molecules, probably due to that the narrow micropores induce strong variation in adsorption potential with the progressive fillings in micropores.

Figure 4.3 Methane isotherms on the Norit AC.

Table 4-2 Isotherm parameters of methane on the Norit AC

Temperature (K)	$C_{\mu s}$ (mmol/g)	b (1/bar)	t
273	20.65	1.58×10^{-2}	0.333
300	11.31	7.78×10^{-3}	0.493

The volumetric storage capacity of methane, CH₄ (v/v), is then calculated based on the methane isotherm capacity and the bulk density of the AC using the following equation.

$$\text{CH}_4 \text{ (v/v)} = (16 \times C_{\mu} \times \rho_c) / 0.65 \quad (4-2)$$

where ρ_c (g/cc) is the bulk density of the carbon, 0.65 (mg/cc) is methane gas density at 298 K and 1 bar.

The standard ASTM (American Society for Testing and Materials) method [108] was used to determine the density of the AC sample, in which the sample was crushed into fine powder and put in a measuring cylinder for its volume determination. The storage capacity was found to be approximately 70 v/v which compares favourably in terms of cost/performance against other designated AC samples reported in the

literature. For example, the capacity of 86 v/v was achieved by [30], in which the ACs was produced via the combination of physical plus chemical activation processes. Methane storage in other two commercial carbons (Picazine and Sigma) also reported favorable results of 77 and 71 v/v, respectively [109]. However, those capacities are far from the commercial target.

4.2 Hydrogen sorption in AC

The hydrogen adsorption on the commercial Norit AC was measured using the high pressure volumetric rig at 77 K over the pressure range 0-10 bar. The hydrogen adsorption isotherm is shown in Figure 4.4. The isotherm is fitted using Langmuir adsorption model, which can be described as:

$$C_{\mu} = C_{\mu s} \frac{b \times P}{1 + b \times p} \quad (4-3)$$

where b (bar^{-1}) is the adsorption affinity, P is the pressure and $C_{\mu s}$ (wt%) is the saturation capacity of the AC, which is the maximum hydrogen uptake determined from Langmuir plot.

It can be observed that the hydrogen adsorption on the AC follows the Langmuir adsorption isotherm. Considering the specific surface area of the carbon ($S_{\text{BET}} = 860 \text{ m}^2/\text{g}$), the approximation maximum of hydrogen storage capacity at 77 K of the carbon can be calculated:

$$C_{\mu s} = S_{\text{BET}} \times 1.78 \times 10^{-3} \text{ wt\%} \quad (4-4)$$

This means, even at 77 K, it is necessary to increase the surface area up to 3,650 m^2/g in order to meet the 2010 DoE target.

Figure 4.4 Hydrogen adsorption isotherm at 77 K of the AC. (Langmuir model parameters: $C_{\mu s}=1.53$ wt%, $b=2.557$ bar⁻¹)

4.3 Hydrogen storage on a commercial SWCNT

Carbon nanotubes (CNTs) have found numerous applications due to their unique mechanical, electrical, and chemical properties. The adsorption properties of CNTs were extensively explored in such applications as chemical/biosensors [110], adsorbents for energy storage [111], and nanofillers in composite membranes [112], etc. For example, hydrogen storage in CNTs has been a much sought-after area, although both encouraging [111] and discouraging [113] results have been reported.

CNTs consist of graphite pores of cylindrical configuration which may present both high adsorption potential and selectivity for molecules with specific structure and dimension. Some experimental and simulation studies showed that CNTs have the potential to achieve high hydrogen capacity [(5 to 14) % weight percentage] at ambient temperature if the structure is optimized [114,115], while some other studies show that the optimal temperature for hydrogen storage delivery should be much lower at ~115 K to meet the DoE standard of 6 wt % at ambient conditions [50].

The adsorption mechanisms in CNTs are also a subject of controversy. While most researchers agree that the cylindrical graphite pores (inner tubes) offer most of the capacities for physical adsorption [114], the role of the external surface, the corners within the tube bundles, the defects, and the functional groups, etc. were not fully understood [116,117]. For example, Lee et al. found the existence of a strong steric barrier for the transport of hydrogen in nanotubes [118]. Ye et al. observed a phase transition in SWNT at 77 K [119]. Lee and Lee reported that excessive hydrogen adsorption may lead to the breakdown of the tube structure [120]. The NREL (National Renewable Energy Laboratory, U.S.A.) demonstrated the ability for SWCNTs to store substantial quantities of hydrogen at ambient conditions via hydrogenation with reduced binding energies [2].

To explore the adsorption properties of SWCNT, a commercial SWCNT and hydrogen gas with high purity have been selected. The SWCNT was acquired from CheapTube Inc., USA. Table 4-3 lists the properties of the sample.

Table 4-3 The properties of a commercial SWCNT

Purity	Ash	OD	Surface area	Length	EC
> 90 %	< 1.5 %	1-2 nm	> 407 m ² /g	5-30 μm	> 10 ⁻² s/cm

Note: OD = Outer diameter; EC = Electrical conductivity

4.3.1 Characterization of SWCNT

N₂ adsorption isotherms at 77 K of the SWCNT sample were shown in Figure 4.5(a). It can be observed that the isotherms show Type II adsorption isotherm (IUPAC classification). The moderate amount of adsorption on the SWCNT at very low pressures indicates the presence of micropores [121]. The specific surface area (S_{BET}) was determined using the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.3. The measured S_{BET} derived from the N₂ is 420 m²/g, which is near to the value the supplier provided. The total pore volume of the sample is ~ 0.70 cc/g and the micropore volume is ~ 0.12 cc/g. Figure 4.5b shows the pore size distribution (PSD) of the SWCNT derived from the N₂ isotherm via the NLDFT method which assumes cylindrical graphite pore geometry. It is seen that the sample has a sharp

volume peak at the pore diameter of ~ 1.1 nm and a minor peak at ~ 2.0 nm, which is consistent with the information in Table 4-3 that tube OD = 1-2 nm. Meanwhile, a large portion of the pore volume (as well as surface area) was seen to be contributed by tubes with the diameter above 2 nm. This apparent discrepancy with the product specifications is probably due to the adsorption at the external surface of the tubes and the void space formed among the CNT bundles, which constitutes a major volume contribution of mesopores. The desorption hysteresis confirms the existence of mesopores volume in the sample. Table 4-4 lists texture properties of the SWNT derived from N_2 adsorption.

Figure 4.5 (a) The N_2 isotherm on SWCNT; and (b) the derived PSD of SWCNT.

Table 4-4 Surface properties of SWCNT derived from N_2 adsorption

BET area (m^2/g)	V_t (cc/g)	V_{mic} (cc/g)	V_{me} (cc/g)
420	0.70	0.12	0.58

4.3.2 CO_2 sorption in SWCNT

For comparison with N_2 sorption isotherms, CO_2 sorption isotherms on the SWNT sample were also measured. Figure 4.6 shows the adsorption isotherms of CO_2 measured on the sample at 273 K (The sample cell was submerged in an ice bath during the experiment). As the adsorption pressure is low ($P_0 = 1.05$ bar), CO_2 adsorbed moderately and no hysteresis was observed between the adsorption and desorption

isotherms. A small hump was seen at $P/P_0 = 0.18$, which may be related to the transition of adsorption from the internal tubes to the external voids/surfaces [117]. Simulation studies are needed to understand the underlining mechanisms at this point.

Figure 4.6 CO₂ isotherm on SWCNT ($P_0 = 1.05$ bar) at 273 K.

Figure 4.7 H₂ isotherm on SWCNT at 77 K. (The fitting parameters of Langmuir isotherm are: $C_{\mu s} = 95$ STP cc/g, $b = 1.93$ bar⁻¹.)

4.3.3 Hydrogen adsorption on the commercial SWCNT

The hydrogen isotherm measured on the SWCNT at 77 K is shown in Figure 4.7, which combines the data from the PSA ($P < 1.05$ bar, solid circles) and the high pressure volumetric rig ($1.05 \text{ bar} < P < 10$ bar, open circles). It is seen that the isotherm data measured with the two rigs agree with each other reasonably well. The hydrogen isotherm data are fitted to the Langmuir equation, Eq. (4-2), where b is the adsorption affinity, P is the pressure and $C_{\mu s}$ is the saturation capacity of the SWNT. The fitting parameters are listed in the caption of Figure 4.7. The isotherm data revealed that the SWCNT presents a H₂ adsorption capacity of ~ 0.9 wt% at 77 K and 10 bar. This capacity is mainly determined by the micropore volume and the tube sizes of the SWCNT sample.

4.4 Summary

Commercial AC sample may present good performance for methane storage, provided that the sample presents a narrow pore size distribution around 0.8-1.1 nm and a surface area $\geq 900 \text{ m}^2/\text{g}$. Such commercial ACs have the advantage of low cost, but are generally low in storage capacities. The structure of such a commercial AC may be further tailored to improve the methane storage capacity, for example, via the chemical/physical activations to open more micropores, or via the chemical vapor deposition to reduce the size of large pores [122]. Both techniques are well developed and worthwhile to try in the future. However, the raw commercial ACs present low volumetric methane capacity.

The commercial SWCNT was found to have a major tube diameter distribution at 1.1 nm, but the external surface and the void space among the CNT bundles constitute the major contribution of mesopore volume. The hydrogen adsorption capacity of the sample is found to be $\sim 0.9 \text{ wt } \%$ at 77 K and 10 bar, which is lower than the Norit AC. This finding is in agreement with the simulation study conducted by Bhatia and Myers [50] that CNT presents no obvious advantage over ACs in energy storage application.

CHAPTER 5 CH₄ STORAGE IN TCS AND TC PELLETS

5.1 Introduction

Natural gas (NG, with methane >70 wt%) is gaining increasingly more attention as a fuel because of its inherent clean burning characteristics, abundant reserve and relatively low price. Activated carbons (ACs) are excellent adsorbents for NG storage in the form of adsorbed natural gas (ANG). For the optimal storage of NG, the AC should be predominantly microporous with the pore size around 0.8-1.0 nm [30,106,123], although mesoporosity is also necessary for the intraparticle transport/diffusion of methane molecules. Templated carbons (TCs) are produced via the pyrolysis of carbonaceous precursors formed in the highly ordered micro-channels of porous media such as zeolites and silicas, etc. These types of carbons have been successfully fabricated for various applications [74,84,83].

This chapter will investigate the methane storage in two as-synthesized TC samples and their pellets fabricated with two different pelletisation technologies.

5.2 Sample preparation and characterization

Two as-synthesized TC samples were employed to study the methane storage performance. They are: (1) a TC derived from sucrose, S1100 and (2) a TC derived from PFA, C1050.

5.2.1 TC S1100 preparation and characterization

5.2.1.1 Preparation

TC S1100 was prepared by soaking ammonium-form zeolite Y (NH₄Y form, SiO₂/Al₂O₃ = 5.1) in sucrose solution, pyrolyzed at 1100 °C and followed by acid wash. The detailed preparation procedures can be found in Chapter 3.

5.2.1.2 SEM/TEM analysis

Figure 5.1 shows the FESEM and TEM images of S1100. The image shown in Figure 5.1a reveals that TC S1100 has the layered-graphite structure with large interparticle voids, which is in agreement with the XRD result that TC S1100 is largely amorphous (See section 5.2.1.3) and the density measurement that its bulk density is low (0.23 g/cm^3 by the ASTM method). The TEM image (Figure 5.1b) of the carbon crystal shows a thick graphite core surrounded by thin graphite shells. Some defects can be clearly seen at the edge of the crystal as well. These observations suggest that the graphite crystal presents a high degree of structural heterogeneity and many amorphous domains.

Figure 5.1 The structure of S1100: (a) FESEM; and (b) TEM.

5.2.1.3 XRD analysis

Figure 5.2a shows the XRD pattern of TC S1100 while the embedded Figure 5.2b shows the XRD pattern of the zeolite $\text{NH}_4\text{-Y}$. The two peaks at around $\sim 25^\circ$ and 43° (2θ) in Figure 5.2a are assigned to the (002) and (100) diffractions of graphitic carbon [124,125], indicating a quasi-crystalline carbon structure. The shift of the peak (002) from 26.3° (2θ) to $\sim 25^\circ$ (2θ) was also observed previously [82]. The peak at 6° (2θ), which is corresponding to the (111) planes of zeolite Y and was observed in TCs

derived from zeolite Y by other studies [80,82], was not clearly seen in the present study, indicating that the structural ordering of the sample is low.

Figure 5.2 The XRD pattern of (a) TC; and (b) zeolite Y.

5.2.1.4 TGA analysis

Figure 5.3 The thermogravimetric analysis of TC: (a) TGA; and (b) DTGA.

The TGA and the derivative thermogravimetric analysis (DTGA) of the sample are presented in Figure 5.3a and Figure 5.3b, respectively. It is seen from Figure 5.3a that the oxidation (combustion) of TC S1100 was nearly complete, indicating that the acid-wash treatment is effective in removing the zeolite template and the sample is a pure carbon. As the weight loss above 250 °C is related to the combustion of amorphous carbons, the broad peak at 550-630 °C (Figure 5.3b) suggests that TC S1100 is highly amorphous.

