

**Gas Adsorption and Diffusion in Porous Coordination Networks:
A Computational Study**

by

Tuğba Nur Öztürk

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Tuğba Nur Öztürk

and have found that it is complete and satisfactory in all respects,
and that any and all revisions required by the final
examining committee have been made.

Committee Members:

Seda Keskin Avcı, Ph. D. (Advisor)

Ersin Yurtsever, Ph. D.

Murat Sözer, Ph. D.

Date:

ABSTRACT

Adsorbents and membranes play a significant role in energy efficient gas separations. Higher energy costs in recent decades have made the adsorption- and membrane-based gas separation processes even more economically competitive with traditional separation methods. Adsorbents having high selectivity and working capacity are needed for effective adsorption-based separation processes. Similarly, membranes exhibiting high selectivity and high gas permeability are required to lower the cost of large scale membrane-based gas separation processes. Developing ideal adsorbents and membranes having desired properties has been the main focus of adsorption and membrane research in the world for a very long time.

Porous coordination networks (PCNs) are a new class of crystalline nanoporous materials constructed from metal organic complexes and organic linkers to create highly porous structures with permanent porosity. Their properties, such as tunable pore sizes, large surface areas, high porosities, good chemical and mechanical stabilities, make them attractive in a large variety of applications such as gas storage, catalysis, and gas separation. During synthesis, different combinations of metal ions and organic linkers lead to a large variety of PCN materials. Although a large number of PCNs has been synthesized to date, the potential performance of PCNs for adsorption-based and/or membrane-based gas separation applications is not studied in detailed. There is currently no study in the literature that examines the membrane-based gas separation properties of PCNs which requires information on gas transport properties in PCNs' pores.

In this thesis, atomic simulations are performed to investigate adsorption-based, diffusion-based and membrane-based separation performances of various PCN materials for industrially important gas separations including CH_4/H_2 , CO_2/CH_4 , CO_2/H_2 , CO_2/N_2 and O_2/N_2 mixtures. To evaluate the adsorption-based and membrane-based separation performances of PCNs, important parameters such as adsorption selectivity, working capacity, regenerability, sorbent selection parameter, diffusion selectivity, permeation selectivity and gas permeability are computed. PCNs' separation performance is compared with other nanoporous materials to assess the potential of PCNs as adsorbents and membranes. The effect of charge assignment method on the calculation of separation properties is also studied. Simple models to predict adsorption, diffusion and permeation selectivities are developed. Additionally, PCN-filled

mixed matrix membranes are investigated performing molecular simulations for separating O₂ from N₂.

To conclude, adsorption-based and membrane-based separation performances of PCNs using atomic simulations are examined for the first time in the literature. Results suggest that PCNs offer considerably high potential to be used as adsorbents and membranes for gas separation applications. This study provides simple models to predict adsorption, diffusion and permeation selectivities of PCNs that will be highly useful for quick screening of PCNs for gas separation applications to identify the promising materials. Time, resources and efforts can be then directed to more detailed examination of these promising materials using experimental manners.

ÖZET

Adsorbent ve membranlar enerji verimlilikli kimyasal ayırma işlemlerinde önemli rol oynarlar. Son yıllardaki yüksek enerji maliyetleri, adsorpsiyon ve membran temelli gaz ayırma uygulamalarını diğer ayırma metotlarına oranla ekonomik olarak daha cazip hale getirdi. Adsorpsiyon temelli ayırma işlemleri için yüksek seçiciliğe ve çalışma kapasitesine sahip adsorbentler kullanılmalıdır. Büyük ölçekli membran temelli gaz ayırma işlemlerinin maliyetini düşürmek için ise yüksek seçicilik ve yüksek gaz geçirgenliğine sahip membranlar gereklidir. İstenilen özelliklere sahip ideal adsorbentleri ve membranları geliştirmek hem endüstri hem de akademi için pek çok bilimsel çalışmanın ana odağı olmuştur.

