Nanoporous Materials for Hydrogen Storage 
and H₂/D₂ Isotope Separation

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I hereby declare that this thesis is my own work and effort and that it has not been submitted anywhere for a degree nor has it been submitted as part of requirements for a degree. Where other sources of information have been used, they have been acknowledged

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Date: 06. April 2014
Abstract

This thesis presents a study of hydrogen adsorption properties at RT with noble metal doped porous materials and an efficient separation of hydrogen isotopes with nanoporous materials. Most analysis is performed via thermal desorption spectra (TDS) and Sieverts-type apparatus.

The chapter 1, classical porous materials and the novel class of metal-organic frameworks (MOFs) are introduced. The brief overview of promising applications for implementing nanoporous materials in hydrogen storage and isotope separation is addressed.

The theory of physical adsorption on a solid surface of porous materials that is relevant to this work is covered in chapter 2. This chapter describes details of the adsorption model (Langmuir, BET), thermodynamic of the adsorption (Van’t Hoff plot), expression of hydrogen storage capacity (excess, absolute and total uptake), metal doping effect on hydrogen adsorption and the fundamentals of quantum sieving.

Chapter 3 describes the theoretical background to the experimental techniques applied. The design of the experimental apparatus is given in details, and the measurement principle, including calibration for each device is explained.

The result and discussion is presented in two parts;

Chapter 4 focuses on metal doped nanoporous materials for hydrogen storage.

Cryogenic hydrogen storage by physisorption on porous materials has the advantage of high reversibility and fast refuelling times with low heat evolution at modest pressures. At room temperature, however, the physisorption mechanism is not able to achieve enough capacity for practical application due to the weak van der Waals interaction, i.e., low isosteric heats for hydrogen sorption. Recently, the “spillover” effect has been proposed by R. Yang et al. to enhance the room temperature hydrogen storage capacity. However, the mechanism of this storage enhancement by decoration of noble metal particles inside high surface area supports is not yet fully understood and still under debate.

In this chapter, noble metal (Pt / Pd) doped nanoporous materials (i.e. porous carbon, COFs) have been investigated for room temperature hydrogen storage. Their textural properties and hydrogen
storage capacity are characterized by various analytic techniques (e.g. SEM, HRTEM, XRD, BET, ICP-OES, Thermal desorption spectra, Sievert’s apparatus and Raman spectroscopy).

Firstly, Pt-doped and un-doped templated carbons possessing almost identical textural properties were successfully synthesized via a single step wet impregnation method. This enables the study of Pt catalytic activities and hydrogen adsorption kinetics on porous carbons at ambient temperature by TDS after H₂/D₂ gas exposure and PCT measurement, respectively. While the H₂ adsorption kinetics in the microporous structure is enhanced by Pt catalytic activities (spillover), only a small enhancement of the hydrogen uptake in Pt doped carbon over pristine carbon is observed indicating a limited role of the spillover effect for practical hydrogen storage.

Secondly, the synthesis of a new organic-inorganic hybrid material “metal doped covalent-organic framework (COF)” via gas phase infiltration method is presented. In this way, COFs can be used as novel scaffolds for the stabilization of nanoparticles with a nearly mono-dispersed size and homogeneous distribution. At room temperature, the hydrogen storage capacity of Pd doped COFs is enhanced by a factor of 2~3 compared to the pristine COFs. This significant enhancement of Pd doped COFs can be assigned to the catalytic hydrogenation of organic fragments such as bicyclopentadiene originating from the Pd precursor.

Chapter 5 focuses on separation of hydrogen isotopes with nanoporous materials.

Separating gaseous mixtures that consist of very similar particles (such as mixture of light gas isotopes or mixtures of noble gases) is one of the challenges in modern separation technology. Especially D₂/H₂ separation is a difficult task since its size, shape and thermodynamic properties share each other. Recently, quantum sieving in confined space has received increased attention as an efficient method for hydrogen isotope separation. Despite many theoretical calculations, however, it has been difficult to identify a feasible microporous material up to now. Among various porous materials, the novel class of microporous framework materials (COFs, ZIFs and MOFs) is considered as the most promising approach for isotope sieving due to ultra-high porosity and uniform pore size which can be tailored in these materials.

Hence, one focus is the investigation of the fundamental correlation between D₂/H₂ molar ratio and pore size at optimized operating conditions by using different nanoporous frameworks. It reveals that the D₂/H₂ molar ratio is strongly depending on pore size, pressure and temperature. The experiments
indicate clearly that the optimum pore diameter for quantum sieving lies between 3.0 Å and 3.4 Å which can be an important guideline for the design and development of feasible porous frameworks for isotope separation. Afterwards, two strategies for satisfying industrial requirements are introduced. Firstly, one way of increasing the operating pressure is presented by using cryogenically flexible COFs. Secondly, a different chemical affinity of isotopes on strong adsorption sites is demonstrated in order to increase the operating temperature for isotope separation. Finally, on the basis of obtained results, multistep cycles of a temperature swing separation process are experimentally simulated with D₂/H₂ mixtures containing only 5% D₂, demonstrating the high potential for an application in hydrogen isotope separation.

**Keywords:** Hydrogen storage • Covalent organic frameworks • Metal organic frameworks • Palladium nanoparticles • Physisorption • Spillover • Quantum sieving • Hydrogen isotopes • Gas adsorption • Isotope separation
Zusammenfassung


In Kapitel 1 werden die klassischen porösen Materialien und die neuartige Klasse der metallorganischen Gerüststrukturen (metal-organic frameworks- MOFs) vorgestellt. Der kurze Überblick befasst sich mit den vielversprechenden Anwendungen nanoporöser Materialien für die Wasserstoffspeicherung und Isotopentrennung.

Die für das Verständnis dieser Arbeit benötigte Theorie der physikalischen Adsorption auf einer Festkörperoberfläche poröser Materialien, wird in Kapitel 2 beschrieben. Dieser Abschnitt beschreibt die Adsorptionsmodelle (Langmuir, BET), die Thermodynamik der Adsorption (Van’t Hoff Diagramm), Termini der Wasserstoffspeicherungskapazität (Exzess-, Absolut- und Totalaufnahme), den Effekt der Metalldotierung für die Wasserstoffadsorption und die Grundlagen des Quantensiebens.

Kapitel 3 beschreibt den theoretischen Hintergrund der verwendeten Experimentiertechniken. Der Aufbau der Messapparaturen und die Messprinzipien inklusive der jeweiligen Kalibrierung werden detailliert erklärt.

Die Ergebnisse und die Diskussion werden in zwei Abschnitten vorgestellt; In Kapitel 4 liegt der Schwerpunkt auf die Wasserstoffspeicherung in mit metall-dotierten nanoporösen Materialien.

Kryogene Wasserstoffspeicherung durch Physisorption in nanoporösen Materialien besitzt den Vorteil hoher Reversibilität, schneller Wiederaufladung bei geringer Hitzeentwicklung und moderaten Drücken. Bei Raumtemperatur jedoch ist der Mechanismus der Physisorption aufgrund der schwachen van der Waals Wechselwirkungen und dadurch niedriger isosterischer Wärme für die Wasserstoffsorption unzureichend, um eine genügend hohe Speicherkapazität für praktische Anwendungen zu erreichen.


Kapitel 5 behandelt die Wasserstoffisotopentrennung durch nanoporöse Materialien. Die Trennung von Gasgemischen aus sehr ähnlichen Teilchen (wie zum Beispiel Gemische leichter Isotope oder Edelgasgemische) ist eine der Herausforderungen der modernen Trennungstechnologie. Insbesondere ist die D₂/H₂ Separation eine schwierige Prozedur, da diese Moleküle gleiche Größe,
Form und thermodynamische Eigenschaften besitzen. Kürzlich hat das Quantensieben in engen Poren Aufmerksamkeit als effiziente Methode der Wasserstoffisotopentrennung erlangt. Trotz vieler theoretischer Berechnungen war es bislang schwierig, passende mikroporöse Materialein zu identifizieren. Unter den verschiedenen porösen Materialien wird die neue Klasse mikroporöser Gerüststrukturen (COFs, ZIFs und MOFs) als der vielversprechendste Ansatz zur Isotopentrennung aufgrund der sehr hohen Porosität und gleichförmigen, einstellbaren Porengröße dieser Materialien angesehen. Somit ist ein Schwerpunkt die Untersuchung der grundlegenden Beziehung zwischen dem $\text{D}_2/\text{H}_2$ Molverhältnis und der Porengröße unter optimierten Arbeitsparameter für verschiedene Gerüststrukturen. Es ist zu erkennen, dass das $\text{D}_2/\text{H}_2$ Molverhältnis stark von der Porengröße, dem Druck und der Temperatur abhängt. Aus den experimentellen Ergebnissen geht klar hervor, dass der optimale Porendurchmesser für das Quantensieben zwischen 3.0 Å und 3.4 Å liegt, was wiederum eine wichtige Richtlinie für das Entwerfen und die Entwicklung neuer mikroporöser Gerüste für die Isotopentrennung gibt. Im Anschluss werden zwei Strategien der Implementierung in industrielle Prozesse vorgestellt. Eine Möglichkeit der Erhöhung des Arbeitsdrucks durch Einsatz kryogener flexibler COFs wird vorgestellt. Eine weitere Option, um die Arbeitstemperatur für die Isotopentrennung zu erhöhen, ist die Nutzung der unterschiedlichen chemischen Affinität der Isotope an starken Adsorptionsplätzen. Abschließend können auf Grundlage der erworbenen Kenntnisse, mehrere Trennungszyklen eines Temperaturwechselverfahrens experimentell mit $\text{D}_2/\text{H}_2$ Gemischen, die nur 5 % $\text{D}_2$ beinhalten, simuliert werden, um das hohe Potential der Wasserstoffisotopentrennung mit dieser Methode zu demonstrieren.
1. General Introduction

Porous matter is classically seen as a material that has voids throughout its entire extent. A typical example of a simple porous system is solid foam which is one type of dispersion described in colloid science. Also, many natural substances such as rocks, soil, zeolites can be considered as porous materials. These porous materials are typically characterized by their porosity, permeability, tensile strength and interface properties. In particular, fluid-solid interface properties are important and responsible for a number of phenomena encountered in biological, chemical and physical processes. Hence, a fundamental understanding of fluid-solid interaction in porous media is essential for meeting a specific demand in many areas of applied science and engineering. This includes the fluid-structure interaction and the surface-induced changes of materials properties in complex chemistry.

As a consequence of several decade's studies on fundamental fluid-solid (physical and chemical) interaction and their mechanical properties, by now, porous materials are becoming very popular in various important fields such as space, automobile, chemical and biomedical applications due to their lightweight structure, mechanical endurance, enhanced mass transfer with chemical reaction and biomimetic properties. Most of these applications require specific textural properties (e.g. pore size, pore volume and surface area). Therefore, a method that allows controlling the textural properties of porous materials is essential, but it has been still a challenge to control the size, shape and functionality of the void space with conventional porous materials (e.g. zeolite) efficiently. Recently, Metal-organic frameworks (MOFs) are newly joined in the field of porous materials, exhibiting varieties of structure-property relation. Owing to their ordered porous structure with an ultra-high surface area, tunable porosity and functionality, MOFs have gained a tremendous interest in many applications such as gas storage, separation, biomedical application, sensor technology or catalysis.

Especially, two particular applications of this ordered porous structure that has great potential are the 1) Solid-state hydrogen storage by physisorption and 2) Hydrogen isotope separation by quantum sieving or chemical affinity sieving.
1.1 Solid-state hydrogen storage

Concerning climate change, resource depletion of fossil fuels and energy security, a growing pressure exists to search for a replacement for fossil fuels. Among various sustainable energy sources, hydrogen has been considered as a clean energy carrier. However, hydrogen storage remains as a major challenge for implementation of a hydrogen economy and in particular for mobile applications. Current technology for hydrogen-powered fuel cell vehicles mainly focuses on hydrogen storage in either compressed gas at room temperature, e.g. $p(H_2) = 700$ bar or liquid state at ambient pressure, i.e. liquefied temperature of 20 K, due to fast refuelling of the vehicles.\textsuperscript{1,2} For the compressed gas at 700 bar corresponding to a cruising range of 500 km, however, a light-weight and high robust tank is inevitably required, leading to an economic issue. Furthermore, the compressed gas tank will be always dangerous in case of a car accident. For liquid hydrogen, due to the low critical temperature of hydrogen (33 K), the storage tank has to be an open system in order to prevent the heavily pressurized tank. Consequently, it requires energy intensive liquefaction process and also faces the technical difficulties such as evaporative hydrogen losses after a short dormancy (boil-off effect).

The alternative to the conventional storage methods is to use solid materials for hydrogen storage. This provides two very different bonding schemes. For example, hydrogen molecules can be physically adsorbed in a porous material by weak Van der Waals (dispersion) interactions or hydrogen can be chemically bound to a light element.\textsuperscript{3-5} In both ways, hydrogen can be safely stored within materials reversibly under moderate pressure. However, the improvements of these methods for mobile applications still require overcoming some technical barriers (e.g. working temperature, kinetic and thermodynamic properties of the material) to meet the DoE revised targets for 2017. As shown in figure 1.1, an efficient on-board hydrogen storage system requires 0.055 kg H\textsubscript{2} per kg (or ~5.5 wt\%) system and 0.040 kg H\textsubscript{2} per L system, gravimetric and volumetric capacity, respectively. Unfortunately, none of the existing systems meet these conditions completely up to now.\textsuperscript{6}
While different types of materials are being explored as hydrogen carriers, hydrogen storage by physisorption in nanoporous materials at modest pressure has a great advantage of offering reversible and fast sorption kinetics over multiple cycles. At cryogenic condition (~77 K), the key to reach high storage capacities in this method is a large internal surface area accessible for hydrogen molecules. Among various nanoporous materials, therefore, porous organic frameworks (e.g. MOFs: Metal-organic frameworks or COFs: Covalent-organic frameworks) are considered as promising materials for non-dissociative hydrogen adsorption due to the extremely large internal surface. In particular, the surface excess gravimetric hydrogen uptake in COF-102\textsuperscript{8} and MOF-210\textsuperscript{9} has already reached to almost 7 wt% and 9 wt% (in materials level), respectively.

1.2. Hydrogen isotope separation

In order to solve key challenges facing the world such as food and energy shortage, climate change and protection of environment it is essential that economically and environmentally sustainable energy sources are required. In this regard, nuclear fusion reactors will be the promising next generation of power generators, and cost-effective production of its energy source, therefore deuterium, a stable
isotope of hydrogen, will play an indispensable role in the near future. Moreover, deuterium is not only considered a potential energy source for the nuclear fusion reactor, but it is also widely used today in many of application such as in neutron moderators for heavy-water nuclear reactors, non-radioactive isotopic tracing, neutron scattering technique as well as a host of others. Despite its great versatile, mole fraction of natural deuterium is only up to 0.0184 % of hydrogen on Earth (the natural abundance of deuterium in the ocean is approximately 156.25 ppm10), and its enrichment from isotope gas mixtures is extremely difficult as its isotopes share identical size, shape and thermodynamic properties. Thus, a large-scale industrial separation of hydrogen isotopes is only possible with a limited number of techniques, such as cryogenic distillation or electrolysis of heavy water produced by the Girdler-sulfide process, but these techniques tend to be time and energy intensive.

![Figure 1.2 Illustration of classical molecular sieve membrane for separating a) one species from mixed gas streams and b) isotope gas mixture.](image)

In general, gas mixtures can also be separated with help of permeable membranes. For classical molecular sieving (figure 1.2a), the driving force is size difference in gas mixtures that consist of very different particle size. The pore size of the membrane is maintained and only gases smaller than the pore can permeate. This membrane gas separation is a very effective and efficient process, and their ease of operation provides a reduction in the process cost of separation. However, in contrast to the normal gas mixture separation, it is not possible to apply the size excluded methods (molecular sieve) for isotope (e.g. H2/D2) separation due to its identical kinetic diameter, shape and thermodynamic properties (figure 1.2b).
Recently, in their seminal work, Beenakker et al.\textsuperscript{11} suggested that quantum sieving is one promising avenue to separate hydrogen isotopes efficiently. It describes that if the difference between entrance pore diameter and size of the gas molecule become comparable to the De Broglie wavelength, it produces a greater diffusion barrier for lighter isotopes (quantum effect). Owing to this effect, at low temperature molecules of the heavier isotope diffuse faster inside porous materials than lighter molecules, resulting in kinetic isotope quantum molecular sieving (figure 1.3). (Details are in chapter 2.4.2) By now only a few porous materials have been tested experimentally for quantum sieving, but it has been difficult to discover a feasible porous material up to now.

In order to design or develop feasible porous materials for isotope separation, a precisely controlled pore size is an essential prerequisite. Hence, among various porous materials, novel class of porous organic frameworks (e.g. MOF, COF) are considered as promising isotope sieving materials due to their ultra-high porosity and uniform pore size which can be tailored.
2. Fundamentals: Physical adsorption or Physisorption

2.1. Ordered porous materials with ultrahigh surface area

Porous materials are of scientific and technological interest in various applications, ranging from catalysts, ion-exchange, sorption, sensing and separation to biotechnology because of their large pore volume, tunable pore size, surface functionality and high surface area. Especially, activated carbon, zeolite or novel hybrid porous materials can reach the specific surface areas of several hundred to several thousand square meters per gram, depending on the materials. In particular, among those materials, research in the ordered crystalline porous materials such as templated carbon (TC), metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs) has been tremendously grown for an application as storage media for various gases (e.g. H₂, CO₂ and CH₄) due to their ultrahigh surface areas, narrow pore size distributions, well-defined pore shapes and channel systems.

**Templated Carbon (TC)**

Porous carbons with controlled porosity in the micro/mesopore range of below 50 nm can be prepared by using micro/meso-structured silica (or zeolite) as templates. The pioneering study in this hard-templatting synthesis strategy toward porous carbon (e.g. CMK) has been first reported by the group of Prof. R. Ryoo.¹² As shown in figure 2.1, the carbon precursor (i.e. organic compound such as sucrose, glucose or fructose) infiltrates through the porous structure of inorganic materials (template), forming as organic/inorganic composites. Then, these organic/inorganic composites are carbonized by pyrolysis. By eliminating the inorganic template completely through destructive distillation with e.g. HF, a large surface area, a high porosity and controlled narrow/ordered pore size distribution (PSD) is obtained. As a result, this novel form of porous carbon has attracted much attention for various applications such as electrode materials for lithium-ion batteries¹³, electrochemical capacitors¹⁴ and hydrogen storage¹⁵. For hydrogen storage by physisorption, in particular, large surface area, large micropore volume and a suitable pore size are highly desirable for high uptake.¹⁶,¹⁷ By means of this technique, therefore, a high BET surface area (up to 4100 m²/g¹⁸) can be achieved, and thereby yield the enhanced hydrogen storage capacity.¹⁵
Metal-organic frameworks (MOFs)

Metal-organic frameworks (MOFs) are a novel class of crystalline porous compounds, consisting of metal ions (connector) linked together by organic bridging ligands (linker)\(^\text{19}\) as shown in figure 2.2. MOFs have attracted tremendous attention over the past years due to the fact that they have large surface areas and tunable pore size.

Figure 2.2 a) Schematic representation of a MOF. b) Basic building units of coordination polymers.
The variety of different connectors and linker shown in figure 2.2b makes it possible to construct a versatile 1-, 2- and 3-dimensional architectures, leading to the various types of MOFs depending on the combination of metal ions and ligands. For synthesis of MOFs, standard coordination chemistry methods (i.e. hydrothermal/solvothermal synthesis) are used, where metal ions are reacted with an organic ligand at low temperature (< 250 °C) (e.g. may be seen as self-assembly). Typically, Zn(II) and Cu(II), the most common metal ions for secondary building unit (SBU), and other transition metals (i.e., Mn, Co, Cr, Ni...) are used for the connector, and various carboxylic acids and nitrogen-heterocyclic compounds are used as the organic building blocks (linker) for the synthesis of MOFs. When these MOFs are synthesized, the pores are usually filled by guest or template molecules. In order to obtain a high porosity, therefore, it is necessary to remove these guest species by heating (activation). Through the activation, exceptionally high surface area materials are also obtained (i.e., MOF-210, DUT-6, UMCM-2 and NU-100) which can be achieved BET surface area up to 6000 m²/g.

This great variety of topologies in MOFs leads to promising applications such as hydrogen storage, separation of hydrogen isotopes, biomedical applications, sensor technology or catalysis and has been well reviewed by O’keeffe and Yaghi. Figure 2.3 shows one of well-known MOFs (MOF-5) in which the octahedral SBUs (Zn₄O clusters) connected with 6 carboxylate linker formed a 3-D cubic network.

![Figure 2.3 A prototypical metal cluster connected with linker for 3D-framework of MOF-5.](image)
Covalent-organic frameworks (COFs)

Covalent-organic frameworks (COFs) are organic analogues of metal organic frameworks (MOFs) and are comprised of light, non-metallic elements such as C, H, O, N and B. Instead of metal-linker coordination bonds as in MOFs, COFs are linked by strong covalent bonds. Yaghi and co-workers showed that self-condensation of aromatic diboronic acids or condensation of aromatic alcohols and aromatic diboronic acids in a controlled way yields crystalline organic polymers. Typically, COFs exhibit high thermal stability, and large surface areas. Figure 2.4 shows prototype of 1-D COFs (COF-1: three boronic acid molecules converge to form a planar six-membered \( \text{B}_3\text{O}_3 \) (boroxine) ring with the elimination of three water molecules). In case of 3-D network COFs, high surface area materials have been also reported (i.e., COF-102, 103) possessing BET surface areas of over 4000 m\(^2\)/g.

![Figure 2.4 A prototypical 1D Covalent Organic Frameworks COFs (COF-1)](image-url)
2.2. Molecular forces and interactions: Van der Waals forces (London dispersion force)

When two molecules approached each other, an equilibrium distance between the two is established due to the force balance between the intermolecular attraction and Pauli repulsion. The short-range Pauli repulsion is simply caused by overlapping electron orbitals, while long-range intermolecular attractions are caused by various forces such as dipole-dipole force, ion-dipole force and Van der Waals forces (Keesom force, Debye force, and London dispersion force). These correlated electron movements of nonpolar or uncharged molecules induce a dipole for a short time. As a dipole, it then can induce again dipoles in its near surrounding (which is frequently described as formation of instantaneous dipoles). Thus, this attractive force, so-called London dispersion forces, is proportional to a certain distance between the molecules. If the molecules are attracted by London dispersion forces towards the solid surface, it is also known as physical adsorption or physisorption. Note that the solid surface is relatively unstable due to a positive surface free energy. Hence, the surface has the tendency to attract molecules to minimize the surface energy.

Following terms concerning physical adsorption will be used (figure 2.5):

**Sorptive** – Molecules in fluid phase that could potentially participate in a physical adsorption

**Adsorbent** – The solid phase constituent participating in a physical adsorption.

**Adsorbate** – The general term for the molecules that have accumulated on a solid surface (adsorbent)

**Adsorption** – The process through which molecules are removed from fluid phase (sorptive) and accumulate on solid constituents at the solid-fluid interface. It is a surface phenomenon.

**Desorption** – The release of molecules from solids into fluid phase

**Coverage** – The extent of surface coverage is normally expressed as the fractional coverage, \( \theta \) (≈ number of adsorption sites occupied / number of adsorption sites available).

![Figure 2.5 Schematic diagram illustrating the location and differences between a sorptive, adsorbate, adsorbent, adsorption and desorption.](image-url)
Physical adsorption is an exothermic process which means that heat is liberated by the formation of new bonds. Simultaneously, the entropy of the system is decreased due to the loss of at least one degree of translational freedom of the molecules. Since physical adsorption is typically characterized by low adsorption enthalpy values (between 1 ~ 10 KJ/mol), it is thermodynamically more favorable at low temperatures. Figure 2.6 shows the potential energy (ε) curve for the adsorption process on porous materials as a function of the distance of an adsorbate from a surface. As defined by International Union of Pure and Applied Chemistry (IUPAC), pores are classified by their internal pore width, i.e., Macropore (Figure 2.6a): pore width greater than 50 nm, Mesopore (Figure 2.6b): pore width between 2 and 50 nm and Micropore (Figure 2.6c): pore width less than 2 nm. The micropores may then be subdivided into two categories, i.e., width less than 0.7 nm (ultramicropores) and width between 0.7 – 2 nm (supermicropores). There is a great difference of the adsorption potential curve between in macro, meso and micropores (Figure 2.6). The macropores are so wide that the potential of opposite walls do not influence each other and therefore can be considered as nearly flat surfaces. On the other hand, the potential of the walls in micro and mesopores start to overlap (indicating not only fluid-surface (micro) but also fluid-fluid interaction (meso)), which may lead to micropore filling and mesopore capillary condensation. This potential overlap gets stronger with decreasing pore width till the potential minima of opposite walls meet each other.

![Figure 2.6 Schematic one-dimensional (1D) model illustrating the molecular adsorption potential, ε, as a function of the distance, d, of an adsorbate from (a) a flat or macroporous surface, (b) mesoporous surface and (c) microporous surface.](image-url)
2.2.1. Gas-solid adsorption model

Typically physical adsorption data are plotted on the basis of relative pressure, \( P/P_0 \) (\( P_0 \) is liquefaction pressure of gas) versus amount adsorbed at a constant temperature of adsorption (isothermal process). The isotherms provide important information regarding the adsorbent and the interaction with the adsorbate in the system such as a fundamental assessment of the surface chemistry involved in the adsorption process and estimation of its textural properties (the surface area, pore volume and pore size distribution). Hence, it leads to different sorption shapes depending on the nature of the adsorbate and adsorbent. The IUPAC classification distinguishes between six sorption isotherms characteristic for different processes. Among those, microporous materials typically exhibit a type I adsorption isotherm as shown in figure 2.7. An initial steep increase (micropore filling) in physical type I adsorption will occur at relative pressure below 0.1, and this adsorption process is usually complete at a relative pressure of ~ 0.5 (adsorption plateau).

![Figure 2.7 Reversible type I physical adsorption isotherm classified by IUPAC.](image)

One should note that the interpretation of adsorption isotherms can yield a large amount of information about the sorption processes, but this is only possible upon careful analysis of the experimental data with employing suitable kinetic theories. A common method for assessing sorption behavior in micropores (pore width < 2 nm) is described below;
**Henry’s law**

In 1803, William Henry formulated a law for low gas coverage. It states when a gas is in contact with the surface of a liquid, the amount of the gas which will go into solution is proportional to the partial pressure of that gas. Likewise, physical adsorption of molecules on a solid surface is also subject to this law. At very low concentration (or low surface coverage), the amount of adsorbed molecules is linearly proportional to the gas pressure (Henry’s region), which is usually defined as:

\[ P_{\text{gas}} = \kappa_H \times n_{\text{ads}} \quad (2.1) \]

where \( P_{\text{gas}} \) is the partial pressure of the gas, \( \kappa_H \) is Henry’s law constant and \( n_{\text{ads}} \) is amount of adsorbed molecules. Note that Henry’s law does not work for gases at high pressure and molecules interacting with the surface.

**Langmuir and BET theory**

The Langmuir model is the most commonly applied theory describing isotherms for gases adsorbed on solids at elevated temperature and pressure. It is a semi-empirical isotherm derived from a proposed kinetic mechanism. Basic assumptions of the Langmuir model are the following:

- Only a monolayer is formed and, therefore, true chemisorption always exhibits a type I isotherm. In case of microporous materials that allow monolayer physisorption, the Langmuir model is also able to describe the type I isotherm.
- The surface of the adsorbent is energetically homogeneous and thereby all the adsorption sites are equivalent
- Adsorbed molecules do not interact
- All adsorption occurs through the same mechanism ( \( A_{\text{gas}} + B_{\text{surface}} \leftrightarrow \text{ad/desorption} \rightarrow AB \) )

Based on the above assumption, the Langmuir equation can be described as the relation between the number of active sites of the surface during an adsorption process, the adsorbate-adsorbent interaction energy \( (b) \) and the pressure of the adsorbate \( (p_i) \), and can thus be written as:

\[ \theta = \frac{\text{occupied site}}{\text{max. adsorption site}} = \frac{N}{N_{\text{mono}}} = \frac{W}{W_{\text{mono}}} = \frac{b(T)p_i}{1 + b(T)p_i} \quad (2.2) \]
where $\theta$ is the fractional coverage (number of sites covered with gaseous molecules), $N$ and $N_{\text{mono}}$ are the number of molecules in the incomplete and complete monolayer, respectively, $W/W_{\text{mono}}$ is the weight adsorbed relative to the weight adsorbed in a completed monolayer, $p_i$ is the adsorbate pressure, $b(T)$ is the empirical equilibrium constant as a function of temperature which contains an exponential term of the form:

$$b(T) = b_0 \cdot \exp\left( -\frac{\Delta h_{\text{at}}}{RT} \right) \quad (2.3)$$

where $b_0$ is the initial equilibrium constant.