5.2.1.5 Structural characteristics

(1) N₂ adsorption

The porous structure of the sample S1100 was initially analysed with N₂ isotherm measured on a pore and surface analyser (Quantachrome, Autosorb-1c) at 77 K. Figure 5.4a shows the nitrogen isotherms measured on TC sample. It can be seen that TC S1100 exhibits considerable high adsorption capacity. Desorption isotherm suggests that TC S1100 possesses a small portion of mesopores, which results in small hysteresis observed in the desorption curve. This mesopore characteristic of TC S1100 can be attributed to such factors as: adsorption on the surface of graphite grains and interparticle voids, the polymer layers formed on the exterior surface of zeolite particles, etc. (See Figure 5.1a)

The pore size distribution (PSD) and cumulative pore volume were derived from the N₂ isotherm via the non-local density functional theory (NLDFT) (See Figure 5.4b and 5.4c). It is seen that TC has a major micropore peak at ~1.1-1.2 nm, close to the optimal pore size range (0.8-1.0 nm) for methane storage. Two minor mesopore peaks are also seen at ~2.6 nm and ~3.8 nm, which result in a mesoporosity ~ 40% in TC S1100.

According to the N₂ adsorption isotherms, the specific surface area (S_{BET}) was determined according to the BET method in the relative pressure range of 0.05–0.3. The total pore volume (V_{t}) was obtained from the volume of nitrogen adsorbed at a relative pressure of 0.95. The micropore volume (V_{mic}) was calculated from the Dubinin–Radushkevich (DR) equation. The mesopore volume (V_{me}) was determined by

subtracting the micropore volume from the total volume. The structural and adsorption characteristics of TC S1100 are listed in Table 5-1.

Figure 5.4 (a) N₂ isotherms at 77 K on TC S1100; (b) PSD and (c) cumulative pore volume of TC S1100 derived by NLDFT method.

Table 5-1 The surface parameters of TC S1100

Sample	BET area (m ² /g)	V _t (cc/g)	V _{mic} (cc/g)	V _{me} (cc/g)
S110 0	1500	1.30	0.78	0.52

Note: V_t, total pore volume; V_{mic}, micropore volume; V_{me}, mesopore volume.

(2) Isopropanol vapor adsorption analysis

From Figure 5.4b, it can be seen TC S1100 has micropores with the size ~1.1 nm. This structure of TC was further characterized by isopropanol vapor adsorption analysis. Isopropanol is a weakly polar molecule with the size of 4.8 Å. Its basic properties are listed in Table 5-2.

Table 5-2 The basic properties of isopropanol

Molecular formula	Molar mass	Density	Boiling point
C ₃ H ₈ O	60.10 g/mol	0.786 g/ml, liquid	82.3 °C

The isotherm was measured at 283 K on the Quantachrome Autosorb-1 by using its standard vapor adsorption function. It is seen in Figure 5.5a that TC adsorbs a considerable amount of the alcohol and presents a desorption hysteresis. The isotherm measurement terminated at P/P₀ = 0.85 because of the extremely slow adsorption rates at higher adsorption pressure. The BET surface area revealed by the isopropanol isotherm is ~ 640 m²/g, considerably lower than that from the N₂ isotherm. This apparent difference can be attributed to the size exclusion effect of small micropores. For example, pores with the size ~ 1.1 nm (center-to-center distance between the graphite pore walls) can possibly accommodate two or more layers of N₂ molecules (with the collision diameter of ~ 0.3 nm), but is capable of hosting only a single layer of isopropanol (0.48 nm). In addition, micropores with the effective size of 0.48 nm or below are unlikely detected with isopropanol molecules. Such a disparity was also reported by Mikhail and Shebl [126], who observed a 50% difference in the BET areas

of a silica gel measured by N₂ (793 m²/g) and isopropanol (437 m²/g) isotherms. The vapor isotherm was then analysed by the Dubinin–Astakhov (DA) equation and the derived PSD was shown in Figure 5.5b. It is seen that the large isopropanol molecule give a narrower pore size range peaking at ~1.8 nm.

Figure 5.5 (a) The isopropanol isotherm on TC; and (b) the derived pore size distribution on TC.

5.2.1.6 Pelletisation with S1100

The as synthesized TC is in the form of very fine flakes (Figure 5.1) which occupy large inter-particle space and result in a low bulk density (0.23 g/cc). To improve the volumetric capacity of TC S1100, carbon pellets (or monolith) were fabricated, which has been known as an effective way to increase the volumetric adsorption capacity, although at the sacrifice of gravimetric capacity. The procedure of pellet fabrication basically follows the method proposed by Wang et al. [127] and Lozano-Castello et al. [30], i.e.: (1) TC flakes were ground into fine powders in a ball miller and sieved with 63μm mesh tray in a sieve-shaker, (2) ~7 wt% of binder (PVA, hydrolyzed, Sigma-Aldrich®) was mixed with the fine TC powder and added with DI water, (3) The slurry was shifted into a small metal mold made of aluminium foils, and (4) The mold was put in a hydraulic press with heating function and subject to 30 bar and 180 °C overnight. Phenolic resin was also tested as a binder for its reported good performance to make carbon monolith [127] but was found inferior to PVA due to its high weight percentage

requirement, the complicated afterwards thermal treatments and the low mechanical strength of the pellets. After the pelletisation, the bulk density of the pellet increases drastically from 0.23 g/cc to 1.10 g/cc.

5.2.2 Preparation and characterization for TC C1050 and its pellet

5.2.2.1 Sample preparation

For preparation of C1050, ammonium-form zeolite Y (NH_4Y , $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.1$) was impregnated with poly furfuryl alcohol (PFA), pyrolyzed at 1050 °C for 4 hours under a N_2 gas flow, and followed by acid treatment to remove the templates. The as-synthesized TC (referred to as C1050) was in the form of very fine powders and was used to fabricate pellets by the following procedure: (1) 400 mg of TC was loaded in a metal bag made of commercial aluminum foils; (2) the system was hot-pressed at 200 °C and 50 MPa for 4 hours using a heated press (Model 4128, Carver Inc., USA); and (3) the system was then cooled in air. The obtained pellet is named as C1050P. To determine the bulk density of TC pellet, a rectangular pellet was carefully cut out of the large pellet with a surgical knife. The pellet was then dried in a vacuum oven overnight at 200 °C. Its density was calculated from its weight and geometrical volume.

5.2.2.2 XRD analysis

The XRD patterns of C1050, C1050P and the zeolite Y template are shown in Figure 5.6a and 5.6b, respectively. The XRD pattern of C1050 is largely featureless without showing the diffraction peaks at 6° (2 θ), which is corresponding to the {111} plane of zeolite Y. What is more, the {002} and {100} diffraction peaks of graphite carbon at 26° (2 θ) and 43° (2 θ) were also hardly noticeable. These observations point to the amorphous nature of TC C1050. In comparison, TC samples derived from zeolite Y by Hou et al. [128] and Chen et al. [85] clearly exhibit the diffraction peaks at 6° (2 θ), indicating the presence of ordered microporous structure. Figure 5.6 also shows the XRD pattern of the C1050P, from which a broad diffraction peak of {002} at 26° (2 θ) can be clearly seen, indicating that C1050P possesses certain degree of the ‘turbostratic’ structure in graphite carbon [129]. Turbostratic carbon (t-carbon) is a variant of hexagonal graphite. The graphite layers of t-carbon may randomly translate to each other and rotate about the normal of graphite layers. This structure change of

C1050P indicates that the densification of TC C1050 leads to the deformation of graphite crystals and the formation of multi-layered graphenes.

Figure 5.6 XRD diffraction pattern of (a) C1050/C1050P; and (b) template zeolite Y.

5.2.2.3 SEM/TEM analysis

Figure 5.7a shows the FESEM image of C1050 powder, from which we see that the sample consists of graphite crystals with the dimensions of a few hundreds nm and with large interparticle voids. The magnified view (Figure 5.7b) confirms that the graphite crystals are largely amorphous. The TEM image in Figure 5.7c suggests that the structure of the graphite crystal is heterogeneous with many defects.

The FESEM image of C1050P in Figure 5.8a shows that the pellet is compact with very little interparticle voids. The magnified view of C1050P in Figure 5.8b further reveals that, compared with the graphite crystals in powdered TC (Figure 5.7b), the compression deformed the graphite crystals of the pellet and the crystals became more irregular in geometry.

Figure 5.7 Morphology of C1050 powder: (a) SEM; (b) SEM magnified; and (c) TEM.

5.2.2.4 Raman analysis

Figure 5.9 shows the Raman spectra of the C1050 and C1050P, respectively, as lines. The D-peak (1350 cm^{-1}) and G-peak (1582 cm^{-1}) correspond to the amorphous and graphite domains of the samples, respectively [130]. It is seen that the height of the D-peak becomes slightly higher than that of the G-peak after compression. A simple calculation reveals that the ratio of the integrated areas (intensities) of D-peak to G-peak (I_D/I_G) increased slightly from the powder (2.12) to the pellet (2.23). This suggests that the hot-pressing increased the structural disorder of TC C1050. This result is supported by the SEM image in Figure 5.8b which shows that the graphite crystals were deformed upon the compression.

Figure 5.8 (a) SEM image of C1050P (Overview); and (b) SEM image of C1050P (Magnified view).

Figure 5.9 Raman spectra of C1050 and C1050P.

5.2.2.5 Structural characteristics

Figure 5.10a shows N₂ isotherms measured on the two samples (powdered TC and its pellet) at 77 K. The desorption hysteresis loop on C1050 indicates the existence of mesopores. This loop, however, is barely perceptible on C1050P, which suggests that hot-pressing is an effective method for reducing the mesoporosity. Figure 5.10b presents the derived PSDs via NLDFT, from which it can be seen that: (1) the mesopores (with sizes ranging from 2 to 5 nm) of C1050 was largely eliminated by hot-pressing, and (2) the major micropore peak was shifted from ~1.4 nm on C1050 to ~1.1 nm on C1050P. The shift of the micropore peak suggests that deformation of the graphite crystals has occurred under the external pressure as low as 50 MPa.

Table 5-3 Structural characteristics of TC C1050 and TC pellet C1050P

Sample	Density (g/cm ³)	S _{BET} (m ² /g)	V _{mic} (cm ³ /g)	S ^a (m ² /cm ³)	V ^a (cm ³ /cm ³)
C1050	0.28	2136	1.034	454	0.28
C1050P	0.98	932	0.544	913	0.54

Note: ^a = on volumetric basis

Figure 5.10 (a) N_2 adsorption isotherms; (b) the derived PSDs and (c) cumulative pore volume of C1050 and C1050P by NLDFIT method.

Figure 5.10c shows the cumulative pore volume of the two samples, indicating that small micropore volume (pore size <1.3 nm) was increased after the pelletisation process. It can be postulated that the large micropores (~1.4 nm) derived from the template zeolite are mechanically fragile and deformable upon compression.

Table 5-3 shows that C1050P has a bulk density of 0.98 g/cm³, which is about 3.5 times the density of the as-synthesized TC powders. The surface area (S_{BET}) and micropore volume (V_{mic}) of C1050P are lower on the gravimetric basis, but are higher on the volumetric basis. The SEM image of C1050P presented in Figure 5.8a shows that the pellet is compact with very little interparticle voids. The magnified view of C1050P in Figure 5.8b further reveals that, compared with the graphite crystals in TC C1050 (Figure 5.7b), the compression deformed the graphite crystals and they became more irregular in geometry. The bulk density of C1050P (0.98 g/cm³) is close to the densities of carbon monoliths for methane storage reported in a few other studies [30,39].

All these findings show the excellent pelletisation property of TC C1050. Hou et al. [128] also found the hot-pressing can change microporosity of their zeolite Y derived TCs and proposed that TCs possess the “soft” mechanical structure. Nishihara et al. recently proposed that zeolite-derived TCs have a 3-D buckybowl-like nanographenes structure [131]. According to this model, it can be deduced that the collapse of this 3-D structure will lead to the formation of multiple-layered graphenes which accommodate slit-like micropores and small micropores (<1.0 nm) and subsequently result in the diffraction peak at 26° (2 θ) observed in Figure 5.6. The formation of the multi-layered graphenes well explains the dramatic decrease in the specific surface area, porosity, as well as the significant increase in the density of the pellet.

From discussion above, the good pelletisation of TC C1050 may be attributed to three factors: (i) the graphite crystals of TC are very fine and relatively uniform in size so that they can be closely packed under compression; (ii) the 3-D buckybowl-like graphenes are fragile/deformable under external pressure; and (iii) the deformed/collapsed 3-D frame lead to the formation of layered graphenes which subsequently bridge with each other via the covalent bonds under the heating. In a comparison study, such a hot-pressing procedure was found unable to pelletize the

commercial Norit AC powders. This is because: (1) the graphite crystals of the conventional AC are non-uniform, and (2) the graphene layer of the normal AC is stacking so that its framework is mechanically ‘hard’.