Gözenekli koordinasyon ağları (PCNler), metal organik bileşiklerle organik bağlayıcıların birleşiminden oluşan kalıcı gözeneklere sahip yeni bir tür kristal nano-gözenekli malzemelerdir. Ayarlanabilir gözenek boyutu, yüksek yüzey alanı, yüksek gözeneklilik, iyi kimyasal ve mekanik dayanıklılık gibi özellikler bu malzemeleri gaz depolama, kataliz ve gaz ayırma gibi uygulamalar için cazip hale getirmektedir. Sentez sırasında, metal iyonlar ve organik bağlayıcıların farklı kombinasyonlarda bir araya getirilerek pek çok yeni PCN geliştirilebilir. Günümüzde sentezlenen pek çok PCN olmasına rağmen, bu malzemelerin adsorpsiyon ve membran temelli gaz ayırma uygulamaları için potansiyel performansları detaylı bir şekilde çalışılmamıştır. Literatürde, PCN'lerin gözeneklerinin gaz iletme özelliklerinin de incelenmesini gerektiren membran temelli gaz ayırma performanslarını inceleyen çalışmalar bulunmamaktadır.

Bu tezde, endüstriyel açıdan önemli olan CH_4/H_2 , CO_2/CH_4 , CO_2/H_2 , CO_2/N_2 ve O_2/N_2 gaz karışımları için, pek çok PCN'lerin adsorpsiyon ve membran temelli ayırma performansları atomistik simülasyonlar kullanılarak araştırıldı. Malzemelerin adsorpsiyon ve membran temelli ayırma performanslarını değerlendirmek için, adsorpsiyon seçiciliği, çalışma kapasitesi, yenilenebilirlik, adsorbent seçme parametresi, difüzyon seçiciliği, membran seçiciliği ve gaz geçirgenliği gibi pek çok önemli parametre çalışılan tüm malzemeler ve gaz karışımları için hesaplandı. PCN'lerin performansları iyi bilinen diğer nano-gözenekli malzemelerle karşılaştırıldı. PCN kafesindeki atomlara kısmi elektrik yükü atayan iki farklı yük atama metodunun, yapılan analizlere olan etkisi incelendi. Adsorpsiyon, difüzyon ve membran seçiciliğini tahmin eden basit modeller geliştirildi. Ek olarak, O_2 'yi N_2 'den ayırmak için PCN dolgulu hibrit membranların performansları, moleküler simülasyonlar kullanılarak incelendi.

Özetle, bu çalışmada PCN'lerin adsorpsiyon ve membran temelli gaz ayırma performansları moleküler simülasyonlar uygulanarak incelendi. Bulunan sonuçlar, PCN'lerin adsorbent ve membran olarak gaz ayırma uygulamalarında yüksek potansiyel taşıdığını göstermektedir. Ayrıca, bu çalışmada adsorpsiyon, difüzyon ve membran seçiciliklerini tahmin eden basit modeller geliştirildi. Bu modeller gaz ayırma uygulamaları için ideal PCN adaylarının hızlı taraması yapılırken kullanılabilir. Böylece süre, kaynak ve çalışmalar ideal malzemelerin deneysel olarak daha detaylı incelenmesi için kullanılabilir.

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NOMENCLATURE

A_i : Accessible surface area	ϕ : Fractional pore volume of PCN
A_{surface} : Surface Area	c : Concentration
D_c : Corrected diffusivity	D : Diffusivity
D_s : Self diffusivity	J : Flux
D_t : Transport diffusivity	L : Membrane thickness
k_B : Boltzmann constant	LCD: Largest cavity diameter
K_H : Henry's coefficient	LPD: Limiting pore diameter
M_A : Molecular weight	N : Number of molecules
N^{ads} : Loading at adsorption pressure	P : Pressure or permeability
N^{des} : Loading at desorption pressure	R : Ideal gas constant or correlation coefficient
P_0 : Saturation vapor pressure	$R(\%)$: Regenerability per cent
P_{MMM} : Permeability of MMM	r : Distance between molecule pairs
P_{polymer} : Permeability of polymer	T : Temperature
Q_{st} : Isostatic heat of adsorption	V : Volume
r_0 : Equilibrium distance	C : Coulomb
r_c : Collision diameter	cm: Centimeter
r_f : Diameter of framework atom	g: Gram
r_p : Probe diameter	K: Kelvin
S_{ads} : Adsorption selectivity	kJ: Kilojoules
S_{diff} : Diffusion selectivity	m: Meter
S_{perm} : Permeation selectivity	ns: nanosecond
S_{sp} : Sorbent selection parameter	Pa: Pascal
V_{pore} : Pore volume	ps: Picoseconds
ΔE : Energy barrier	s: Second
ΔN : Working Capacity	Å: Angstrom
ε : Energetic potential parameter	Ar: Argon
ε_0 : Permittivity of free space	CH ₄ : Methane
λ : Ratio of permeabilities of PCN and MMM	CO: Carbon monoxide
μ : Chemical potential	CO ₂ : Carbon dioxide
σ : LJ size parameter	H ₂ : Hydrogen
ϕ : Volume fraction of filler in MMM	N ₂ : Nitrogen
Γ : Thermodynamic correction factor	O ₂ : Oxygen
Λ : Thermal wavelength	