The Langmuir equation (2.2) can be rearranged in the following form;

$$\frac{p_i}{W} = \frac{1}{b(T)W_{\text{mono}}} + \frac{p_i}{W_{\text{mono}}} \quad (2.4)$$

A plot of $p_i/W$ versus $p_i$ yields a straight line of slope $1/W_{\text{mono}}$ and intercept $1/b(T)W_{\text{mono}}$. From this plot, both $b(T)$ and $W_{\text{mono}}$ can be obtained for calculating the surface area of the sample.

The Langmuir model is frequently applied to describe type I monolayer adsorption isotherms for microporous sorbents. However, monolayer formation occurs only at low relative pressures. Under high pressure, this assumption breaks down as gas molecules attract more and more molecules towards each other. In this regard, the BET theory\textsuperscript{31} proposed by Brunauer, Emmett and Teller (BET) describes a more realistic multilayer adsorption process.

The BET model is an extension of the Langmuir model that accounts for multilayer adsorption. To the assumptions of the Langmuir theory, therefore, the BET theory adds two supplementary assumptions;

- The uppermost layer is in equilibrium with vapor phase and the number of layers becomes infinite at saturation pressure.
- The adsorption energy for first monolayer and higher layers is heat of adsorption and heat of condensation, respectively.

Hence, the BET equation can be expressed in the usual linearized form:

$$\frac{p_i}{W(p_0-p_i)} = \frac{1}{W_{\text{mono}}C} + \frac{C-1}{W_{\text{mono}}C} \times \frac{p_i}{p_0} \quad (2.5)$$

where $p_0$ is the saturation pressure and the $C$ is constant contains an exponential term of the form;

$$C \approx \exp\left( -\frac{\Delta h_{\text{mono}}-\Delta h_{\text{multi}}}{RT} \right) \quad (2.6)$$
Hence, constant $C$ depends on the difference between the adsorption enthalpy of first layer ($\Delta h_{\text{mono}}$) and multilayers ($\Delta h_{\text{multi}}$), so-called net heat of adsorption, and its value varies from solid to solid. In particular, low $C$ values represent a weak gas adsorption. A plot of the $p/W(p_i-p_0)$ versus relative pressure should also yield a straight line (equation 2.5) which will be used for determination of the BET surface area from an experimental isotherm.

2.2.2. Determination of the textural properties by BET method

Specific surface area calculation

The specific surface area (SSA) is an important characteristic for microporous materials, which is typically determined from adsorption of nitrogen, argon or carbon dioxide. This SSA can be obtained by the Brunauer-Emmett-Teller (BET) method. As shown in equation 2.5 and figure 2.8, the plot of $1/[W(p_i/p_0)-1]$ versus $p_i/p_0$ should be a straight line with slope $s = (C-1)/W_{\text{mono}}C$ and intercept $i = 1/W_{\text{mono}}C$ in the relative pressure range of 0.05 to 0.35. Hence we can solve $C$ and $W_{\text{mono}}$ from the slope and intercept of plot, simultaneously. Note that the adsorption strength can also be estimated by the value of constant $C$ (i.e., $C = 2 \sim 50$ polymers, organics / $C = 50 \sim 200$ oxides, silicates / $C$ over 200 activated carbons, zeolites).

![Figure 2.8 a) Gas adsorption isotherm and b) Plot of $1/[W(p_i/p_0)-1]$ versus $p_i/p_0$](image)

In general, relative pressure range from 0.05 to 0.35 is indeed well suited for BET plot of meso/macropore materials. However, in case of materials possessing micropores, such a broad relative pressure range ($P/P_0 = 0.05 \sim 0.35$) may result in various portions which can be linear, and therefore it is not clear which linear portion gives the correct results. Hence, in order to determine the appropriate BET pressure range for obtaining monolayer content of microporous materials, two consistency criteria should be followed as suggested by Rouquerol et al.\textsuperscript{32}: (1) the straight line fitted to
the BET plot must have a positive intercept (i.e., no negative value of C), and (2) the pressure range should be chosen within the regions of that $W_{\text{mono}}(1 - p/p_0)$ is continuously increasing with $p/p_0$. In addition to these criteria, it is strongly recommended to use at least 3 data points (preferably five data points). From these criteria, we obtain the monolayer content $W_{\text{mono}}$:

$$W_{\text{mono}} = \frac{1}{x + 1}$$  \hspace{1cm} (2.7)

Thus, total surface area ($S_t$) can be calculated

$$S_t = \frac{W_{\text{mono}}N_A\Lambda_{\text{m}}}{\rho_p}$$ \hspace{1cm} (2.8)

where $N_A$ is Avogadro constant (6.022 * 10^{23} mol^{-1}), $M_v$ is molar volume (22414 mL) and $\Lambda_{\text{m}}$ is cross-sectional area of probe molecule (i.e., $N_2$: 0.162 nm^2 and Ar: 0.142 nm^2).

When $S_t$ is divided by the sample mass (in gram), then the specific surface area is obtained.

**Cross-sectional area of hydrogen molecule**

One of the most important parameters for BET surface area calculations from H\textsubscript{2} adsorption isotherms at temperatures near the boiling point is the cross-sectional area of the probe molecule (H\textsubscript{2}), which is a function of the density of the adsorbed phase. Unfortunately, the cross-sectional area of the hydrogen molecule ($\Lambda_{\text{H}_2}$) is unknown, thus $\Lambda_{\text{H}_2}$ can be derived from the density of the adsorptive in the hexagonal closest packing (HCP) of bulk liquid state.

$$\Lambda_{\text{H}_2} = f \left( \frac{M_{\text{H}_2}}{\rho_{\text{H}_2}N_A} \right)^{2/3}$$ \hspace{1cm} (2.9)

where HCP packing factor $f$ is 1.091, the density of liquid hydrogen $\rho_{\text{H}_2}$ is 0.071 g/cm\textsuperscript{3} and the hydrogen molar mass $M_{\text{H}_2}$ is 2.016 g/mol.

Therefore, the cross-sectional area of hydrogen ($\Lambda_{\text{H}_2}$) is calculated for hexagonal closest packing of the bulk liquid with a molecular volume of 28.4 cm\textsuperscript{3} mol\textsuperscript{-1} (20 K) which yields $\Lambda_{\text{H}_2} = 14.2$ Å\textsuperscript{2}.

**Specific pore volume**

The specific pore volume (SPV) is the total internal void volume per unit mass of adsorbent which can be approximated according to Gurvich’s rule\textsuperscript{33}:

$$\text{SPV} = \frac{n_{\text{max}}}{\rho_{\text{cond}}}$$ \hspace{1cm} (2.10)

where $n_{\text{max}}$ is the maximum uptake per material mass before liquefaction and $\rho_{\text{cond}}$ is the liquid density of the probe molecule.
2.3. Hydrogen storage by physisorption

2.3.1. Hydrogen storage capacity: Excess, absolute, and total adsorption

The physical hydrogen storage capacity in porous materials is typically presented as “surface excess quantity” and given a thermodynamic meaning by use of Gibbs dividing surface. As adsorbed gas concentration in pores is difficult to quantify directly, assumptions are needed regarding the concentration of surface excess amount. The three definitions of adsorptions (absolute, total and surface excess) are schematically shown in figure 2.9. The absolute uptake is the amount of gas adsorbed solely (region in figure 2.9a) in pores. The Gibbs surface excess uptake is the absolute amount of gas adsorbed in pores minus the amount of gas that would be present in the pores in the absence of adsorbent-adsorbate interaction. The total uptake is the total amount of gas introduced to the sample cell (absolute amount of gas adsorbed in pores plus gas phase in pores). Note that the surface excess amount (iii in figure 2.9c) exhibits a maximum as a function of pressure because the excess uptake decreases at high pressure as bulk gas density increases, and thereby the quantity defined as gas phase (B in figure 2.9b) also increases.

![Figure 2.9 Schematic representation of the relation between the a) ‘absolute’, ‘total’ and b) surface ‘excess’ adsorbed amount. c) Typical isotherms for (i) total, (ii) absolute and (iii) excess hydrogen uptake.](image-url)
Calculation of excess adsorption

In order to obtain the excess uptake, all measured data points should be corrected the thermal gradient arisen from the differences between cooled sample cell (i.e. 77 K ~ 117 K) and gas reservoir with pressure transducer (298 K) during isotherm measurements. For removing an influence of the thermal gradient, non-adsorbing samples (sea sand) possessing the same sample volume were measured under identical conditions. By subtracting these two measurements, the influence of the temperature gradients as well as systematic errors can be corrected.

The adsorbed amount is reported in wt% which is defined as mass of hydrogen $m_{H}$ adsorbed onto the sample per mass of the system, which consists of the sample mass $m_{\text{sample}}$ and the adsorbed hydrogen.

$$ wt\% = \frac{100m_{H}}{m_{\text{sample}} + m_{H}} $$ (2.11)

Calculation of absolute adsorption out of excess adsorption

The excess adsorption on porous materials is the only experimentally accessible variable by all conventional techniques. Therefore, the absolute adsorption is calculated from the excess adsorption with approximated excess volume of the adsorbed layer and adsorbed gas density. If we assume that the density of the adsorbed layer is close to the density of the liquid, then the excess volume, $V_{\text{excess}}$, of the adsorbed layer can be approximated as

$$ V_{\text{excess}} = \frac{n_{\text{excess}} \cdot M_{\text{H2}}}{\rho_{\text{H2}}} $$ (2.12)

In addition, we should also consider the amount of gas that would be present in the pores due to the external pressure in the absence of adsorbent-adsorbate interaction. This can be calculated from the corrected ideal gas equation

$$ n_{\text{gas}} = \frac{p \cdot V_{\text{excess}}}{Z \cdot R \cdot T} $$ (2.13)

with the correction (compression) factor for non-ideal gas $Z$

$$ (1.000547 - (6.07 \cdot 10^{-7})T + (0.000912 - (1.0653 \cdot 10^{-6})T) \cdot P + ((7.373407 - 0.0901T) \cdot 10^{-7}) \cdot P^2 ) $$ (2.14)

where pressure, $P$, is given in atm, $T$ is temperature and $R$ is a gas constant.

The absolute adsorbed amount, $n_{\text{absolute}}$, is therefore:

$$ n_{\text{absolute}} = n_{\text{gas}} + n_{\text{excess}} = n_{\text{excess}} \cdot (1 + \frac{p \cdot M_{\text{H2}}}{Z \cdot \rho_{\text{H2}} \cdot R \cdot T}) $$ (2.15)
Measurement error reporting

In order to quantify uncertainty, the standard deviation, \( \text{StdDev} (P, T) \), is calculated and is used for an error bar. The uncertainty of the measurement is therefore given by;

\[
\text{StdDev} (P, T) = \sqrt{\frac{(1^\text{st measurement} - \text{average})^2 + (2^\text{nd measurement} - \text{average})^2 + \cdots + (N^\text{th measurement} - \text{average})^2}{N}}_{P, T}
\]

(2.16)

\[
\text{average} (P, T) = \frac{(1^\text{st measurement} + 2^\text{nd measurement} + \cdots + N^\text{th measurement})}{N}_{P, T}
\]

(2.17)

where function “sqrt()” denotes to non-negative square root of its argument and \( N \) is number of measurement.

2.3.2. Enthalpy of adsorption

Physisorption is generally considered as exothermic process, and this liberated heat energy is called isosteric enthalpy of adsorption or heat of adsorption. In cryogenic hydrogen storage applications, the heat of adsorption is a very important characteristic and has to be identified because hydrogen uptake in the low pressure range is strongly governed by this value.

The temperature dependence of the adsorption/desorption equilibrium vapor pressure is governed by Clausius-Clapeyron equation as shown below;

\[
\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)
\]

(2.18)

where \( R \) is gas constant, \( P \) is the equilibrium gas pressure and \( \Delta H \) the adsorption enthalpy change.

This Clausius-Clapeyron equation allows the estimation of the vapor pressure at temperature \( T_2 \), if the vapor pressure \( P_1 \) and the enthalpy of vaporization are known at temperature \( T_1 \). In addition, the isosteric heat of adsorption can be determined by an integration of the Clausius-Clapeyron equation as function of the surface coverage. Carrying out the integration, the Claudius-Clapeyron relation is now commonly rearranged in the Van’t Hoff form\(^{35} \) for calculating physisorption enthalpy.

\[
\Delta H = R \left(\frac{\partial \ln(P)}{\partial T}\right)_\theta
\]

(2.19)

where \( P \) is the equilibrium gas pressure, \( \Delta H \) the reaction enthalpy and \( \theta \) is the surface coverage.
From the absolute adsorption isotherms for different temperatures, the logarithm of the pressures values at a fixed surface coverage $\theta$ can be plotted versus the reciprocal temperature $1/T$ yielding a linear correlation with a slope proportional to the enthalpy of adsorption. As an example for a porous carbon sample, the evaluation of the H$_2$ heat of adsorption is shown in figure 2.10. Figure 2.10a for different uptakes measuring in the heat of adsorption as function of surface coverage.

![Figure 2.10 Determination of the isosteric heat of adsorption; a) the fully reversible absolute hydrogen uptake isotherms in porous carbon at temperatures between 77 K and 117 K, b) $\ln(P)$ versus $1/T$ plot and c) the isosteric heat of adsorption shown as a function of the surface coverage normalized to saturation uptake.](image)

**2.3.3. Linear correlation between H$_2$ uptake and surface area; Chahine’s rule**

In cryogenic (77 K) hydrogen storage applications, the maximum hydrogen uptake at higher pressures typically depends on the specific surface area (SSA) of the microporous material, also known as Chahine’s rule which describes a linear correlation between the excess hydrogen uptake and SSA with a slope of 1 wt% H$_2$ per 500 m$^2$/g. Therefore, microporous materials possessing high SSA will be necessary for physisorptive hydrogen storage.
Materials such as zeolite, activated carbons and metal-organic frameworks have been tested as effective storage candidates. It shows that the best surface area of zeolite and activated carbons are about 1000 and 3000 m$^2$ g$^{-1}$, respectively (figure 2.11). Thus, further enhancement of surface area needs to be accomplished in order to improve gravimetric hydrogen density.

Within the novel class of metal–organic frameworks (MOFs), crystalline materials exhibiting ultra high porosity with well-defined pore structure can be synthesized. Moreover, extremely large inner surface areas exceeding the best activated carbons can be also achieved. As shown in figure 2.11, there are several MOFs showing higher hydrogen uptakes than best activated carbon due to their larger SSA. Even SSA of more than 6000 m$^2$ g$^{-1}$ have been recently reported in the literature, achieving a hydrogen excess uptake of 7.92 wt% (55 bar, MOF-210$^{38}$), and 9.05 wt% (56 bar, NU-100$^{39}$), respectively. Therefore, this represents a huge step forward to materials for physisorptive hydrogen storage system.

It is noteworthy that hydrogen uptake for high SSA (over 3000 m$^2$ g$^{-1}$) materials falls the below the values predicted by chahine’s rule. It implies that these materials may have not reached the saturation
yet or errors in the determination of the appropriate BET pressure range can lead to deviations from the linear correlation as already explained in chapter 2.2.2.

### 2.3.4. Metal-doped porous materials

**Increase of hydrogen adsorption enthalpy**

One pathway for increasing the hydrogen adsorption enthalpy is to introduce active sites (e.g. exposed metal site or polarization site) into porous frameworks. In MOFs possessing open metal sites, the adsorption enthalpy can be enhanced over 10 kJ/mol\(^40,41\) (e.g. CPO-27) by employing various unsaturated metal sites (e.g. Li, Mg, Co, Zn, Fe and Cu), leading to high surface affinity to hydrogen molecules. Furthermore, G. E. Froudakis et al.\(^42\) and O. M. Yaghi et al.\(^43\) have theoretically studied that both insertion of lithium alkoxide groups in COFs and metalated (PdCl\(_2\)) Imine-COFs can lead to a significant enhancement of the hydrogen uptake, exceeding the DOE 2017 target for hydrogen uptake at RT. Therefore, this approach could be one of the possibilities in future.

**Hydrogen spillover**

Recently, R. Yang and co-workers observed the enhanced storage capacity and reported the hydrogen uptake of 4 wt%\(^41\) in Pt bridged MOFs at room temperature and 100 bar which they ascribed to the so-called “Spillover” effect (figure 2.12).\(^44,45\).

![Figure 2.12 Hydrogen spillover in a catalyst supported porous system: (i) molecular hydrogen adsorption on a metal catalyst; (ii) dissociation of molecular H\(_2\) into the atomic H, and spilt-over the adsorbent; (iii) hydrogen storage as an atomic state.](image)

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‘Hydrogen spillover’ is a well-known phenomenon in the field of catalysis, which the dissociative chemisorption of hydrogen molecules on metal nanoparticles, followed by migration of atomic hydrogen onto the metal surface. In case of hydrogen storage applications, however, this storage enhancement mechanism by decoration of noble metal particles inside high surface area supports is not yet fully understood and still under debate.\textsuperscript{46-52} Firstly, no consistent explanation exists for the migration of atomic hydrogen from metal particles into the high surface area support. Furthermore, measurements of the hydrogen storage capacity scatter from an enhancement of several times to negligible within the experimental uncertainty. As a result, some groups who have examined the spillover effect have reported significant enhancements\textsuperscript{53,54} but some others have denied any enhancement\textsuperscript{13,51,55} at room temperature. As for instance, C. M. Ghimbeu et al. reported that the significant uptake enhancements on Pd doped zeolite templated carbon (Pd-ZTC) mainly come from the presence of PdO layer (reduction of PdO with the formation of Pd and water) on small Pd nanoparticles at room temperature below 1 bar.\textsuperscript{56} Similarly, C. I. Contescu et al. also reported that the presence of Pd in activated carbon fibers (Pd-ACF) induced the spillover process and then some of the spilt-over hydrogen have been chemically bonded to the carbon support edge (e.g. C-H bonds) at room temperature and high pressure (20 bar), which cannot be desorbed even after outgassing at 300 °C.\textsuperscript{44}

Another reason for the discrepancies between different groups may be caused by inaccurate or erroneous measurement. For instance, D. Broom et al.\textsuperscript{57} well elaborated the experimental challenges for determination of gas adsorption using Sievert-type apparatus at elevated pressures where the accuracy of the equation of state, propagation of errors and adsorption of impurities become significant factors. Hence, they pointed out that the special care for those problems (e.g., leaks in the apparatus, the impurities in the gas phase, error propagation at high P and etc…) is required to avoid common pitfalls. Recently, international Round-Robin Test (RRT) on porous carbon\textsuperscript{58} showed a huge scatter particularly at high pressure for RT isotherms measured by different laboratories, indicating difficulty of reliable results.
2.4. Hydrogen isotope separation

Conventional molecular sieves are often utilized in industry for the purification of gas mixtures consisting of different molecular sizes. However, separation of hydrogen isotopes requires special efforts because of its identical size, shape and thermodynamic properties. Therefore, separation of isotope mixtures is only possible with limited techniques such as cryogenic distillation and Girdler sulfide (GS) process.

2.4.1. Current technology for H\textsubscript{2}/D\textsubscript{2} separation

Cryogenic distillation

Cryogenic distillation is extensively used in the field of industrial gas separations for many years, and is operated at extremely low temperature and high pressure to separate components according to their different boiling temperatures. The basic principle of distillation consists of three steps; 1) generation of the two phase system, 2) mass transfer across the interface and 3) separation of the two phases. Figure 2.13 shows the schematic diagram of H\textsubscript{2}/D\textsubscript{2} separation by cryogenic distillation. This method is advantageous with respect to direct production of liquid D\textsubscript{2} or pure D\textsubscript{2} gas. However, it requires very high energy for the refrigeration and its separation factor is rather low (1.5\textsuperscript{58} at 24 K and 3\textsuperscript{60} at 20 K) due to the small difference in boiling points (20.3 K and 23.7 K for H\textsubscript{2} and D\textsubscript{2}, respectively). Moreover, water vapor has to be removed from the gas mixture before the cryogenic cooling process in order to avoid blockage from freezing in the cryogenic equipment. This can add additionally to the cost of the process.

![Schematic diagram of H\textsubscript{2}/D\textsubscript{2} separation by cryogenic distillation](image)

Figure 2.13 Schematic diagram of H\textsubscript{2}/D\textsubscript{2} separation by cryogenic distillation
Chemical exchange (Girdler-Sulfide process)

The chemical exchange technique makes use of different chemical reaction rates. Although hydrogen and deuterium possess same number of electrons (thus, it is thought to be chemically identical), they undergo chemical reactions at different rates because of their difference in atomic masses. For that reason, Girdler-sulfide (GS) dual-temperature method is commonly used to produce heavy water in large commercial enrichment plants. This method is an isotopic exchange process between $\text{H}_2\text{S}$ and ordinary water (containing small portion of heavy water), which eventually produces $\text{D}_2\text{O}$ through multiple processing cycles.

Figure 2.14 shows GS process flow-sheet. Hydrogen sulfide gas is circulated in closed tower, and mixes with ordinary water at cold tower (c.a. 303 K). Then small portion of heavy water inside ordinary water reacts with hydrogen sulfide, producing deuterium sulfide. This product is transferred to the hot tower (c.a. 403 K), and reacts with ordinary water again enriching heavy water. This cycle is repeated in order to obtain enriched heavy water.

In GS method, ordinary water can be enriched to 20–30% deuterium. In order to obtain pure heavy water (~99.75%), it is needed to be fed to a vacuum distillation system. This results in a highly energy intensive process with a separation factor of only ~2.3. Moreover, an additional electrolysis process is required to obtain the pure deuterium from heavy water, resulting in extremely high product costs.
2.4.2. A novel strategy for H$_2$/D$_2$ separation

Quantum sieving

Recently, quantum sieving in nanopores was proposed as one possibility to separate H$_2$/D$_2$ isotope mixture efficiently and effectively. This concept was first introduced by Beenakker et al. (1995)$^{11}$ on the basis of the simple model for the adsorption of isotope molecules with hard core diameter in a cylindrical pore with a square well potential. They proposed that isotope separation in nanopores can be possible when the difference between pore ($d$) and molecular size ($\sigma$) becomes comparable to the de Broglie wave length of isotope molecules ($\lambda$) where the molecules are restricted in their transverse motion in a given space$^{11}$ (figure 2.15a and equation 2.20).

$$\lambda \approx d - \sigma$$  \hspace{1cm} (2.20)

Figure 2.15b shows the zero point energy ($E_0$) of a molecule and the adsorption potential depth ($\epsilon$) in a narrow pore. As a result of equation 2.21, the $E_0$ of a molecule in a narrow pore is inversely proportional to the de Broglie wave length (equation 2.20) and the atomic mass ($m$) of isotope, exhibiting that $E_0$ increases with decreasing $d$.\textsuperscript{11}

$$E_0 \sim \frac{1}{m(d-\sigma)^2}$$  \hspace{1cm} (2.21)

In figure 2.15b, $\epsilon$ is additionally illustrated as a function of pore diameter (e.g., molecule in a slit channel) starting from its value ($\epsilon_{fs}$) at a flat surface. The variation of $\epsilon$ by the potential overlap is well demonstrated in figure 2.15c. For example, when $d$ is large enough, the potential of opposite walls do not influence each other and can be considered as nearly two independent flat surfaces, $\epsilon_{fs}$, (denoted 1 in figure 2.15b-c). This potential overlap gets stronger with decreasing pore width till the potential minima of opposite walls meet each other (denoted 2 in figure 2.15b-c). If $d$ is further reduced, the potential depth starts to decrease (denoted 3 in figure 2.15b-c), and finally when $d$ is the same or smaller than $\sigma$, the molecule is physically impossible to penetrate the pore. It is also noted that $\epsilon$ becomes negative before the $d = \sigma$ is reached (figure 2.15b), indicating that the electrostatic repulsion of the electron shells between pore and molecule already occurs for the pore just slightly larger than the molecule, making adsorption difficult.

Assuming equilibrium with the gas in free space, the density of particles (molecules) inside the channel (pore) per unit length can be estimated as shown below equation 2.22\textsuperscript{11}
\[
\sum_{}^{} \left( d - \sigma \right)^2 \sum \exp\left( -\frac{E_0}{kT} \right) \geq \sigma
\]

Free volume per unit length of the channel (pore) Boltzmann factor

where \( n_v \) is the gas density outside the channel (pore), \( k \) is Boltzmann constant and \( T \) is absolute temperature.

At region A in figure 2.15b (where \( d - \sigma \) is closed to \( \lambda \)), the zero point energy (or motion), \( E_{0h} \) of gas molecules overcompensates the attractive molecule-surface interaction, \( \varepsilon \) (i.e. \( E_0/\varepsilon > 1 \)), resulting in the quantization of the transverse motion of gas molecules in the pore\(^{11}\). Hence, according to equation 2.22, the molecular density in the channel (pore) will be reduced by a Boltzmann factor \( \exp\left(\frac{\varepsilon - E_0}{kT}\right) < 1 \). Since the only difference between isotopes is their mass, the \( E_0 \) for lighter isotopes is higher than for heavier ones and thereby the lighter isotope further decreases its density in the channel (pore) compared to the heavier isotope.

![Figure 2.15](image)

**Figure 2.15** a) Scheme of quantum confinement effect. b) Behavior of the well depth \( \varepsilon \) and zero-point energy \( E_0 \) as function of channel diameter.\(^{11}\) c) Adsorption potential depth as function of pore diameter.

This foregoing description proposed by Beenakker\(^{11}\) can be applied to hydrogen isotope separation by using microporous materials possessing pore diameter similar to kinetic diameter of the hydrogen isotope under cryogenic conditions. At this nanopore, hydrogen isotopes encounter a penetration barrier because of the \( E_0 > \varepsilon \), and this barrier will differ for isotopes due to the mass (and thereby \( E_0 \)) difference. Thus, at sufficiently low temperature (where exhibiting the higher differences between the quantized energy levels of \( H_2 \) and \( D_2 \) adsorbed in a nanopore), the molecular diffusivity of the isotopes will differ\(^{62}\) inside the porous material, resulting in the separation of the isotopes. That is so-called quantum sieving.
This idea was later expanded upon by several research groups using both theory and experiment. For instances, Y. Wang et al. (2009) elaborated these effects in detail using more realistic model of path integral formalism with Silvera-Goldman potential, demonstrating high D$_2$/H$_2$ selectivity (S ~ 16.6) in carbon slit pore (5.6 Å) with an adsorbed D$_2$ density of 33.2 kg/m$^3$ at 40 K, 1 bar. P. Kowalczyk et al. (2009) elucidated pore size effects on localization of hydrogen isotopes at 33 K in very small carbonaceous square-shaped pores by using path integral-grand canonical Monte Carlo simulations. They discovered that in the small pore width, the D$_2$ molecules tend to be more localized at the center of the pore than H$_2$ molecules, leading to the less broadening of the D$_2$ density matrix (figure 2.16). It also implies that effective particle diameter of D$_2$ is smaller than H$_2$. The steepness of the interaction potential by small pores (denoted 3 in figure 2.15c) is the main reason for this high localization. Moreover, they reported that the smaller size of the pore width, the higher is the difference between the kinetic energy of H$_2$ and D$_2$ (e.g. the lower kinetic energy for D$_2$ due to the heavy mass in small pore), resulting in a different diffusivity.

![Figure 2.16](image)

Figure 2.16 Density matrix of H$_2$ (left) and D$_2$ (right) adsorbed at 33 K in infinitely long structure less square-shaped carbon pores of widths: 2.6 and 3.1 Å (from top to bottom). (Taken from figure 5 of ref. 60)
Subsequently the foregoing theoretical results have been experimentally confirmed by Bhatia et al. (2010), exhibiting the quantum kinetic effect on carbon molecular sieves (CMS) with quasi-elastic neutron scattering for pure H\textsubscript{2} and D\textsubscript{2}. As shown in figure 2.17, the D\textsubscript{2} diffuses faster than H\textsubscript{2} below 100 K in Takeda 3 Å CMS, and the difference in diffusivity gets stronger close to the base temperature of 30 K.