5.2.2.6 Tensile strength of C1050P

The mechanical strength of C1050P was also demonstrated. The picture embedded in Figure 5.12 shows that a small TC pellet (size: 6mm ×10mm×0.5mm; weight: ~25mg) can well support the weight a metal nut (weight: ~2.5 gram). The tensile strength of C1050P was measured using a horizontal micro-tensile test rig (See Figure 5.11). Figure 5.12 presents the result of the tensile test with a small pellet and from which the tensile strength of C1050P was calculated as ~1 MPa. In comparison, the ultimate tensile strength of concrete is ~3 MPa (en.wikipedia.org/wiki/Tensile). This shows C1050P has good mechanical strength. It is also interesting to see that the fracture took place at the elongation of ~12%, confirming that the pellet has the soft mechanical structure. The pellet was also found to hold well after the repeated degassing-adsorption processes, during which the pressure fluctuated from 10^{-4} Torr to 35 bar and temperature varied from room temperature to 250 °C.

Figure 5.11 Photo for the tensile test rig.

Figure 5.12 C1050P loading test result and its photo (embedded).

5.3 Methane adsorption in S1100 and its pellet

5.3.1 Methane adsorption in TC S1100

Figure 5.13 presents the adsorption isotherms of methane on TC S1100 at three temperatures (263, 273 and 300 K) and with the pressure up to 40 bar. It can be seen that the sorption amount of TC S1100 at 300 K and 35 bar can reach 8.0 mmol/g and it is still far from the saturation capacity at the upper limit of the experimental pressure. The shape of the methane isotherm on TC is also found to be very different from a typical type I isotherm (such as the methane isotherms on the Norit AC, shown in Chapter 4, Figure 4.3). This is probably due to the strong surface heterogeneity of TC towards methane gas. Toth isotherm model was therefore used to fit the isotherm data, which takes the form of Eq. (4-1). The fitting results are shown in Figure 5.13 as lines while the optimally obtained fitting parameters are listed in Table 5-4. It is seen that the Toth equation fits the isotherm data reasonably well but gives unrealistic high saturation capacities ($C_{\mu s}$) for TC S1100. The reason is that the experiment pressure is too low to exert reasonable constraints on the derived adsorption capacities. The value of the heterogeneity parameter, t , further indicates that TC S1100 ($t = 0.32$ at 300 K) presents strong surface heterogeneity towards methane molecules.

Figure 5.13 Methane isotherms on TC powder and TC pellet.

Table 5-4 Toth isotherm parameters of methane on a TC sample, S1100

Temperature	$C_{\mu s}$ (mmol/g)	b (1/bar)	t
263K	215.22	2.23×10^{-2}	0.240
273K	196.32	1.22×10^{-2}	0.259
300K	170.15	5.49×10^{-3}	0.319

5.3.2 Methane adsorption in TC S1100 pellet

For the purpose of assessment of methane volumetric storage capacity of TC S1100, the sample density was measured. The helium density was measured with a pycnometer while the bulk density of carbon powder was analysed using the ASTM method. The measured value of helium density is 2.15 g/cm^3 ; however that of bulk density is as low as 0.23 g/cm^3 . The gravimetric and volumetric methane adsorption capacities of TC S1100 are listed in Table 5-5 and compared with a few other AC samples reported in the literature (See Table 5-5). It is seen that TC S1100 presents a good gravimetric capacity (8.0 mmol/g) at 35 bar and 298 K. This value indicates that TC S1100 presents higher methane density of 0.16 g/cm^3 (calculated from methane uptake divided by the micropore volume) than that of ACs via KOH activation ($0.13\sim 0.15 \text{ g/cm}^3$) [30].

Figure 5.13 also shows the methane isotherm data (squares) on the prepared TC pellet (made with PVA as binder) and the photo of a piece of TC pellet. The methane sorption capacity of TC S1100 pellet was found to decrease from 8.0 to 4.5 mmol/g at 300 K and ~ 35 bar. The volumetric capacity of TC S1100 pellet was calculated to be $\sim 93 \text{ v/v}$, which compares favourably with most other samples listed in Table 5-5. Although the capacity of TC S1100 is still below that of KUA31751, an AC pellet fabricated from AC prepared via KOH activation, TC S1100 has good potential to improve and possibly to outperform. This is because the PSD and microporosity can be largely manipulated in case of TC, via the choice of template, precursor, and pyrolytic conditions. Judging from Figure 5.4, TC S1100 has a portion of mesopores ($\sim 40\%$ by volume fraction) as well as a portion of micropores in the size range of $13\text{-}20 \text{ \AA}$, which can be potentially tailored (via the choice of template, precursor, and pyrolytic conditions, etc.) to improve the methane capacity [78]. For TC S1100, during pyrolytic

process, additional lower temperature CVD method (~973 K) is expected to improve impregnation of the carbon sources into the nano-channels of the template [132]. Other studies also reported TCs with surface area up to 4,000 m²/g (although the average micropore size is a bit large) [72]. TCs with both high surface area and high volume fractions of small micropores should present much improved storage capacity for ANG application.

Table 5-5 Methane sorption capacities on various AC samples

AC adsorbents	Storage capacity @300K and 35bar		Method of preparation
	Gravimetric (mmol/g)	Volumetric (v/v)	
S1100 flakes	8.0	43	Template synthesis
S1100 pellets	4.5	93	PVA binder, 180 °C
CMK-3 [96]	5.2 (at 298K)	-	Template synthesis (Silica)
Coconut shell-AC [34]	7.4	86	Chemical (H ₃ PO ₄ /ZnCl ₂) & physical (CO ₂) activations
KUA31751 [133]	12	141 (at 298K, pellet)	Chemical activation (KOH)

5.4 Methane adsorption in C1050 and C1050P

5.4.1 Methane adsorption isotherms in C1050

Figure 5.14 shows the methane isotherms (symbols) measured on TC C1050 at 263, 273 and 298 K, respectively, with the pressure up to 35 bar. It can be seen that the isotherms can be fitted using Langmuir model (Lines), which takes the form of Eq. (4-2). The optimal parameters are listed in Table 5-6. It can be observed that TC C1050 is not saturated at the upper limit of the experimental pressure. At 298 K and 35 bar, the storage capacity can reach ~11 mmol/g [246 cc (STP)/g], which is much better than that of self-ordered mesoporous carbon (CMK-3) [96] and also better than that of TC S1100.

Table 5-6 Langmuir model parameters of methane adsorption in C1050

Temperature (K)	$C_{\mu s}$ (mmol/g)	b (bar ⁻¹)
263	17.73	0.0691
273	17.12	0.0549
298	14.66	0.0634

Figure 5.14 Adsorption isotherm of methane on TC C1050.

5.4.2 Methane adsorption performance of C1050P

Figure 5.15 presents methane isotherms on C1050 (open circles) and C1050P (dots) measured, respectively, at 35 bar and 298 K. The volumetric storage capacities were calculated and listed in Table 5-7. The methane isotherms were fitted to Langmuir equation [See Eq. (4-2)] with the optimal parameters listed in Table 5-7. The methane volumetric capacity on C1050P was found to be 127 v/v, which was approximately doubled that on C1050 (TC powder). It can be observed from Table 5-3 that the methane volumetric storage capacity is directly relative to surface area and micropore volume on the volumetric basis. For ANG application, these two parameters are more important than conventional S_{BET} and V_{mic} on the weight basis. This high volumetric methane capacity gives further supports on the pelletisation method developed in this study. Compared with the other pelletisation techniques, the simplified hot-pressing method uses normal laboratory equipment and is able to effectively reduce the

mesoporosity of TC C1050. TC C1050P presents good methane storage capacity on volumetric basis and excellent mechanical strength.

Table 5-7 Comparison of methane storage capacity of C1050 and C1050P

Sample	$C_{\mu s}$ (mmol/g)	b (bar ⁻¹)	Storage capacity at 35bar 298K ,cc(STP)/g	Storage capacity at 35bar 298K, (v/v)
C1050	14.66	0.0634	246	69
C1050P	7.184	0.0952	130	127

Figure 5.15 Methane isotherm data (symbols) on C1050 and C1050P at 35 bar and 298 K and the optimal fittings (lines) via Langmuir equation.

5.5 Summary

The sucrose-derived TC has a surface area of $\sim 1,500 \text{ m}^2/\text{g}$ and a methane adsorption capacity of 8.0 mmol/g at 300 K and 35 bar . The low bulk density of the as-synthesized carbon powder was improved by the fabrication of carbon pellets (with a PVA binder) on which a volumetric methane storage capacity of 93 (v/v) was achieved. TC sample prepared with PFA as carbon source (C1050) presents a surface area of $2136 \text{ m}^2/\text{g}$ (by N_2 sorption) and a gravimetric capacity of 10 mmol/g . TC C1050 also has good

pelletisation performance. TC pellet fabricated via the binderless technology presented good mechanical strength and a methane capacity ~ 127 (v/v). This shows TC and the binderless pelletisation technology developed are very promising for the ANG application. It was also found that the hot-pressing can effectively reduce the mesoporosity of the carbon powder and, meanwhile, change the microstructure and morphology of the graphite crystals.

CHAPTER 6 HYDROGEN STORAGE IN TCS

6.1 Introduction

Template synthesis is a promising technology for preparing activated carbon (AC) samples with large surface area and with relatively uniform porous structure [13,69,74,84]. These templated carbons (TCs) have been demonstrated to have a good potential application in methane storage (Chapter 5). Hydrogen storage in these nanoporous carbons is also of particular interest. This chapter presents the hydrogen adsorption results on the two TCs described in Chapter 5. The hydrogen isotherms were measured at various temperatures and based on which the heat of hydrogen adsorption was calculated.

6.2 Hydrogen adsorption in the sucrose derived TC (S1100)

6.2.1 Structural characteristics of TC S1100

From Chapter 5, structure characteristics of S1100 can be summarized as follows: TC S1100 has a quasi-crystalline carbon structure with lower structural ordering. TC S1100 has the layered-graphite structure with large interparticle voids, which results in its low bulk density (0.23 g/cm^3). TEM observations suggested that TC S1100 has graphite crystal structure with a high degree of structural heterogeneity and many amorphous domains. Thermo-gravimetric analysis (TGA) of the sample indicated that TC S1100 is basically zeolite free after acid treatment. The BET surface area of TC S1100 is $\sim 1,500 \text{ m}^2/\text{g}$. The micropore volume is $0.78 \text{ cm}^3/\text{g}$ and mesopore volume is $0.52 \text{ cm}^3/\text{g}$.

It is noted in Figure 5.4b that TC S1100 does not possess any small micropores (0.6-0.9 nm), which also play important role in hydrogen storage. To double check these small pores, CO_2 adsorption was measured on the sample at 273 K and analyzed with

the NLDFT method (in which CO₂ molecules are treated as the 3-centered fluid with L-J 12-6 as well as electrostatic interaction potentials) [134] and Horvath-Kawazoe (HK) method [135], respectively. The CO₂ isotherm is presented in Figure 6.1 on logarithmic scale as symbols ($P_1=1.05$ bar is the maximum sorption pressure that the PSA can reach) while the derived PSDs are shown in the figure also as the solid line (NLDFT) and dashed line (HK), respectively. It can be seen that both methods confirm the existence of small micropores in the size range of 0.6-0.9 nm which are desirable for hydrogen storage. Moreover, the PSD derived by NLDFT method presents micropore peaks at 0.4~0.5 nm which are invisible in that derived by the HK method. The PSD from NLDFT is more reasonable as it considers both adsorbate-adsorbate and adsorbate-adsorbent interactions. The PSD from HK method, however, only take into account of the adsorbate-adsorbent interaction and assumes a linear isotherm.

The above findings suggest that CO₂ adsorption is a more reliable method for the structural characterization of adsorbents with small micropores, such as the zeolite-templated carbons. This finding is in line with the expectations, because (1) CO₂ molecule is more strongly adsorbed and smaller in dimension (at favorable orientation) than N₂ molecule, and (2) the high adsorption temperature (273 K) facilitates CO₂ molecule to penetrate into small micropores with much faster kinetic rates than N₂ molecules at 77 K. Another possible reason (although speculative at this point) is that TC S1100 may have some ink-bottled micropores (The pore has access to the external only via narrow constriction). Such a structural feature is common for carbon molecular sieves (CMS), of which the ultramicroporosity and the strong pore mouth barrier limit the use of N₂ adsorption at 77 K [136]. Therefore, CO₂ adsorption at ambient temperature should be preferred for characterizing the small micropores (0.6-0.9 nm) in carbonaceous materials for hydrogen storage.