COM: Center of mass
 CBAC: Connectivity-based atom contribution
 CCDC: Cambridge crystallographic data centre
 CPU: Central processing unit
 DDEC: Density derived electrostatic and chemical method
 DFT: Density functional theory
 EMD: Equilibrium molecular dynamics
 EQeq: Extended charge equilibration method
 GCMC: Grand canonical Monte Carlo
 MMM: Mixed matrix membranes
 MOF: Metal organic framework
 NMR: Nuclear magnetic resonance
 PCN: Porous coordination network
 PQEQ: Periodic charge equilibration method
 PFG: Pulsed field gradient
 PSA: Pressure swing adsorption
 REPEAT: Repeating electrostatic potential extracted atomic method
 Qeq: Charge equilibration method
 QM: Quantum mechanics
 STP: Standard temperature and pressure
 TSA: Temperature swing adsorption
 UFF: Universal force field
 VSA: Vacuum swing adsorption
 ZIF: Zeolite imidazolate framework

Chapter 1: Introduction

Separation and purification of gas mixtures have become important processes in several chemical and industrial applications [1]. Traditional gas separation techniques include distillation, absorption, adsorption and membranes. Among these techniques, adsorption-based and membrane-based gas separation methods have received significant attention from academy and industry. Both processes compete with distillation and absorption as alternative methods for several processes including carbon dioxide removal from gas streams [2].

Separation is a process that divides a mixture into two or more components [3]. Since separation is not a favored process by second law of thermodynamics, it requires major energy consumption. In addition to energy consumption, another factor that is needed to be minimized is the capital cost. Adsorption-based and membrane-based separation processes do not require phase changes. This allows them to be easily staged with a lower cost with respect to other separation methods. Unlike other techniques, adsorption- and membrane-based separation processes do not require corrosive organic solvents. As a result, these separation techniques are energy-efficient and environmentally friendly processes.

Adsorption-based gas separation processes can be performed in three ways: pressure swing adsorption (PSA), temperature swing adsorption (TSA) and vacuum swing adsorption (VSA) [4]. In PSA processes, adsorption is performed at high pressure whereas desorption is performed at ambient pressure. In TSA processes, adsorption occurs at ambient temperature, whereas desorption is performed at a higher temperature. In VSA processes, adsorption and desorption are performed at ambient and vacuum pressure, respectively. The operating conditions, such as adsorption pressure, desorption pressure and temperature, can be determined based on the types of adsorbate and the choice of the gas mixture to be separated. In adsorption-based processes, gas separation is achieved based on the differences of

adsorption capability of different components in the adsorbent [3]. Therefore, the performance of any such process is directly correlated with the characteristics of the adsorbent in adsorption equilibrium and kinetics. In addition to common requirements such as thermal stability, chemical stability, mechanical strength and no tendency to promote undesirable chemical reactions, a promising adsorbent should possess good adsorption capacity and selectivity as well as favorable adsorption kinetics and regenerability. To fulfill these requirements, the adsorbent should have a high surface area and large pore sizes for porous materials which allow adsorbate molecules to reach the interior surface.