![Figure 2.17](image)

Figure 2.17 Diffusion coefficients for H\textsubscript{2} and D\textsubscript{2} in Takeda 3 Å CMS, as a function of temperature (loading: 0.5 mmol/g), showing typical error bars. Inset: depicts the pore size distribution of the CMS obtained from the interpretation of experimental high pressure CO\textsubscript{2} adsorption data. (Taken from figure 2 of ref. 62)

In quantum sieving, therefore, the pore size plays an important role for determining the diffusion kinetics and thereby overall separation. By now only a few porous materials like carbons, zeolites, and metal-organic frameworks (MOFs) have been experimentally tested for their ability to separate hydrogen isotopes by quantum sieving. Until recently, however, the highest experimentally demonstrated separation factor at 77 K was 3 with an adsorbed capacity of 0.2 mmol g\textsuperscript{-1} by using MS13X zeolite. Table 2.1 shows experimental results of the selectivity on various porous materials reported in literature.
Chemical affinity sieving

As alternative to quantum sieving, it may also be possible to use thermodynamic effects to separate hydrogen isotope mixtures. In general, molecules with the strongest chemical affinity with the pores (or specific adsorption sites) are adsorbed while the ones with weaker interaction are not. This holds as long as the pore size is large enough for penetration of both gases, and no diffusion barrier exists inside the porous material. Similarly, isotope molecules may also adsorb on strongly attracting sites of the host material with different affinities as the different molecular masses leads to different zero point energies (ZPE), and thereby different adsorption enthalpies \( \Delta H \) of the isotopes.

In the case of adsorbed molecular hydrogen on the surface, six degrees of freedom contribute to the ZPE and the partition function, and thus to the enthalpy. These are the vibration of the center of the hydrogen molecule towards the adsorption site of the host, the vibration of the intramolecular bond, two rotational and two translational degrees of freedom. Depending on the affinity strength of the adsorption site, the latter four degrees could be hindered. The first degree of freedom (vibration of adsorbed \( \text{H}_2 \) on adsorption sites) is the one that is most strongly influenced by the host material. Hence, significant difference in their adsorption enthalpies may provide the preferential uptake of heavier isotopes, leading to a large separation factor even at liquid nitrogen temperature (77K) and above.

Figure 2.18 Qualitative plot of the strength of the adsorption sites. Zero point energies are shown qualitatively for \( \text{H}_2 \) (black) and \( \text{D}_2 \) (red). The strength of each binding site is demonstrated by the depth of potential well.
Figure 2.18 shows the physisorption potential energy of hydrogen isotopes on porous materials possessing three different adsorption sites, describing qualitatively the zero point energies for hydrogen isotopes (e.g. H\textsubscript{2} (black line) and D\textsubscript{2} (red line)). The strength of each binding site is represented by the depth of the potential well. It can be found that the steeper the interaction potential, the larger is the difference between the zero point energy of H\textsubscript{2} and D\textsubscript{2}. As already mentioned before, the different molecular masses imply different zero point energies (ZPE), meaning different adsorption enthalpies $\Delta H$. Consequently, the larger the difference in adsorption enthalpies $\Delta H$, the heavier isotope will adsorb more preferentially at strong binding sites, resulting in a separation of isotopes. This can be called chemical affinity sieving.

In short, figure 2.19 shows simplified models for hydrogen isotope separation, exploiting basically the difference in the zero point energy (ZPE) of H\textsubscript{2} and D\textsubscript{2}. Two different separation mechanisms are involved;

i) **Quantum sieving** (figure 2.19a) is based upon the different diffusivity of H\textsubscript{2} and D\textsubscript{2} as lighter isotope possesses the higher kinetic energy than heavier ones at the pore entrance (resulting in the lower H\textsubscript{2} density in pore) when the difference between pore size and molecular size becomes comparable to the de Broglie wave length at sufficiently low temperature.

ii) **Chemical affinity sieving** (figure 2.19b) is based upon preferential adsorption of heavier isotopes on strong adsorption sites inside porous materials because of the difference in adsorption enthalpy between the isotopes.

![Figure 2.19 Models of simplified a) quantum sieving and b) chemical affinity sieving](image-url)
Table 2.1: Summary of the experimentally reported quantum molecular sieving separability on various porous materials.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Aperture</th>
<th>T</th>
<th>P</th>
<th>$w^a$</th>
<th>$S_{\text{IAST}}^b$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous coordination polymer</td>
<td>LPE$^c$ (8.7*8.7)</td>
<td>40 / 77</td>
<td>0.02</td>
<td>5.8 / 1.2</td>
<td>3.0 / 1.3</td>
<td>66</td>
</tr>
<tr>
<td>(CuBOTf)</td>
<td>SPE$^d$ (0.2*0.2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microporous mixed MOFs (M'MOF 1)</td>
<td>5.6 * 12</td>
<td>77 / 87</td>
<td>&lt; 0.2</td>
<td>1.15 / 1.18</td>
<td>-</td>
<td>67, 70, 71</td>
</tr>
<tr>
<td>12-connected MOFs</td>
<td>10</td>
<td>77</td>
<td>1</td>
<td>1.1</td>
<td>-</td>
<td>72</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>9 / 5</td>
<td>77</td>
<td>0.02</td>
<td>1.23</td>
<td>-</td>
<td>73</td>
</tr>
<tr>
<td>Coordination frameworks (Cu2L2)</td>
<td>7.3</td>
<td>77</td>
<td>0.1</td>
<td>1.2</td>
<td>-</td>
<td>74</td>
</tr>
<tr>
<td>CPO-27 (Ni)</td>
<td>10</td>
<td>77</td>
<td>NZP$^e$</td>
<td>4.6</td>
<td>5</td>
<td>75</td>
</tr>
<tr>
<td>Loosely-assembled SWCNT</td>
<td>28.5 ± 0.72</td>
<td>40 / 77</td>
<td>$10^4$</td>
<td>5 / 3.8</td>
<td>-</td>
<td>76</td>
</tr>
<tr>
<td>CMS Takeda 3A</td>
<td>5.88 (2.78)</td>
<td>30</td>
<td>0.5mmol loading</td>
<td>Diffusivity ratio : 3.5</td>
<td>-</td>
<td>62</td>
</tr>
<tr>
<td>Activated Carbon Fibers (ACFs)</td>
<td>~ 6 A</td>
<td>77</td>
<td>$10^{-3}$</td>
<td>1.2</td>
<td>-</td>
<td>77</td>
</tr>
<tr>
<td>SWCNT</td>
<td>12.6</td>
<td>77</td>
<td>$10^{-3}$</td>
<td>1.2</td>
<td>-</td>
<td>77</td>
</tr>
<tr>
<td>SWCNT bundles</td>
<td>Interstitial site &lt; 7 A</td>
<td>77</td>
<td>1</td>
<td>~1.2</td>
<td>-</td>
<td>78</td>
</tr>
<tr>
<td>Carbon molecular sieve CMK-3</td>
<td>35</td>
<td>77</td>
<td>1</td>
<td>1.15</td>
<td>-</td>
<td>79</td>
</tr>
<tr>
<td>CMS Takeda 3A</td>
<td>77</td>
<td>5*10^{-3} ~ 1</td>
<td>1.063</td>
<td>1.097</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>Porous Carbon Substrate (PCS)</td>
<td>77</td>
<td>5*10^{-3} ~ 1</td>
<td>1.063</td>
<td>1.097</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>Activated Carbon Fibers (ACFs)</td>
<td>10.9 A</td>
<td>20</td>
<td>1</td>
<td>~1.11</td>
<td>2.25</td>
<td>81</td>
</tr>
<tr>
<td>Fluorinated-ACFs</td>
<td>8.8 A</td>
<td>20</td>
<td>1</td>
<td>~1.27</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

45
<table>
<thead>
<tr>
<th>Compound</th>
<th>Aperture (Å)</th>
<th>T (K)</th>
<th>P (bar)</th>
<th>( w^a ) ((n_{D_2}/n_{H_2}))</th>
<th>( S_{IAST}^b )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS13X RHO</td>
<td>8.6</td>
<td>77</td>
<td>5*10^{-3}</td>
<td>-</td>
<td>3.05*</td>
<td>65</td>
</tr>
<tr>
<td>AlPO4-5</td>
<td>10*11.4</td>
<td>77</td>
<td>1</td>
<td>1.1</td>
<td>1.1</td>
<td>77</td>
</tr>
<tr>
<td>Molecular Sieve Y</td>
<td>7</td>
<td>77</td>
<td>0.139</td>
<td>1.18</td>
<td>-</td>
<td>82</td>
</tr>
<tr>
<td>3A</td>
<td>3</td>
<td></td>
<td></td>
<td>1.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4A</td>
<td>4</td>
<td></td>
<td></td>
<td>1.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5A</td>
<td>5</td>
<td>77</td>
<td>1</td>
<td>1.12</td>
<td>-</td>
<td>79</td>
</tr>
<tr>
<td>Y</td>
<td>6~7</td>
<td></td>
<td></td>
<td>1.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a: the \( D_2/H_2 \) molar ratio based on the pure gas adsorption isotherms, b: 1:1 \( D_2/H_2 \) mixture selectivity from pure gas adsorption isotherms using idealized adsorption solution theory (IAST), c: Large Pore Entrance, d: Small Pore Entrance, e: Near Zero coverage Pressure and f: experimentally determined mixture selectivity using flow method (flow rate: 0.08 mL(STP)/min).
3. Experimental methods

3.1. Volumetric device for Pressure-Composition-Temperature characteristics (PCTs)

The volumetric method for hydrogen storage measurement, known as Sievert’s method, uses temperature-pressure-volume correlations to determine hydrogen concentration and the storage capacity of a material. Here, an automated Sievert’s type apparatus (Setaram-HyEnergy PCTPro-2000) was used with a so-called micro-doser (MD) from HyEnergy which can allow us to measure the storage properties accurately with only small amount of sample (~100 mg). The PCTPro-2000 with a micro-doser is capable of performing PCT measurements with the hydrogen gas at a maximum pressure of 20 bar, and sample temperatures in the range 77 K ~ 550 K. A general illustration of this volumetric apparatus (PCTPro-2000) with the main components is shown in Figure 3.1.

![Illustration of an automated Sievert's type apparatus (PCTPro-2000) with a micro-doser.](image)

The setup is equipped with a turbo pump (Vacuum) for evacuation of the sample/reservoir volume and cleaning of the lines. There is a ventilation line (Vent), which takes all the excess pressure from the system that the vacuum pump cannot handle. The PCTPro-2000 consists of a gas reservoir (supply volume) connected to helium or hydrogen inlet and also connected to a sample container. The gas inlets are controlled by a rotating valve providing 3 possible operations. By rotating the MD’s manual
actuator into the ‘bypass’, a common procedure such as purging, evacuation or charging can be performed. During measurements the valve is automatically switched from the ‘sample’ to the ‘source’ position. The ‘sample’ position indicates that the sample container is closed and the pressure transducer is measuring the pressure in the volume of the container. The ‘source’ position indicates that the pressure transducer is measuring the supply volume and connection line from the apparatus (PCTPro-2000) while the sample container is closed.

The adsorbed amount of hydrogen can be determined by the real gas equation of state based on the pressure drop in a calibrated volume of reservoir and sample container at constant temperature. The skeletal volume of the materials, \( V_{skc} \) (density of materials) must be known in advance by a helium expansion test.

Initially, hydrogen gas is introduced into the reservoir (supply volume) under a pressure of \( P_{res}, T_{res} \). Then the reservoir is connected to the sample container. Once the thermal equilibrium in the system is reached, the pressure \( (P_{sys}) \) and temperature \( (T_{sys}) \) are recorded again. Therefore, the quantity of hydrogen gas \( (n) \) present in the reservoir as an initial gas content and in the system as a final gas content can be determined as follows;

\[
 n = \frac{P \cdot V}{Z \cdot R \cdot T} \quad (3.1)
\]

where \( Z \) is compression factor (equation 2.14) for corrected ideal gas equation\(^{34}\);

And the hydrogen gas uptake can be calculated by subtracting the initial gas content \( (n_i) \) from final gas content \( (n_f) \).

\[
 \Delta n = n_i - n_f \quad (3.2)
\]

By substituting equation (3.1) into equation (3.2), the total quantity of hydrogen gas adsorbed in a sample can be determined as given in equation (3.3)

\[
 \Delta n = \frac{P_{res}V_{res}}{Z(P_{res}T_{res})R_{res}} - \frac{P_{sys}V_{sys}}{Z(P_{sys}T_{sys})R_{sys}} \quad (3.3)
\]

where \( V_{res} \) is the reservoir (supply) volume and \( V_{sys} \) represents the reservoir volume plus sample container \( (V_{con}) \) volume minus skeletal volume \( (V_{skc}) \) of the materials. Thus, \( V_{sys} \) can be expressed by

\[
 V_{sys} = V_{res} + V_{con} - V_{skc} \quad (3.4)
\]
where the reservoir volume of MD in PCTPro200 containing volume of the connection pipe line and manometer yields $V_{res} = 0.51 \text{cm}^3$. The sample container volume ($V_{con}$) is $1.265 \pm 0.005 \text{ cm}^3$. The skeletal volume ($V_{ske}$) of the materials will be obtained by a helium expansion test prior to the measurement. A typical sample mass for MD measurement is in the range of 100–200 mg.

![Diagram of the cooled system](image)

**Figure 3.2** Schematic system of the upgraded PCTPro2000 micro-doser (MD) for cooling system. a) Dipping method with dewar cryostat for cooling at liquid nitrogen (77K) and liquid argon (87 K) temperature. b) Cooling system for temperatures above 87K where the sample container is enclosed by a copper block (orange) and partially sank in the liquid nitrogen. The liquid nitrogen level is constantly controlled by automatic liquid N$_2$ refilling system.

Hydrogen storage by physisorption on porous materials requires low temperature, typically around liquid nitrogen temperature, due to the very weak Van der Waals interaction energy. Therefore, the original setup is upgraded by a heating and cooling device to regulate the sample temperature. This upgraded setup will allow the measurement of adsorption and desorption isotherms (0-20 bar) at
various temperature (77 to 300 K). Especially, over wide temperature range for isotherms (77 K ~ 117 K) will provide a minimized uncertainty (errors) of measurement for an adsorption enthalpy calculation and yield reliable results. Figure 3.2 shows the details of upgraded PCTPro2000 MD setup.

For isotherms at 77 K and 87 K, the sample container is submerged into the liquid nitrogen or argon, respectively (fig. 3.2a). For temperatures above 87 K, the sample container is enclosed by a copper block (orange) and partially submerges in the liquid nitrogen (fig. 3.2b). The liquid nitrogen level is controlled within 0.2 cm height by an automatic liquid N\textsubscript{2} refilling system. The copper block includes a K-type thermocouple and a heater for monitoring and adjusting the temperature. By a PID control a constant temperature within ±1 K can be maintained over the whole temperature range.

### 3.1.1. Cold volume calibration

The calibration of the sample container volume is a crucial step for obtaining reliable measurements. By a helium expansion test, the sample container volume ($V_{\text{con}}$) containing porous sample at RT can be directly determined by measuring the pressure change on dosing the helium gas from the known reservoir volume ($V_{\text{res}}$) into the sample container. At low temperatures, however, this direct helium expansion test results in inaccurate values of $V_{\text{con}}$ for microporous materials due to a significant helium adsorption. Therefore, the indirect method such as ‘volume correction using a non-porous material’ is applied.

Using $V_{\text{con}}$ obtained at RT, the apparent hydrogen uptake of non-porous material (sea sand) with various masses is measured in the temperature range of 77 - 117 K. Since the volume occupied by the sample is denoted as skeletal volume ($V_{\text{ske}}$), the $V_{\text{con}}$ (and thereby the apparent hydrogen uptake) is function of $V_{\text{ske}}$ at given temperature and pressure, $V_{\text{con}}(V_{\text{ske}})$.

Figure 3.3 shows the apparent concentration of hydrogen gas up to 20 bar in the temperature range of 77 K ~ 117 K using 1.26 cm\textsuperscript{3} of $V_{\text{con}}(V_{\text{ske}})$. The apparent hydrogen uptake is linearly increasing with the pressure. This apparent hydrogen concentration can be converted into a volume, and is defined as the ‘cold volume’. Figure 3.4 shows the linear fit of the cold volume for low temperatures. Therefore, using this cold volume, the influence of the thermal gradient for each sample temperature can be corrected.
Figure 3.3 PCT measurements at various temperatures showing the apparent hydrogen concentration using $V_{con(V_{ske})}$ determined at room temperature.

Figure 3.4 Cold volume as a function of $V_{con(V_{ske})}$ for different temperatures.

The hydrogen uptake at ‘low temperatures’ is determined by measuring the porous sample and a non-adsorbing material (sea sand) possessing the same volume. By subtracting these two measurements, the difference between the total amounts of gas introduced to the sample container (gas adsorbed in pores plus gas phase in pores) and the total gas phase that would be present in the sample container can be obtained. This quantity is the so-called excess amount of hydrogen $n_{excess(p,T)}$ and is simply given by
\[ n_{\text{excess}}(p,T) = n_{\text{experiment}}(p,T) - n_{\text{sea sand}}(p,T) \]  

where \( n_{\text{experiment}}(p,T) \) is the raw data of hydrogen uptake measurement for the porous sample and \( n_{\text{sea sand}}(p,T) \) is the hydrogen uptake for the sea sand.

Figure 3.5 shows an example of the application of cold volume corrections to hydrogen adsorption data (in wt\% uptake) for a porous carbon at 77 K. It shows that the cold volume correction at low temperatures can be significant even at pressures below 20 bar. Therefore a special care is required.

Figure 3.5 Hydrogen adsorption by porous carbon at 77 K exhibiting a) raw data \( (n_{\text{experiment}}(p,T)) \) without cold volume correction and b) excess hydrogen uptake \( (n_{\text{excess}}(p,T)) \) corrected for cold volume.
3.2. Low-pressure, high-resolution hydrogen adsorption isotherm measurement

The Quantachrome Autosorb-1 is a fully automated set-up based on the Sieverts’ method. The working principle is almost identical to the PCTPro2000 in the foregoing section. The Autosorb-1 has the capability of measuring adsorbed or desorbed volumes of gases at pressures in the range \(1 \times 10^{-7}\) bar to 1 bar through the five sensitive pressure transducers. Thus, precise measurement with small sample quantity (ca. 20 mg) can be achieved. Furthermore, applying the Autosorb-1 software, the measured volume-pressure data can be used to calculate the various textural properties of porous materials such as sorption isotherm, (BET, Langmuir) specific surface area, pore size distribution and pore volume calculation.

This commercial Autosorb-1 is mainly designed for measuring the quantity of gas (such as N\(_2\), Ar or CO\(_2\)) adsorbed on solid surface “above” the liquid nitrogen temperature (~77 K) as those gases are liquid at 77 K under atmospheric pressure. On the other hand, the liquid nitrogen temperature is not sufficient for the case of hydrogen isotherms, and thus a novel cryostat has been developed which can reach temperatures below the liquefaction of hydrogen gas. Therefore, the original liquid bath cryostat for nitrogen is replaced by a helium flow cryostat as shown in figure 3.6.

Figure 3.6 a) Schematic diagram of volumetric adsorption apparatus b) Experimental set-up of low-pressure high-resolution hydrogen adsorption system. Commercial Autosorb-1 is equipped with a helium flow cryostat with temperature controller (ITC503, Oxford). c) Close-up view of the helium flow cryostat equipped with Autosorb-1.
Figure 3.7 shows the inner part of the helium flow cryostat. The sample chamber is under ultra-high vacuum (UHV) and the sample is located at the bottom of the sample cell inside copper block. In order to minimize the empty volume inside the sample cell, a glass cylinder is used to fill up the upper part of sample cell volume.

Figure 3.7 Schematic representation of an inner part of the helium flow cryostat for hydrogen adsorption at 19.5 K.

For cooling, the liquid helium flows through the copper block, and a heating element in the copper block is used for achieving higher temperature. A platinum resistor (PT-111) as a temperature sensor is placed in the copper block close to the sample cell and the temperature is stabilized by temperature controller (ITC503, Oxford). This helium flow cryostat can reach a minimum temperature of approximately 11 K.

3.2.1. Temperature sensor calibration

The temperature dependence of the electrical resistance of metals (e.g. Pt) can be used for measuring the temperature. Above 70 K, the platinum resistor follows a linear resistance-temperature relationship, leading to good temperature calibration above 70 K. However, there is a deviation of linear resistance-temperature relationship at low temperatures, which depends on the residual resistance of the individual platinum resistor. In addition, the location of platinum resistor inside copper block is not exactly at the sample location, leading to a slight temperature gradient between the sample and the sensor at low temperatures.
By measuring the liquefaction pressure of different gases such as hydrogen, deuterium nitrogen and argon, the real temperature in the sample cell can be obtained since temperature-pressure correlation is well-known based on the phase diagram of each gas\(^{83}\). Figure 3.8 shows the correlation between real temperature and sensor reading, which was used to correct the temperature gradient. Note that it is assumed that above 200K the temperature gradient between the platinum resistor and sample cell is negligible and the resistance increases with the temperature according to DIN IEC 751 temperature/resistance table for platinum sensors.

![Figure 3.8 Temperature sensor calibration by measuring the liquefaction pressure for various gases such as hydrogen, deuterium and nitrogen in the empty sample cell; \(T_{\text{sensor}}\) is liquefied temperature recorded by platinum resistor and \(T_{\text{real}}\) is the actual liquefied temperature from phase diagram of each gas. The red line is the polynomial 4\(^{th}\) order fit of calibration.](image)

### 3.2.2. Cold volume calibration

The sample cell volume can be directly determined by helium expansion test. Initially the valve is closed and helium is fed into the defined reservoir volume (19.667 cm\(^3\)). After thermal equilibrium is reached, temperature and pressure are recorded. Afterwards, the valve is open to the sample cell, and temperature and pressure are recorded again. This direct helium expansion method allows calculating the sample cell volume by using helium real gas equation and the change of pressure after connecting the two volumes. This yields a sample cell volume of \(V_{\text{cell}} = 10.085 \pm 0.003\) cm\(^3\).
For all isotherms at cryogenic condition, a temperature gradient (from RT to low T) exists along the sample cell volume which needs to be corrected. For simplicity, it is assumed that the sample cell volume is divided into two temperature zones; imaginary cold zone \( V_{\text{cold}} \) at the sample temperature and room temperature zone \( V_{\text{RT}} \),

\[
V_{\text{cell}} = V_{\text{cold}} + V_{\text{RT}}
\]  

This \( V_{\text{cold}} \) can be determined through a gas expansion measurement in the empty sample cell. First, the empty sample cell, \( V_{\text{cell}} \), is filled with initial pressure \( P_{\text{ini}} \) at room temperature \( T_{\text{RT}} \) and the valve is closed, resulting in a constant amount of gas, \( n_{\text{ini}} \). Then, the sample cell is cooled down to 13 K. Afterwards, the pressure is monitored while the temperature of the sample cell is raised slowly to RT. Once the thermal equilibrium in the system is reached, pressure \( P(T) \) of the empty sample cell at each temperature \( T \) are recorded.

Thus, \( V_{\text{cold}} \) can be represented as the volume containing the amount of gas, \( n(T) \) at temperature \( T \).

\[
V_{\text{cold}}(T) = \frac{n(T)R^T Z_p(T)}{p(T)}
\]  

where \( R \) is gas constant \((83.1447 \text{ cm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})\) and \( Z_p(T) \) is the compression factor (equation 2.14) for corrected ideal gas equation.

An amount of initial gas, \( n_{\text{ini}} \) at RT can be calculated by;

\[
n_{\text{ini}} = \frac{P_{\text{ini}} V_{\text{cell}}}{R T_{\text{RT}} Z_p(T)}
\]  

As the valve is closed, the amount of gas is constant \((n(T) = n_{\text{ini}})\). Hence, from equation 3.7 and 3.8, the cold zone volume at \( T \) can be derived as;

\[
V_{\text{cold}}(T) = \left( \frac{P_{\text{ini}} V_{\text{cell}}}{R T_{\text{RT}} Z_p(T)} \right) \cdot \left( \frac{R^T Z_p(T)}{p(T)} \right)
\]  

By this approach, the imaginary cold zone volume at 19.5 K can be determined to be \( V_{\text{cold}} = 0.65 \text{ cm}^3 \). For temperatures above the boiling temperature, further correction of \( V_{\text{cold}} \) is done empirically. By that, the polynomial 4th order fit of the cold zone volume \( V_{\text{cold}} \) is obtained as shown in figure 3.9 which can be used for calibration of the \( V_{\text{cold}} \) as a function of temperature. In figure 3.10, the molar volume variation in a sample cell as a function of loading pressure for different temperatures is shown using corrected \( V_{\text{cold}} \).
Figure 3.9 Cold zone volume ($V_{\text{cold}}$) calibrations as a function of temperature.

Figure 3.10 Molar volume of a gas (i.e. H$_2$) in a sample cell as a function of loading pressure for different temperatures.
3.3. Thermal desorption spectroscopy (TDS)

Thermal desorption spectroscopy (TDS), also known as temperature programmed desorption (TPD) is a standard surface science technique, providing information on the binding energies of atomic and molecular species adsorbed on a solid surface. The basic process of thermal desorption is that an adsorbate leaves the substrate and enters the gas phase by transferring the thermal energy to the adsorbed species when the surface is heated (see figure 3.11). Thus, desorption takes place if a molecule has enough thermal energy to overcome the activation barrier for releasing the adsorbate from the substrate. Consequently, adsorbates that have a strong binding energy desorb at high temperature, and adsorbates that have a weak binding energy desorb at low temperature.

![Figure 3.11 Illustration of adsorption and desorption process](image)

Figure 3.12 shows the experimental setup of cryogenic TDS designed in order to measure desorption spectra of physisorbed hydrogen or deuterium at 20 K. The in-house designed TDS setup consists of mainly 3 parts; (1) ‘Sample chamber’ made by stainless steel in the central part. The chamber should be under the high vacuum (10^{-6} mbar). (2) ‘Sample cell’ in the bottom of the device connected tightly to copper block. For the cooling to 20 K, the copper block is directly connected to the cold finger of a liquid helium flow cryostat. (3) ‘Quadrupole mass spectrometer (QMS) - Spectra satellite 100 D-HP’ on the top of the device in order to analyze desorbed gas molecules directly.

QMS operates by ionizing desorbed gas molecules to generate charged molecules and measuring their mass-to-charge ratios (m/z). The amount of ionized molecules depends on the partial pressure of the individual species. Thus, the detector records the abundance of each m/z via an electron multiplier with a very linear m/z-electric signal relationship. For high flux or partial pressure (over 10^{-5} mbar),
however, this linearity between partial pressure and analyzed m/z may deviate and it gives inaccurate result. Hence, it is important to maintain a partial pressure below $10^{-5}$ mbar in the chamber during measurements. In case of porous materials with high gas uptake, the sample masses of less than 3 mg are usually enough to keep the partial pressure below $10^{-5}$ mbar. Note that QMS used here can detect desorbing mass signal in the range from 1 to 100 amu with a sensitivity of $2 \times 10^{-11}$ mbar.

The heating element is wrapped around the copper block, and the temperature of the sample is measured by a platinum resistor (Pt-103). An additional thermocouple (NiCr-Ni) is used as a reference to monitor the temperature during the experiment. Inside the cryostat, temperature is measured by a Pt-100 resistor and AuFe512 thermocouple. Temperature is controlled by a Proportional-Integral-Derivative (PID) temperature control program. With a PID controller the sample can be heated linearly from 20 K to approximately 600 K with different heating rates (0.01 K/s to 0.1 K/s).

Figure 3.12 a) Schematic diagram of thermal desorption spectroscopy. b) Experimental set-up of TDS
3.3.1. Theoretical description of TDS

A basic assumption in TDS is that the desorption rate of an adsorbate is proportional to the corresponding measured partial pressure. In this regard, the pumping speed of the system should be high enough so that no gasses will re-adsorb during desorption. Furthermore, using TDS spectrum with different heating rate, the kinetic information of an adsorbate can be also obtained\(^{84-88}\).

Please note following general remarks:

1. The area under a desorption peak is proportional to the amount of initially adsorbed species (or proportional to the surface coverage).
2. Desorption peak temperature is related to the enthalpy of adsorption (or to the strength of binding to the surface).
3. Kinetics information of desorption can be obtained from the peak profile and the coverage dependence of the desorption characteristics.

The process of thermal desorption can be formally described in terms of an Arrhenius-type equation, known also as the Polanyi-Wigner desorption rate equation:

\[
I(T) \propto \frac{dM}{dt} = \frac{d\theta_M}{dt} = v(\theta_M) \cdot \theta_M^n \cdot \exp\left(\frac{-E_{des}(\theta_M)}{RT}\right)
\]  

(3.10)

where

\(I(T)\) = intensity of the mass spectrometer signal at a given temperature \(T\)
\(\frac{dM}{dt}\) = desorption rate of a given species \((M)\)
\(v(\theta_M)\) = frequency factor
\(\theta_M\) = instantaneous coverage
\(n\) = kinetic order or desorption order
\(E_{des}(\theta_M)\) = activation energy for desorption as function of \(\theta\) (through a Boltzmann factor)
\(R\) = gas constant
\(T\) = temperature

This basically states that the desorption rate \(\frac{dM}{dt}\) of a given species \((M)\) is related to the actual surface coverage \((\theta)\) and to the kinetic order of the process \(\langle n \rangle\) by a power law. It also depends on the desorption energy \((E_{des})\) through a Boltzmann factor.