CO₂ sorption at 273 K presents the advantage for characterizing small micropore not only for TCs but also for other carbonaceous adsorbents. For example, Mandoki et al. [137] reported that the hydrogen uptakes are directly proportional to the micropore volumes of the carbon samples derived from CO₂ isotherm at 273 K (however, this is not applicable to N₂ isotherm at 77 K). Jagiello and Thommes [138] found that CO₂ adsorption is more applicable in characterizing small micropores of carbonaceous adsorbents. As small micropores provides the main CH₄/H₂ adsorption capacity, CO₂

adsorption at 273 K should be preferably used to characterize the structure of the adsorbent for the application, or at least used to double check the structural information derived from N₂ isotherm at 77 K. The N₂ adsorption at 77 K, on the other hand, is more convenient and reliable for characterizing large micropores (1-2 nm) and mesopores. Such large pores may also be characterized by CO₂ adsorption at 273K but requires a bulk phase pressure considerably higher than the upper limit of the bulk phase pressure (~ 1 bar) in the current commercial PSA rig.

Figure 6.1 CO₂ isotherm at 273K ($P_1 = 1.05$ bar) and the derived PSDs with NLDFT (—) and HK (--) method.

6.2.2 Hydrogen adsorption isotherms

Hydrogen isotherms were measured on TC S1100 sample at three temperatures [77 K (liquid N₂ temperature), 194.5 K (dry ice temperature) and 303 K (room temperature)], respectively. For 77 K, the isotherms were first measured with the PSA rig up to 1 bar and then measured with the high pressure rig up to 50 bar. Figure 6.2 shows the isotherm data as symbols. It is noted that the two sections of the isotherm data at 77 K agree with each other reasonably well. It is seen that, at 77 K, the hydrogen adsorption increases quickly until $P = 10$ bar with a capacity of ~ 12 mmol/g (~ 2.4 wt%), then the isotherm becomes flat quickly and the capacity reaches 2.7 wt% at 50 bar. At room temperature and 50 bar, the hydrogen uptake is about 0.8 wt%.

Figure 6.2 Hydrogen adsorption isotherm data (symbols) and the model fittings with the Toth equation (lines). [The isotherm parameters for 77 K data are: $C_{\mu s} = 15.5$ (mmol/g), $b = 9.03$ (bar⁻¹), and $t = 0.491$.]

The isotherm data were fitted, respectively, to the Toth isotherm equation described in Section 4.1.2 [Eq. (4-1)]. The fittings are shown in Figure 6.2 as solid lines and the optimal isotherm parameters for the experimental data at 77 K are listed in the figure caption. It can be seen that the hydrogen capacity decreases significantly at dry ice temperature (~ 0.2 wt% at 10 bar) while the isotherm is largely linear at 303 K. The Toth isotherm parameter ($t = 0.491$ at 77 K) indicates that TC S1100 is heterogeneous

towards hydrogen molecules. The saturation capacity of 15.5 mmol/g indicates that the maximum hydrogen uptake at 77 K can be up to 3.1 wt%.

6.2.3 Isostatic heat of hydrogen adsorption

Isostatic heat of hydrogen adsorption is an important parameter characterizing the interaction between hydrogen molecules and the carbon adsorbent. The heat of adsorption of hydrogen is generally low on commercial ACs due to the high volume fraction of macro- and meso- pores in these commercial products. Bhatia and Myers have estimated an optimal heat of hydrogen adsorption about 15 kJ/mol for carbonaceous adsorbents, considering the storage and delivery of hydrogen between 30 and 1.5 bar [50].

The definition of isosteric heat of adsorption is obtained from the Vant Hoff equation [139]:

$$Q_{iso}/RT^2 = -(\partial \ln P / \partial T)_q \quad (6-1)$$

where Q_{iso} is the isosteric heat of adsorption (kJ/mol), T is the temperature (K), P is the adsorbate pressure (bar), q is the constant adsorption amount, and R is the universal gas constant.

Integrating Eq. (6-1) gives:

$$\ln p = -\frac{Q_{iso}}{RT} + C \quad (6-2)$$

where C is the integration constant. Hydrogen adsorption isotherms at 77 K, 195 K and 303 K were used to calculate the heat of hydrogen adsorption. The hydrogen adsorption isotherms were first converted to hydrogen adsorption isosteres (P versus T at a given adsorption amount) and then Q_{iso} was calculated from the slopes of the isosteres according to Eq. (6-2).

Figure 6.3a plots Q_{iso} versus the adsorbed phase concentration of hydrogen while the embedded Figure 6.3b shows the range of the experimental isotherm data involved in the computation (that is, interpolation within the experimental data was employed to

draw the smooth curve of Figure 6.3a. Extrapolation outside the range of experimental data, however, was not used). The value of heat of adsorption of hydrogen in TC S1100 can be as high as 8 kJ/mol. It is observed that the heat of adsorption decreases quickly from ~ 8 kJ/mol to 5 kJ/mol as the hydrogen bulk pressure increases from $\sim 10^{-3}$ bar to 0.2 bar.

The heat of adsorption is predominantly dictated by the pore size and $Q_{iso} = 8$ kJ/mol suggests that TC S1100 possesses a portion of micropores in the size range of 0.65 nm – 0.7 nm [52]. Such a value is a bit higher than the common carbonaceous adsorbents (e.g., commercial activated carbons) in which the pore sizes disperses in a large range and the average Q_{iso} is generally around 6 kJ/mol [50]. However, Rao et al [140] showed that the heat of adsorption is 4.39 kJ/mol for hydrogen molecules adsorbing onto a graphite basal plane, which suggests that the heat of adsorption can be as high as 8.8 kJ/mol in a slit graphite pore. Table 6-1 compares the Q_{iso} of various carbons. It can be observed that the Q_{iso} of C1050 (See section 6.3.3) and S1100 are comparable with other TCs. For example, Yang et al [80] also found that $Q_{iso} > 8$ kJ/mol in their TC sample at low loadings. Yushin et al. [52] even found that the heat of adsorption could reach 11 kJ/mol in their carbide-derived carbons (CDCs). It is noted that the pores in the CDC may not be slit-shaped.

Table 6-1 Comparison of Q_{iso} of various carbons

Sample	Q_{iso} (kJ/mol)	Ref.
CDC carbon	11	[52]
Normal commercial AC	~ 6.0	[50]
TC, derived from zeolite beta	~ 8.2	[80]
S1100	8.0	This project
C1050	7.8	This project

Figure 6.3 The isosteric heat of adsorption of H₂ on (a) TC; and (b) the isotherm data used in computation.

6.3 Hydrogen adsorption in the PFA-derived TC (C1050)

6.3.1 Structure characteristics of TC C1050

From Chapter 5, the structural characteristics of C1050 were examined and can be summarized as:

(1) TC C1050 is essentially amorphous in structure and the graphite crystals have heterogeneous surface with significant defects;

(2) TC C1050 has high surface area (2136 m²/g) and good micropore volume (1.034 cc/g);

(3) The derived PSD via NLDFT method from N₂ adsorption indicates that TC C1050 has major micropore peak at ~1.3 nm and mesopores ranging from 2~4 nm.

For the purpose of characterization of small micropores in C1050 sample, the adsorption isotherms of Ar at 77 K and CO₂ at 273 K were measured using the pore and surface analyzer. Figure 6.4 compares the isotherms of N₂, Ar and CO₂ on TC C1050

and their related PSDs and cumulative pore volume distributions derived via the NLDFT with the assumptions that the pores are slit-shaped and the adsorbate-pore interaction is dispersive.

It can be observed from the PSD derived from N₂ adsorption (Figure 6.4d) that TC C1050 has a major micropore peak at ~1.3 nm and two small mesopore peaks were found at 2.6 and 3.8 nm, respectively. Figure 6.4b and 6.4e present Ar isotherm measured at 77 K and the PSD derived from Ar isotherm. It can be seen that, Ar isotherm predicts a higher distribution density of micropores, and a peak of small micropores at ~ 0.6-0.7 nm, which was undetected by N₂ adsorption. Compared with the N₂ molecule, Ar is an inert monoatomic gas with smaller molecular dimension and higher critical temperature (150.9 K). These properties enable Ar molecules to penetrate the small micropores with faster kinetics and less diffusion barriers so that the small micropores (as well as the ink-bottled pores) were better probed.

Next, CO₂ isotherm measured at 273 K was employed to derive the PSD of TC C1050. CO₂ molecules are assumed to be a 3-centered fluid with both dispersive and electrostatic interaction among the fluid molecules [141]. Figure 6.4c and 6.4f show the CO₂ isotherms and PSD. It can be seen that CO₂ adsorption expectedly reports three micropore peaks, located at the pore size of 0.5 nm, 0.6 nm, and 0.85 nm, respectively. The micropore peaks at 0.6-0.9 nm were partly agreed by the PSD derived from Ar adsorption (Figure 6.4e). It should be noted that, in the measurements of the 3 isotherms, the lowest pressure is same at ~ 0.005 Torr. It might be possible for Ar or even N₂ molecule to detect the small micropores with considerably lower adsorption pressure (e.g. At 10⁻⁵ Torr). But the measurement will take very long time and the PSA may not function properly at such a low pressure range. Therefore, this exercise further confirms the previous results obtained on the sucrose-derived TC (S1100) that CO₂ adsorption is a more reliable method for the characterization of small micropores. This is expected as CO₂ molecule is more strongly adsorbed and smaller in dimension (at the favorable orientation) than N₂ and Ar molecules. This result is also in agreement with the study by Sweatman and Quirke that N₂ sorption at 77K is diffusion limited or even frozen in such small micropores [142].

The surface properties of TC C1050 were derived from the three adsorption isotherms and listed in Table 6-2. It is interesting to see that Ar adsorption predicts a slightly higher surface area and a larger micropore volume than N₂. This is due to the better accessibility of Ar molecules in the porous network of TC. The difference in the BET areas detected by molecules with different dimensions was also observed in the previous experiments and attributed to the effect of size exclusion (See Chapter 5). It can be seen from Table 6-2 that CO₂ adsorption reports a very small surface area and micropore volume (0.035 cc/g from *DR* plot). This is because its maximum bulk adsorption pressure is low (~1 bar, or P/P₀~0.02) and the adsorption takes place primarily in the small micropores at such a small relative pressure, which is shown in Figure 6.4c. According to the reference [142], considerably high adsorption pressure is needed for CO₂ molecule to detect the large pores of TC at ambient temperature, which is well beyond the working range of the present commercial PSA rig. The high surface area (~2500 m²/g by Ar sorption) and good micropore volume (1.034 cc/g) obtained from N₂ adsorption suggests that TC C1050 is a good candidate for energy storage. The existence of the mesopore volume means that the storage capacity of TC C1050 can be further improved.

Table 6-2 Textural properties of C1050 derived from N₂, Ar and CO₂ adsorption isotherms

Adsorbate	BET area (m ² /g)	Micropore volume (cc/g)	Total Pore volume (cc/g)
N ₂	2136	1.034	1.556
Ar	2545	1.129	1.402
CO ₂	125	0.035	0.035

Figure 6.4 Sorption isotherms, derived PSDs and cumulative pore volume of C1050: (a) (d) (g) N₂ isotherm at 77 K; (b) (e) (h) Ar isotherm at 77 K; and (c) (f) (i) CO₂ isotherm at 273 K.

6.3.2 Hydrogen adsorption isotherms

The hydrogen adsorption isotherms were also measured on C1050 at three temperatures (77 K, 195 K and 303 K), respectively. The hydrogen isotherm at 77 K was measured with the PSA rig up to 1 bar and with the high pressure volumetric rig up to 50 bar.

Figure 6.5a shows the hydrogen isotherm on TC C1050 at the three temperatures as the symbols. Some discrepancy can be seen between the hydrogen isotherm measured on the PSA rig (at 77 K, < 1 bar) and that measured on the high pressure volumetric rig

(77K, 0.3 to 50 bar), but the agreement was reasonable. At 77 K, hydrogen adsorption increases quickly until 10 bar with the storage capacity of 13.2 mmol/g (~ 2.6 wt%). This capacity increases to ~ 3.1 wt% at the pressure of 50 bar. The capacity is seen to decrease significantly at the dry ice and room temperatures (~ 1.0 wt% at room temperature and 50 bar).

Compared with other storage technologies such as metal-organic framework or metal hydrates, H₂ capacity of TC is comparable but at the lower end. For example, the above mentioned two technologies reported storage capacities of 6.9 wt% on MOF-5 (77K and 100 bar) [143] and 5.6 wt% on MgH₂/2LiNiH₂ [144], respectively. However, physical adsorption in carbonaceous adsorbent presents such advantages of low cost, good reversibility, and safety.

The hydrogen isotherms were then fitted, respectively, to the Toth equation [Eq. (4-1), Section 4.1.2]. The fittings are shown in Figure 6.5a as solid lines while the optimal parameters (for the isotherm data at 77 K only) were listed in the figure caption. The isotherm parameter ($t = 0.474$) indicates that TC C1050 is heterogeneous towards hydrogen molecules at 77 K.

Figure 6.5 H₂ adsorption isotherms and isosteric heat of C1050: (a) H₂ adsorption isotherms at three temperatures [Solid line = Toth model ($C_{ps} = 17.3$ mmol/g, $b = 8.66$ kPa⁻¹, $t = 0.474$, at 77 K), Dashed line = Cuong & Do's model]; and (b) Isosteric heat of H₂ adsorption on C1050. (The embedded figure shows the isotherm data used in computation of the isosteric heat.)