In a membrane-based separation process, components are separated from the mixtures by differential permeation through membrane. In such processes, permeate side of membrane is generally kept at ambient pressure, whereas the feed pressure is set to be higher than the permeate pressure. The keystone of these processes is the membrane itself. Although the criteria for selecting the membrane material for a specified gas separation are circuitous, several factors should be ensured including durability, mechanical integrity, separation efficiency [5]. Intrinsically, a good membrane candidate should possess not only high selectivity but also high permeability. In a typical membrane-based separation processes, membranes can be classified into three types: polymeric membranes, inorganic membranes and mixed matrix membranes. Polymeric membranes have the advantages of desirable mechanical properties and economical processing capabilities. However, there exists a trade-off between gas selectivity and permeability in polymeric membranes [6]. Inorganic membranes are usually formed from metals, ceramics, zeolites and nanoporous materials. They exhibit long-term stability at high temperatures, well-defined pore structures and resistance towards solvents. On the other hand, their industrial applications are limited due to the fact that it costs more to produce inorganic membranes compared to polymeric membranes. Lastly, mixed matrix membranes (MMMs) consist of inorganic materials as fillers dispersed in polymeric membranes [5]. They exhibit high separation capabilities of the inorganic materials as well as the desirable mechanical properties and economic advantages of the polymers [7].

Porous coordination networks (PCNs) are a new class of nanoporous materials which are highly promising for adsorption-based and membrane-based gas separation processes since they have high surface areas, large pore volumes, tunable pore sizes and good thermal and mechanical stabilities. Additionally, they can be good candidates as fillers in MMMs for gas

separation applications because of their capabilities of high selectivity and permeability for the specified component of the mixture.

In this thesis, adsorption-based and membrane-based gas separation performances of PCNs have been investigated using atomistic simulations. Separation of CH_4/H_2 , CO_2/H_2 , CO_2/CH_4 and CO_2/N_2 mixtures have been studied for PCN-6, PCN-6', PCN-9-Co, PCN-9-Fe, PCN-9-Mn, PCN-10, PCN-11, PCN-13, PCN-14, PCN-16, PCN-16', PCN-18, PCN-19, PCN-20, PCN-26, PCN-39, PCN-46, PCN-80, PCN-121, PCN-131', PCN-221-Cu, PCN-221-Hf, PCN-222, PCN-224-Ni and PCN-225. Additionally, performances of PCN-9-Co, PCN-121 and PCN-131' have been analyzed as adsorbents, membranes and fillers in MMMs to separate O_2 from N_2 . Parameters such as adsorption selectivity, diffusion selectivity, permeation selectivity, permeability, working capacity, sorbent selection parameter, regenerability are calculated to evaluate PCNs for adsorption- and membrane-based gas separation applications. Chapter 2 explains the importance of separation of gas mixtures specified earlier and reviews the literature on PCNs. Chapter 3 defines the theory behind the adsorption and diffusion phenomena and describes the calculation details of Grand Canonical Monte Carlo (GCMC) and Equilibrium Molecular Dynamics (EMD) simulations and the structural properties of PCNs such as pore volume, pore size and surface area. Additionally, the definitions of adsorbent and membrane evaluation parameters and mixed matrix membrane models are briefly described. Chapter 4 provides the validation of accuracy of the simulations by comparing the results with available experimental data. It also demonstrates the gas separation analysis with four PCNs for adsorption-based and membrane-based processes and investigates the effect of charge assignment methods for this analysis. In Chapter 5, an extended analysis of performances of twenty five PCNs is introduced for adsorption based and membrane-based gas separation applications. Additionally, for CH_4/H_2 and CO_2/H_2 mixtures, simple models to predict the adsorption, diffusion and membrane selectivity of PCNs are proposed in Chapter 6. Lastly, PCN-filled performances of MMMs to separate O_2 from N_2 are discussed in Chapter 7.

Chapter 2: Literature Review

2.1. Gas Storage and Separation

Porous coordination networks (PCNs) have attracted the interest of both academia and industry in several applications including gas storage, gas separation, catalysis, drug storage and sensing [8]. Among those applications, gas storage and separation are the most mature application areas of PCNs since those processes have been used in industry and energy research.