During TDS measurement, sample is heated linearly;
\[ T(t) = T_0 + \frac{dT}{dt} t = T_0 + \beta t \]  
(3.11)

\[ \beta = \frac{dT}{dt} = \text{const.} \]  
(3.12)

where \( \beta \) is the heating rate in \([\text{K} \cdot \text{s}^{-1}]\), \( T_0 \) is the start temperature in K and \( t \) is the time in [s].

Therefore, the activation parameters can depend on the temperature itself and on the heating rate \( \beta \).

Substituting the time \( t \) in Polanyi-Wigner equation (eq. 3.10) by \( dt = (1/\beta) \cdot dT \) (eq. 3.12), an equation 3.10 becomes;

\[ -\frac{d\theta_M}{dT} = \frac{v \theta_M^n}{\beta} \exp\left(-\frac{E_{des}}{RT}\right) \]  
(3.13)

Hence, the rate contains a coverage term \( (\theta_M^n) \) and energy term \( \exp\left(-\frac{E_{des}}{RT}\right) \).

![Image](image.png)

**Figure 3.13** Correlation between surface coverage, desorption signal and activation energy as a function of temperature. If higher \( 'E_{des}' \) or smaller \( 'v' \) is applied, then \( 'T_m' \) will shift to higher \( T \). If faster heating rate is applied, then \( 'T_m' \) will shift slightly to higher \( T \).

Figure 3.13 shows the correlation between surface coverage and activation energy as a function of temperature. It clearly shows that a little desorption occurs at low \( T \) due to the \( E_{des} \gg RT \). Thus, the intensity of the desorption signal is very small, \( I(T) \sim 0 \). At high \( T \), \( \exp(-E_{des}/RT) \) rises rapidly, resulting in \( I(T) > 0 \). By raising \( T \) further (or decreasing surface coverage), \( I(T) \) is reached the maximum, then starts to decrease. Eventually, all molecules desorbed at very high \( T \), leading to \( I(T) = 0 \).
In Polanyi-Wigner equation (eq. 3.13), most terms are quite straightforward. For example, the factors such as \([E_{\text{des}}, v, \beta \text{ and } \theta_M]\) affect desorption peak temperature, and factors such as \([v, \beta \text{ and } n]\) additionally influence to peak shape. A factor of \(\theta_M\) affects peak area. Most importantly, desorption rate or peak are strongly influenced by desorption order, \(n\). Details are following:

- Zero-order desorption kinetics \((n=0):\)
\[
- \frac{d\theta_M}{dT} = \frac{v}{\beta} \cdot \exp \left( \frac{-E_{\text{des}}}{RT} \right) \tag{3.14}
\]

Equation 3.14 implies that desorption rate does not depend on coverage and increases exponentially with \(T\). It typically shows that all \(\theta_M\) have common initial leading edge and rapid drop beyond \(T_m\). The peak temperature \(T_m\) moves to higher \(T\) with \(\theta_M\). Zero-order kinetic can be seen in thick multi-layer or in quasi-equilibrium coexistence between 2D diluted adatom gas and 2D solid phase (figure 3.14a). It is also sometimes occurred if strong adsorption site is existed (pseudo zero-order).

- First-order desorption kinetics \((n=1):\)
\[
- \frac{d\theta_M}{dT} = \frac{v}{\beta} \cdot \theta_M \cdot \exp \left( \frac{-E_{\text{des}}}{RT} \right) \tag{3.15}
\]

Equation 3.15 implies that desorption rate is proportional to instantaneous coverage, and desorption peak will show balance of coverage term and energy term as shown the desorption signal in figure 3.13 and 3.14b. This is normal desorption order for non-dissociative molecular adsorption (i.e. physisorption - usual attempt frequency, \(v\), is ca. \(10^{13} \text{ s}^{-1}\)). Thus, \(T_m\) is usually constant with increasing \(\theta_M\), but increases with high \(E_{\text{des}}\). Desorption peak shape shows asymmetric characteristic.

- Second-order desorption kinetics \((n=2):\)
\[
- \frac{d\theta_M}{dT} = \frac{v \theta_M^2}{\beta} \cdot \exp \left( \frac{-E_{\text{des}}}{RT} \right) \tag{3.16}
\]

Equation 3.16 implies that desorption rate is proportional to \(\theta_M^2\), and desorption peak will also show balance of coverage term and energy term. This is only strictly observed for re-combinative desorption (i.e. associative molecular desorption). Thus, \(T_m\) moves to lower \(T\) with increasing \(\theta_M\), trailing common edges of peaks. Desorption peak shape shows nearly symmetric characteristic (figure 3.14c).
Note that there are also ‘pseudo second-order’ desorption kinetics observed for strong repulsive interadsorbate interaction and ‘fractional-order (0 < n < 1)’ desorption kinetics observed for cluster formation on surface or desorption from edges of cluster. Therefore, it implies that complicated kinetics can yield other exponents.

![Figure 3.14 schematic examples of a) zero-order desorption kinetic, b) first-order desorption kinetic and c) second-order desorption kinetic](image)

3.3.2. Analysis of TDS

Redhead analysis

Basic assumption of this approach is that ‘γ’ and $E_{des}$ parameters are independent of coverage and temperature, and desorption follows 1st order kinetics. The activation energy is approximately related to the temperature $T_{max}$ and, thus, equation 3.15 can be rewritten to:

$$\Delta E_{des} = R T_{max} \left[ \ln \frac{\nu}{\beta} - \ln \frac{\Delta E_{des}}{RT_{max}} \right]$$

(3.17)

Note that $\ln(\Delta E_{des}/RT_{max})$ and $\nu$ in bracket is commonly estimated as $\sim 3.64$ and $10^{13} \text{s}^{-1}$, respectively. From equation 3.17, plot of $T_{max}$ vs. $\beta$ can be obtained by measuring $T_{max}$ for various heating rates ($\beta$) at fixed initial coverage. Therefore, a slope of straight line is determined to be $-E_{des}$.

Plot of ln(rate) vs. 1/T and Leading edge analysis

A desorption spectrum (Polanyi-Wigner equation) can be also rearranged to the an Arrhenius plot directly;
Thus, a graph of $\ln\left(\frac{-d\theta_M}{dt}\right)$ versus $1/T$ will produce a straight line of slope $-E_{\text{des}}/R$ for activation energy and intercept $ln(v) + n \cdot ln(\theta_M)$ for frequency factor if the correct order ($n$) is chosen. In case of leading edge analysis, $I(T)$ is measured for various coverage and evaluated only leading edge of peak. For this calculation, first part of desorption trace is usually employed (less than 4~5 % desorption coverage) where surface coverage does not change appreciably ($\theta \approx \theta_0$).

### 3.3.3. Experimental procedures for TDS

**The integrated-signal approach for quantitative TDS measurements**

In a thermal desorption experiment for physisorbed hydrogen gases, Polanyi-Wigner equation follows 1$^{st}$ order kinetics (see equation 3.15). It is also critical that the pumping speed of system must be constant during entire measurement procedures. Therefore, the molar flow rate of the gas evolving from a sample is directly proportional to the output signal of the mass spectrometer (indicated as partial pressure signal in the chamber)

$$I(t) = \alpha \cdot \frac{dn(t)}{dt}$$ (3.19)

where $\alpha$ is a proportionality factor for a specific gas ($H_2$) and $n(t)$ is the number of molecule desorbed at the time $t$.

The quantitative calibration is possible based on the integration of equation 3.19 over ‘time’ (Note that it must be ‘time’ not ‘temperature’.)

$$\int_{t_0}^{t} I(t) \, dt = \alpha \int_{t_0}^{t} \frac{dn(t)}{dt} \, dt$$ (3.20)

where $t_0$ is initial time and $t$ is end of measurement time.

The value of a proportionality factor, $\alpha$, can be determined by associating an area under the output signal $I(t)$ to a known amount of specific gas generated in the chamber. Since TDS spectra presented here is hydrogen isotopes signal, ‘$\alpha$’ will serve as a calibration constant for hydrogen isotopes.
Calibration constant for hydrogen isotopes

For the quantitative calibration of mass spectrometer signal, approximately 0.23 g of Pd$_{95}$Ce$_5$ was used. Internal friction measurements showed that in diluted PdCe alloy H-Ce complex are formed up to a concentration of H atom per Ce atom without the formation of Pd hydride.\textsuperscript{90} This H-Ce complex is quite stable under the ambient conditions compare to Pd hydride due to the formation of trapping sites by the introduction of Ce into Pd lattice\textsuperscript{91,92} Owing to this relatively stable Pd-Ce-H system, the loaded alloy can be handled under ambient conditions for a short period of time.

The calibration procedure was performed as follows.
(1) The Pd$_{95}$Ce$_5$ alloy was etched prior to the calibration procedure by aqua regia (nitric acid hydrochloride: HNO$_3$+3HCl).
(2) Due to their sensitiveness to oxidation, Pd$_{95}$Ce$_5$ alloy was annealed by ramping from RT to 600 K, 0.1 K/s under UHV.
(3) Weigh the Pd$_{95}$Ce$_5$ alloy and then be loaded it in the TDS sample chamber
(4) Expose to mild pure H$_2$ or D$_2$ atmosphere (150 mbar) at 350 K for 2 h.
(5) After 2hr gas loading, cool the sample temperature to RT. (used by either air-cooled or liquid N$_2$)
(6) Take out the Pd$_{95}$Ce$_5$ alloy from the chamber and weigh again. After weighing, the alloy is loaded in the chamber again. This process should be done very quickly (preferably within 4 min). The mass difference before and after loading is equal to the amount of gas that was taken up by the alloy.
(7) Subsequently a desorption spectrum from RT to 600 K was recorded with a heating rate of 0.1 K.
(8) In order to obtain reliable data, the step 3 to 7 should be repeated at least 3 times. The obtained mean amount of gas is directly corresponded to the mean area under the desorption peak. From this, we could calculate a calibration constant, $\alpha$ in [mol/area] or [Nr. molecule/area], for hydrogen and deuterium.
(9) The calibration constants should be determined repeatedly after changing the mass spectrometer setting, repair work on the spectrometer or exchange of filament.
Instructions for the TDS experiment

Previous TDS methods for hydrogen storage application are focused on investigating pure gas storage capacities and adsorbate-adsorbent interactions represented as the temperature of the peak maximum $T_m$ (figure 3.15a and figure 3.16a)\textsuperscript{93,94}. In case of quantum sieving application, however, a measurement procedure has to be modified to be more optimized for $\text{H}_2/\text{D}_2$ mixture separation (figure 3.15b and figure 3.16b-c). Furthermore, depending on the size of pore aperture or the existence of the strong binding site, the measurement procedure can be split into two (Mode I and Mode II). Figure 3.15 and figure 3.16 show the detailed procedures for each measurement.

![Figure 3.15](image)

**Figure 3.15** Three types of the TDS measurement procedure; a) Normal procedure for pure $\text{H}_2$ or $\text{D}_2$ desorption study. b) Procedure of quantum sieving for $\text{H}_2/\text{D}_2$ mixture separation (Mode I: the microporous materials possessing strong diffusion limitation effect. Mode II: the microporous materials possessing strong binding site but no diffusion limitation.)

![Figure 3.16](image)

**Figure 3.16** Temperature profile over time for each measurement mode shown in figure 3.15. $T_{\text{exp}}$ is the loading temperature of gas mixture (typically between $20 \text{ K} \sim 80 \text{ K}$).
Normal procedure for pure gas desorption study: normal mode (figure 3.15a and 3.16a)

a) Sample is activated under the UHV. Note that the activation temperature will be determined depending on the stability of each sample. Normally, temperature of 400~420 K for 3~4 h are applied.

b) After activation, the sample is exposed to pure H$_2$ or D$_2$ pressure (ca. 25 mbar) at RT. Few minutes of loading time for adsorption will be enough for microporous materials possessing large cavity. However, a bit longer loading time will be required for the case of microporous materials possessing small pore (below 3.5 Å).

c) Afterwards, the sample is cooled down to ca. 20 K. Adsorption occurs during the cooling process. In the case of porous materials with small pore (below 3.5 Å), adsorption equilibrium may not be reached if the cooling process is too fast because of the diffusion limitation.

d) After reaching 20 K, the chamber is evacuated for removing residual gases and thereby achieved the vacuum again.

e) Finally, a linear heating ramp (0.1 Ks$^{-1}$) is applied in order to thermally activate desorption. The desorbing gas is continuously detected using a quadrupole mass spectrometer, recognizing a pressure increase in the sample chamber when gas desorbs.

Procedure of quantum sieving for H$_2$/D$_2$ mixture separation with MOFs possessing small aperture (below 3.5 Å): mode I (figure 3.15b and 3.16b)

a) Sample is activated under the UHV. Note that the activation temperature will be determined depending on the stability of each sample.

b) After activation, the sample is cooled down to exposure temperature (typically between 20 K to 80 K) under vacuum.

c) Then, sample is exposed to D$_2$/H$_2$ mixture at the exposure temperature for a defined exposure time.

d) Afterward, sample is quickly cool down to ca. 20 K. Then the chamber is evacuated for removing residual gases and thereby achieved the vacuum again.

e) Finally, a linear heating ramp (0.1 Ks$^{-1}$) is applied in order to thermally activate desorption. The desorbing gas is continuously detected using a quadrupole mass spectrometer, recognizing a pressure increase in the sample chamber when gas desorbs.
(3) Procedure of quantum sieving for H\textsubscript{2}/D\textsubscript{2} mixture separation with MOFs possessing strong adsorption site: mode II (figure 3.15b and 3.16c)

a) Sample is activated under the UHV. Note that the activation temperature will be determined depending on the stability of each sample.

b) After activation, the sample is cooled down to exposure temperature (typically 20 K to 80 K).

c) Then, sample is exposed to D\textsubscript{2}/H\textsubscript{2} mixture at the exposure temperature for a defined exposure time.

d) Afterward, the chamber is evacuated to remove residual gases at exposed temperature, and then quickly cool down to ca. 20 K.

e) Finally, a linear heating ramp (0.1 Ks\textsuperscript{-1}) is applied in order to thermally activate desorption. The desorbing gas is continuously detected using a quadrupole mass spectrometer, recognizing a pressure increase in the sample chamber when gas desorbs.

\textbf{H\textsubscript{2}/D\textsubscript{2} mixture selectivity determined by TDS}

During the adsorption process of gaseous (binary) mixture, an adsorbed amount of each species on the surface of porous solids may vary at given pressure and temperature depending on the heat of adsorption, giving the possibility for separation.

Hence, the selectivity A species relative to B species in A/B mixture is typically defined as the ratio of molar fraction in the adsorbed phase (x) and gas phase (y),

\[ S = \frac{x_A/x_B}{y_A/y_B} \] \hspace{1cm} (3.21)

In the TDS system, porous materials are exposed to 1:1 D\textsubscript{2}/H\textsubscript{2} mixture (up to 60 mbar in chamber). As the volume of hydrogen uptake in the sample mass (ca. 3 mg) is usually a few cm\textsuperscript{3} and the volume of our TDS chamber is larger than 1 L, the volume change by adsorption and thereby the partial pressure change in gas phase is nearly negligible. After 1:1 D\textsubscript{2}/H\textsubscript{2} mixture exposure, therefore, the sample chamber is evacuated in order to remove residual gases that are not adsorbed on the surface of porous materials. Since the ratio of molar fraction in the gas phase (y) can be neglected and assumed
as 1:1 mixture, the selectivity of D<sub>2</sub> relative to H<sub>2</sub> in 1:1 D<sub>2</sub>/H<sub>2</sub> mixture in TDS measurement is given by the ratio of amount of D<sub>2</sub> over H<sub>2</sub> desorbed into vacuum.

As shown in figure 3.17, the area under the desorption peak is proportional to the desorbing amount of gas, which can be quantified after careful calibration (by Pd<sub>95</sub>Ce<sub>5</sub> alloy) of the TDS apparatus.

Thus, the selectivity of A species relative to B species in A/B mixture can be determined to be

\[
S_{A,B} = \frac{A_{\text{area}} C_A}{B_{\text{area}} C_B}
\]  

(3.22)

where \(A_{\text{area}}\) and \(B_{\text{area}}\) is the area under the desorption peak of each species, respectively. \(C_A\) and \(C_B\) is calibration constants of the each species.

Figure 3.17 Thermal desorption spectrum from gas mixture of two species, A and B.
Part 1

Solid-state hydrogen storage
4. Investigation of adsorption properties at RT on metal doped porous materials

4.1. Introduction

Efficient hydrogen storage at ambient condition is one of the key requirements for automotive application. Thus, one of the most overlooked features is a heat of adsorption on surfaces which largely determines the total uptake at ambient temperatures. For increasing the interaction energy, various methods such as incorporating a high number of unsaturated metal centers and ligand exchange have been proposed for enhancing the storage capacity. Recently, as a part of this, the “spillover” effect has been proposed by R. Yang et al.\textsuperscript{44,45} to enhance the room temperature hydrogen storage capacity. However, the mechanism of this storage enhancement by decoration of noble metal particles inside high surface area supports is not yet understood and still under debate\textsuperscript{46-52}.

In this work, the hydrogen adsorption properties and storage capacity of noble metal decorated porous materials have been thoroughly studied with various techniques such as powder X-ray diffraction, low-pressure high-resolution hydrogen and nitrogen BET, Raman and thermal desorption spectroscopy. For that, Pt-doped and un-doped templated carbons possessing almost identical textural properties have been successfully synthesized. This enables the study of Pt catalytic activities and hydrogen adsorption kinetics on porous carbons at ambient temperature. Afterwards, the synthesis of a new organic-inorganic hybrid material “metal doped covalent-organic framework (COF)” is presented. This new hybrid material enables to establish COFs as novel templates for the stabilization of nanoparticles and to study the hydrogen storage properties of metal doped COF surfaces. Through these investigations, new aspects of the “spillover process” in microporous materials for hydrogen storage enhancement are addressed and an alternative explanation is given.
4.2. Materials and characterization

4.2.1. Direct synthesis of platinum doped templated carbon

Synthesis of platinum doped silica templated carbon

The hierarchically structured porous particles of silica, which serve as the template of the carbon, were kindly provided and characterized by the group of P.B. Atanassov (University of New Mexico, USA) and synthesis description of porous silica is following.

The hierarchical porous structures can be obtained by templating silica microparticles with a specially designed surfactant micelle/microemulsion mixture (so-called microemulsion-templated method) as described by Carroll et al.95 (figure 4.1). The silica precursor solution was prepared by dissolving 1.82 g of cetyltrimethylammonium bromide (CTAB) in 20 g of DI water at 40 °C until the solution was clear. Next, 5.2 g of tetraethylorthosilicate (TEOS) and 0.57 g of 1 N hydrochloric acid were added to the mixture at room temperature for 30 min to hydrolyze and dissolve the TEOS monomer. The oil phase was prepared by dissolving a modified polyether-polysiloxane/dimethicone copolyol surfactant with the trade name ABIL EM 90 (Degussa) in hexadecane (3 wt %). The aqueous siliceous precursor solution was then added to the oil phase and subsequently emulsified by brisk shaking of the vial. The emulsion was transferred to a 1000 mL round-bottom flask and heated to 80 °C under a reduced pressure of 70 mTorr for 3 h. The particles were collected and centrifuged, and the supernatant oil removed, followed by calcination in air at 500 °C for 5 h to remove the templating surfactant.95

Figure 4.1 Sketch of liquid silica precursor emulsion system. a) Aqueous silica precursor emulsion drops (light gray) in hexadecane oil (dark gray). Microemulsion droplets form and occupy the internal drop volume (small dark gray circles). b) Single aqueous silica precursor drop. Cetyltrimethylammonium bromide (CTAB) is above the critical micellization concentration (CMC), forming micelles (red) in addition to microemulsion droplets (dark gray). c) Oil/water interface with adsorbing surfactants from the two immiscible phases.95 (* Taken from figure 1 of ref. 95)
The porous silica particles exhibit a honeycomb-like structure possessing open access cavities to the porous network. The pore size analysis suggests the presence of larger (mostly 10−30 nm) and smaller (> 5 nm) pores. The BET (N$_2$) surface area is determined to be ~ 1000 m$^2$/g.

The obtained porous silica can be used as templates for the fabrication of porous carbon or noble metals doped porous carbon. The different steps for the synthesis of templated porous carbon (TC) and platinum decorated TC are given in the following and shown in figure 4.2.

The silica template was impregnated with an aqueous solution of sucrose and sulfuric acid. Afterward, it was dried at RT for overnight. Next day, a heat treatment was performed in oven at 100−150 °C under air. In case of Pt decorated carbon preparation, aqueous solution of Chloroplatinic acid hexahydrate, sucrose and sulfuric acid was additionally added to achieve an 8 wt% Pt infiltration into the sample. This was followed by pyrolysis at 800 °C in a N$_2$ atmosphere for 4 h, with a heating rate of 3 °C per min. After pyrolysis, the silica template was removed by dissolving (etching) in 6 M KOH for 4 days. The material was then filtered, washed 8 times with DI water, and dried in the oven at 70 °C overnight.

After finishing the synthesis of platinum decorated templated porous carbon, the precise Pt amount was analyzed by inductively-coupled-plasma optical-emission spectroscopy (ICP-OES). Hence, the determined Pt content in carbon sample was 6.8 wt% ± 0.4 which is in good agreement with the input of Pt prior to the synthesis (8 wt%).

![Diagram](https://example.com/diagram42.png)

**Figure 4.2 Templated synthesis of hierarchically structured carbon from sucrose. For the Pt decorated carbon, solution of chloroplatinic acid was impregnated slowly before the pyrolysis under nitrogen atmosphere.**
**Powder X-ray diffraction**

The crystal structure of templated carbon (TC) and Pt-doped templated carbon (Pt/TC) were identified by powder X-ray diffraction (PXRD) using CuKα radiation. Measurements were carried out in transmission mode and by using glass capillaries. As shown in figure 4.3, TC is amorphous, but after Pt impregnation, Pt(111), Pt(200), Pt(220), Pt(311) and Pt(222) peaks are clearly found at 2θ = 39.8, 46.3, 67.5, 81.3 and 85.8 in the XRD pattern. One should note that, in addition to the Pt Bragg peaks, a number of very low intensity can be observed in figure 4.3a. From PXRD Rietveld refinement of Pt/TC, these low intensity peaks are determined to be platinum silicide (Pt_{12}Si_b) as shown in figure 4.3b. Although platinum silicide (Pt_{12}Si_b) is detected, the amount of platinum silicide (Pt_{12}Si_b) is very small as Si was below the detection limit in the ICP-OES.

![Figure 4.3 a) PXRD patterns of (i) Pt/TC and (ii) TC, b) PXRD rietveld refinement of Pt/TC sample](image)

This small amount of Platinum Silicide (Pt_{12}Si_b) can be formed during the impregnation of the chloroplatinic acid solution into the silica template where the solution of sucrose is not impregnated. Thus, Platinum Silicide (Pt_{12}Si_b) is not embedded inside TC and expected to stay on the outer surface of TC independently which is not relevant to the spillover effect. Chemical information obtained by elemental mappings with STEM/EDX analysis of the nanoparticles embedded in the porous matrix confirmed this by showing ‘only’ Pt and C elemental maps (figure. 4.4b).

**Scanning transmission electron microscopy**

A TEM study (figure 4.4) has been carried out (by the group of S. Bals, EMAT, University of Antwerp, Belgium) in order to understand the Pt distribution in the porous carbon. Bright-field TEM (BFTEM) image reveals the presence of Pt particles that are dispersed throughout the carbon matrix (see figure 4.4a). In addition, it is seen that the size of the particles varies significantly through the matrix, and the
large-sized particles often form agglomerates with each other (see figure 4.4a). Such agglomeration of the particles is observed to be less apparent when the size of Pt particles decreases (see figure 4.4b). In addition, High-resolution scanning transmission electron microscopy (HRSTEM) images (see figure 4.4c) indicate that both smaller and bigger sized particles are single crystals. The lattice fringe spacing of the small sized particle estimated to be \( \sim 2.3 \, \text{Å} \), corresponding to the interplanar distance of the (111) planes of platinum.

Figure 4.4 a) BFTEM image reveals the presence of Pt particles in a carbon matrix. b) STEM image shows the presence of Pt particles with different sizes and their dispersion in the matrix. The inset presents the color mixed EDX elemental maps of both Pt and C elements at a position given on the STEM image. c) The lattice fringes of the particles are observed at the HRSTEM image showing the crystallinity of the particles. d) Visualization of the 3-dimensional reconstructions reveals the distribution of the Pt particles within the carbon matrix. e) Othoslice image collected from a position shown at the visualization of the 3-dimensional reconstructions f) of Pt/TC reveal the voids around bigger size Pt particles.

The 3-dimensional dispersion of the Pt nanoparticles within the carbon matrix was investigated using electron tomography. For that, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was used to obtain the 2-dimensional projection images. Since the
intensity in the projection images acquired using HAADF-STEM scales with the atomic number Z of the elements present in the sample, it is thus possible to obtain both structural and analytical information. As a result, an intensity difference is expected between the Pt nanoparticles and the carbon matrix. The visualization of the 3-dimensional reconstruction (see figure 4.4d) that was obtained for Pt nanoparticle loaded carbon matrix together with a slice through the reconstructed volume (see figure 4.4e-f) reveal how the particles are dispersed in the volume. It is seen that the smaller size particles dispersed randomly and well embedded within the carbon matrix. In addition, there were also existed few bigger particles, and large voids come into sight around these bigger size particles (see figure 4.4f). It means that the initially impregnated Pt precursors are partially agglomerated inside meso-pore silica template before carbonization, and then these agglomerated particles play a role as a support inside cavity for suppressing any shrinkage during carbonization. Similar observations were also reported in literature.96-98

Textural properties (nitrogen BET)
Specific surface area measurements at 77 K were carried out using a Quantachrome Autosorp-1 MP instrument with N\textsubscript{2} gas. The TC and Pt/TC samples (~100 mg) were priorly degassed at 420K for overnight. The specific surface area was obtained by the Brunauer-Emmet-Teller (BET) method. The pressure range for BET calculation was chosen according to Rouquerol’s suggestions.99 The total pore volume and the micropore volume were computed from the density functional theory (DFT) method and the MP micropore method, respectively. The pore size distribution (PSD) was obtained from the adsorption branch of the nitrogen isotherm using the non-local density functional theory (NLDFT). The nitrogen adsorption/desorption analysis and pore size distribution (PSD) of the TC and Pt/TC samples are shown in figure 4.5. In the sorption curve a small hysteresis occurs for both samples over a wide relative pressure range. A broad PSD (between 0.7 and 100 nm) of TC and Pt/TC can be seen as shown in figure 4.5b. The Pt/TC exhibits an almost identical nitrogen uptake and a stronger hysteresis compared to pristine TC. The nitrogen BET specific surface area (SSA) for TC and Pt/TC were determined to be 877 m\textsuperscript{2}/g and 882 m\textsuperscript{2}/g, respectively.
Figure 4.5 a) Nitrogen sorption curves of (i) TC (square black) and (ii) Pt/TC (circle red) at 77K. (closed symbols show the adsorption and open symbols show the desorption isotherm). b) NLDFT analysis of nitrogen adsorption isotherm suggesting various (from micro to meso) pore size distribution.