Finally, TC C1050 was characterized by H₂ sorption isotherm at 77 K with the model proposed by Nguyen and Do [145]. The model employs isotherm data at supercritical temperature and over a wide pressure range and has been used for the structural characterization of activated carbons, carbon molecular sieves, and carbon membranes [146]. Basically, the model assumes that physical adsorption in slit-shaped graphite pores consists of pore phase and adsorbed phase. Each phase has the potential energies related to the pore size and the position in the pores. The model fitting to the isotherm data was listed in Figure 6.5a as the dashed lines while the distribution of sorption capacities in pores of various dimensions were presented schematically in Figure 6.6. It can be seen that the model correctly predicts the small micropore peaks at 0.5-1 nm (detected by CO₂ sorption) and the mesopore peaks at 3-4 nm (detected by N₂ sorption), although the contribution of the mesopores seems a bit high.

Figure 6.6 The distribution of H₂ sorption capacity of C1050 derived by Cuong & Do's model.

6.3.3 Isosteric heat of hydrogen adsorption

The hydrogen isosteric heat of adsorption, Q_{iso} , was calculated using the Eq. (6-1) and plotted in Figure 6.5b versus the surface loading. The experimental data involved in the computation were plotted in the embedded figure. It is seen that the heat of adsorption drops quickly from ~7.8 kJ/mol to 5 kJ/mol as the surface loading increase to 4 mmol/g. The high value of the Q_{iso} is comparable to that of the previous sucrose-derived TC (S1100). As discussed before, this high value of heat of adsorption is an

indication of hydrogen adsorption in small micropores (0.6-0.9 nm) which is critical for the optimal hydrogen adsorption capacity at the ambient conditions.

6.4 Comparisons of the hydrogen adsorption performance for TCs

Table 6-3 compares the hydrogen storage performance and the surface area of some reported TC samples. It can be observed that C1050 has good hydrogen storage next to CB850h, a TC prepared via CVD at 1123 K using zeolite beta as solid template and acetonitrile as carbon precursor. The CB850h has a very high surface area of 3,189 m²/g and pore volume of 2.41 cm³/g, which may imply the better infiltration to the template by the CVD process and the possible improvement of the impregnation method. TCs prepared by CVD normally have high surface area, large pore volume and high order-ness. However, for zeolite Y template, CVD derived TCs are ordered with micropore peak at 1.4 nm (corresponding to the replica of the template), which present high capacity for hydrogen storage at cryogenic temperature but not at ambient temperature.

Table 6-3 Comparison of the hydrogen adsorption performance of some TCs and one AC

Material	S _{BET} (m ² /g)	Hydrogen Adsorption (wt%)		Carbon synthesis method		Temp. (K)
		(77K, 1bar)	(303K, 50 bar)	Carbon source	Template	
C-Chem ^[88]	1200	2	-	sucrose	SBA-15	1073
CB850h ^[80]	3150	2.6	-	acetonitrile	zeolite beta	1123
C-Y-2 ^[87]	2340	1.6	-	PFA+propylene	zeolite Y	-
CY800 ^[79]	1825	2	-	acetonitrile	zeolite Y	1073
C-1223-6 ^[91]	2749	2.24	-	sucrose	SBA-15	1173
S1100	1500	1.71	0.8	Sucrose	zeolite Y	1373
C1050	2135	2.24	~1.0	PFA	zeolite Y	1323
KUA5 ^[54]	3183	2.0	0.5

Figure 6.7 Comparison of PSD (a) and cumulative pore volume (b) for two TCs. [The PSDs (Large micro-/meso- pores) were derived from N₂ adsorption via NLDFT method.]

Figure 6.8 Distribution of small micropore in two TCs (a) and corresponding cumulative pore volume (b). (The PSDs were derived from CO₂ adsorption via NLDFT method.)

At room temperature, all TC and AC samples present relatively low adsorption capacity, which suggests that some breakthrough technology are needed for TCs to reach the hydrogen storage target set by DoE.

For C1050 and S1100, the two TCs have similar values of heat of hydrogen adsorption at low loading. It can be observed that the surface area of C1050 is significantly higher (~1.4 times) than that of S1100, but the storage capacity of C1050 is only about 1.17 times that of S1100 at 77 K and 50 bar. This emphasizes the important role of microporosity as well as the pore size in hydrogen uptake. Figure 6.7 compares the PSDs of the large micropores and mesopores in two TCs. It is seen that S1100 has

lower pore volume but more micropores with smaller pore sizes (with the size close to 1 nm). Figure 6.7 further compares the small micropores in the two TCs, in which the PSDs were derived from CO₂ isotherms measured at 273 K via the NLDFT.

It can be clearly seen that S1100 has a higher volume of small micropore pores at ~0.82 nm, which is more in favor of hydrogen uptake. Therefore, the structural characteristics of S1100 (high volume of small micropores and small average pore size in big micropores) is more closer to the optimal porous structure of carbon for hydrogen storage and is therefore able to present a comparable hydrogen storage capacity even with a much smaller surface area. Therefore, future target for this technology is to boost the volume fraction of small micropores, even at the *sacrifice* of some surface area.

6.5 Summary

Two templated carbons was synthesized, characterized, and investigated for hydrogen storage. The hydrogen adsorption capacity was measured as ~2.0-2.5 % at 77 K and 10 bar, which is among the high end of capacities reported on other TCs. Hydrogen uptakes of 0.8~1.0 wt% were achieved at 303 K and 50 bar, which is better than most of the conventional KOH chemical activation AC. The prepared TCs present the isosteric heat of adsorption of as high as ~ 8 kJ/mol at the low surface loading. Such high value of heat of adsorption indicates a strong interaction between the adsorbed hydrogen molecules and the carbon surface and point to the existence of small micropores in TC samples. CO₂ adsorption at 273 K and Ar sorption at 77K were found superior to the popularly-used N₂ adsorption at 77 K in characterizing such small micropores and surface areas, respectively. To reach high hydrogen storage capacity, a carbon should have a good balance among its surface area, microporosity, as well as its pore size.

CHAPTER 7 PORE STRUCTURE DEVELOPMENT OF TC AND ITS EFFECTS ON H₂/CH₄ ADSORPTION

7.1 Introduction

A number of molecular simulation studies predicted a possible hydrogen storage capacity of 6.0 wt% for carbonaceous adsorbents with an ideal structure, such as nanographite platelets with an interlayer spacing of ~0.8 nm [11]. Bhatia and Myers [50] predicted the optimal structure for hydrogen storage as the carbon with slit-shaped micropores with a center-center pore width of 0.92 nm and with the surface area of ~2630 m²/g. The maximum hydrogen storage/deliverable capacity of such an idealized carbon can be >6.0 wt% at a cryogenic temperature.

The process of graphitization in an AC depends on the nature of the carbon precursor material, the activation agent and more importantly, the thermal treatment temperature (Figure 2.1, Chapter 2) [147]. The carbonization temperature for TC synthesis will strongly affect the structure of the derived TC, which in turn dictates its hydrogen adsorption performance. This Chapter will investigate the effect of carbonization temperature on the development of the porous structure of the derived TC samples. Meanwhile, the important structural characteristics for hydrogen/methane adsorption of TCs will also be discussed.

7.2 Sample preparation

Three TC samples were fabricated using the ammonium-zeolite Y as the template and PFA as the carbon source. Three carbonization temperatures (900 °C, 1050 °C and 1150 °C) were chosen for sample fabrication to study its effect on pore evolution. The three derived TCs were named as C900, C1050 and C1150, respectively. The detailed procedures of sample preparation were described in Section 3.1.2, Chapter 3.

7.3 Sample characterization

7.3.1 SEM analysis

Figure 7.1 SEM images of (a) C1150 (10k); (b) C1150 (30k); (c) C900 (10k); (d) C900 (30k); (e) C1050 (10k); and (f) C1050 (30k).

Figure 7.1 shows the SEM images of the three TC samples with magnifications of 10k and 30k. It can be observed that all TC samples are comprised of large interparticle

voids and carbon crystals which are largely amorphous in structure. The sizes of the graphite crystals range from ~100 nm to ~ 1000 nm. No obvious difference was found in the morphologies of the graphite crystals in the as-synthesized three TC samples.

7.3.2 XRD analysis

Figure 7.2 shows the XRD patterns of C1150, C1150, C900 and zeolite Y (inset one). It can be observed that the C1050 and C1150 have the similar XRD patterns and there are no obvious diffraction peaks at 26° (2θ) ($\{002\}$ diffraction of graphitic carbon) and 43° (2θ) ($\{100\}$ diffraction of graphitic carbon), which implies the amorphous nature of the two TCs. Compared with C1050 and C1150, a small XRD peak at around 6° (2θ) for C900 is clear. The peak at around 6° is corresponding to $\{111\}$ planes of zeolite Y (See the inset XRD pattern in Figure 7.2). This suggests that some degree of regularity is higher in TC C900 and a too high carbonization temperature is not favourable to the development of this regularity. Figure 7.2 also shows broad low intensity peak at 26° (2θ) in the XRD pattern of C900.

Figure 7.2 XRD patterns of C1050, C1150, C900 and zeolite Y (the inset one).

7.3.3 Adsorption experiments

The porous structure of the three TC samples was first investigated with nitrogen adsorption isotherm at 77 K. For comparison purpose, the pore size distributions (PSDs) and the pore volumes were derived from the nitrogen isotherms using the non-local density functional theory (NLDFT). The total pore volume (V_T) was obtained from the cumulative volumes of pores smaller than 50 nm. The micropore volume (V_{mic}) was obtained from the cumulative volumes of pores smaller than 20 nm. The mesopore volume (V_{me}) was determined by subtracting the micropore volume from the total volume.

Figure 7.3 Nitrogen adsorption isotherms on the three TCs (Solid symbol = adsorption; hollow symbol= desorption).

Figure 7.3 shows the nitrogen adsorption isotherm data (symbols) measured on the three TCs at 77 K. It is seen that the adsorption isotherm of C900 is more of type I and those of C1050 and C1150 are more of type IV, according to the IUPAC classification [148]. In general, the type I isotherm represents predominantly physical adsorption on microporous adsorbents. Type IV isotherm, on the other hand, is more related to the adsorption onto a mesoporous surface with multilayer adsorption and followed by capillary condensation. The nitrogen uptake in C1050 is about 1000 cc-STP/g at the relative pressure of $P/P_0 = 0.95$, which is significantly higher than those of C900 and C1150. All the three adsorption isotherms increase quickly and present relatively high N_2 adsorption capacity (>300 cc(STP)/g) at the relative pressure $P/P_0 < 0.1$, which suggests the presence of a significant portion of micropores in the three TC samples.

The clear hysteresis loops on the desorption isotherms of C1050 and C1150 suggest the existence of mesopores in their structures. Such hysteresis was also observed on a number of TCs reported in literature [80,84] and the formation of mesopore volume was largely attributed to such factors as the interparticle voids of template particles and the incomplete carbon precursor's infiltration into the nano-channels of the zeolite template, etc. However, the experimental results in this Chapter will further demonstrate (as shown in later parts) that the carbonization temperature also plays a critical role in the formation of mesopores in TCs.

For the purpose of comparison, the surface texture properties of the three TCs were also derived from the nitrogen adsorption isotherms at 77K using NLDFT and were summarized in Table 7-1, together with those of a TC pellet (C1050P, See Chapter 5) and S1100. The conventional BET surface was not used in comparison due to the uncertainty in choosing the pressure range for the isotherm on microporous adsorbents [149,150]. It can be seen that all three TC samples present high NLDFT surface area (~660-1290 m²/g) and large pore volume (0.65~1.40 cm³/g). C1050 has the highest surface area and micropore volume. C900 has the highest microporosity but the lowest surface area. C1150 has the lowest microporosity but the highest mesoporosity. Please note that, the microporosity in Table 7-1 accounts for only 'big' micropores (1.0-2.0 nm) and does not include the contribution of small micropores (0.6-0.9 nm), due to the diffusion barrier of N₂ molecules into such small micropores at 77K.

Table 7-1 Texture properties of TC samples and their H₂ uptake capacities

Sample	Surface area (pore<5.4nm) from NLDFT	V _{mi} , micropore volume from NLDFT	V _{me} , mesopore volume	Microporosity	H ₂ uptake at 77 K, 1 bar
	(m ² /g)	(cm ³ /g)	(cm ³ /g)	R _{mi} ^b	(wt%)
C900	823	0.45	0.20	0.69	1.78
C1050	1292	0.57	0.83	0.41	2.24
C1150	958	0.33	0.77	0.30	1.66
C1050P ^a	664	0.34	0.22	0.60	1.38
S1100	951	0.42	0.50	0.46	1.71

^aC1050P is a TC pellet derived from C1050 (See Chapter 5); ^bR_{mi}=V_{mi}/(V_{mi}+V_{me})

7.3.4 Pore size distributions (PSDs)

The pore size distributions (PSDs) of the three TCs were derived from their N₂ isotherms at 77K via NLDFT and presented in Figure 7.4a, 7.4b, and 7.4c, respectively with the cumulative pore volume (also derived from NLDFT) shown in the embedded figures. It is seen that C900 has a relatively concentrated distribution of micropores in the range of 1.1-1.2 nm and little mesopore volume in the size range of 2.0-4.0 nm. When the carbonization temperature increases from 900 °C to 1050 °C, the micropore peak becomes sharper and shifts towards the pore size range of ~1.3 nm and, meanwhile, the mesopores start to develop in the size range of 2.5 to 5 nm. This indicates that the high carbonization temperature enhances the formation of both big micropores and mesopores. It is noteworthy that the both micropore and mesopore volumes decrease when the carbonization temperature was further increased from 1050 °C to 1150 °C, which makes the surface area of C1150 is only ~70% that of C1050. This phenomenon was also observed in other researches and was ascribed to the partial collapses of the structure of micropores at the higher carbonization temperature [83].