Pure gases such as CH_4 , CO_2 , H_2 , N_2 and O_2 have crucial roles in various industrial applications. For example, there exists an escalating need for H_2 in chemical manufacturing and petroleum refining applications [9]. The oxidation product of H_2 is water and therefore H_2 storage is attractive [10]. Since pure H_2 and CH_4 can be used in energy applications, materials which can store those gases have essential role in energy-related applications. Pure N_2 can be used in many applications including aerospace applications, laser cutting applications, automotive and transportation equipment, chemical processes, medical and pharmaceutical applications. Additionally, it is a key agent in food industry applications such as cooling and food freezing processes. It can also be used as replacement of air in the processes where oxidation is undesirable because N_2 is an inert gas [11]. Another important gas is pure O_2 which is widely used in medical applications and industrial applications including space suit production and chemical processes. Such applications lead us the fact that the storage of single component gases is very important and can be used for several purposes. In this thesis, adsorption-based separation performances of PCNs for CH_4 , CO_2 , H_2 , N_2 , and O_2 gases have

been studied in order to specify the good adsorbent candidates to be used in these applications.

Gas separation is another significant application area of PCNs. In this thesis, PCNs have been studied to separate CH_4/H_2 , CO_2/CH_4 , CO_2/H_2 , CO_2/N_2 and N_2/O_2 mixtures since they have important roles especially in industrial applications. Capturing CH_4 from H_2 , is crucial to purify synthesis gas obtained from steam reforming of natural gas. As well as CH_4/H_2 separation, to separate CO_2 from CO_2/H_2 mixture is also relevant in H_2 recovery processes from plants and refineries [12-14]. Since clean energy research has gained importance because of the exhaustion of fossil oil deposits and the growing threat of global warming, several research groups search for clean energy carriers such as H_2 and CH_4 as well as they attempt to find a way to reduce CO_2 emissions [13]. Apart from the H_2 and CH_4 storage studies, CO_2 capture has been put on the urgent agenda due to several other reasons including large-scale industrial applications. To capture CO_2 from CO_2/CH_4 and CO_2/N_2 is important in natural gas purification and carbon capture from flue gas, respectively. Conjointly, separation of N_2/O_2 , also known as air separation, is employed to supply O_2 for the gasification of a wide range of hydrocarbon feedstock to generate synthesis gas for the production of fuels, chemicals and many others [15].

Adsorption-based and membrane-based separation techniques are advantageous ways of gas storage and separation processes. Both processes are based on the ability of some natural and synthetic materials. For adsorption-based separation applications, those materials should adsorb the desired gas molecules with the desired amount whereas in the membrane-based processes, material's capabilities of both adsorption and diffusion of the desired component are crucial. In this thesis, PCNs have been investigated using atomically detailed simulations and the adsorbent and membrane candidates for gas storage and separation studies of mixtures specified earlier have been identified.

2.2. Porous Coordination Networks (PCNs)

Porous coordination networks (PCNs), commonly known as metal organic frameworks (MOFs), are a new group of nanoporous materials that have tunable pore sizes, large surface areas, high porosities, and good chemical and mechanical stabilities. Apart from the gas storage and separation applications, they can be used in several applications such as catalysis,

drug delivery, ion exchange, hosts for metal colloids and nanoparticles, luminescence, magnetism, nonlinear optics and sensor technology [8].