Raman spectroscopy

In figure 4.6, the Raman spectrum of TC and Pt/TC (performed by A. Schulz from MPI-FKF), measured with an excitation wave length of \( \lambda = 532 \) nm, shows two broad peaks centered at 1343 and 1596 cm\(^{-1}\), which can be assigned to the disorder induced C-C single bond (sp\(^3\) hybridization) (D-band) and the vibration of sp\(^2\) hybridized carbon (G-band), respectively. In addition, the peak of the G-band slightly shifts downwards by Pt decoration. It should be noted that the wavenumber recorded in the range of 500~4000 cm\(^{-1}\) can cover almost all possible Raman active vibration modes of functional groups. In particular, the possible vibration mode of \( v(C-H), v(\equiv(C-H)), v(C-OH), v(C-O-C)_{\text{asym}} \) and \( v(C-O-C) \), corresponding to the 2800-3000 cm\(^{-1}\), 3000-3100 cm\(^{-1}\), 3300 cm\(^{-1}\), 1050-1150 cm\(^{-1}\), 1060-1150 cm\(^{-1}\), 800-970 cm\(^{-1}\), respectively has been examined (bottom in figure 4.6), and exhibits the absence of any noticeable peak shift or peak formation, confirming the almost identical surface chemical composition of two samples.
Figure 4.6 Raman spectra of Pt/TC and TC sample. The Raman spectra were taken in backscattering geometry in a JobinYvon LabRam 1800 single-grating spectrometer equipped with a razor-edge filter and a Peltier-cooled CCD camera. Green laser with a wavelength of 532 nm has been used for excitation. The laser beam was focused through a 50x microscope objective to a ~5 μm diameter spot on the sample surface.
4.2.2. Palladium doped COF-102 via gas phase infiltration

**Synthesis of palladium doped Covalent Organic Frameworks (COF-102)**

The sample was kindly provided and characterized by the group of R. A. Fischer (Uni. Bochum, Germany) and synthesis description is following. The reaction for COF-102 was carried out in a glass tube equipped with a Teflon stop-cock at the top, measuring o.d. × i.d. = 80 × 64 mm² and length around 18 cm. The dioxane and mesitylene solvents were dried over activated molecular sieves (3 Å). The tube was charged with 300 mg (0.60 mmol) of tetra(4-(dihydroxy)borylphenyl)methane and 6.0 mL of a 1:1(v/v) mixture of mesitylene:dioxane solvent under argon. The tube was degassed at liquid N₂ temperature for 5 min and sealed under vacuum. The self-condensation of tetra(4-(dihydroxy)borylphenyl)methane was carried out at 85 °C by aging the reaction tube for 4 days. The obtained white color solid was filtered from the reaction mixture using a G2 crucible inside a glove box. The isolated final product was washed with 60 mL of THF and stored overnight in a fresh THF solvent. The solvent was removed under vacuum at room temperature; later the framework (COF-102) was heated at 150 °C under vacuum (10⁻³ mbar) overnight to remove the guest molecules, yielding 160-170 mg of COF-102 (figure 4.7).

For decorating Pd inside the porous framework (COF-102), highly volatile and light sensitive [Pd(η³-C₃H₅)(η⁵-C₅H₅)] as a precursor for Pd nanoparticles were used for the gas phase infiltration method (figure 4.7b). In this method, the inclusion compounds, [Pd(η³-C₃H₅)(η⁵-C₅H₅)]@COF-102 are decomposed by heat or light to yield Pd@COF-102 composite materials. The major advantage associated with this approach is that the homogeneously distributed high metal loading can be achieved in a single loading step. In a typical loading experiment, activated COF-102 was placed along with [Pd(η³-C₃H₅)(η⁵-C₅H₅)] precursor in two separate glass boats in a Schlenk tube under vacuum (~10⁻³ mbar) as shown in figure 4.7b. The molecular dimensions of [Pd(η³-C₃H₅)(η⁵-C₅H₅)] are ~ 2.2, 2.3, and 4.1 Å in the x, y, and z directions, which are much smaller than pore openings (above 1 nm) of COF-102 framework. Therefore, the diffusion of precursor into COF-102 matrix is highly feasible. The color of the COF-102 matrix changed immediately to light red color and then to dark red, due to the infiltration of [Pd(η³-C₃H₅)(η⁵-C₅H₅)] into COF-102 matrix. The reaction Schlenk tube was kept at room temperature for 3 h in a dark cupboard. From elemental analysis data, the number of [Pd(η³-C₃H₅)(η⁵-C₅H₅)] molecules per
COF-102 formula unit was determined close to 2. The \([\text{Pd}(\eta^3-\text{C}_3\text{H}_5)(\eta^5-\text{C}_5\text{H}_5)])@\text{COF-102}\) was subjected to UV light irradiation for 16 h at room temperature, changing the color of the sample from dark red to black indicating the formation of Pd nanoparticles. Subsequently, a thermal treatment under vacuum at 400 K for 12 h was performed in order to remove any physisorbed organic by-products. A range of samples with varying amounts of Pd content were synthesized (30 wt%, 9.5 wt%, and 3.5 wt%).

Figure 4.7 a) Schematic representation of the synthesis of the Pd@COF-102 hybrid material; the ctn structure of COF-102 is shown on the bottom right side; carbon, boron, oxygen atoms are represented with black, yellow and red colors, respectively. On the bottom left hand side of the figure, the reaction carried out inside the porous of COF-102 for the synthesis of Pd nanoparticles is shown. b) Schematic representation of gas-phase infiltration method

**Powder X-ray diffraction and Infrared spectroscopy**

The powder XRD pattern of (ii) Pd30wt%@COF-102 (figure 4.8a) reveals the characteristic reflections of host-matrix along with a very broad peak around 2θ = 39.7° assigned to ~2.5 nm sized Pd nanoparticles as estimated from the Scherrer equation. These characterization data suggest that small Pd nanoparticles are formed and present along with (i) pristine COF-102 (figure 4.8a) in Pd30wt%@COF-102. In addition, figure 4.8b shows the comparison of PXRD patterns of (i) pristine COF-102, Pd3.5wt%@COF-102 and Pd9.5wt%@COF-102.
Figure 4.8 Powder X-ray powder diffraction patterns (PXRD) were measured on a D8 Advance Bruker AXS diffraction (Cu Kα -radiation, room temperature, Göbel mirror, step, data points) in θ–2θ geometry. Measurements were carried out in capillary mode and by using glass capillaries (0.7 mm diameter). The glass capillaries were filled with the samples inside a glove box, closed with grease and later flame sealed immediately outside the box. a) PXRD pattern of (i) activated COF-102; (ii) Pd30wt%@COF-102 hybrid material; the inset shows a broad peak corresponding to Pd nanoparticles. b) Powder XRD patterns of (i) COF-102, (ii) Pd3.5wt%@COF-102, and (iii) Pd9.5wt%@COF-102 samples.

Figure 4.9 Infrared(IR) spectra were measured on a bruker Alpha-P FT-IR instrument in the ATR geometry with a diamond ATR unit, inside a glove box. a) IR spectrum of (i) activated COF-102; (ii) Pd30wt%@COF-102 hybrid material after heating at 130 °C under vacuum. The peaks from zoomed region correspond to left over by-products such as bicyclopentadiene b) IR spectrum comparison of (i) activated COF-102; (ii) 3.5 wt Pd@COF-102; (iii) 9.5 wt% Pd@COF-102 samples.

The IR spectrum (figure 4.9a) of the (ii) Pd30wt%@COF-102 also showed no signs of decomposition of COF-102; the IR spectrum perfectly matches with that of the pure matrix of (i) COF-102. Additional bands were noted around 3000 cm⁻¹ which could be due to left over organic fragments from the decomposition of the organometallic precursor (details are given in Results). In addition, figure 4.9b shows the comparison of IR spectrum of (i) pristine COF-102, Pd3.5wt%@COF-102 and Pd9.5wt%@COF-102. All samples possess, within the detection limit, identical PXRD and IR spectra indicating that the framework structure remained intact after loading with Pd.
Scanning transmission electron microscopy

In order to get complete insight about the distribution of the nanoparticles in the COF-102 matrix, extensive transmission electron microscopy (TEM) studies were carried out (by the group of G. Van Tendeloo, EMAT, University of Antwerp, Belgium) on Pd@COF-102 as shown in figure 4.10-12.

Figure 4.10 a) BF-TEM image of an unloaded COF-102 crystal. The crystal exhibits only a small degree of high-index faceting and is quite rounded. b) Electron diffraction ring pattern of pristine COF-102 crystals. c) BF-TEM image of heavily Pd loaded COF-102 crystals (30 wt%). The crystals exhibit only a small degree of low index faceting. Due to the high loading with Pd nanoparticles the crystals are almost opaque to the electron beam. d) Size distribution of the Pd nanoparticles in Pd30wt%@COF-102; particle sizes measured from HAADF-STEM images have been used for the size distribution. The average particle size calculated to be 2.4 ± 0.5 nm.

Usually, Pd@COF-102 is not stable enough under the TEM electron beam to be able to obtain electron diffraction information. However, it is possible to obtain a weak diffraction pattern from empty COF-102 (figure 4.10a-b) indicating its composition and crystallinity. Bright field-TEM (figure 4.10c) and high angle annular dark field and scanning transmission electron microscopy (HAADF-STEM) (figure 4.11a) images of Pd30wt%@COF-102 show the presence of crystalline COF-102 crystals. The COF host materials are systematically and heavily loaded with nearly monodispersed and evenly distributed Pd nanoparticles. Their average size is measured to be 2.4 ± 0.5 nm (figure 4.10d). Larger agglomerates of Pd are not found.
Figure 4.11 a) HAADF-STEM of Pd30wt%@COF-102; image reveal the even distribution of Pd particles throughout the framework crystals. b) HRHAADF-STEM image of a Pd nanoparticles imaged along its [110] zone axis at atomic resolution. c) Fourier transform of the area highlighted by the white frame in b) showing evidencing that the particle in b) is cubic Pd(0). d) HRHAADF-STEM image of the Pd nanoparticles imaged along its [100] zone axis. e) shows the indexed Fourier transform of the area in the white box in d). f) HRHAADF-STEM image of the same crystal showing a five-fold twinned Pd nanoparticle. Its five-fold symmetry is highlighted by white arrows; the scale bars in b), d), and f) are 5 nm. g) HR-TEM of Pd30wt%@COF-102; The inset shows the Fourier transform of the area highlighted by the white frame. Only reflexes of cubic Pd(0) are present and highlighted in the top right corner of the inset. The particles were monodisperse, no large agglomerates were found. h) Tomographically reconstructed volume, the Pd particles are rendered in gold, the COF framework in soft off-white. i) Orthoslice through the three dimensional reconstruction of a loaded Pd30wt%@COF-102. The particles visible as white dots are clearly present in the whole crystals without any preferential distribution in size or position.

The evaluated structure of the Pd nanoparticles is cubic Pd(0) (Fm-3m, Space Group 225) as shown by indexing fast fourier transforms (FFTs) of particles imaged in HAADF-STEM (figure 4.11b-f) and HR-TEM (figure 4.11g) along zone axis orientations. Some imaged particles exhibit the presence of single or multiple twins (e.g. the five-fold twinned nanoparticle in figure 4.11f).

To determine the 3D distribution of the Pd nanoparticles within the COF-102 crystals, electron tomography was performed. An overview of the reconstruction of a loaded crystal together with a slice through the reconstructed volume in figure 4.11h-i reveals that the particles are densely and homogeneously distributed throughout the whole COF-102 crystals. Larger particles at or closer to the surface that are quite common in loaded MOF systems are absent (see figure 4.11i).
distribution of particles inside COF-102 crystals is established from this tomography data. In fact this composite system is, if not the only one, one of the very rare examples of metal particle loaded porous crystalline materials with very narrow particle size distribution and an absence of larger agglomerates even at higher loadings (30 wt%). This suggests that COF-102 is an excellent template for the stabilization and host matrix of highly monodisperse nanoparticles. Similar observations are made for the samples with lower Pd content. At a loading of 3.5 wt% the nanoparticles are also well monodispersed. The amount of Pd loading has no effect on the particle size (around 1-4 nm) in Pd@COF-102 hybrid material (figure 4.12).

![BF-TEM image of Pd3.5wt%@COF-102 crystal with quite evenly distributed particles.](image)

**Specific surface area**

The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) method. The nitrogen adsorption/desorption analysis of the (i) COF-102, (ii) Pd3.5wt%@COF-102 and (iii) Pd30wt%@COF-102 samples are shown in figure 4.13 From the isotherms of the N$_2$ sorption measurements, a BET surface area of 3750 m$^2$/g, 3415 m$^2$/g and 1419 m$^2$/g was calculated, respectively. The decrease in surface area corresponds to a filling of the pores in the framework with Pd nanoparticles.
Figure 4.13 N₂ sorption isotherms of (i) COF-102, (ii) Pd3.5 wt%@COF-102, and c) Pd30wt%@COF-102 carried out using Quantachrome Autosorp-1 MP instrument. The samples were priorly degassed at 373 K for 12 h. Pressure range for BET calculation were chosen according to Rouquerol’s suggestions. Closed symbols show the adsorption isotherm and open symbols show the desorption isotherm. The pore volume decreased with increase in Pd Loading, suggesting incorporation of Pd inside COF-102 crystals.
Table 4.1: Overview of metal content, nanoparticle size, the nitrogen BET specific surface area (SSA), pore size distribution and skeletal density from He adsorption for the materials investigated.

<table>
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<tr>
<th>Compound</th>
<th>Metal content (wt%)</th>
<th>Metal particle size (nm)</th>
<th>BET$_{N_2}$ SSA (m$^2$/g)</th>
<th>Pore size distribution (nm)</th>
<th>Skeletal He density (g/cm$^3$)</th>
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<td>COF-102</td>
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<td>-</td>
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<td>1.2</td>
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<tr>
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<td>1 - 4</td>
<td>-</td>
<td>1.2</td>
<td>1.35</td>
</tr>
<tr>
<td>Pd/COF-102</td>
<td>30</td>
<td>2.4 ± 0.5</td>
<td>1419</td>
<td>1.2</td>
<td>-</td>
</tr>
</tbody>
</table>

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4.3. Influence of Pt doped templated carbon on hydrogen adsorption

4.3.1. Results

Low-pressure, high-resolution $H_2$ adsorption isotherm

The textural properties of TC and Pt/TC were analyzed by nitrogen adsorption at 77 K (figure 4.5a), and its BET surface area was determined to be 877 m$^2$/g and 882 m$^2$/g, respectively, showing one of the very rare examples possessing almost identical specific surface area (SSA) and pore volume (Vp) despite of Pt decoration. These almost identical textural properties of TC and Pt/TC are also cross checked by hydrogen adsorption isotherms (figure 4.14), exhibiting $H_2$ BET SSA of 1306 m$^2$/g and 1364 m$^2$/g for TC and Pt/TC, respectively. However, there is huge SSA difference between $H_2$ and $N_2$ BET measurements. Even considering the difference in probe size between $N_2$ and $H_2$, the approx. 35 % larger of SSA from $N_2$ BET to $H_2$ BET indicates the existence of numerous micropores smaller than nitrogen molecule size. The pore size distribution (PSD) analysis (figure 4.5b) exhibiting a high intensity below 0.7 nm (that is below detection limit of nitrogen gas) also supports this conclusion.

Figure 4.14 a) Low-pressure high-resolution hydrogen adsorption (closed symbol) / desorption(open symbol) isotherm at 19.5 K for TC (square black) and Pt/TC (circle red). b) Comparison of hydrogen (19.5 K) and nitrogen (77 K) sorption isotherm.
**Thermal Desorption Spectroscopy**

Thermal desorption spectra are recorded after cooling the samples from RT to 30 K under 1:1 hydrogen/deuterium isotope mixture atmosphere (10 mbar), see procedure details in chapter 3.3.3. Figure 4.15 shows thermal desorption spectra after adsorption of a 1:1 H$_2$/D$_2$ mixture for TC and Pt/TC in the range between 30 K and 140 K, recorded with a heating rate of 0.1 K/s. Above 140 K no significant desorption of hydrogen isotopes is occurring. Note that the signal of the mass spectrometer is normalized by the sample mass and shows clearly that a stronger HD signal for Pt/TC (figure 4.15b) is observed compared to TC (figure 4.15a), indicating the catalytic activity of Pt.

![Figure 4.15 Thermal desorption spectra of 1:1 H$_2$/D$_2$ mixture on a) TC and b) Pt/TC with heating rate 0.1 K/s. The signal of the mass spectrometer is normalized by the sample mass. H$_2$ (square black), HD (circle red) and D$_2$ (triangle blue)](image)

**High-pressure hydrogen adsorption isotherms**

Excess hydrogen storage capacity of TC and Pt/TC is examined by high-pressure ad / desorption isotherms up to 20 bar for 77 K and 298 K (figure 4.16). For 77 K, hydrogen uptake of both TC and Pt/TC are almost identical (~2.2 wt% at 20 bar) with fully reversible sorption curves as shown in figure 4.16a. In contrast to 77 K, hydrogen uptake of Pt/TC (~0.30 wt% ± 0.02) at 298 K is slightly enhanced over TC (~0.29 wt% ± 0.01). However, this slightly enhanced H$_2$ uptake is in the range of measurement error and a relatively strong hysteresis starting from the high pressure region is also observed in Pt/TC while TC exhibits only a weak hysteresis below 2 bar as shown in figure 4.16b. One should note that TC and Pt/TC samples are measured three times in adsorption and desorption (see figure 4.16c-d) under identical P, T conditions, resulting in a calculated standard deviation (error bars).
4.3.2. Discussion

Silica-templated carbon without and with Pt nanoparticles have been prepared in one carbonization step. The wet impregnation of the Pt precursor prior to carbonization allowed the preparation of a Pt-doped carbon possessing almost identical textural properties, i.e. surface area and micropore volume as the pure templated carbon allowing the investigation of catalytic activities and hydrogen adsorption kinetics. Furthermore, structural and textural characterization performed by PXRD and TEM confirms that the Pt nanoparticles are homogeneously dispersed within the carbon template.

Hydrogen uptake at RT

The hydrogen storage capacity of Pt/TC at 298 K is slightly enhanced only ~ 5 % compared to TC. Moreover, its uptake of Pt/TC is scattered within the experimental uncertainty between different measurements (see figure 4.16c). As Sievert’s type measurement is often observed to be uncertainty
in particular for the materials that are based on physisorption due to various sources of errors (e.g. volume calibration, temperature gradients, impurities, equilibrium wait times, error propagation at high pressure, leaks, sample density and etc...). This small enhancement (less than 5%) can be also considered as experimental errors and therefore could not observe any significant spillover effect. In addition, this negligible enhancement with strong hysteresis may also come from the chemical reaction between hydrogen and carbon host (e.g. C-H bonding). Table 4.2 summarizes a hydrogen capacity comparison of these two samples.

**Hydrogen catalytic effect**

An almost identical hydrogen storage capacity of Pt/TC and TC at 77 K (figure 4.16a) means that Pt catalytic activity may be suppressed or slow down due to the low temperature, and even if there is any catalytic activity, the enhanced hydrogen adsorption by Pt decoration is almost negligible due to the significant amount of physisorptive hydrogen molecules at low temperature. As a result, SSA and pore volume mainly contribute to the cryogenic (77 K) H₂ storage capacity.

On the other hand, Pt catalytic effect is more active at high temperature (RT) as supported by TDS measurements. Comparing the TC and Pt/TC in TDS spectra (figure 4.15), it is shown that the HD signal is strongly enhanced by Pt decoration which can be an evidence of the catalytic activity of Pt by dissociation of H₂ and D₂ to atomic hydrogen or deuterium and recombination to HD molecules. As R. Prins also reported, however, this H-D exchange is no fully proof of spillover (that is the migration of atomic hydrogen on large surface porous materials) as H-D exchange occurs frequently on both Pt particles and defect sites of carbon located near Pt.

**Hydrogen adsorption kinetics**

For hydrogen storage applications, it is essential not only to study hydrogen storage capacity, but it is also crucial to characterize hydrogen adsorption kinetics, especially in the case of microporous materials. The hydrogen adsorption rate of each sample was measured at RT and presented in figure 4.17 as function of the adsorption rate at various hydrogen pressures (e.g. 1.2, 3.3 and 5.5 bar) over equilibrium time. It is found that adsorption rate of Pt/TC is faster than TC at initial loading pressure of range up to 5.5 bar as shown in figure 4.17b, c and d.
Since over 400 m$^2$/g of H$_2$ BET SSA (compared with N$_2$ BET SSA) of Pt/TC and TC are only measurable by H$_2$ molecule, this can be deduced an existence of numerous microporosity below kinetic diameter of N$_2$ molecule. As a consequence, an adsorption and diffusion of hydrogen is expected to be influenced mainly by this microporosity due to comparable pore size over hydrogen molecule. Therefore, the slow adsorption kinetic of TC is mainly ascribed to micro porosity, creating also the weak hysteresis at low pressure due to a kinetic diffusion limitation as shown in figure 4.17b. Despite of this hysteresis, the adsorption isotherm of TC at 298 K is fully reversible after evacuation for overnight (figure 4.17d). On the other hand, since both materials possess microporosity below the kinetic diameter of N$_2$ molecule, fast adsorption rate of Pt/TC over TC can be mainly ascribed to the presence of Pt nanoparticles although the reduction of microporosity filled by Pt nanoparticles is also partially influenced (see TEM study in figure 4.8). Hence, a strong binding energy between hydrogen molecules and the surface of Pt nanoparticle is able to accelerate molecular hydrogen diffusion, and then dissociated atomic hydrogen preferentially chemisorb around surface irregularities$^{102}$, leading to fast adsorption kinetic of Pt/TC.

Figure 4.17 Rate of adsorption for hydrogen on Pt/TC and TC at 298 K with various pressure; a) Gravimetric hydrogen uptake of the TC (square black) and Pt/TC (circle red) at RT. b) ~ 1.2 bar, c) ~ 3.3 bar and d) ~ 5.5 bar versus full equilibrium time at each pressure.
4.4. Influence of Pd doped COF-102 on hydrogen adsorption

4.4.1. Results

High-pressure hydrogen adsorption isotherms
Hydrogen adsorption isotherms at 77 K for pristine COF-102, Pd3.5wt%@COF-102 and Pd9.5wt%@COF-102 samples are presented in figure 4.18. Pristine COF-102 has a hydrogen storage capacity of 5.27 wt% at 20 bar and 77 K which is in good agreement with the previous work of Yaghi and co-workers. After decoration of Pd on COF-102, however, the hydrogen uptake on Pd3.5wt%@COF-102 and Pd9.5wt%@COF-102 is decreased to 4.60 and 4.38 wt%, respectively. The loss of gravimetric excess hydrogen uptake at low temperature can be correlated with the increase of the specific weight by Pd doping and the decrease of the specific surface area and micropore volume. At room temperature, the hydrogen uptake for the pristine COF-102 is much lower than at 77 K. As shown in figure 4.19, the uptake on pristine COF-102 is around 0.16 wt% at 20 bar. After decoration of Pd on COF-102, however, the hydrogen storage capacity is enhanced by a factor of 2~3, when compared to the pristine material. The uptake on Pd3.5wt%@COF-102 and Pd9.5wt%@COF-102 is around 0.38 wt% and 0.42 wt% at 20 bar, respectively.

Figure 4.18 Excess hydrogen isotherm sorption curves of the Pd-free COF 102 (square), Pd 3.5wt%@COF-102 (circle) and Pd 9.5wt%@COF-102 (diamond) at 77 K. (Filled symbol: adsorption, open symbol: desorption)
Figure 4.19 Hydrogen isotherm sorption curves of the Pd-free COF 102 (square), Pd 3.5wt%@COF-102 (circle) and Pd 3.5wt%@COF-102 (diamond) at 298 K. (Filled symbol: adsorption, open symbol: desorption)

Figure 4.20 Reversibility of hydrogen uptake of 9.5wt% Pd containing COF-102 sample; circle, squares, diamond and triangles stand for first (RT), second (77K), third (RT) and fourth (77K) cycle respectively. Samples were evacuated in vacuum at room temperature for overnight prior to each measurement.

Note that the adsorption isotherm of Pd@COF-102 was completely reversible after fully evacuating for overnight, although there appeared to be a hysteresis at RT within a complete measurement time of 150 min. Several ad/desorption cycles are shown in figure 4.20 which the 3rd and 4th adsorption
isotherm at RT and 77K is in good agreement with the 1st and 2nd adsorption isotherm, indicating no change of the textural properties of Pd@COF-102 during hydrogenation.

**Hydrogen adsorption kinetics**

Owing to a relatively strong hysteresis in isotherm of Pd doped COF-102 (figure 4.19) especially in the low pressure region (> 6 bar), adsorption kinetics of Pd 9.5wt% doped COF-102 and the pristine material are compared (figure 4.21). Pristine COF-102 shows for adsorption and desorption nearly the same equilibrium time independent of pressure. In contrast, during adsorption the equilibrium time in Pd@COF-102 is much longer at pressures below 6 bar. Above 6 bar and during desorption the equilibrium time of Pd@COF-102 is almost equivalent with pristine COF-102. This remarkably longer equilibrium time in the Pd-doped COF-102 may be an indication for the occurrence of an unknown chemical reaction at low pressure while physical interaction prevails at high pressure.

![Figure 4.21 Kinetics of COF-102 and Pd9.5wt%@COF-102. (Close: Adsorption, Open: Desorption) – Triangle and diamond is isotherm graph of Pd9.5wt%@COF102 and COF102, respectively. Equilibrium time: Required time that the H₂ pressure is reached the Equilibrium (Black square is for COF-102 and red circle is for Pd9.5wt%@COF-102).](image)
Solid-State $^{13}$C/MAS Nuclear Magnetic Resonance ($^{13}$C-MAS-NMR)

Figure 4.22 shows a close comparison of the Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance ($^{13}$C-MAS-NMR) spectrum of H$_2$ loaded and unloaded Pd@COF-102. Both Pd and PdHx@COF-102 generate resonances at chemical shifts in the peak position of 66, 128, 134 and 151 ppm. First resonances (66 ppm) is correspond to the carbon 1 of triangular B$_3$O$_3$ rings in COF-102, and the rest 3 resonances is consistent with the chemical shifts induced on carbon 2-4 by benzene rings (figure 4.23). Additionally, a resonance in the peak position at around 45 ppm is generated in Pd@COF-102 (figure 4.22a). After hydrogen loading (PdHx@COF-102), this resonance shifts in the peak position from at 45 ppm to 34 ppm.

![Figure 4.22 13C-NMR(MAS) spectrum of a) Pd@COF-102 hybrid material; b) PdHx@COF-102.](image)

<table>
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<tr>
<td>1</td>
<td>66</td>
</tr>
<tr>
<td>2</td>
<td>151</td>
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<tr>
<td>3</td>
<td>128</td>
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</table>

Figure 4.23 Chemical shift values of pristine COF-102 in $^{13}$C-NMR(MAS) spectrum. (taken from ref. 103)
4.4.2. Discussion

Pd doped COF and MOF comparison for hydrogen uptake

The investigation of noble metal doped frameworks was initiated by the publication of R. Yang et al.\textsuperscript{41}, claiming 4 wt\% of H\textsubscript{2} uptake at RT and 100 bar. However, their result has been never independently reproduced and is questioned by other groups\textsuperscript{55,104}. Nevertheless, several groups found a small enhancement of the H\textsubscript{2} storage capacity. Figure 4.23 shows the direct comparison of H\textsubscript{2} adsorption isotherms at 298 K with various Pd contents impregnated in COFs (this work) and MOFs (taken from the literature\textsuperscript{105,106}). For example, M. Latroche et al.\textsuperscript{117} investigated the H\textsubscript{2} storage properties for Pd10wt\%@MIL-100(Al). They reported that the H\textsubscript{2} uptake in the Pd10wt\%@MIL-100(Al) is ca. 0.2 wt\% at 20 bar which is almost twice that of the pristine MIL-100(Al) at room temperature. Similarly, M. P. Suh et al.\textsuperscript{118} also reported the H\textsubscript{2} storage properties for Pd3.0wt\%@[SNU-3]\textsuperscript{0.54+}(NO\textsubscript{3}-)\textsubscript{0.54} exhibiting H\textsubscript{2} uptake of ca. 0.1 wt\% at 20 bar, RT. On the other hand, the H\textsubscript{2} uptake of Pd3.5wt\%@COF-102 and Pd9.5wt\%@COF-102 in this work is 0.38 wt\% and 0.42 wt\% at 20 bar, respectively. Therefore, the observed gravimetric H\textsubscript{2} uptake of Pd@COF-102 hybrid material is much higher at a pressure of 20 bar compared to those of similar systems\textsuperscript{105,106}.

![Figure 4.23 Comparison of H\textsubscript{2} adsorption isotherms at 298 K with various Pd contents impregnated in COFs and MOFs: 3.5 wt\% Pd containing COF 102 (circle), 9.5 wt\% Pd containing COF 102 (diamond), 10 wt\% Pd containing MIL-100(Al) (triangle : taken from ref.\textsuperscript{105} and 3 wt\% Pd containing [SNU-3]\textsuperscript{0.54+}(NO\textsubscript{3}-)\textsubscript{0.54} (square : taken from ref.\textsuperscript{106}).](image)

Porous materials doped with Pd can store hydrogen through the physisorption on the framework and chemisorption via Pd hydride formation. Considering the hydrogen uptake of both physisorption (figure 4.19) and Pd hydride, however, the small enhancement of hydrogen uptake for Pd@COF-102 is
expected as only small quantities of hydrogen is required for the small Pd contents (i.e. 3.5 wt% and 9.5 wt%) inside COF-102 (e.g. one Pd atom is able to take far less than one hydrogen atom for Pd hydride formation (PdHx, typically x ≤ 0.6)). Hence, this remarkable enhancement compared to pristine COF-102 can be partially considered by Pd hydride formation, and some other mechanism must be involved for improving the hydrogen storage capacity of the Pd@COF-102.