The effect of carbonization temperature on the porous structural development is also reflected in the changes of microporosity and surface area. It can be seen in Table 7-1 and Figure 7.4 that: while the microporosity drops constantly from C900 (0.69) to C1150 (0.3), the change in surface area took a complicated trend of increasing dramatically before pulling back. This suggested that, although the high carbonization temperature is necessary for the development of high surface area and pore volume, a too high carbonization temperature will result in the collapse of micropores and a decrease in the surface area (largely due to the collapse of big micropores). Therefore, an optimal carbonization temperature should exist and from the experimental results above, this temperature is likely located between 950 °C to 1050 °C.

Figure 7.4 Pore size distribution and cumulative pore volume of (a) (b) C900; (c) (d) C1050; and (e) (f) C1150.

Table 7-2 Characteristics of small micropores in TCs derived from CO₂ sorption isotherm at 273K

TC	Surface area (m ² /g)	Volume of small micropores, V _{mis} (cc/g)	Microporosity, R _{mis}
C900	302	0.080	13.7%
C1050	125	0.036	3.0%
C1150	169	0.058	7.3%
S1100	173	0.059	8.1%

Note: (1) The volume is from DR plot; (2) $R_{mis} = V_{mis}/(V_{mi})$

As discussed previously in Chapter 6, N₂ adsorption at 77K can only detect big micropores (>1.0 nm) in TCs. To check the evolution of the small micropores (<1.0 nm) in the three TCs during the pyrolysis process, CO₂ isotherm at 273 K was measured on the three TC samples and shown in Figure 7.5 on the logarithmic scale. The corresponding surface area of the small micropores and *DR* pore volumes were listed in Table 7-2 for each TC sample.

The small micropores have been known to play a dominant role in hydrogen adsorption at ambient temperature [151]. Although they have better hydrogen storage performance than big micropores, it should be noted that their volume increase is insignificant (~0.02 cc/g or about 2% in the total volume) compared with the loss in the total micropore volume (as high as ~0.24 cc/g) in the sample, when the carbonization temperature increases from 1050 °C to 1150 °C. From C900 to C1050, although the volume of small micropore decreases by ~0.05 cc/g, the overall micropore volume increases by 0.12 cc/g. As the results, C1050 still present better hydrogen capacity than C900 at 77K and 1 bar (Table 7-1).

Figure 7.5 CO₂ isotherm at 273K ($P_0 = 1.05$ bar) for the 3 TC samples.

Figure 7.6 Variation of the pore volume of TCs with carbonization temperature. (1= 900 °C; 2 = 1050 °C; 3 = 1150 °C)

From above discussion, it can be seen that, during the pyrolysis process, the development in the micropore volume, surface area, and pore size are interconnected and is a complicated issue. Figure 7.6 shows graphically the change in micropore and mesopore volume with respect to the carbonization temperature, from which one can conclude that carbonization temperature plays a dominant role in the development of both the microporous and mesoporous structures of TCs. High temperature tends to

open more big micropores and some mesopores (therefore increase the overall surface area and pore volume), but a too high carbonization temperature will result in the collapse of micropores and result in the formation of large mesopores. As small micropores present strong adsorption affinity for hydrogen molecule while big micropores provide high surface area and pore volume, a good balance is needed between the two factor in the future adsorbents.

7.3.5 The degree of graphitization

Raman spectroscopy was used to characterize the degree of graphitization of the 3 TCs. Figure 7.7 shows the Raman spectra measured on C900, C1050 and C1150. It can be observed that the D band (Raman shift = 1350 cm^{-1} , corresponding to the amorphous carbon domain) and G band (Raman shift = 1582 cm^{-1} , corresponding to the graphite carbon domain) varies on the three TC samples carbonized at different temperatures. It is seen that the height of the G-peak becomes slightly higher than that of the D-peak after carbonization temperature increased from 900°C to 1150°C . A simple calculation demonstrates that the ratio of the integrated areas (intensities) of D-peak to G-peak (I_D/I_G) decreased from 2.32 (C900) to 1.71 (C1150) (See Table 7-3). This trend is consistent with the literature that, as the carbonization temperature increases, more amorphous carbon domains were converted to graphite carbons (Figure 2.1). The development in the PSDs of the three TCs (Figure 7.4) further suggests that this graphitization process is accompanied with the formation of more mesopores and the collapse of some micropores at the higher carbonization temperature.

Table 7-3 Raman D and G band features of three TCs

Sample	D-peak (cm^{-1})	G-peak (cm^{-1})	I(D)/I(G)
C900	1339	1583	2.32
C1050	1339	1596	2.12
C1150	1346	1587	1.71

Figure 7.7 Raman spectra of TCs

7.4 Hydrogen adsorption isotherms

Figure 7.8 shows the hydrogen adsorption isotherms of the three TCs at 77 K in the pressure range of 0-1.05 bar. The desorption isotherms were found to overlap with the adsorption isotherms on all the three TC samples.

It can be observed that C1050 has the highest hydrogen uptake of about 2.25 wt% at 1 bar. It also can be seen from Figure 7.8 that the hydrogen adsorption isotherm of C900 is slightly higher than that of C1150, although C1150 has a higher surface area than C900. This is attributed to the fact that the micropore volume of C900 is much higher than that of C1150 (See Figure 7.4 and 7.5). It is interesting to see that C900 even presents a higher adsorption capacity than C1050 when the adsorption pressure is below 0.2 bar. This is because that the volume of small micropores is the highest in C900 (Figure 7.5). These small micropores were quickly filled at low adsorption pressure and thereafter the big micropores play a major role. This observation again emphasizes the importance of the balance between the pore size and micropore volume in addition to the high surface area for hydrogen storage in carbonaceous materials, as discussed in the previous section.

Figure 7.8 Hydrogen adsorption isotherms on the 3 TCs at 77 K.

The high pressure (up to 40 bar) hydrogen adsorption isotherms were also measured on the three TCs at 77 K with the high pressure volumetric rig. The isotherms are shown in Figure 7.9 as symbols. Some discrepancy can be seen between the hydrogen isotherm measured on the PSA rig (closed cycles, pressure < 1 bar) and that measured on the high pressure volumetric rig (open cycles, pressure= 1-40 bar), but the agreement was reasonable. The isotherms were then fitted, respectively, to the Toth equation, which takes the form of Eq. (4-1). The fitting parameters are listed in Table 7-4. It can be observed that C1050 has the highest saturation capacity of 17.3 mmol/g, which corresponds to a hydrogen storage capacity of ~3.5 wt %. It can be observed that at higher pressure, the hydrogen storage capacity of C900 is similar as that of C1150. This implies that micropore volume plays a major role on hydrogen uptake rather than the total pore volume or BET surface area.

Table 7-4 The Toth model fitting parameters of TCs

Sample	b (kPa ⁻¹)	t	C _{us} (mmol/g)
C900	129.2	0.296	14.9
C1150	18.7	0.413	13.7
C1050	8.66	0.474	17.3

Figure 7.9 H₂ high pressure adsorption isotherms at 77 K: (a) C1050; (b) C1150; and (c) C900.

7.5 Benchmark parameters for hydrogen adsorption in TCs

The basic or “benchmark” parameters for adsorption in ACs are usually the BET surface area and pore volume. Figure 7.10 shows the relationship between adsorbed amount of hydrogen (at 77 K and 1 bar) and TC samples’ measured BET surface areas (calculated from $P/P_0 = 0.05-0.3$). This trend line is somehow similar to those reported in the literature [19,152], but with the abnormality that C900 with the lower BET surface area presents a higher hydrogen adsorption capacity than C1150. This, as the previous discussion, points to the importance of the micropore volume and the micropore size. Compared with C1150, C900 is superior in terms of both total

micropore volume (<2 nm) and the volume of small micropore volume (<1 nm). This indicates the most important (benchmark) parameter for hydrogen storage is the micropore volume. Surface area gives its way to the 2nd place as the benchmark parameter.

Figure 7.10 Hydrogen capacity (at 77 K and 1 bar) as a function of the BET surface area.

Figure 7.11 Hydrogen capacity (at 77 K) as the function of the NLDFT-micropore volume.

Figure 7.11 shows the correlation between the hydrogen adsorption capacity (at 77 K) and the micropore volume (NLDFT accumulative pore volume) for the three TC samples. It can be observed that an approximately linear relationship between the micropore volume and the hydrogen uptake exists. This is in agreement with the findings of Armandi et al. [88] with their carbon adsorbents derived from SBA-15 silica template. It is noteworthy to point out that they measured the micropore volumes using the t-plot method [153] while this study employed the micropore volume from NLDFT method. It can be concluded here that the micropore volume (especially small micropore volume) is a better benchmark for carbonaceous adsorbents designated for hydrogen storage. From this point of view, the use of ordered microporous carbon (OMC) in hydrogen storage capacity is analysed below.

According to the work of Kyotani et al [73], the PSD of the OMC will be dominated by the periodicity of the template zeolite Y (at ~1.4 nm). However, this pore size has

been proved to be too large for hydrogen storage in a number of researches [50,73,151]. The optimal pore sizes for H₂ storage should be around 0.6-0.9 nm, much smaller than the majority of micropores formed in the ordered periodicity of zeolite channels. Therefore, the highly ordered OMC with the micropore size peak at 1.4 nm (corresponding to the replica of the zeolite Y template) and a surface area up to 4000 m²/g presents no obvious advantage in hydrogen storage application. As a comparison, the activated carbon Maxisorb (Table 2-1) possesses a surface area of ~3100 m²/g, which presents a hydrogen capacity ~ 6.0% at 77 K and 12 bar, but a capacity only ~0.67 % at ambient temperature and 100 bar [154]. This capacity is lower than that of C1050/S1100 at similar conditions (~0.8-1.0 wt%, listed in Chapter 6). This further stresses the importance of micropores of smaller sizes (with the size of 0.6-1.2 nm) in the improved hydrogen uptake at ambient temperature. The results in this project indicate that the success for the carbon adsorbents in hydrogen storage application are not to increase the ‘order-ness’ of TC or further increases the surface area (the theoretical limit of the physical surface area for a ideal carbon consisting slit-shaped graphite-pores should be around 2630 m²/g [50,151]), but to increase the volume fraction of small micropores, which may be achievable by optimizing the pyrolysis conditions.

7.6 Methane adsorption performance

Figure 7.12a and 7.12b show TCs’ methane adsorption capacity (at 298K, 35bar) as the function of BET surface area from N₂ sorption and the methane isotherms (symbols) measured on C900, C1150 and C1050 at the temperature of 298 K and the adsorption pressure up to 40 bar. It can be observed that the three TCs are not saturated at the upper limit of the experimental pressure. The isotherms were fitted using Langmuir model (Lines), which was described in Eq. (4-2) of Chapter 4. The optimal isotherm parameters are listed in Table 7-5. It can be seen from the Table that C1050 and C900 have similar adsorption affinities; however the saturation capacity of C900 is only ~60% of that of C1050, which is proportional to the ratio of their BET surface areas listed in Table 7-5.

Figure 7.12 (a) Methane adsorption capacity (at 298 K and 35 bar) as the function of BET surface area from N₂ sorption and (b) Methane adsorption isotherms on the three TCs at 298 K.

At 298 K and 35 bar, the best carbon is C1050 and its storage capacity can reach ~11 mmol/g, which is much better than that of self-ordered mesoporous carbon (CMK-3) [96]. Figure 7.12b also shows that, at pressures up to 8 bar, C900 adsorbs slightly more methane than C1150; but as the adsorption pressures further increases, C1150 presents better methane uptake capacity. These observations emphasize the importance of surface area for methane storage and may be explained as the follows: methane molecules are relatively strongly adsorbed in both micropores and mesopores so that increasing the

overall pore volume of TCs is important to improve the methane storage capacity at high pressure. Therefore, surface area is a better indicator (benchmark parameter) for the carbonaceous adsorbents designated for methane storage.