PCNs are crystalline porous materials like zeolites and aluminophosphates. Unlike zeolites which are purely inorganic compounds, PCNs belong to organic-inorganic hybrid compound class. PCNs consist of metal atoms (or metal clusters) as nodes linked through organic linkers. They generally have low densities ($0.1\text{-}1.5\text{ g/cm}^3$) and high surface areas ($400\text{-}4500\text{ m}^2/\text{g}$). PCNs can be synthesized with desired topological features by prearranging the linkers in place using framework-templating strategy [16]. PCNs are generally synthesized from molecular building blocks in solution or hydro/solvothermal methods. Their metal clusters are usually formed in situ and linkers are often preformed. Geometry and connectivity of the linker dictate the structure of the PCN [17]. Several synthesis methods have been developed for those materials. Starting from the same reaction mixtures, various structures can be synthesized using different methods. Namely, these synthesis methods affect the reaction time, products, particle size and morphology [18]. As stated earlier, the most common methods have been reported as hydrothermal and solvothermal synthesis [17]. In addition to these, various methods including micro-wave assisted, electrochemical, mechanochemical and sonochemical synthesis techniques have been used to synthesize PCNs [17,18]. These conventional methods have established a new bridge between the coordination chemistry and synthetic organic chemistry [19]. Among the most conventional methods, hydrothermal synthesis can be described as the use of water as a solvent in a sealed reaction container when the temperature is raised above 100°C . In the solvothermal synthesis, a sealed reaction vessel and temperature above the boiling point of the solvent are used [20].

2.3. Literature Review on PCNs

Since adsorption-based gas separation performances of PCNs are generally assessed based on the results of single-component gas uptake studies, several experimental studies investigated the single gas uptake of PCNs. Most of the studies in the literature have focused on H_2 storage in PCNs. For example, Ma et al. synthesized catenated PCN-6 and noncatenated counterpart, PCN-6', to compare their H_2 uptakes [21,22]. They suggested that new adsorption sites and small pores formed as a result of catenation may strengthen the overall interaction between H_2 molecules and the pore walls, thereby increasing the apparent surface area and H_2

uptake. PCN-10, PCN-11, PCN-12, PCN-12', PCN-12-Si, PCN-14, PCN-15, PCN-16, PCN-16', PCN-26, PCN-46, PCN-68, PCN-80 and PCN-82 are the other materials which have been tested and identified as promising candidates for H₂ storage due to their nanoscopic cages [23-32]. PCN-20 and PCN-105 were also reported to exhibit high H₂ uptake capacity due to their large surface areas and existence of mesoporous cages with narrow windows [33,34]. Many research groups have also focused on uptake capacities of PCNs for other gas molecules. For example, adsorption isotherms of several gases such as Ar, CH₄, CO, CO₂, H₂, N₂ and O₂, were experimentally measured in many materials, PCN-9-Co, PCN-9-Fe, PCN-9-Mn, PCN-13, PCN-17, PCN-18, PCN-19, PCN-21, PCN-46, PCN-53, PCN-56, PCN-57, PCN-58, PCN-59, PCN-61, PCN-66, PCN-68, PCN-69, PCN-121, PCN-122, PCN-125, PCN-921 and PCN-922 [16,30,35-48]. Several PCNs have been identified to be promising for CO₂ capture such as PCN-5, PCN-46, PCN-61, PCN-68, PCN-123 and PCN-124 [30,43,49-52]. Makal et al. studied single-component gas adsorption capacities of PCN-38 and PCN-39 and showed that PCN-39 exhibits selective adsorption for H₂ over CO, CO₂ and N₂ [53]. Moreover, Liu et al. examined single-component adsorption of CO₂ and N₂ in PCN-72 and concluded that this material can be a promising adsorbent for CO₂ capture from flue gas [54]. Liu and co-workers synthesized PCN-426-Mg which collapsed upon activation procedure. By using this PCN as a template, they also synthesized two robust PCNs named as PCN-426-Cr and PCN-426-Fe and measured their N₂ adsorption isotherms [55]. Additionally, Zhang et al. synthesized PCN-521 and 523 which are the first examples of Zr/Hf MOFs with tetrahedral linkers and concluded that PCN-521 has the largest BET surface area (3411 m²/g), pore size (20.5 Å×20.5 Å×37.4 Å) and void volume (78.5%) of MOFs formed from tetrahedral ligands [56]. In another study, Zhang and coworkers synthesized PCN-530 whose constructional unit was adenine and offered a general perspective about synthesis of nucleic-acid-based incorporated MOFs [57].