Elucidation of the enhancement mechanism for hydrogen storage capacity

A consistent explanation for the remarkable enhancement of Pd@COF-102 compared to the pristine material is following; the 6 wt% increase of the Pd content between 9.5 wt% Pd@COF102 and 3.5 wt% Pd@COF-102 results in an increase in the H₂ uptake of 0.036 wt% at 20 bar, as shown in iii-(a), figure 4.24. Under the assumption that this increase is solely due to Pd hydride formation, an upper limit for the ratio of atomic hydrogen and Pd can be calculated, leading to a Pd/H = 0.6. Considering the 20 bar, the ratio of 0.6 H/Pd in Pd nanoparticles agrees well with literature (e.g. between 0.2 to 0.55 H/Pd for the different Pd sized (2 to 9 nm) at 1 bar H₂ and 300~310 K. Hence, from this Pd/H ratio of 0.6, the maximum amount of hydrogen adsorbed by Pd hydride formation can be calculated for Pd 3.5wt%@COF102 (0.02 wt% of H₂), as shown in iii-(b), figure 4.24. Furthermore, the amount of physisorbed hydrogen (0.16 wt% of H₂) coming from the pristine material can be subtracted (figure 4.24, i). The further enhancement of the hydrogen adsorbed at 20 bar is 0.2 wt% and has to be related to an additional mechanism (figure 4.24, ii).

Figure 4.24 hydrogen isotherm sorption curves of the Pd-free COF 102 (square), Pd 3.5wt%@COF-102 (circle) and Pd 3.5wt%@COF-102 (diamond) at 298 K. (i) Amount of H₂ adsorbed by physisorption process, (ii) Amount of H₂ adsorbed by unknown mechanism, and (iii) Amount of H₂ adsorbed by Pd hydride: iii-a is due to the 6 wt% of Pd difference = 0.036 wt% of H₂ / iii-b is due to the 3.5 wt% of Pd impregnated in COF-102 = 0.02 wt% of H₂.
Hydrogenation of the organometallic Pd precursor

Based on a relatively strong hysteresis in isotherm of Pd doped COF-102 at RT (figure 4.19) with slow adsorption kinetic at low pressure (figure 4.21), it can be carefully presumed that residual organic fragments coming from the decomposed products of the organometallic Pd precursor might still exist inside COF-102, leading to a remarkable enhancement of H₂ adsorption and hysteresis. A close comparison of the ^13C-MAS-NMR spectrum of H₂ loaded and unloaded Pd@COF-102 supports this conclusion (figure 4.22), exhibiting a slight shift in the peak position (from 45 to 34 ppm) in NMR after H₂ loading. Thus, the question arises what kind of residuals exist in Pd@COF-102. The decomposition (UV-light/thermal) pathways for the [Pd(η⁳-C₃H₅)(η⁵-C₅H₅)] precursor have been well studied in the literature⁹⁸⁻¹¹⁰. Based upon these studies, the major decomposition pathway for [Pd(η³-C₃H₅)(η⁵-C₅H₅)] under UV-light is shown in figure 4.25.

![Figure 4.25](image)

Figure 4.25 Most probable reaction pathways for decomposition of the [Pd(η₃-C₃H₅)(η₅-C₅H₅)] precursor in the presence of UV-light. The samples are heated at 400 K under vacuum. (Tᵢ = boiling temperature).

Initially the Pd precursor complex was loaded inside the framework via gas phase infiltration, and then decomposed under UV-light. At the end, the compound was heated under a vacuum at 400 K. Therefore, the most of allyl and cyclopentadieny radical product such as propylene, propane, biallyl, benzene and cyclopentadiene should be evaporated, but dicyclopentadiene which has low volatility (b.p. ~443 K) might have stuck to the surface of Pd nanoparticles (figure 4.26). NMR signals also
confirmed the existence of dicyclopentadiene possessing peak positions at 136, 132, 50, 46, 45, 41, and 34 ppm. The first two chemical shifts (in peak position of 136 and 132 ppm) are overlapped with COF-102 framework peaks so that it is not visible, and the other peaks are broadened, see figure 4.22. The existence of dicyclopentadiene inside Pd@COF102 is also cross checked by TDS measurements (figure 4.27a), showing one clear desorption peak of 132 m/z.

Figure 4.26 hydrogen isotherm sorption curves of the Pd-free COF 102 (square), Pd 3.5wt%@COF-102 (circle) and Pd 9.5wt%@COF-102 (diamond) at 298 K. (i) Amount of H₂ adsorbed by physisorption process, (ii) Amount of H₂ adsorbed by hydrogenation of residual organics, and (iii) Amount of H₂ adsorbed by Pd hydride: iii-a is due to the 6 wt% of Pd difference = 0.036 wt% of H₂ / iii-b is due to the 3.5 wt% of Pd impregnated in COF-102 = 0.02 wt% of H₂.

In addition, all the by-products of [Pd(η⁵-C₅H₅)(η⁵-C₅H₅)] are removed by heating temperatures above 473 K, but the Pd@COF-102 hybrid lost its crystalline nature (figure 4.27b) under this experimental condition. At current stage, the exact amount of left over organic residual cannot be quantified, but the TGA data (figure 4.27c) suggests the presence of less than 5 wt% organic fragments after activation at 403 K under vacuum.

This alkene chemistry such as hydrogenation/dehydrogenation of organic fragments on Pd surfaces (single crystalline as well as supported nanoparticles) has been already investigated by several research groups. For instance, A. Doyle et al.¹¹¹ has been compared the surface chemistry of ethane and trans-2-pentene on Pd (111) single crystal and Pd nanoparticles by TDS. They observed that a number of hydrocarbon transformations, such as dehydrogenation and H-D exchange occur on both
Pd systems. But the alkene hydrogenation to alkane only occurs on the Pd nanoparticles under low-pressure conditions. In addition, D. Stacchiola et al.\textsuperscript{112} also has been studied the adsorption of propylene on Pd (111) by using TDS and IR. They reported that the highly reactive nanosized Pd surfaces leads to strong adsorption of alkenes in di-\(\sigma\) configuration even at temperatures as low as 80 K. With increasing temperature up to room temperature (250–325 K), the molecular desorption and dehydrogenation (i.e. adsorbed alkene: propylene) take place through \(\beta\)-H elimination depending on the reaction conditions via \(\eta^1\)-alky species.

Therefore, the significant excess of 0.2 wt% of \(\text{H}_2\) uptake at 298 K, 20 bar can be attributed to hydrogenation/dehydrogenation of organic fragments permanently present on the Pd nanoparticles surface in Pd@COF-102.

![Figure 4.27](image)

*Figure 4.27 a) Thermal desorption profile of mass 132 for dicyclopentadiene inside Pd@COF102 after loading hydrogen gas (Heating rate of 0.1 K/s). b) Powder XRD pattern of the Pd@COF-102 sample after annealing overnight at 250 °C under vacuum. The loss of the crystallinity is clearly evident from the absence of sharp peaks. c) TGA profile of (i) pure COF-102; (ii) Pd@COF-102, after irradiation with UV light*

Overall, the hydrogen adsorption in COF hybrid materials at RT consists of three different mechanisms, i.e. hydrogen physisorption on the framework, hydride formation in the Pd nanoparticles and an additional enhancement due to organic residue. It is important to note that obtained results support an alternative explanation with novel perspectives of the “spillover process” in porous materials to explain the significantly enhanced hydrogen storage properties at ambient conditions. Table 4.2 summarizes a hydrogen storage capacity of Pd@COF samples at 77 K and RT.
Table 4.2 Overview of the hydrogen specific surface area (SSA), specific total pore volume (SPV) and hydrogen excess uptake at 19.5 K / 77 K / RT for the materials investigated.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Metal content (wt%)</th>
<th>BET$_{H_2}$ SSA (m$^2$/g)</th>
<th>Hydrogen SPV$_{0.9}$ (cm$^3$/g)</th>
<th>H$_2$ excess uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC</td>
<td>-</td>
<td>1306</td>
<td>0.61</td>
<td>4.14</td>
</tr>
<tr>
<td>Pt/TC</td>
<td>6.8</td>
<td>1364</td>
<td>0.62</td>
<td>4.17</td>
</tr>
<tr>
<td>COF-102</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pd/COF-102</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pd/COF-102</td>
<td>9.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
4.5. Conclusion

Pt doped carbon

- Pt-doped (Pt/TC) and un-doped (TC) templated carbons have been successfully synthesized via one carbonization step. The content of Pt in carbon matrix is 6.8 wt% and Pt nanoparticles are randomly dispersed and well embedded within the carbon matrix.

- The textural properties analyzed by both H₂ and N₂ BET show almost identical specific surface area (SSA) and pore volume (Vp) of Pt/TC and TC. However, there is huge SSA difference (ca. 35 %) between H₂ and N₂ BET measurements, indicating an existence of numerous micropores smaller than nitrogen molecule size.

- This microporosity leads to slow adsorption and diffusion of hydrogen in TC at RT, whereas the adsorption kinetic is enhanced for the Pt-doped TC.

- Furthermore, after exposure to 1:1 H₂/D₂ mixture, thermal desorption spectroscopy measurements show a clear signal for HD molecules, indicating the catalytic activity of Pt nanoparticles.

- At room temperature, the hydrogen storage capacity of Pt/TC exhibits a negligible enhancement with a strong hysteresis, suggesting no connection between the spillover effect and a feasible hydrogen storage enhancement.

Pd doped COFs

- Pd nanoparticles have been successfully incorporated in microporous COF-102 by gas phase infiltration and photo decomposition of [Pd(η³-C₃H₅)(η⁵-C₅H₅)] leading to Pd@COF-102 hybrid material without any decomposition of the COF structure. Regardless of the amount of Pd loading (3.5~30 wt%), the size of the Pd nanoparticles is the same (2.4 ± 0.5 nm) and they are homogeneously distributed throughout the whole COF-102 crystal.
- At room temperature, the hydrogen uptake on pristine COF-102 is around 0.16 wt% at 20 bar. After decoration of Pd on COF-102, the hydrogen storage capacity is enhanced by a factor of 2−3, exhibiting 0.38 wt% and 0.42 wt% for Pd3.5wt%@COF-102 and Pd9.5wt%@COF-102, respectively.

- Porous materials doped with Pd can store hydrogen through the physisorption on the framework and chemisorption via Pd hydride formation. Considering the hydrogen uptake of both physisorption (0.16 wt%) and Pd hydride (< 0.06 wt%), the enhanced hydrogen uptake of Pd@COF-102 cannot be explained.

- The additional enhancement of ca. 0.2 wt% can be assigned to the catalytic hydrogenation of residual organic fragments such as bicyclopentadiene originating from the Pd precursor.
Part 2

Separation of hydrogen isotope with nanoporous materials
5. Separation of hydrogen isotope with nanoporous materials

5.1. Introduction

In order to design and develop feasible nanoporous materials for hydrogen isotope separation by quantum sieving, a fundamental study for correlations between selectivity and pore size at various temperature and pressure is an essential prerequisite. However, despite many theoretical and computational studies performed recently with the aim of identifying optimum pore size at various pressure\textsuperscript{113 114 60 115 116}, these results show a large variation concerning best pore size and operating conditions (see table 5.1). Furthermore, experiments as guideline are rare and typically not measured under the idealized conditions used in the computer simulation. Therefore among various nanoporous materials, crystalline organic frameworks, as MOFs, COFs or ZIFs, possessing a uniform and well-defined pore structure are the most promising candidates to investigate the correlation between pore size and aperture and their effectiveness for quantum sieving. Furthermore, their crystalline framework also enables precise control (or tuning) of aperture size (e.g. decorating functional group at pore) and functionality (i.e. open metal sites) by accurate design of structures at the molecular level.

In this work, the feasibility of the microporous frameworks as isotope sieves is outlined. Various frameworks materials, COFs, ZIFs and MOFs, are characterized by various techniques such as powder X-ray diffractometry, low-pressure high-resolution hydrogen and nitrogen BET and cryogenic thermal desorption spectroscopy. For the first time, a fundamental correlation between selectivity and pore diameter at optimized operating conditions has been experimentally investigated by using different frameworks. Afterwards, two strategies for satisfying industrial requirements are introduced. Firstly, one way of increasing the operating pressure is presented by using cryogenically flexible COFs. Secondly, different chemical affinity of isotopes on strong adsorption sites is demonstrated in order to increase the operating temperature.
Table 5.1: Theoretical and computational studies for identifying optimum pore size of quantum sieving.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Optimized Aperture (Å)</th>
<th>T (K)</th>
<th>P (bar)</th>
<th>Method</th>
<th>Interaction Potential</th>
<th>Selectivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylindrical carbon pore</td>
<td>6.23</td>
<td>77</td>
<td>10</td>
<td>FH-GCMC&lt;sup&gt;a&lt;/sup&gt; &amp; IAST&lt;sup&gt;b&lt;/sup&gt; (Grand Canonical Ensemble)</td>
<td>Feynman-Hibbs / Lorentz-Berthelot mixing rules</td>
<td>9.9</td>
<td>117</td>
</tr>
<tr>
<td>Idealized carbon slit pores</td>
<td>5.82</td>
<td>77</td>
<td>10</td>
<td>FH-GCMC &amp; IAST (Grand Canonical Ensemble)</td>
<td>Feynman-Hibbs / Lorentz-Berthelot mixing rules</td>
<td>3.6</td>
<td>117</td>
</tr>
<tr>
<td>Idealized carbon slit pores</td>
<td>5.6</td>
<td>40 / 77</td>
<td>10</td>
<td>PI-GCMC&lt;sup&gt;c&lt;/sup&gt; &amp; IAST (Grand Canonical Ensemble)</td>
<td>Path Integral / Silvera-Goldman</td>
<td>~18 / ~6</td>
<td>115</td>
</tr>
<tr>
<td>Idealized carbon slit pores</td>
<td>5.7</td>
<td>40 / 77</td>
<td>10</td>
<td>IAST</td>
<td>-</td>
<td>~16 / ~6</td>
<td>115</td>
</tr>
<tr>
<td>Idealized carbon slit pores</td>
<td>5.7</td>
<td>20</td>
<td>NZP&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Direct diagonalization of the single particle Hamiltonian</td>
<td>Lorentz-Berthelot mixing rules</td>
<td>2050</td>
<td>114</td>
</tr>
<tr>
<td>Idealized carbon slit pores</td>
<td>5.6</td>
<td>40</td>
<td>NZP</td>
<td>Direct diagonalization of the single particle Hamiltonian</td>
<td>Lorentz-Berthelot mixing rules</td>
<td>70</td>
<td>114</td>
</tr>
<tr>
<td>Idealized carbon slit pores</td>
<td>5.6</td>
<td>77</td>
<td>NZP</td>
<td>Direct diagonalization of the single particle Hamiltonian</td>
<td>Lorentz-Berthelot mixing rules</td>
<td>7.6</td>
<td>114</td>
</tr>
<tr>
<td>Idealized carbon slit pores</td>
<td>2.6</td>
<td>77</td>
<td>NZP</td>
<td>PI-GCMC (Grand Canonical Ensemble)</td>
<td>Path Integral / Primitive Action / Lorentz-Berthelot mixing rules</td>
<td>-</td>
<td>60</td>
</tr>
</tbody>
</table>

<sup>a</sup> Feynman-Hibbs variation, <sup>b</sup> Grand Canonical Monte Carlo simulations, <sup>c</sup> Idealized Adsorption Solution Theory, <sup>d</sup> Near Zero coverage Pressure.
5.2. Materials and characterization

5.2.1. ZIF-7, ZIF-8, COF-1 and COF-102

By using a new class of highly ordered porous frameworks (Four different zeolitic imidazolate / covalent organic frameworks with a different aperture size; ZIF-7, ZIF-8, COF-1 and COF-102), a fundamental correlation of D₂ selectivity and pore size at optimized operating conditions (T, p) can be experimentally discovered.

Zeolitic Imidazolate Frameworks (ZIFs) are composed of tetrahedrally-coordinated transition metal ions (Zn is used here but others can also be used such as Fe, Co or Cu) connected by organic imidazole linkers. On the other hand, Covalent Organic Frameworks (COFs) are made entirely from light elements (H, B, C, N, and O) that are known to form strong covalent bonds.

Zeolitic imidazolate frameworks (ZIF-7)

The sample was kindly provided by K. Park (Uni. Liverpool, U.K) and synthesis description is following. ZIF-7 was synthesized by modifying the reference given in ref 118. Benzimidazole (BzIm) (500 mg, 4.23 mmol) and zinc nitrate tetrahydrate (1500 mg, 5.75 mmol) were dissolved in 150 ml of dimethylformamide (DMF). The solution was transferred in 200 ml glass jar and tightly capped. The jar was heated at a rate of 5 °C/min to 130 °C in a programmable oven, held at this temperature for 48 hrs, then cooled at rate of 0.4 °C/min to room temperature. White crystalline solid was collected by filtration and washed with DMF (20 ml X 3) and dried in air. (Yield: 680 mg)

Figure 5.1 shows the crystal structure of ZIF-7 with the ZnN₄ tetrahedra units covalently joined by bridging imidazole linkers (Benzimidazole). This porous ZIF-7 with the sodalite (SOD) cage structure possesses small channels of approximately 3.0 Å in aperture diameter.

The crystal structure of ZIF-7 was identified by powder X-ray diffraction (PXRD) using Mo radiation (figure 5.2). The measurement was carried out in transmission mode and by using glass capillaries. The PXRD pattern for ZIF-7 is in very good agreement with literature values 118. One should note that N₂ sorption measurement at 77 K for ZIF-7 shows virtually no adsorption at low pressure (<1 bar) due to the bigger size of the kinetic diameter of the nitrogen molecule than the aperture.
Zeolitic imidazolate frameworks (ZIF-8)

Commercially available sample of ZIF-8 (Basolite Z1200) is kindly provided by BASF SE. Figure 5.3 shows the crystal structure of ZIF-8 with the ZnN₄ tetrahedra units covalently joined by bridging imidazole linkers (2-methylimidazole). This porous ZIF-8 with the sodalite (SOD) cage structure possesses an aperture diameter of approximately 3.4 Å.
Figure 5.3 Crystal structure of ZIF-8. Hydrogen atoms are omitted for clarity. Carbon (black), zinc (blue tetrahedral) and nitrogen (green).

Figure 5.4 The fully reversible nitrogen adsorption/desorption isotherm of ZIF-8 at 77 K, exhibiting the characteristic IUPAC type I adsorption isotherm, which is typical for microporous materials. Closed symbol indicates adsorption and open symbol indicates desorption isotherm.

Nitrogen adsorption-desorption isotherm at 77 K was carried out using a Quantachrome Autosorp-1 MP instrument (figure 5.4). The ZIF-8 sample was priorly degassed at 420K for overnight. The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) method. The pressure range for BET calculation was chosen according to Rouquerol’s suggestions. The BET specific surface area of 1264 m$^2$/g was calculated.
Covalent organic frameworks (COF-1)

The sample was kindly provided by the group of Prof. R. A. Fischer (Uni. Bochum, Germany) and synthesis description is following. 1,4-benzene diboronic acid (BDBA) was purchased from sigma Aldrich and Tetra(4-(dihydroxy)borylphenyl)methane was prepared from tertraphenylmethane according to literature procedure. COF-1 was prepared following the procedure reported by Yaghi et al.\textsuperscript{103,119} The synthesis was carried out in a glass tube equipped with a Teflon stop-cock, measuring o.d. × i.d. = 80 × 64 mm\textsuperscript{2} and length around 18 cm. The glass tube was loaded with 1,4-benzene diboronic acid (BDBA) (300 mg) and 12 mL of a 1:1 v:v solution of mesitylene:dioxane. The tube was degassed at liquid N\textsubscript{2} temperature and Teflon stop-cock was closed under vacuum. The self-condensation reaction was carried out by aging the reaction tube for 3-4 days at 85 °C. The obtained product was filtered from the reaction mixture using a G2 crucible inside a glove box. The isolated white product was washed with 50 mL of THF and stored overnight in a fresh THF solvent. The solvent was removed under vacuum and later the framework was heated at 150 °C under vacuum (10\textsuperscript{–3} mbar) for 12-14 h to remove the solvent molecule from the pores. (Yield: ~210 mg)

Figure 5.5 shows the crystal structure of two dimensional COF-1 which forms a planar six-membered B\textsubscript{3}O\textsubscript{3} (boroxine) ring with aperture diameter of 9.0 Å.

![Figure 5.5 Crystal structure of COF-1. Carbon (black), oxygen (red), boron (yellow) and hydrogen (gray)](image_url)
The crystal structure of COF-1 was identified by PXRD using CuKα radiation. Figure 5.6 shows the PXRD pattern for COF-1 with the stacking of the layer in AA eclipsed arrangement with $P6/mmm$ space group symmetry which is in very good agreement with literature values\textsuperscript{119}. Nitrogen gas isotherm for COF-1 was measured at 77 K (figure 5.7). The COF-1 sample was priorly degassed at 420K for overnight. The Brunauer-Emmett-Teller (BET) method was applied to the isotherm which resulted in the BET specific surface area of 748 m$^2$/g.

![Figure 5.6 Powder XRD pattern (Cu source) of COF-1 with the stacking of the layers in AA eclipsed stacking arrangement with $P6/mmm$.](image1)

![Figure 5.7 The fully reversible nitrogen adsorption/desorption isotherm of COF-1 at 77 K, exhibiting the characteristic IUPAC type I adsorption isotherm, which is typical for microporous materials. Closed symbol indicates adsorption and open symbol indicates desorption isotherm.](image2)
Covalent organic frameworks (COF-102)

For COF-102 the synthesis details have been already described in chapter 4.2.2. Figure 5.8 shows the crystal structure of three dimensional COF-102 which forms a triangular B₃O₃ (boroxine) ring with pore diameter of 12.0 Å. The crystal structure of COF-102 was identified by PXRD using CuKα (figure 5.9) which matches perfectly with literature values⁸. From the isotherms of the N₂ sorption measurements (figure 5.10), a BET surface area of 3707 m²/g was calculated for COF-102 using BET method.

Figure 5.8 Crystal structure of COF-102. Carbon (black), oxygen (red), boron (yellow) and hydrogen (gray)

Figure 5.9 Powder XRD pattern of COF-1 (Cu source).
Figure 5.10 The fully reversible nitrogen adsorption/desorption isotherm of COF-102 at 77 K, exhibiting the characteristic IUPAC type I adsorption isotherm, which is typical for microporous materials. Closed symbol indicates adsorption and open symbol indicates desorption isotherm.
5.2.2. Cryogenically flexible pyridine on COF-1

For hydrogen isotope separation by quantum sieving, the aperture size plays a vital role in determining the overall separation. Thus, pyridine molecules (Py) are incorporated in the pore walls of COF-1 (C₃H₂BO) in order to reduce the aperture size effectively. This Py@COF-1 is synthesized by the Lewis base (Py) assisted condensation of 1,4-benzenediboronic acid (BDBA) (figure 5.11).

**Synthesis of pyridine decorated covalent organic frameworks (Py@COF-1)**

The sample was kindly provided and characterized by the group of Prof. R. A. Fischer (Uni. Bochum, Germany) and synthesis description is following. Benzenediboronic acid (0.5g, 3.0 mmol) was suspended in diethylether (10 ml). Upon addition of pyridine (0.25 mL, 3.1 mmol), the suspension was flash frozen at 77 K and evacuated. Then, the mixture was stored at 40°C overnight. The obtained white precipitate was filtrated and washed with excess ether. Thus obtained white solid (Py@COF-1) was dried under vacuum at room temperature overnight.

Elemental analysis calculated for 0.66 pyridine molecules per formula unit of COF-1 i.e. C₃H₂BO•1/3C₅H₅N.

*Calculation:* C: 61.44, H: 4.05, N: 5.12.

*Found:* C: 62.1, H: 4.00, N: 5.75

![Diagram of synthesis process](image)

Figure 5.11 Synthesis of Py@COF-1 from 1,4-benzenediboronic acid via Lewis base assisted pathway.
Sample characterization (PXRD, IR, NMR, TGA and SEM)

Figure 5.12 shows powder XRD pattern of Py@COF-1 obtained after 12h of reaction time. Although, the powder pattern of Py@COF-1 contains some broad peaks, the presence of several well defined peaks indicates an ordered structure. Importantly, the peak at 2\(\theta\)=26.8° corresponds to a typical \(\pi-\pi\) stacking distance, similar to the parent COF-1, indicating a close packed structure of Py@COF-1. Owing to the strongly broadened diffraction peaks, an exact crystal structure of Py@COF-1 could not be determined.

![Figure 5.12 Powder XRD pattern of Py@COF-1 (Cu source).](image)

The infrared (IR) (figure 5.13a), \(^{11}\)B and \(^{13}\)C nuclear magnetic resonance (NMR) (figure 5.13b and d) spectra of this compound are in very good correlation with the respective spectrum of the model compound (Ph\(_3\)B\(_3\)O\(_3\)•Pyridine). Thermal gravimetric analysis (TGA) (figure 5.13c) of Py@COF-1 shows a weight loss of 29 (± 2) % around 150 °C, corresponding to loss of one Py molecule per one boroxine ring. This is corroborated by C, H, N analysis data which is consistent with a molecular formula of C\(_3\)H\(_2\)BO•1/3C\(_5\)H\(_5\)N.
Figure 5.13 a) The comparison of IR spectra of COF-1, Py@COF-1 and Ph3B3O3•Pyridine (model compound). The close similarity between Py@COF-1 and Ph3B3O3 • Pyridine model compound is clearly evident. The peaks between 1600~1450 cm⁻¹ in spectrum Py@COF-1 are assigned to C-C and C-N stretching frequencies of pyridine. b) ¹¹B NMR(MAS) spectra of COF-1, Py@COF-1 and Ph3B3O3•Pyridine (model compound). c) TGA profile of Py@COF-1. The initial weight loss is consistent with C3H2BO•1/3C5H5N. d) ¹³C NMR(MAS) spectrum of Py@COF-1 and COF-1.

The SEM image (figure 5.14a) reveal a plate like morphology, similar to the parent COF-1. Complete removing of pyridine from Py@COF-1 gave pristine COF-1 (figure 5.14b and figure 5.15).

Figure 5.14 a) SEM image of Py@COF-1. b) Powder XRD patterns of pyridine@COF-1 at various temperatures.
Figure 5.15 Characterization of COF-1 obtained from Py@COF-1 activated at 180 ºC; a) IR spectrum b) $^{11}$B NMR(MAS) spectrum c) $^{13}$C NMR(MAS) spectrum d) $N_2$ adsorption/desorption profile at 77 K. The calculated BET surface area is 804 m$^2$/g.

**Computational study (molecular simulation)**

In order to understand the structural information of Py@COF-1 at the atomic level, a molecular simulation is employed and analyzed by the group of R. Schmid (Uni. Bochum, Germany).

Here, MOF-FF$^{120}$, a first principles derived force field (FF), is applied to describe the interactions in the system. The study begins with a small system in which the initial structures are generated using 1 x 1 x 2 supercell containing 2 layers of COFs. Each layer consists of 4 and 6 units of boroxine and phenylene ring, respectively. The system is created based on the experimentally justified assumption that one pyridine is bonded to one boron of the boroxine ring.
Since the pyridine can be attached to one boroxine ring at 6 different positions (3 for top and 3 below) (figure 5.16a), in total, 68 different structures are possible. An automated genetic algorithm based on global minimum search approach (known as GA) is used to screen only the potential structures from all possible initial structures. Afterward, the screened structures are optimized. The simulation is carried out in a periodic condition with a cutoff of 4 Å for the non-bonded van der Waals and the electrostatic interactions. Since, it is difficult to find the right cell parameters from such a small system with a very short cutoff, a larger system is required. Therefore, after obtaining the best conformation of Py@COF-1 from 1x1x2 supercell, the small system is extended to have bigger size of 2x2x8. The bigger system has 32 formula units (f.u.), and allows a proper simulation of the interlayer interaction. (figure 5.16 and 5.17)
Figure 5.17 a) bent structure of a single layer. b) close packing of two layers. c) and d) top view of the ABAB stacking pattern of the layers (blue top layer and red bottom layer).