Table 7-5 The Langmuir isotherm parameters of CH₄ on 3 TCs

TC sample	q _m (mmol/g)	b (bar ⁻¹)	S _{BET} (m ² /g)	adsorption capacity (mmol/g) at 298K,35bar
C900	8.63	0.063	1245	6.12
C1150	13.42	0.0347	1520	7.65
C1050	14.66	0.0634	2135	10.98

7.7 Summary

TCs were synthesized at different carbonization temperatures using zeolite Y as template and PFA as carbon source. Carbonization temperature was found to play a significant role in the development of the porous structure and the degree of graphitization in the derived TCs. High carbonization temperature generally increases the degree of graphitization and improves the surface area and pore volume; but a too high carbonization temperature will result in the collapse of micropores and the formation of more mesopores. An optimal carbonization temperature exists which balance the surface area, pore size and pore volume of the derived TC.

Small micropores play an important role in hydrogen storage. Their volume fraction is generally low but can be manipulated via the thermal treatment process. Mesopore volume is not useful for hydrogen storage but play some role in methane adsorption. The methane adsorption capacity was found to be better correlated by the surface area while the hydrogen capacity is better represented by the micropore volume.

CHAPTER 8 ADSORPTION KINETICS ON TC SAMPLES

8.1 Introduction

Another important aspect for energy gas storage is the rate of adsorption. The energy storage capacity must be realized for both the discharging and charging processes rapidly. For example, one of the DoE technical targets for hydrogen storage system (for the year of 2010) is that the refueling time should be less 5 min [11]. This obviously emphasizes the importance of the adsorption kinetics in practical applications. Compared with hydrogen, methane is a molecule with large molecular dimensions and with relatively high value of heat of adsorption. Its adsorption rate on carbon pellet or powder is of more practical concern.

This Chapter will present the study of methane adsorption kinetics on two TC samples, C1050 and C1050P. Adsorption kinetic data were measured in a batch adsorber system, which simulates the charging process of a practical gas storage tank.

8.2 Mathematical models for adsorption kinetics

8.2.1 LDF model

The linear driving force (LDF) model is popularly used in the study of pressure swing adsorption (PSA) and in the methane storage in coal beds [155,156]. The model presents good simplicity and is versatile for the study of kinetics in various systems. The LDF model equation can be written in terms of the adsorbed phase concentration as:

$$\frac{dC_{\mu}(t)}{dt} = k_L [C_{\mu}^*(t) - C_{\mu}(t)] \quad (8-1)$$

where t is the uptake time, $C_{\mu}(t)$ is the (average) adsorbed phase concentration, k_L is the rate constant of adsorption, and $C_{\mu}^*(t)$ is the adsorbed phase concentration that would be

equilibrated with the instantaneous bulk phase pressure, $P(t)$. Sircar and Hufton [157] derived the analytical solution for the LDF model of Eq. (8-1). The fractional uptake, $f(t)=M_t/M_\infty$, for the adsorption in a *constant volume* (V) batch adsorber can be written as:

$$f(t) = \frac{M_t}{M_\infty} = \frac{C_\mu(t) - C_\mu(0)}{C_\mu^\infty - C_\mu(0)} = 1 - \exp\left[-\frac{1+\alpha}{\alpha} k_L t\right] \quad (8-2)$$

where M_t and M_∞ are the amount of adsorbate adsorbed at time t and at the final equilibrium, respectively, and α is the ratio of the volume of the adsorber to the volume capacity of the adsorbent. The relation $1/(1+\alpha) = M_\infty/VC_e$ was used in a number of researches with the LDF model (where C_e is the bulk phase concentration at the equilibrium) [156,157,158]. The constant pressure uptake experiment is a special case of Eq. (8-2) when $\alpha = \infty$ (which corresponds to $V \rightarrow \infty$). This fractional uptake can be equivalently written (with the assumption that the bulk and the adsorbed phases are uniform and are in instant equilibrium with each other) in terms of the bulk phase pressure as:

$$f(t) = \frac{M_t}{M_\infty} = \frac{C_\mu(t) - C_\mu(0)}{C_\mu^\infty - C_\mu(0)} = \frac{P^* - P(t)}{P^* - P_\infty} = 1 - \exp[-(1+\beta)k_L t] \quad (8-3)$$

where $P(t)$ is the bulk phase pressure at time t , P^* is the bulk phase pressure (the instantaneous pressure in the system upon the dosing) or the system pressure at $t = 0$, P_∞ is the final equilibrated bulk pressure in the system, and $\beta = mHRT/V$ is the ratio of the adsorption capacity of the adsorbent to the volume of the batch adsorber (here, H is the Henry's law constant, See the Appendix). Eq. (8-3) is termed as LDF-Henry model, which is equivalent to Sircar and Hufton's solution with $\beta=1/\alpha$. To clearly demonstrate the assumptions and the definition of the parameters, the derivation of the LDF model with respect to the adsorption pressure, Eq. (8-3), was presented in the Appendix.

The model solutions assume a homogeneous surface, uniform temperature, and the bulk phase is in equilibrium with the adsorbed phase. By comparing the fractional uptake of the mathematical model with respect to the experimental data (the observed pressure decay of the system), the rate constant, k_L , of the LDF model can be derived for the system. To check the importance of the assumption of isotherm linearity in LDF-

Henry model, the nonlinear Langmuir isotherm was also employed for Eq. (8-1) to study the kinetic data. The LDF-Langmuir model was solved numerically.

8.2.2 FD model

The other popular model for the batch adsorption kinetics is the Fickian diffusion (FD) model, which is more rigorous and stemmed in the assumption that the driving force for diffusion is the chemical potential gradient [159]:

$$J_{\mu}(r,t) = -D \left(\frac{\partial C_{\mu}}{\partial r} \right) \quad (8-4)$$

where J_{μ} is the adsorbed phase flux, $D = B \left[\frac{d \ln P}{d \ln C_{\mu}} \right]_T$ is the Fickian diffusion coefficient, which is concentration dependent. With the assumption of linear adsorption isotherm ($C_{\mu} = H \times P$, here H is the Henry's law constant, P is the bulk pressure) and the isothermal adsorption process, Eq. (8-4) can be simplified and the mass balance equation on the particle can be written as:

$$\frac{\partial C_{\mu}(r,t)}{\partial t} = \frac{D}{r^s} \frac{\partial}{\partial r} \left[r^s \frac{\partial C_{\mu}}{\partial r} \right] \quad (8-5)$$

where s is the geometric shape factor of the particle ($s = 0, 1, 2$ for slab, cylindrical and spherical shaped particles, respectively). Eq. (8-5) was previously solved by Crank for a batch system with *constant volume* and *constant pressure*, respectively [158].

The fractional uptake on the *fine powder* adsorbent in a *constant volume* system can be written as:

$$f(t) = \frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(1+\alpha)}{(9+9\alpha+\alpha^2 q_n^2)} \exp \left[-\frac{D q_n^2 t}{R^2} \right] \quad (8-6)$$

where α is defined in the same way as Eq. (8-2), q_n represents the positive roots of the transcendental equation, $\tan(q_n) = \frac{3q_n}{3+\alpha q_n^2}$, R is the radius of the particles (assumed to be small spherical particles with uniform radius R), and D/R^2 is the diffusion time

constant. The method of solution of the transcendental equation was attached in the Appendix.

The fractional uptake on a slab particle (with the thickness of $2l$) in a constant volume system is:

$$f(t) = \frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{(1+\alpha+\alpha^2 q_n^2)} \exp\left[-\frac{Dq_n^2 t}{l^2}\right] \quad (8-7)$$

where q_n is the positive roots of the transcendental equation, $\tan(q_n) = -\alpha q_n$.

In this thesis studies, Eq. (8-3), Eq. (8-6) and Eq. (8-7) were used to analyze the kinetic data measured in the batch system, respectively, to derive the rate constant (k_L) or the diffusion constant (D/R^2 , D/l^2) of the system.

8.3 Experiments

The adsorption kinetics of methane was measured for C1050 powder and C1050P pellet, respectively, at 298K. For the powder C1050, the adsorption kinetics were measured at five different dosing pressures ($P_0 \approx 1, 3, 6, 8, 16$ bar), respectively; for the C1050P, the adsorption kinetics were measured at five different dosing pressures ($P_0 \approx 1, 4, 6, 13, 20$ bar). The measurements were conducted from low dosing pressure to high dosing pressure successively. The procedures of kinetic measurement were described in Section 3.3.3, Chapter 3.

8.4 Results and discussions

Figure 8.1 shows the methane adsorption isotherms (symbols) measured on C1050/C1050P at 298K. As the analytical solutions of LDF and FD models require linear isotherms, Henry's law equation was fitted to the isotherm data at various pressure ranges (also used to study the effect of isotherm linearity). The optimal isotherm parameters of Langmuir equation and Henry's law equation were listed in

Table 8-1. The Henry's law isotherms for methane sorption on C1050 at different pressure ranges were shown schematically in Figure 8.1 as the dashed lines (H1 to H5).

Table 8-1 Isotherm parameters of methane sorption on C1050/C1050P at 298K

Sample	Langmuir		Henry's law (mmol/bar/g)						
	mmol/g	bar ⁻¹	H _{overall} /	H1 /	H2 /	H3 /	H4 /	H5	
C1050	14.7	0.0643	0.341	/ 0.881	/ 0.771	/ 0.661	/ 0.545	/	0.469
C1050P	7.18	0.0952	0.191	/ 0.847	/ 0.553	/ 0.309	/ 0.258	/	0.207

Figure 8.1 CH₄ isotherms at 298K on C1050/C1050P (— Langmuir isotherm; --Henry's law isotherm for different pressure ranges).

Figure 8.2 shows the pressure decay (real pressure) versus time in the adsorber loaded with C1050 at 298 K. The experimental data (symbols) at five successive dosing pressures ($P_0 = 1.1, 3.0, 5.7, 8.4, 16.8$ bar) were fitted simultaneously to the LDF-Henry model (lines) with the overall Henry's constant listed in Table 8-2. It is seen that the model adequately fits the pressure decays at various dosing pressure over long time scale with $k_L \sim 0.04$ 1/s.

Figure 8.2 Methane uptake on C1050 powder at 298 K and the fittings of LDF-Henry model.

Figure 8.3 Fractional uptake of methane on C1050 at various dosing pressures (symbols) and model fittings (lines).

The model fitting of the real experimental pressure decay may heavily favor the high pressure data if the absolute errors between the model and experimental data are used as the objective function for optimization. In comparison, fractional uptake (which is converted from the pressure decay) is a more rigorous form of sorption kinetics and is used here to examine the model performance. The average relative error (ARE) was used to evaluate the goodness of model fittings, which is defined as:

$$ARE = \frac{100}{N} \sum_{n=1}^N \left(\left| \frac{Model - Exp \ data}{Exp \ data} \right|_n \right) \quad (8-8)$$

where N is the number of experimental points. Figure 8.3 shows the fractional uptakes of methane on C1050 (calculated from the pressure decay data in Figure 8.2). It can be seen from Figure 8.3 that the sorption equilibrium is reached quickly (<300s) for all five dosing pressures and the uptake rate increases steadily as the dosing pressure increases. The fittings of LDF-Henry model (with the Henry's constants for each dosing, or H1 to H5 as listed in Table 8-1) were shown in Figure 8.3 as the solid lines while the fitting results were listed in Table 8-2. It is seen that the model fittings (AREs) improved gradually at higher dosing pressures.

Table 8-2 Optimal model parameters and the average relative errors (ARE) of fittings

	P_0 (bar)	LDF-Henry		LDF-Langmuir		FD model	
		k_L , (1/s)	ARE%	k_L , (1/s)	ARE%	D/R^2 , (1/s)	ARE%
C1050 (powder)	1.1	0.0244	20.87	0.0246	14.61	0.00133	27
	3.0	0.0322	5.11	0.0331	5.10	0.00187	11.6
	5.7	0.0338	4.90	0.0355	4.89	0.00199	11.9
	8.4	0.0395	1.42	0.0421	1.42	0.00240	4.75
	16.8	0.0410	2.41	0.0448	2.41	0.00247	2.95
C1050P (pellet)	1.1	0.0318	5.11	0.0329	5.11	0.0103	9.51
	4.0	0.0449	4.82	0.0480	4.82	0.0153	7.63
	6.3	0.0611	2.47	0.0611	2.48	0.0211	3.79
	13.0	0.0681	2.00	0.0752	2.01	0.0236	3.07
	20.5	0.0835	1.34	0.0931	1.34	0.0239	2.05

For comparison reason, LDF-Langmuir model was also used to simulate the kinetic data on C1050. The model simulation was shown in Figure 8.3 as the dashed lines (which are overlapped with the solid lines) while the optimal parameters were listed in Table 8-2. It is seen that the use of the nonlinear Langmuir isotherm will not considerably improve the performance of LDF model (because the isotherm is largely linear, especially at low sorption pressure). The derived rate constants (k_L) are very close in values for LDF model with linear or nonlinear isotherms.

The fractional methane uptakes on C1050P pellet (in slab geometry with the thickness of 0.5 mm) were also measured at 298K under five dosing pressures ($P_0 = 1.1$, 4.0, 6.3, 13.0, and 20.5 bar). Figure 8.4 shows the pressure decay versus time in the adsorber loaded with C1050P at 298 K. The optimal model parameters (k_L) and ARE for C1050P at different dosing pressures were listed in Table 8-2. It can be observed that both LDF-Henry and LDF-Langmuir models fit the methane uptake kinetics on the pellet well, as indicated by the AREs. Figure 8.5 presents the experimental data (symbols) and model fittings (solid line for LDF-Henry, dashed line for LDF-Langmuir) for the fractional uptake. The experimental data and the model fittings were found to present similar trends as those observed on C1050.