The simulated PXRD of the final structure model compares very well with the experimental data (figure 5.18). The experimental peaks are broadened probably also due to defects in the Py position, which could lead to stacking faults and a certain disorder. Overall, the theoretically predicted structure is a very good, but somewhat idealized atomistic, structure model for Py@COF-1. The simulated surface area using N$_2$ and H$_2$ molecules is 0 m$^2$/g, indicating the extremely dense phase of Py@COF-1.

Figure 5.18 Comparison of simulated and experimental powder XRD patterns of Py@COF-1.
Textural properties (nitrogen and hydrogen adsorption isotherms)

From the nitrogen (77 K) and hydrogen (19.5 K) adsorption/desorption analysis of Py@COF-1, BET specific surface area of nitrogen and hydrogen are 20.5 m²/g and 48 m²/g, respectively (figure 5.19 and 5.20), indicating that the gas molecules cannot penetrate the structure which is in good agreement with computational study.

![Graph showing nitrogen adsorption/desorption isotherm at 77 K](image)

Figure 5.19 Low pressure N₂ adsorption/desorption isotherm at 77 K of Py@COF-1. The calculated BET surface area is 20.5 m²/g⁻¹.

![Graph showing hydrogen adsorption/desorption isotherm at 19.5 K](image)

Figure 5.20 Low pressure H₂ adsorption/desorption isotherm at 19.5 K of Py@COF-1. The calculated BET surface area is 48 m²/g⁻¹.

Figure 5.21 shows the high pressure (up to 20 bar) hydrogen adsorption isotherms of a) Py@COF-1; b) after removing pyridine from Py@COF-1 at 100 °C under vacuum; c) pristine COF-1. In accordance
with PXRD data (figure 5.14b), complete removing of pyridine from Py@COF-1 exhibits almost identical storage property of pristine COF-1.

Figure 5.21 H₂ adsorption/desorption isotherm at 77 K up to 20 bar. a) Py@COF-1; b) after removing pyridine from Py@COF-1 at 100 °C under vacuum; c) pristine COF-1. After complete removal of pyridine from pyridine@COF-1, the H₂ uptake is very close to COF-1. This means that complete stripping of pyridine from Py@COF-1 gave neat COF-1.
5.2.3. MOFs with open metal site (CPO-27-Co)

The redox-active metal-organic framework with open metal site, CPO-27-Co, was selected for testing the separation of D₂/H₂ mixtures as its isosteric heat of adsorption is among the highest recorded values⁴⁰ for physisorptive materials.

Commercially available sample of CPO-27-Co is kindly provided by BASF SE.

Figure 5.22 shows the crystal structure of CPO-27-Co exhibiting a three-dimensional honeycomb-like network. The large hexagonal 1D channel possesses about 10 Å in diameter defined by the space between the van-der-Waals radii of the wall atoms inside the channel. Thus, it provides a large enough window for small H₂ and D₂ molecules to enter without any diffusion barrier.

Figure 5.22 Crystal structure of CPO-27-Co.

Figure 5.23 Powder XRD patterns of CPO-27-Co at RT. a) CuKα radiation, b) Mo radiation.
The crystal structure of the CPO-27-Co was identified by powder X-ray diffraction (PXRD) using CuKα and Mo radiation (figure 5.23) in range of 2θ = 5º - 60º. Measurements were carried out in transmission mode and by using glass capillaries. The PXRD patterns for CPO-27-Co is in good agreement with measurements in the literature\textsuperscript{121,122}. Scanning electron microscope (Figure 5.24) show the morphology of crystallized CPO-27-Co, exhibiting around 2 μm length hexagonal rod-shapes.

![Figure 5.24 SEM (scanning electron microscope) image of crystallized CPO-27-Co](image)

Nitrogen adsorption-desorption isotherm at 77 K was carried out using a Quantachrome Autosorp-1 MP instrument (figure 5.25). The CPO-27-Co sample was priorly degassed at 420K for overnight. A BET specific surface area of 1012 m\textsuperscript{2}/g was calculated using the Brunauer-Emmett-Teller (BET) method in the pressure range according to Rouquerol's suggestions.\textsuperscript{99}
5.3. Structure-property relationship for H$_2$/D$_2$ separation by quantum sieving

Four different Zeolitic Imidazolate / Covalent Organic frameworks (ZIF-7, ZIF-8, COF-1 and COF-102) are used to investigate the quantum sieving effect. Diameters of the pore aperture are 3.0 Å, 3.4 Å, 9.0 Å and 12 Å for ZIF-7, ZIF-8, COF-1 and COF-102, respectively (table 5.2). Note that ZIF-7 was chosen for minimum pore aperture since the kinetic diameter of the hydrogen molecule is around 2.83-2.89 Å$^7$, whereas the COFs possess far larger pore aperture, which allow to assess the D$_2$ over H$_2$ molar ratio in dependence of aperture and operating conditions.

5.3.4. Results

Low-pressure, high-resolution H$_2$ and D$_2$ adsorption isotherms

Figure 5.26-29 shows low pressure adsorption isotherms for H$_2$ and D$_2$ on ZIF-7, -8, COF-1 and -102 for various temperature between 19.5 K and 70 K. All isotherms except ZIF-7 are type I in the IUPAC classification, indicating highly microporous materials. In case of ZIF-7 (Figure 5.26), H$_2$ or D$_2$ cannot penetrate the framework due to the comparable size of the pore aperture and the kinetic diameter of the hydrogen isotope molecule. On the other hand, due to the larger pore aperture size of ZIF-8, COF-1 and COF-102 adsorption and desorption are fully reversible.

![Figure 5.26 Low pressure isotherm for H$_2$ and D$_2$ adsorption on ZIF-7 at various temperature (range of 19.5 K - 70 K) and pressure (range of 0 - 1 bar); open symbol indicates D$_2$ and closed symbol indicates H$_2$.](image)
Figure 5.27 Low pressure isotherm for H\textsubscript{2} and D\textsubscript{2} adsorption on ZIF-8 at various temperature (range of 19.5 K - 70 K) and pressure (range of 0 - 1 bar); 19.5 K (square black), 30 K (circle red) 40 K (triangle blue), 50 K (inverse triangle green), 60 K (diamond pink) and 70 K (side triangle orange); open symbol indicates D\textsubscript{2} and closed symbol indicates H\textsubscript{2}

Figure 5.28 Low pressure isotherm for H\textsubscript{2} and D\textsubscript{2} adsorption on COF-1 at various temperature (range of 19.5 K - 70 K) and pressure (range of 0 - 1 bar); 19.5 K (square black), 30 K (circle red) 40 K (triangle blue), 50 K (inverse triangle green), 60 K (diamond pink) and 70 K (side triangle orange); open symbol indicates D\textsubscript{2} and closed symbol indicates H\textsubscript{2}

Figure 5.29 Low pressure isotherm for H\textsubscript{2} and D\textsubscript{2} adsorption on COF-102 at various temperature (range of 19.5 K - 70 K) and pressure (range of 0 - 1 bar); 19.5 K (square black), 30 K (circle red) 40 K (triangle blue), 50 K (inverse triangle green), 60 K (diamond pink) and 70 K (side triangle orange); open symbol indicates D\textsubscript{2} and closed symbol indicates H\textsubscript{2}
The corresponding values for H\textsubscript{2} adsorption at 19.5 K, 0.7 bar are 23 mmol/g (ZIF-8), 20 mmol/g (COF-1) and 59 mmol/g (COF-102), respectively, and for the D\textsubscript{2} adsorption at 19.5 K, 0.2 bar are 24 mmol/g (ZIF-8), 20 mmol/g (COF-1) and 63 mmol/g (COF-102), respectively (table 5.2). These corresponding values at 19.5 K, 0.7 bar for H\textsubscript{2} and 19.5 K, 0.2 bar for D\textsubscript{2} are the maximum saturation uptakes before liquefaction.

**Table 5.2 Textural characteristic of the ultramicroporous frameworks considered in this work\textsuperscript{a}**

<table>
<thead>
<tr>
<th>Name</th>
<th>(P_{\text{size}}) ([\text{Å}])</th>
<th>(N_2) (\text{SSA}_{\text{BET}}) ([\text{m}^2/\text{g}])</th>
<th>(D_2 / H_2) uptake @ 19.5 K ([\text{mmol/g}])</th>
<th>Compositon</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-7</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>(\text{Zn(PhiIM)}_2)</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>3.4</td>
<td>1265</td>
<td>24 / 23</td>
<td>(\text{Zn(MeIM)}_2)</td>
</tr>
<tr>
<td>COF-1</td>
<td>9.0</td>
<td>748</td>
<td>20 / 20</td>
<td>(\text{C}_3\text{H}_2\text{BO})</td>
</tr>
<tr>
<td>COF-102</td>
<td>12.0\textsuperscript{b}</td>
<td>3707</td>
<td>63 / 59</td>
<td>(\text{C}<em>{25}\text{H}</em>{32}\text{B}_2\text{O}_8)</td>
</tr>
</tbody>
</table>

\(\text{P}_{\text{size}}\): effective pore aperture diameter (considering the van der Waals radius of atoms in the framework), \(N_2\) \(\text{SSA}_{\text{BET}}\): nitrogen BET specific surface area at 77 K, \(D_2\) and \(H_2\) uptake: \(D_2\) uptake at 19.5 K, 0.2 bar and \(H_2\) uptake at 19.5 K, 0.7 bar – note that liquefaction pressure at 19.5 K is 0.78 bar and 0.27 bar for \(H_2\) and \(D_2\), respectively.

\(\text{in case of COF-102, it is hard to determine the size of the pore aperture due to its geometric complexity. However since a pore aperture size is quite similar to a pore size, we assume that it is same.}\)

**Enthalpy of adsorption**

The isosteric heat of adsorption applying the Clausius-Clapeyron equation was calculated by using the adsorption isotherms at different temperature from 19.5 K to 70 K. For comparison of the different materials, the isosteric heat of adsorption is shown (figure 5.30) in dependence of the surface coverage. Note that the surface coverage is normalized by maximum hydrogen uptake at 19.5 K. Analysis of \(D_2\) and \(H_2\) adsorption enthalpy gives similar maximum values of 5~6 kJ/mol for ZIF-8 and COF-1, and lower values of 4 kJ/mol for COF-102 near zero surface coverage, respectively. With increasing \(H_2\) or \(D_2\) loading up to 90 % coverage, all values are decreasing closely to 2 kJ/mol. This result is consistent with the typical value of \(H_2\) adsorption enthalpy for other MOFs showing a decrease of the heat of adsorption with increasing hydrogen uptake.\textsuperscript{123}

For smaller pore diameters, the interaction potential starts to overlap with the opposite pore side leading to a higher heat of adsorption for smaller pores as observed for ZIF-8 and COF-1. In addition, \(D_2\) shows a slightly higher adsorption enthalpy than \(H_2\) in ZIF-8 and COF-1. In contrast, owing to the large pore size of COF-102, the heat of adsorption between \(D_2\) and \(H_2\) is almost identical over the whole range of coverage.
Figure 5.30 The isosteric heat of hydrogen and deuterium adsorption for ZIF-8 (black square), COF-1 (red circle) and COF-102 (blue triangle) as a function of the surface coverage. Closed symbol is hydrogen and open symbol is deuterium.

5.3.5. Discussion

Despite many computational suggestions for the optimal pore size of quantum sieving, it has been difficult to obtain an experimental demonstration due to difficulties of preparing samples with the same properties as the idealized ones used in the computational analyses. In this regard, ordered porous organic frameworks are ideal candidates to study a fundamental correlation between the \( \text{H}_2/\text{D}_2 \) separation and pore structure at various temperatures and pressures, which lead to an optimum pore aperture as well as operating conditions for effective \( \text{H}_2/\text{D}_2 \) separation by quantum sieving.

D\(_2\) and H\(_2\) adsorption on porous frameworks

In adsorption isotherms of ZIF-8, COF-1 and -102, \( \text{D}_2 \) uptake is always higher than \( \text{H}_2 \) in the whole temperature and pressure range as shown in figure 5.27-29 although with increasing temperature the difference between \( \text{D}_2 \) and \( \text{H}_2 \) gets smaller. This indicates that \( \text{D}_2 \) is favorably adsorbed on the entire surface of these microporous materials compared to \( \text{H}_2 \) at sufficiently low temperature. The main reason for this high \( \text{D}_2 \) uptake over \( \text{H}_2 \) is due to a difference between \( \text{H}_2 \) and \( \text{D}_2 \) in mass effect on the vibrational energy level normal to the surface and dispersion energy.\(^{67}\) Consequently, this results in the stronger \( \text{D}_2 \)-surface interaction than \( \text{H}_2 \)-surface interaction, leading to the high \( \text{D}_2 \) adsorption density.
Adsorption molar ratio

A simple experimental quantification of the enhanced adsorption of D\textsubscript{2} over H\textsubscript{2} is to divide the adsorbed quantity of D\textsubscript{2} by H\textsubscript{2} (D\textsubscript{2} over H\textsubscript{2} adsorption molar ratio) at the same pressure. Hence, the molar D\textsubscript{2}/H\textsubscript{2} ratio at temperature range of 19.5 K - 70 K and pressure range of 0 - 1 bar are shown in figure 5.31. The molar D\textsubscript{2}/H\textsubscript{2} ratio of COF-102 is just slightly larger than 1 at all temperatures only because of a favorable D\textsubscript{2} adsorption on the surface. It means that the quantum sieving effect (which the transverse motion of the molecule has to be quantized) of hydrogen isotope in microporosity is nearly negligible. However, a completely different behavior can be seen when the diameter of the pore aperture is decreased from 12 Å to 9 Å. At low temperatures, 19.5 K ~ 40 K, the molar D\textsubscript{2}/H\textsubscript{2} ratio at near zero coverage pressure is remarkably larger than for higher pressures (figure 5.31). This result implies that the quantum sieving effect can be already observed at a pore aperture of 9 Å and a maximum molar D\textsubscript{2}/H\textsubscript{2} ratio of 7 is reached at 19.5 K. This molar ratio is more enhanced when the diameter of the pore aperture is decreased to 3.4 Å (ZIF-8) and a maximum molar D\textsubscript{2}/H\textsubscript{2} ratio of about 11 is reached at 19.5 K under zero coverage pressure. Moreover, the pressure range at 30 K and 40 K is also shifted to higher pressures compared to COF-1 (9 Å). One should note that this molar D\textsubscript{2}/H\textsubscript{2} ratio is based on pure gas equilibrium isotherms, and if the kinetic effect is exploited for an isotope mixture, the kinetic D\textsubscript{2} selectivity for D\textsubscript{2}/H\textsubscript{2} isotope mixture will be significantly enhanced. Most importantly, these experimental results indicate clearly that the optimum pore diameter for quantum sieving must be larger than 3.0 Å and should be smaller than 3.4 Å. In contrast, computer simulations report different values for the optimum pore diameter of 6.23 Å\textsuperscript{117}, 5.6~5.7 Å\textsuperscript{114,115} or 2.6 Å\textsuperscript{60}, which may be caused by the different theoretical methods applied as shown in table 5.1. Furthermore, different potentials for the hydrogen molecule and carbon surface have been used yielding small variations in the effective pore diameter (e.g. 0.6 Å), which will influence the selectivity significantly\textsuperscript{124}. 
Figure 5.31 Comparison of the molar D$_2$/H$_2$ ratio as function of the effective pore size of organic frameworks at temperature range of 19.5 K - 70 K and pressure range of 0 - 1 bar.
5.4. Optimization of aperture for quantum sieving via cryogenically flexible COF-1

Previously, a fundamental correlation between the quantum sieving effect and the pore structure of framework materials has been established by using COFs and ZIFs. It clearly shows that the aperture size plays a vital role in determining the overall separation. Hence, a novel strategy to reduce effectively the aperture size by incorporating pyridine molecules (Py) in the pore walls of COF-1 (Py@COF-1) is now presented for enhancing the operating pressure.

5.4.1. Results

**Low-pressure, high-resolution H\textsubscript{2} and D\textsubscript{2} adsorption isotherms**

Figure 5.32 shows low pressure adsorption isotherms for hydrogen on Py@COF-1 at low temperatures (19.5 K - 70 K). In general, for hydrogen physisorption on porous materials the isotherms have increased uptake with decreasing temperature. However, isotherms of Py@COF-1 exhibit a unique sorption behavior. As for instance, gas uptake starts at 30 K with exhibiting a hysteresis. The observed hysteresis gets stronger till 40 K, then weaker above 50 K. The maximum hydrogen uptake is found at 50 K (2 mmol/g at 1 bar). These hystereses indicate the slow diffusion kinetics between 30 and 70 K (figure 5.32), implying also non-equilibrium isotherms within measureable time. Identical phenomena are also observed in case of D\textsubscript{2} pure gas adsorption, but the adsorbed amount is higher and the hysteresis below 40 K is even stronger than for H\textsubscript{2} (figure 5.33). The maximum deuterium uptake is also found at 50 K (2.3 mmol/g at 1 bar).
Figure 5.32 Hydrogen adsorption and desorption isotherms of Py@COF-1: closed symbol is adsorption and open symbol is desorption at various temperature at (a) 19.5 K, (b) 30 K, (c) 40 K, (d) 50 K, (e) 60 K and (f) 70 K. Note that pressure measured at 19.5 K is up to 0.7 bar as liquefaction pressure of hydrogen at 19.5 K is 0.78 bar.

Figure 5.33 Deuterium adsorption and desorption isotherms of Py@COF-1: closed symbol is adsorption and open symbol is desorption at various temperature at (a) 19.5 K, (b) 30 K, (c) 40 K, (d) 50 K, (e) 60 K and (f) 70 K. Note that pressure measured at 19.5 K is up to 0.2 bar as liquefaction pressure of deuterium at 19.5 K is 0.27 bar.
Raman spectroscopy

The Raman spectra were taken in backscattering geometry in a JobinYvon LabRam 1800 single-grating spectrometer equipped with a razor-edge filter and a Peltier-cooled CCD camera. A linearly polarized He"/Ne" mixed-gas laser with a wavelength of 632.817 nm are used for excitation. The laser beam was focused through a 50x microscope objective to a ~ 5 μm diameter spot on the sample surface. The power of the incident laser was kept less than 1 mW to avoid laser-induced heating. In order to determine the precise phonon frequencies at every temperature, Ne emission lines were recorded between all measurements. For data analysis, Bose-Einstein thermal factor \( (n(\omega) = \text{Bose-Einstein factor}) \) was considered for all data and all phonon peaks were fitted by Lorentzian profiles, convoluted with the spectrometer resolution function (a Gaussian line of 2 cm\(^{-1}\) full width at half maximum (FWHM)).

\[
[n(\omega) + 1] = [1 - e^{-\frac{h\omega}{k_B T}}]^{-1}
\]

where \( h \) is Planck constant, \( \omega \) is Raman shift and \( k_B \) is Boltzmann constant.

![Raman Spectra](image)

Figure 5.34 Room temperature Raman spectra on powdered Py@COF-1 and COF-1 with the phonon frequencies in Pyridine from Ref. 125.

Room temperature Raman spectra of Py@COF-1, COF-1 and Pyridine molecule (Py) are presented in figure 5.34 and compared in the mode range between 50 cm\(^{-1}\) and 3200 cm\(^{-1}\). Spectra have been
corrected by Bose-Einstein thermal factor and normalized by the maximum intensity of phonon at ~1600 cm\(^{-1}\). The inset in figure 5.34 shows the Raman spectra for low frequency. It clearly shows that the phonon modes at 50 cm\(^{-1}\) and 100 cm\(^{-1}\) of Py@COF-1 are not visible on pristine COF-1 and molecular pyridine. Thus, these modes may originate from the coupling between decorated pyridine molecules and COF-1 frameworks.

**Cryogenic thermal desorption spectroscopy (TDS) for physisorption study**

Desorption spectra of H\(_2\)/D\(_2\) isotope mixture have been recorded for Py@COF-1 by employing a home-built thermal desorption spectroscopy (TDS) apparatus, which is calibrated for H\(_2\) and D\(_2\) (see procedure details in chapter 3.3.3). Figure 5.35 and 5.36 show H\(_2\) and D\(_2\) TDS spectra of Py@COF-1 for various loading pressures (1 mbar - 26 mbar) and exposure temperatures, T\(_{\text{exp}}\), (22 K - 70 K) in the desorption temperature, T, range between 20 and 100 K, above 100 K no significant desorption of hydrogen isotopes is occurring. Note that one mixture measurement of TDS at given temperature and pressure provide each H\(_2\) and D\(_2\) signal individually, and the H\(_2\) (figure 5.35) and D\(_2\) (figure 5.36) signals are presented separately to show the dependence of loading temperature and pressure. For all of the measurements the area under the desorption curve, which is directly proportional to the amount of molecules, is significantly higher for D\(_2\) than for H\(_2\).

The desorption study of physisorbed molecular hydrogen usually provides information on the binding energies of molecular species adsorbed on a solid surface. Thus, strong interactions of the hydrogen molecule with the adsorbent desorb at relatively high temperature, and a weak interaction of the hydrogen molecule with the adsorbent desorb at relatively low temperature. Moreover, if different adsorption sites exist inside porous material, only strong adsorption sites are occupied first after loading at very low pressure, whereas additional maxima at lower desorption temperature appear for higher loading pressures, indicating that weaker adsorption sites are additionally occupied for higher hydrogen uptake\(^{34}\). Namely, TDS spectra typically show the sequential filling from strong (high desorption T) to weak (low desorption T) adsorption sites, exhibiting one, two or multiple maxima.

However, H\(_2\) and D\(_2\) TDS spectra of Py@COF-1 shown in figure 5.35 and 5.36 vary in shape, magnitude and desorption temperature depending on the exposure temperature and loading pressure. This is contrary to what is expected for the sequential filling of adsorption sites by physisorption. For instance, in the H\(_2\) and D\(_2\) spectra for different loading pressure and exposure temperature (T\(_{\text{exp}}\)
(figure 5.35 and 5.36), the desorption maximum is shifted to higher desorption temperatures for higher exposure temperature. Furthermore, the amount of desorbed D₂ (figure 5.36) is increasing with rising pressure up to $T_{\text{exp}} = 40$ K. In contrast, the H₂ uptake (figure 5.35) is decreasing with rising pressure at $T_{\text{exp}} = 22$ and 30 K and at $T_{\text{exp}} = 40$ K the uptake shows a minimum at 7 mbar.

![Loading pressure diagram](image)

Figure 5.35 Thermal desorption spectra of hydrogen on Py@COF-1 with heating rate 0.1 K/s. H₂ desorption rate after loading with a 1:1 H₂/D₂ mixture for pressures of 1 mbar, 3 mbar, 7 mbar, 14 mbar and 26 mbar) and loading temperatures of 22 K (square black), 30 K (circle red) 40 K (triangle blue), 50 K (inverse triangle green), 60 K (diamond pink) and 70 K (side triangle orange). Note that one mixture measurement of TDS at given temperature and pressure provide each D₂ and H₂ signal individually, and the D₂ and H₂ signals are presented separately to show the dependence of loading temperature and pressure. (figure 5.35 and 5.36)
5.4.2. Discussion

Gas adsorption BET measurements performed on the Py@COF-1 show that neither N\textsubscript{2} at 77 K (figure 5.19) nor H\textsubscript{2} at 19.5 K (figure 5.20) can penetrate Py@COF-1 whereas the parent COF-1 (figure 5.7 and 5.28) is fully accessible for these molecules. This indicates that the incorporating pyridine molecule (Py) in the pore walls of COF-1 (Py@COF-1), and thereby reducing aperture size, produces the highly dense structure. An analysis of the isotherms results in BET areas of 20.5 m\textsuperscript{2}/g and 48 m\textsuperscript{2}/g.
applying N\textsubscript{2} and H\textsubscript{2}, respectively, implying the blocked apertures as theoretically evident from the dense structure (figure 5.17).

**Cryogenically flexible Py@COF-1**

Excess hydrogen storage capacity of Py@COF-1 is examined by high-pressure isotherms up to 20 bar. For 77 K, hydrogen uptake of Py@COF-1 shows around 0.5 wt% at 20 bar (figure 5.21a). Thus, based on linear relationship between excess hydrogen uptake and SSA (also known as Chahine’s rule: 1 wt% per 500 m\textsuperscript{2}/g), the specific surface area of Py@COF-1 can be estimated to about 250 m\textsuperscript{2}/g at 77 K. However, an analysis of the low pressure H\textsubscript{2} isotherm results in BET surface area of 48 m\textsuperscript{2}/g at 19.5 K (figure 5.20). This discrepancy indicates the high accessibility of hydrogen ‘only’ at high temperature (77 K), whereas at 19.5 K the hydrogen cannot access the highly dense structure of Py@COF-1. In addition, a varying degree of hysteresis and adsorbed amount in low pressure isotherms (figure 5.32 and 5.33) might also indicate changes in the effective aperture size experienced by the adsorbate, implying a flexible aperture of Py@COF-1.

A close comparison of the Raman spectra between Py@COF-1 and pristine COF-1 also supports the cryo-flexible nature caused by Py molecules. A low energy Raman active phonon modes (50 cm\textsuperscript{-1} and 100 cm\textsuperscript{-1}) which can originate neither from the free Py nor pristine COF-1 is carefully analyzed. The phonon mode at 50 cm\textsuperscript{-1} of Py@COF-1 sample for selected temperatures are displayed in figure 5.37, and the temperature dependence of the mode frequency is inset in figure 5.37 with the fit following a conventional phonon anharmonic model, \textit{i.e.} decay into two acoustic modes with identical frequencies and opposite momenta\textsuperscript{126,127}

\[
\omega_{ph}(T) = \omega_b - C \left[1 + \frac{2}{e^{\frac{\hbar \omega}{k_B T}} - 1}\right]
\]

where C is a positive constant in phonon anharmonic model, \(\omega_b\) is the bare phonon frequency.

The 50 cm\textsuperscript{-1} phonon mode hardens with decreasing temperature down to 30 K, and then softens down to the base temperature of 10 K (figure 5.37). The observed phonon softening implies a redistribution of the electronic state at below 30 K which predominantly contributes the phonon self-energy, suggesting a re-orientation of the Py molecule with respect to the backbone of COF-1. Consequently, this close comparison of the Raman spectra between Py@COF-1 and pristine COF-1 provides the
additional confirmation of the cryogenically flexible nature caused by Py molecules. Owing to this unique phenomenon, the hysteresis in isotherms starts to be observed at 30 K until the reversible isotherm appears at 70 K due to the fully open aperture for hydrogen. (Note that it was unfortunately not able to make a fit with a single Lorentzian profile for 100 cm\(^{-1}\) phonon mode which might be caused by an overlap of several peaks.)

It should be also noted that flexible frameworks reported in literature are typically accompanied by a volume change of the framework (e.g., structural deformation of MIL-53), whereas the flexibility described in here implies only a kinetic effect caused by the pyridine molecules in the pore (no structural deformation).

![Figure 5.37 The phonon mode at 50 cm\(^{-1}\) of Py@COF-1 sample for selected temperatures. Gray dots are the raw data, and black line is the fit following the procedure described in the text. Phonon intensity has been normalized and the spectra have been shifted vertically for clarity. The inset shows the temperature dependence of the mode frequency and the red line is the result of a conventional phonon anharmonic model. Note the anomalous frequency softening below 30 K.](image)

**Adsorption molar ratio**

From the pure gas isotherms (figure 5.32 and 5.33), the D\(_2\)/H\(_2\) molar ratios are assessed (figure 5.38b), and compared with pristine COF-1 (figure 5.38a). For the pristine COF-1, the highest molar ratio is only observed at near zero coverage pressure and decays rapidly for higher pressures. In contrast, for Py@COF-1 the molar ratio shows a maximum at about one order of magnitude higher pressures for
temperatures between 19.5 K and 40 K. Therefore, incorporating pyridine molecules (Py) in the pore walls of COF-1 enhanced the molar ratio at higher pressures.