Figure 8.4 Methane uptake on C1050P at 298 K and the fittings of LDF-Henry model.

Figure 8.5 Fractional uptake of methane on C1050P at various dosing pressures (symbols) and model fittings (lines).

It is seen in Figures 8.3 and 8.5 that the uptake rates are slightly higher on the pellet than those on the powders at the similar dosing pressure. As C1050 powder is much smaller in size ($\sim 0.5\mu\text{m}$ in diameter) than C1050P pellet ($500\mu\text{m}$ in thickness), the fast kinetics on C1050P is attributed to the effect of sorption heat, as explained below:

Firstly, C1050 is in the form of fine carbon flakes with large interparticle void and low bulk density, which present high surface area but poor thermal conductivity. In comparison, C1050P is compact with a much higher density, so it is more efficient in the conductive heat transfer. The study of Kuwagaki et al. revealed that the thermal conductivity of granular ACs ranges from 0.18 to $0.25\text{ Wm}^{-1}\text{K}^{-1}$ while that of graphite is about $150\text{ Wm}^{-1}\text{K}^{-1}$ [160]. The bulk densities of C1050 and C1050P are approximately half of those granular ACs and graphite, respectively. Therefore, it can be deduce that the thermal conductivity of C1050P is much higher than that of C1050. With the low sample loadings ($\sim 250\text{mg}$) in metal sample cell ($\sim 50\text{ g}$, in the form of $\frac{1}{2}$ inch OD stainless steel tube capped with flanges), the pellet can dissipate the sorption heat quickly via conduction, and therefore, results in the observed fast kinetics.

Secondly, the methane sorption capacity is higher on C1050 than C1050P on gravimetric basis, which suggests that more sorption heat will be generated at the similar dosing pressure. This, together with lower thermal conductivity of the sample, further supports the slow kinetics on C1050.

Figure 8.6 presents the isosteric heat of methane sorption on C1050, which was calculated from methane isotherms measured at different temperatures (inset). It is seen that: (1) Q_{iso} can be as high as 22 kJ/mol at the low surface loading, (2) Q_{iso} then decreases quickly and is relatively constant at ~ 14 kJ/mol for the loading between 3-8 mmol/g, and (3) Q_{iso} drops quickly when loading is higher than 8 mmol/g. With the study of Schidler and LeVan [161], these isosteric heats can be roughly attributed to the sorption in slit-shaped graphite pores with the sizes of ~ 0.8 nm (for 22 kJ/mol) and ~ 1.2 nm (14 kJ/mol), respectively. The isosteric heat is also well substantiated by the PSDs of C1050, as C1050 has a major micropore peak at ~ 1.4 nm (Figure 5.10b, derived from N_2 sorption) and a minor peak of small micropores at 0.6-0.9 nm (Figure 6.4f, derived from CO_2 sorption)

Figure 8.6 Isosteric heat of methane sorption on C1050 (Inset shows methane isotherms at 263K, 273K and 298K).

The above discussion explains the observed fast kinetics on the pellets and lays the importance that the dissipation of sorption heat in dictating the overall sorption kinetics. It is expected that, for a real storage tank filled with large quantity of adsorbent pellets/monoliths, the effect of sorption heat will be prominent and the heat transfer will be the rate-limiting step for the charging process. Designs that facilitate the heat dissipation in the fuel tank may be necessary for the quick charging in ANG technology.

Figure 8.7 Methane uptake on C1050 powder at 298 K and the fittings by FD model.

Figure 8.8 Methane uptake on C1050P at 298 K and the fittings by FD model.

The FD model (with the Henry's law constant for each dosing) was used to simulate the fractional uptakes on C1050 and C1050P, respectively. Figures 8.7 and 8.8 show the experimental pressure (symbols) and the model fittings (lines) for C1050 and C1050P respectively. The optimal model parameters and AREs are listed in Table 8-2 while the model performance for the first dosing pressure ($P_0 = 1.1$ bar) was plotted in Figure 8.3 and 8.5 as the dotted lines, respectively. It is seen that FD model fit the uptake of the first dosing point unsatisfactorily with the ARE $\sim 27\%$ on C1050 and $\sim 10\%$ on C1050P. As the dosing pressure gets higher, FD model improves quickly and the AREs become comparable to those of LDF. The poor model fittings are attributed to the surface heterogeneity of the adsorbents. At low loading, sorption takes place primarily in small micropores, in which the sorption affinity and sorption heat changes greatly with the variation of pore sizes. The assumption of homogeneous surface is poorly fulfilled (i.e., the powdered AC can not be represented by a single value of diffusion time constant, D/R^2), even the linear isotherm assumption is largely applicable. On the other hand, C1050P is modeled as a slab particle with uniform structure. From its SEM image (Figure 5.8b, Chapter 5), this seems a reasonable assumption. However, the variation in local pore sizes and the sorption heat will discount its model performance.

The diffusion time constant (D/R^2) was seen to increase with dosing pressure on both carbon samples, which suggests that the diffusion coefficient, D , is concentration dependent. The magnitude of the time constant was found $\sim 2.0 \times 10^{-3} \text{ s}^{-1}$ on C1050. In

comparison, this value for gas sorption is generally in the order of $\sim 0.1 \text{ s}^{-1}$ on commercial activated carbons and $\sim 1.0 \times 10^{-3} \text{ s}^{-1}$ on zeolite crystals [162]. The similar value of the diffusion constants suggests that TC C1050 takes the structural resemblance to its zeolite template (small, microporous crystals). For C1050P, even its diffusion time constant is about ten times that of C1050, its apparent diffusion coefficient (D) would be much larger because the diffusion path in the pellet ($\sim 0.25 \text{ mm}$) is much larger than that of the powders ($\sim 0.25 \text{ }\mu\text{m}$). This apparent discrepancy in the diffusion coefficient has been mainly attributed to the effect of sorption heat in previous discussions.

It is seen in Table 8-2 that both LFD and FD models can fit the experimental data reasonably well especially at high dosing pressure. This is because the small micropores, which present strong sorption potentials, were preferentially filled as the dosing pressure increases so that the key model assumptions (isothermal, homogeneous surface and linear isotherm) are better fulfilled at high dosing pressure. At such conditions, the LDF and FD model may perform equivalently as pointed out by Liaw et al. [163] that the parabolic concentration profile within the particle will lead FD model to the LDF model. Tien [164] also pointed out that the relationship between these two models: Eq. (8-3) is an approximation of Eq. (8-6). At low dosing pressure, LDF performs better because of its flexibility to cope with the heat effect (it is simply a first order rate equation) and the loss of local features at the particle level [157].

It has been demonstrated that the ratio $\Omega_k = k_L/(D/R^2) \approx 15\text{-}16$ for a constant pressure and ideal sorption system [139,157]. This ratio depends on dosing pressure in a constant volume batch system such as the one used in this research. For C1050, Ω_k ranges from 18.3 at low dosing pressure to 16.5 at high dosing pressure, which is in agreement with the best fit relationship provided by Sircar and Hufton [157]. Therefore, LDF model is recommended for the study of uptake kinetics due to its simplicity and versatility in fitting the kinetic data on both the powdered TC and the TC pellet. The FD model is theoretically sound but requires more rigorous assumptions such as: homogeneous particle sizes, linear isotherm, and constant temperature. It is difficult for the batch experiments to fulfill all these assumptions.

8.5 Summary

Both LDF and FD model can adequately describe the methane uptake kinetics on the two types of TC samples, C1050 and C1050P. Isotherm non-linearity was found not to play a significantly role in the model performance. The adsorption kinetics on the TC pellet is observed to be slightly faster than that on the as-synthesized powdered TC. This points the importance of the adsorption heat and the heat transfer, which dictates the sorption (charging) kinetics of methane adsorbate onto the TC samples. The LDF model is recommended for the modeling of the adsorption kinetics onto the TC and the TC pellet, due to its simplicity and versatility.

CHAPTER 9 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

9.1 Conclusions

This thesis focuses on fabrication of a number of nanoporous activated carbons using the template synthesis technique and studies on their performance in energy storage applications. The results show that the template synthesis technology is promising in producing carbon adsorbents for CH₄/H₂ storage applications.

For methane storage: TC prepared using sucrose as carbon source presents a surface area of ~1500 m²/g and a methane adsorption capacity of 8.0 mmol/g at 300 K and 35 bar. The low bulk density of the as-synthesized carbon powder has been improved by the fabrication of carbon pellets (with a PVA binder) on which a volumetric methane storage capacity of 93 (v/v) was achieved. TC prepared with PFA as carbon source presents a surface area of 2136 m²/g and an adsorption capacity of ~11 mmol/g at 300 K and 35 bar. The carbon pellet fabricated via the proposed binderless technology present good mechanical strength with a methane capacity ~ 127 (v/v), which is a very promising result.

From the characterized structures of TCs, the above two TC samples were found to still have ~ 40% of the total pore volume as mesopores, which can be potentially tailored into micropores to boost their methane storage capacities. Therefore, TCs are promising adsorbents to achieve the DoE target for ANG applications.

For hydrogen storage: TC samples exhibit a hydrogen storage capacity of ~ 2.5 wt% at 77 K and 10 bar and ~ 3 wt% at 77 K and 50 bar. The TCs were found to possess a fraction of small micropores (0.6-0.9 nm), which presents the isosteric heat of adsorption of as high as ~ 8 kJ/mol at a low surface loading. Such small pores are critical for the hydrogen storage and the fraction of their pore volume should be optimized to enhance the hydrogen storage capacity in the future. This project has

demonstrated that CO₂ adsorption at 273 K is a better technology for characterizing such small pores, which is advantageous to the conventional N₂ adsorption at 77 K.

The development of the porous structures in TCs was investigated with a series of three TCs (with zeolite Y as a template and PFA as a carbon source) produced at different carbonization temperatures. The TCs have high surface areas (1245 - 2300 m²/g), high pore volumes (0.65 - 1.4 cm³/g) and a significant proportion of micropores. The carbonization temperature was found to play a dominant role in the development of TCs' porous structures and the degree of graphitization. The hydrogen uptake capacity of the TCs was found to be more dominated by the volume fraction and the size of micropores, rather than by the surface area. Experimental results suggest that there exists an optimal carbonization temperature at which the as-synthesized TC can present a good balance between the micropore volume, pore size and surface area. A too high carbonization temperature will decrease the micropore volume and increase the mesopore volume of the TCs.

At room temperature and 50 bar, the TC has a hydrogen storage capacity of ~ 1.0 wt%, which is better than the commercial AC but still indicates a long way for us to reach the DoE target. More efforts are needed to optimize the structure of TCs (high microporosity and more volume fraction of small micropores in the size range of 0.6-0.9 nm) for hydrogen storage applications.

Adsorption kinetics of methane was investigated on the TC powders and TC pellets. It was found that the linear driving force (LDF) model can be conveniently used to describe the batch adsorption kinetics on both the powdered and the pellet carbons, even the heat of adsorption plays an important role in the overall sorption kinetics. The LDF model is recommended for the future applications.

For other commercial carbonaceous adsorbents: Commercial AC with a narrow pore size distribution around 0.8-1.1 nm and a high surface area ≥ 900 m²/g may present good performance for methane storage. Such commercial products have the advantage on economical side. But more researches are needed to modify their pore and surface textures for the possible ANG applications. The high purity commercial single wall carbon nanotube (SWCNT) was found to have a low hydrogen adsorption capacity ~0.9

wt % at 77 K and 10 bar, which is much lower than that of TCs. The SWCNT is less practical than TCs in hydrogen storage applications.

9.2 Recommendations for future studies

This project only initiated the first few steps for the research on energy storage in TCs. More future studies are needed to improve the developed technology. The emphasis should be to optimize the porous structure of TCs, considering that the as-synthesized TCs still have a large portion of mesopore volumes, which can be potentially modified to micropores to enhance the adsorption capacities. The following research directions are suggested:

1. Studying the effect of template on the structure of the derived TCs. Templates with smaller microporous channels (e.g. ZSM-5) can be tested.
2. Using the gas CVD technology to impregnate the carbon sources into the micro-channels of the templates and comparing this method with the liquid phase impregnation method in the structural development of TCs.
3. Tailoring the porous structure of TCs: conventional activation/CVD technologies can be used to fine-tune the micro-/meso- pores in TCs. This has been proved to be effective in the literature [78,165].
4. Optimizing the pelletisation technology for methane storage: A detailed study is needed on the bulk density and storage capacity of the carbon pellets with respect to the temperature, compression pressure and particle sizes.
5. Studying the multicomponent adsorption equilibrium and adsorption/delivery kinetics for methane storage on TCs/TC pellets: The experimental data (NG with ethane, CO₂, propane, SO₂, etc.) should be measured and analyzed with mathematical models for practical applications.

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