Figure 5.38 (a) The molar adsorption ratio \( n_{D_2}/n_{H_2} \) of pristine COF-1 in pressure range of 0 - 1 bar and temperature range of 19.5 K - 40 K. (b) The molar adsorption ratio \( n_{D_2}/n_{H_2} \) of Py@COF-1 in pressure range of 0 - 1 bar and temperature range of 19.5 K - 40 K. The yellow dotted line is to guide the eye.

\[ D_2 \text{ selectivity for } H_2/D_2 \text{ isotope mixture} \]

The \( D_2 \) selectivity is directly investigated for a \( H_2/D_2 \) isotope mixture by employing TDS apparatus (see procedure details in chapter 3.3.3). Figure 5.39 shows \( H_2 \) and \( D_2 \) TDS spectra of Py@COF-1 for 26 mbar loading pressure (sampling from figure 5.35 and 5.36) in the desorption temperature, \( T \), range between 20 and 100 K. For the lowest exposure temperature \( (T_{exp}) = 22 \) K, the \( D_2 \) spectrum shows the highest desorption rate at \( T = 25 \) K, which can be assigned to liquid deuterium or \( D_2 \) weakly adsorbed in multilayers.\(^{93}\) For higher exposure temperatures the spectrum is shifted to higher desorption temperatures. The missing low temperature part of the spectrum is simply caused by desorption of weakly adsorbed molecules already during the evacuation at \( T_{exp} \). In accordance with the observations of hysteresis in the pure gas isotherms, an increase of desorption temperature with \( T_{exp} \) can be attributed to the flexible nature of the framework, which eventually gives different effective apertures.
(pore opening phenomenon) at each $T_{\text{exp}}$ and thereby increasing accessibility for gas molecules (figure 5.40).

![Figure 5.39 H\text{2} and D\text{2} TDS spectra (heating rate 0.1 K/s) of Py@COF-1 after exposure to a 26 mbar 1:1 H\text{2}/D\text{2} mixture for different exposure temperature ($T_{\text{exp}}$) = 22 K (square black), 30 K (circle red) 40 K (triangle blue), 50 K (inverse triangle green), 60 K (diamond pink) and 70 K (side triangle orange).](image)

From TDS, the direct mixture selectivity can be determined from the ratio of desorbed amount of D\text{2} over H\text{2} ($S_{D2/H2}$). The selectivity for 1:1 D\text{2}/H\text{2} mixture (figure 5.26a) is significantly greater than those of molar ratio from pure gas isotherms (figure 5.21b). This is because (i) the heavier D\text{2} favors to adsorb on the surface due to the mass difference$^{67}$; and (ii) D\text{2} diffuses faster compared to the H\text{2} through the cryogenically flexible aperture (which maximizes the quantum sieving effect) into the nanoporous material at low temperatures$^{11}$. Owing to these two effects, $S_{D2/H2}$ at $T_{\text{exp}} < 30$ K increases with loading pressure and reaches to $S_{D2/H2} = 9.7 \pm 0.9$ at 26 mbar. Table 5.3 summarizes the $S_{D2/H2}$ value for all exposure temperatures and pressures of 1 to 26 mbar. The high selectivity at $T_{\text{exp}} < 30$ K can be ascribed to a combined effect of quantum sieving and liquefaction of D\text{2}. The observed selectivity is far more superior compared to commercial cryogenic distillation process ($S_{D2/H2} \sim 1.5$ at 24 K$^{59}$). Eventually $S_{D2/H2}$ drops down to 3.1 $\pm$ 0.5 at 70 K, but its selectivity and amount of adsorbed D\text{2} (figure
5.41b) are still comparable to the Niimura et al.‘s result which is very recently reported highest experimental value. They investigated quantum sieving effects in zeolite and carbon-based materials, and their dynamic D$_2$ selectivity of 3.05 with adsorbed capacity of 0.2 mmol/g at 77 K are achieved in MS13X zeolite. Finally, the relatively high selectivity ($S_{D_2}/H_2 \sim 5.4 \pm 0.8$) combined with large D$_2$ uptake (~ 0.7 mmol/g) at $T_{exp} = 40$ K (figure 5.41b) indicates the optimum condition of the cryogenically flexible aperture for quantum sieving.

Figure 5.40 Illustration of the flexible nature of the framework. It gives different effective apertures at each $T_{exp}$ (pore opening phenomenon) and thereby increasing accessibility for gas molecules.
Figure 5.41 a) Thermal Selectivity as a function of loading pressure for different $T_{exp}$. b) $T_{exp}$ dependence of the highest selectivity and corresponding adsorbed $D_2$ amount. (Corresponding pressures of selectivity are shown in the table 5.3)

Table 5.3 Separation performance ($S_{D_2/H_2}$) of the equimolar $D_2/H_2$ mixture at given exposure temperature and loading pressure

<table>
<thead>
<tr>
<th>Pressure [mbar]</th>
<th>22K</th>
<th>30K</th>
<th>40K</th>
<th>50K</th>
<th>60K</th>
<th>70K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.1 ± 0.2</td>
<td>2.4 ± 0.1</td>
<td>2.5 ± 0.4</td>
<td>2.0 ± 0.2</td>
<td>1.9 ± 0.2</td>
<td>2.1 ± 0.3</td>
</tr>
<tr>
<td>3</td>
<td>3.7 ± 0.3</td>
<td>3.3 ± 0.2</td>
<td>3.2 ± 0.5</td>
<td>2.6 ± 0.2</td>
<td>2.5 ± 0.3</td>
<td>2.6 ± 0.4</td>
</tr>
<tr>
<td>7</td>
<td>5.6 ± 0.5</td>
<td>5.4 ± 0.3</td>
<td>5.4 ± 0.8</td>
<td>3.4 ± 0.3</td>
<td>2.6 ± 0.3</td>
<td>2.9 ± 0.4</td>
</tr>
<tr>
<td>14</td>
<td>7.4 ± 0.7</td>
<td>7.1 ± 0.4</td>
<td>4.5 ± 0.7</td>
<td>3.8 ± 0.3</td>
<td>2.9 ± 0.4</td>
<td>2.9 ± 0.4</td>
</tr>
<tr>
<td>26</td>
<td>9.7 ± 0.9</td>
<td>7.9 ± 0.4</td>
<td>4.1 ± 0.6</td>
<td>3.4 ± 0.3</td>
<td>3.3 ± 0.4</td>
<td>3.1 ± 0.5</td>
</tr>
</tbody>
</table>

Please note that the values in red box are shown in figure 5.41b.
5.5. Chemical affinity sieving exploiting the attractive open metal sites

Despite many theoretical suggestions on the quantum sieving, almost all physisorptive porous materials that have been examined at 77 K exhibited a rather low isotope separation factor (table 2.1). Hence, as alternative to quantum sieving, it is also possible to exploit the difference in the zero point energy for the adsorbed isotopes for hydrogen isotope separation. Since the different molecular masses imply different zero point energies (ZPE), and thereby different adsorption enthalpies \( \Delta H \), this significant \( \Delta H \) could result in appreciable selectivity even at liquid nitrogen temperature (77K) and above. Therefore, CPO-27-Co possessing numerous strong adsorption sites is investigated as the strong attraction between the unsaturated Co(II) centers and hydrogen keeps these sites occupied at relatively high temperature, and that may result in high separation factor even above 77 K.

5.5.1. Results

Low-pressure, high-resolution \( \text{H}_2 \) and \( \text{D}_2 \) adsorption isotherms

The pure \( \text{H}_2 \) and \( \text{D}_2 \) gas adsorption isotherms of CPO-27-Co are measured at various temperatures between 19.5 K and 70 K (figure 5.42). Fully reversible type I isotherms without hysteresis have been observed, indicating a highly microporous material and no kinetic diffusion hindrance. The corresponding saturation uptake for \( \text{H}_2 \) and \( \text{D}_2 \) adsorption at 19.5 K is 17.8 mmol/g (0.7 bar) and 20.0 mmol/g (0.2 bar), respectively. The steep initial increase at low pressure implies a strong affinity of the material for \( \text{H}_2 \) and \( \text{D}_2 \). As clearly shown in figure 5.42, the adsorbed amount of \( \text{D}_2 \) is always higher than that of \( \text{H}_2 \). This phenomenon caused by mass difference has been also observed for other porous frameworks (ZIFs and COFs), and explained already in the foregoing chapter 5.3.2.
Figure 5.42 High resolution low pressure D$_2$ (open symbols) and H$_2$ (filled symbols) adsorption isotherms for CPO-27-Co at various temperatures, i.e. a) 19.5 K (black square), 40 K (blue triangle), 60 K (pink diamond) and b) 30 K (red circle), 50 K (green inverse-triangle), 70 K (orange side-triangle).

Figure 5.43 High isosteric heat of hydrogen (black) and deuterium (red) adsorption for CPO-27-Co as function of the surface coverage. The solid lines are polynomial fits of H$_2$ and D$_2$ heats of adsorption.

**Enthalpy of adsorption**

Applying the Clausius-Clapeyron equation, the isosteric heat of adsorption has been calculated by using the adsorption isotherms at different temperatures from 19.5 K to 70 K as function of surface coverage normalized by saturation uptake at 19.5 K. For clarity, a 4$^{th}$ order polynomial fit (solid line in
figure 5.43) of the H\textsubscript{2} and D\textsubscript{2} enthalpies as function of coverage has been applied. The analysis of the D\textsubscript{2} and H\textsubscript{2} adsorption enthalpies gives different maximum values of 7.3 kJ/mol and 6.1 kJ/mol at ~15 % coverage, respectively. With increasing H\textsubscript{2} or D\textsubscript{2} loading, both adsorption enthalpies decrease and eventually converge to the same value (2 kJ/mol at 90 % coverage). The adsorption enthalpy calculation below ~15 % coverage (ca. 2~3 mmol/g) is limited due to the sudden high initial uptake at T < 40 K caused by strong interaction with the metal sites at low pressures. Thus, high temperature (77 K ~ 125 K) H\textsubscript{2} isotherms are additionally measured. The hydrogen heat of adsorption at low coverage is found to be slightly higher than 10 kJ/mol (see figure 5.44) which is in good agreement with literature values\textsuperscript{122,128}.

![Figure 5.44](image)

**Figure 5.44** a) Absolute hydrogen uptake in CPO27-Co at temperatures between 77 K and 125 K. b) Isosteric heat of hydrogen adsorption for CPO27-Co.

**Cryogenic thermal desorption spectroscopy (TDS) for physisorption study**

In order to identify preferred adsorption sites on CPO-27-Co and to estimate the adsorption strength at these sites, the cryogenic TDS measurements are performed after exposure to pure H\textsubscript{2} and D\textsubscript{2} atmospheres under identical experimental conditions (see procedure details in chapter 3.3.3). Figure 5.45 shows the H\textsubscript{2} and D\textsubscript{2} desorption spectra in the range of 17 K to 140 K, recorded with a heating rate of 0.1 K/s. In accordance with pure gas isotherms, the pure D\textsubscript{2} TDS signal is higher than that for H\textsubscript{2}. By integration of the area under the desorption curve, the total amount of desorbed H\textsubscript{2} and D\textsubscript{2} can be determined to be 16.0 mmol/g and 18.7 mmol/g, respectively.
As already explained in the foregoing chapter 5.4.1, the sequential gas filling from strong to weak adsorption sites is typically observed in the TDS measurements. The occurrence of three desorption maxima in both H\textsubscript{2} and D\textsubscript{2} desorption spectra (figure 5.45) points to the existence of three energetically different adsorption sites. Liu et al.\textsuperscript{129} investigated hydrogen adsorption site in unsaturated metal centers in MOFs (CPO-27) on different deuterium gas loading at 30 K by neutron powder diffraction experiments. They identified 3 different hydrogen adsorption sites on CPO-27 (figure 5.46). The strongest adsorption site (Site I) is offered by the unsaturated metal cluster and is filled first. This is followed by adsorption site II which is on the top of the triangle of oxygen atoms. With increasing gas loading, adsorption site III gets further occupied which is on the top of the benzene ring. By comparison with neutron powder diffraction measurements, therefore, each maximum in TDS can be directly assigned to an adsorption site in the CPO-27-Co framework (as the adsorption strength decreases along the series; open metal site > triangle of oxygen atoms > benzene ring, see figure 5.45). Furthermore, the D\textsubscript{2} spectrum is slightly shifted to higher desorption temperatures compared to the H\textsubscript{2} spectrum, indicating the difference of binding energy between the two molecules and the host surface (e.g. D\textsubscript{2}–surface interaction is higher than H\textsubscript{2}–surface interaction).

Figure 5.45 Pure gas H\textsubscript{2} and D\textsubscript{2} thermal desorption spectra of CPO-27-Co with 0.1 K s\textsuperscript{-1} heating rate. With help of neutron powder diffraction measurements, CPO-27-Co identifies the three adsorption sites.
Figure 5.46 Left: Identification of the three adsorption sites on CPO-27-Co. Site I is the metal site, site II is the triangle of oxygen atoms and site III is the benzene ring. Right: Adsorption sites along the x axis

TDS spectra for H_2/D_2 isotope mixture

Desorption spectra after exposure to a 1:1 H_2/D_2 isotope mixture have been recorded for CPO-27-Co (see procedure details in chapter 3.3.3). Figure 5.47 show H_2 and D_2 mixture TDS spectra of CPO-27-Co for various loading pressures (3 mbar - 60 mbar) and exposure temperatures, T_{exp}, (20 K - 80 K) in the desorption temperature, T, range between 17 and 110 K, above 110 K no significant desorption of hydrogen isotopes is occurring. Note that signals of m/z values of 1 (H) and 3 (HD) were always monitored during entire measurements, but their intensities were negligible compared to m/z values of 2 (H_2) and 4 (D_2) under exposure condition of 20~80 K for 10 min.

As shown in figure 5.47, the hydrogen isotope desorption starts close to T_{exp} as all free molecules are released already during the evacuation process that was carried out at the same temperature. The area under the desorption curve, which is directly proportional to the amount of molecules, is significantly higher for D_2 than for H_2 in all of the measurements. Furthermore, the influence of loading pressure on H_2/D_2 mixture TDS signal was studied especially in the low T (< 60 K) region where two sites (triangle of oxygen atoms and benzene ring) possessing low binding enthalpy of H_2 and D_2 are relevant. For instance, in the H_2 and D_2 spectra for different loading pressure (3-60 mbar) (T_{exp} = 20 ~ 50 K in figure 5.47a-d), the D_2 signal gets stronger with increasing loading pressure at T < 60 K, whereas the reverse is the case for the H_2 signal. Regardless of the applied pressure, however, D_2 is preferentially occupied at T > 60 K where the open metal sites are relevant.
Figure 5.47 Thermal desorption spectra on CPO-27-Co with heating rate 0.1 K/s at 1:1 H\textsubscript{2}/D\textsubscript{2} mixture loading pressure (3 mbar; inverse triangle green, 10 mbar; triangle blue, 30 mbar; circle red and 60 mbar; square black) for H\textsubscript{2} (line) and D\textsubscript{2} (dot), and loading temperature at; a) 20 K, b) 30 K, c) 40 K, d) 50 K, e) 60 K, f) 70 K and g) 80 K.

Figure 5.48 shows the H\textsubscript{2}, D\textsubscript{2} and total (H\textsubscript{2}+D\textsubscript{2}) gas uptake (integration of the area under the desorption curve in figure 5.47) as a function of T\textsubscript{exp} for different equimolar mixture loading pressure (3-60 mbar). D\textsubscript{2} uptake increases with increasing loading pressure at T\textsubscript{exp} < 60 K while the total uptake
remains almost constant. At $T_{\text{exp}} \geq 60$ K, $D_2$ uptake and the total uptake almost converge to the each other.

5.5.2. Discussion

The experimental isotherms and TDS analysis indicate that the hydrogen isotope is strongly physisorbed in the framework. Hence, chemisorption can be ruled out as the formation of HD from the $H_2/D_2$ mixtures was not observed at the thermodynamic conditions of the experiments.

Zero point energies (ZPE) for $H_2$ and $D_2$ on CPO-27-Co are qualitatively shown in figure 5.49 by quantum-mechanical adsorption calculation which performed by the group of Prof. Heine. The strength
of each binding site is demonstrated by the depth of potential well. Similar to the experimental observation in TDS, the binding energy and ZPE difference between adsorbed H$_2$ and D$_2$ molecules is highest at the open metal site.

![Diagram showing energy levels for different binding sites.](image)

**Figure 5.49** Qualitative plot of the strength of the adsorption sites. Zero point energies are shown qualitatively for H$_2$ (line) and D$_2$ (dotted line). The strength of each binding site is demonstrated by the depth of potential well.

**Adsorption molar ratio**

From pure gas adsorption isotherms (figure 5.42), the D$_2$/H$_2$ molar ratio can be directly determined as a function of temperature and pressure (figure 5.48). To test our hypothesis on the role of the open metal sites, the molar ratio of CPO-27-Co is compared to a covalent-organic framework (COF-1), possessing similar pore size (9 Å) and no open metal sites. For both materials, the highest D$_2$/H$_2$ molar ratio is observed at near zero coverage pressure decaying rapidly for higher pressures. In case of COF-1, however, the molar ratio is increasing with decreasing temperature, whereas the reverse is the case of CPO-27-Co.

In general, the quantum sieving effect is more evident at lower temperature as shown in figure 5.50b (COF-1), but an increase of molar ratio with temperature as shown in figure 5.50a (CPO-27-Co) indicates that the D$_2$/H$_2$ molar ratio strongly related to the coverage of the adsorption sites which is function of pressure and temperature. As a result, hydrogen isotope adsorption on CPO-27-Co at high temperature with low pressures is mostly relevant to the open metal sites, yielding the maximum D$_2$/H$_2$
molar ratio of 7 at near zero coverage pressure and 70 K. To the best of our knowledge this is the highest experimental value at this relatively high temperature reported to date.

Figure 5.50 Comparison of the molar ratio \( \left( \frac{n_{D_2}}{n_{H_2}} \right) \) at temperature range of 19.5 K - 70 K and pressure range of 0 - 1 bar. a) CPO-27-Co (aperture: 10 Å) and b) COF-1 (aperture: 9 Å).

**D\(_2\)** selectivity for H\(_2\)/D\(_2\) isotope mixture

The D\(_2\) selectivity in equimolar isotope mixture is directly measured in TDS experiments. Figure 5.51 shows H\(_2\) and D\(_2\) TDS spectra of CPO-27-Co after an exposure to 30 mbar of a 1:1 H\(_2\)/D\(_2\) mixture at \( T_{\text{exp}} \) of 30 K to 60 K (sampling from figure 5.47). The desorption starts close to \( T_{\text{exp}} \) as all free molecules are released already during the evacuation process that was carried out at the same temperature. For all measurements the area under the D\(_2\) desorption curve is remarkably higher than that below the H\(_2\) counterpart, and their ratio is directly reflecting the selectivity. Since the binding enthalpy of H\(_2\) and D\(_2\) at two sites (triangle of oxygen atoms and benzene ring) is rather weak, H\(_2\) and D\(_2\) desorption at these sites mostly occurs below 60 K (figure 5.51a-d). The enthalpy difference between D\(_2\) and H\(_2\) is significantly greater at strong adsorption sites, i.e., at the open metal sites. Those are the only sites with relevant occupation at high desorption temperature, \( T \), (\( T > 60 \) K in figure 5.49a-d). Under an equimolar isotope mixture atmosphere, open metal sites are predominantly occupied by D\(_2\), and therefore afterwards only a D\(_2\) desorption signal can be observed.
Figure 5.51 H₂ (black, filled symbols) and D₂ (red, open symbols) desorption spectra of 30 mbar (1:1 H₂/D₂ mixture) loading on CPO-27-Co with a heating rate of 0.1 K/s. Exposure temperature (T_{exp}) at a) 30 K, b) 40 K, c) 50 K and d) 60 K.

Figure 5.52 shows the selectivity, S_{D₂/H₂}, of CPO-27-Co and their corresponding adsorbed D₂ amount after exposure to 30 mbar of a 1:1 H₂/D₂ mixture as function of T_{exp}. In accordance with high molar ratio at 70 K and zero coverage pressure determined from pure gas isotherms (figure 5.50), the TDS experiments also show a high S_{D₂/H₂} at high exposure temperature, T_{exp} ≥ 60 K. It is clear that S_{D₂/H₂} at T_{exp} ≤ 50 K is less than 4 due to the little difference between D₂ and H₂ adsorption enthalpies at weak binding sites, whereas S_{D₂/H₂} at T_{exp} ≥ 60 K, thus governed by the strong binding sites, increases dramatically and reaches the highest values of 11.8 ± 1.3 at T_{exp} = 60 K. Although at T_{exp} = 80 K S_{D₂/H₂} decreases to 6.3 ± 0.6 and the amount of adsorbed D₂ gets relatively smaller to 1.3 mmol/g, it is still the highest value ever reported above liquid nitrogen temperature, and far more superior compared to the commercial cryogenic distillation process (S_{D₂/H₂} ~ 1.5 at 24 K^{(28)}). Table 5.4 summarizes the S_{D₂/H₂} values for all exposure temperatures and pressures ranging from 3 to 60 mbar.

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Equimolar hydrogen isotopes mixture (30 mbar) selectivity as a function of $T_{\text{exp}}$ and its corresponding amount of adsorbed D$_2$.

Based on the significantly enhanced selectivity, 3 cycles of a temperature swing (range of 80 K - 110 K) separation process have been experimentally simulated. Since the natural abundance of deuterium is much lower than in a 1:1 D$_2$/H$_2$ ratio, a mixture containing only 5 % D$_2$ has been prepared. Thus, a 5:95 D$_2$/H$_2$ mixture is exposed to CPO-27-Co above liquid nitrogen temperature. After evacuation the adsorbed gas is desorbed by increasing the temperature to 110 K showing already a D$_2$ concentration of almost 80 % after this first cycle. For the second cycle the samples were exposed to this D$_2$ enriched mixture and likewise for the third cycle. The result is presented in Figure 5.53, showing clearly that within only 3 separation cycles D$_2$ is enriched from 5 % to 95 %. Indeed, this result demonstrates the strong capability of CPO-27-Co for a practical application of hydrogen isotope separation.
Figure 5.3 Development of D₂ Mole fraction (%) in 5% D₂ / 95% H₂ mixture as an initial bulk concentration at T_{exp} = 80 K and 30 mbar as function of separation cycle.

Table 5.4 Experimental separation performance (S_{D₂/H₂}) of the equimolar D₂/H₂ mixture at given exposure temperature (T_{exp}) and loading pressure (mbar)

<table>
<thead>
<tr>
<th>T_{exp} (K)</th>
<th>60 mbar</th>
<th>30 mbar</th>
<th>10 mbar</th>
<th>3 mbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.4 ± 0.0</td>
<td>3.0 ± 0.0</td>
<td>1.9 ± 0.3</td>
<td>1.0 ± 0.0</td>
</tr>
<tr>
<td>30</td>
<td>4.8 ± 0.3</td>
<td>3.7 ± 0.2</td>
<td>2.2 ± 0.3</td>
<td>1.0 ± 0.0</td>
</tr>
<tr>
<td>40</td>
<td>5.5 ± 0.5</td>
<td>4.5 ± 0.6</td>
<td>2.6 ± 0.5</td>
<td>1.2 ± 0.0</td>
</tr>
<tr>
<td>50</td>
<td>6.0 ± 1.0</td>
<td>4.5 ± 0.5</td>
<td>2.9 ± 0.3</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>60</td>
<td>12.5 ± 1.3</td>
<td>11.8 ± 1.3</td>
<td>5.8 ± 1.0</td>
<td>3.9 ± 1.5</td>
</tr>
<tr>
<td>70</td>
<td>8.2 ± 0.6</td>
<td>8.4 ± 0.3</td>
<td>5.5 ± 0.4</td>
<td>4.0 ± 0.2</td>
</tr>
<tr>
<td>80</td>
<td>6.1 ± 0.6</td>
<td>6.3 ± 0.6</td>
<td>5.4 ± 0.7</td>
<td>4.9 ± 0.6</td>
</tr>
</tbody>
</table>

H₂/D₂ separation in MOFs for Industrial application

Based on the experimental results obtained so far, a deuterium enrichment process that could be directly applied in industrial applications is proposed (figure 5.34). The procedure as follows;

In natural hydrogen gas, a very low content of D₂ is existed. So deuterium will occur predominantly as HD. From theoretical calculation performed by the group of Prof. Heine (figure 5.35), CPO-27-Co also shows a high HD selectivity over H₂. Thus, using a temperature-swing process, the gas covering the
MOF surface is released into a new reservoir (step I in figure 5.34). Repeating this process, HD is purified within 8 cycles at 77 K from an initial concentration of 1% (figure 5.35).

It has been reported that the open metal sites activate hydrogen molecules and thus are capable of isotope exchange reactions\textsuperscript{130}. Thus, the nearly pure HD gas can be catalytically converted to a statistical distribution of H\textsubscript{2}/HD/D\textsubscript{2} as 1:2:1 in an isotope exchange reaction, e.g. in CPO-27-Co at sufficiently high temperature, or on any other hydrogen activating catalyst (step II in figure 5.34).

Finally, this 1:2:1 mixture of H\textsubscript{2}/HD/D\textsubscript{2} is separated in only few cycles using the same material (step III in figure 5.34). HD is recycled for catalytic conversion, and D\textsubscript{2} is separated as product.

Figure 5.34 Suggested procedure for an industrial deuterium production process. Flue gas with enriched deuterium content (predominantly present as HD) is purified in several cycles to HD. This gas is catalytically transformed and produces a 25% D\textsubscript{2} fraction. The pure D\textsubscript{2} product is again separated in CPO-27.

Figure 5.35 Theoretical calculation for cyclical selection of HD over H\textsubscript{2} starting with typical concentration of HD 1 % as in an industrial process.
5.6. Conclusion

Structure-property relationship for isotope separation

- The fundamental correlation between $D_2/H_2$ molar ratio and pore size in the temperature range of 19.5 K - 70 K and pressure range of 0 - 1 bar has been investigated by using various porous frameworks (ZIF-7, -8 and COF-1, -102).

- The $D_2/H_2$ molar ratio is strongly dependent on pore size, temperature and pressure. (The molar ratio increase typically at lower temperature and near zero pressure coverage.)

- The experimentally determined optimum pore diameter for quantum sieving lies between 3.0 Å and 3.4 Å. Moreover, for a pore diameter of 3.4 Å, a high $D_2/H_2$ molar ratio (~11) can be observed at 20 K and near zero pressure coverage.

Optimization of aperture for quantum sieving

- Pyridine decorated COF-1 (Py@COF-1) is successfully synthesized using a Lewis base approach.

- This material possesses a highly dense packing structure with pyridine molecules attached on the pore walls of COF-1, reducing the aperture size and pore volume.

- Hydrogen adsorption measurement at 19.5 K and 77 K show an increase of the accessible surface are from 48 m$^2$/g to 250 m$^2$/g, indicating the hydrogen cannot penetrate this dense structure of Py@COF-1 at 19.5 K. Moreover, the phonon softening in Raman spectroscopy and a varying degree of hysteresis in low pressure isotherms indicate changes in the effective aperture size experienced by the adsorbate, implying a flexible aperture of Py@COF-1.

- Due to the flexible aperture of the framework, the pore diameter is optimized for quantum sieving and a high selectivity for 1:1 $D_2/H_2$ mixture is observed.

- The relatively high selectivity ($S_{D2/H2} \sim 5.4$) combined with large $D_2$ uptake (~ 0.7 mmol/g) at a exposure temperature of 40 K indicates the optimum condition of the cryogenically flexible aperture for quantum sieving.
Chemical affinity sieving exploiting open metal sites

- CPO-27-Co possessing strong binding sites (~10 KJ/mol for hydrogen on open metal sites) has been experimentally investigated for isotope separation.

- Direct TDS comparison between D₂ and H₂ desorption peak assigned to the open metal sites shows that the D₂ spectrum is shifted to higher desorption temperatures compared to the H₂ spectrum, indicating a difference of binding energy between the two isotopes.

- Due to the different molecular masses, the hydrogen isotopes adsorb on open metal sites with different affinities, i.e. different adsorption enthalpies of the isotopes. Moreover, this strong attraction between the unsaturated Co(II) centers and hydrogen keeps these sites occupied at relatively high temperature (even above 77 K). Therefore, strong binding sites lead to large adsorption enthalpy differences that result in high separation factors at temperatures above 77 K.

- At an exposure temperature of 60 K with 30 mbar in CPO-27-Co, 1:1 D₂/H₂ mixture selectivity of 12 is the highest value ever measured, and this strategy (exploiting open metal sites) shows extremely high separation efficiencies even above 77 K.

- Remarkably, CPO-27-Co can enrich very efficiently from low (5% D₂ : 95% H₂ isotope mixtures) to high D₂ concentrated isotope mixtures (95% D₂ : 5% H₂) within only 3 separation steps at a practical temperature of 80 K (S_{D₂/H₂} of ~ 6.3 ± 0.6).
6. References


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Publication List


9. S. B. Kalidindi†, H. Oh†, M. Hirscher, C. Wiktor, G. V. Tendeloo, D. Esken and R. A. Fischer, “Metal@COFs: Covalent organic frameworks as templates for Pd nanoparticles and hydrogen storage properties of Pd@COF-102 hybrid material”, Chemistry - A European Journal, Vol. 18, Issue 35, 10848-10856, 2012 (Frontispiece Cover Article) († These authors contributed equally to this work: co-first authors)