Selective gas adsorption behavior of PCNs has been predicted by examining experimental single-component adsorption isotherms. For example, Ma et al. measured adsorption isotherms for N₂, H₂, CH₄ and CO₂ in PCN-5 and concluded that PCN-5 exhibits selective adsorption for CO₂ over CH₄ (adsorption selectivity of 7 at 195 K and 1 bar) based on the single-component adsorption isotherms [49]. Lu et al. showed that adsorption selectivity of PCN-80 for CO₂ over N₂ is about 11.8 at 296 K [23]. PCN-131' was reported to exhibit high adsorption selectivity for CO₂ over CH₄ whereas isostructural materials PCN-305, PCN-306,

PCN-307 and PCN-308 were reported to show CO₂ selectivity over CH₄ and N₂ [58,59]. CO₂/N₂ (CO₂/CH₄) adsorption selectivities were calculated as 52 (7.2) for PCN-305, 40 (7.5) for PCN-306, 50 (8.8) for PCN-307 and 37 (7.8) for PCN-308 at 273 K. These selectivities were calculated from the experimental single-component adsorption isotherms by using the ideal adsorbed solution theory (IAST) for CO₂/N₂ (15/85) and CO₂/CH₄ (50/50). Park et al. calculated adsorption selectivity of PCN-124 for an equimolar CO₂/CH₄ mixture using IAST method as 15 at 1 bar and 273 K and as 19.5 at 1 bar and 295 K [52]. Ma et al. synthesized four isostructural microporous PCNs named PCN-17-Dy, PCN-17-Er, PCN-17-Y and PCN-17-Yb and calculated adsorption selectivity of O₂/N₂ and H₂/CO [60]. The adsorption selectivities for O₂/N₂ (H₂/CO) were reported as 2.3 (1.9), 2.5 (1.5), 1.9 (1.7) and 9.0 (3.6) at 1 bar for PCN-17-Dy, PCN-17-Er, PCN-17-Y and PCN-17-Yb, respectively based on single-component adsorption isotherms.

Apart from the adsorption studies, several studies have investigated the catalytic abilities of PCNs. Fang and coworkers synthesized PCN-100 and PCN-101 showed typical type IV behavior, indicating their mesoporous nature. They stated that mesoporous materials such as PCN-100 can be applied in the elimination of heavy metal ions from waste liquid. In addition, they concluded both PCN-100 and PCN-101 exhibit size-selective catalytic activity toward the Knoevenagel condensation reaction [61]. Feng et al. synthesized Hf-PCN-221-Co, Zr-PCN-221 and Zr-PCN-221-Fe and concluded that PCN-221 catalyzes the oxidation of cyclohexane with very high selectivity toward ketone and alcohol products [62]. In another study, Feng et al. synthesized PCN-222 and stated that the integration of a high density of catalytic centers, ultra-large open channels, and the extraordinary chemical stability of PCN-222 suggests a flashing future for building MOF-based platforms for enzyme-mimic catalysis [63]. Feng and coworkers studied high catalytic activity of PCN-224-Co for the CO₂/propylene oxide coupling reaction and expressed that PCN-224-Co can be used as a recoverable heterogeneous catalyst [64]. In the same study, they also synthesized PCN-224, PCN-224-Fe and PCN-224-Ni and concluded that PCN-224 series not only show the highest BET surface area (~2600 m²/g) among all the reported porphyrinic MOFs but also remain intact in pH=0 to pH=11 aqueous solution. Similarly, Jiang et al. synthesized a PCN named PCN-225 and reported that this PCN can potentially be applied in fluorescent pH sensing

applications due to its exceptionally high stability and pH-dependent fluorescent intensity [65].

As the literature summarized earlier suggests, various PCNs have been synthesized by different research groups and single-component gas uptake capacities of these PCNs are generally determined by experimental methods. In addition to those studies, the number of computational studies on gas adsorption in PCNs rapidly increases in the literature. For example, Barbarao et al. studied adsorption and diffusion of alkane isomer mixtures (C_4 and C_5) for catenated and noncatenated MOFs, IRMOF-13, IRMOF-14, PCN-6 and PCN-6' using Grand Canonical Monte Carlo GCMC and molecular dynamics (MD) simulations [66]. They concluded that adsorption and diffusion selectivities can be enhanced by catenation. In a different study, Babarao and coworkers computationally examined the adsorption selectivity of PCN-6 and PCN-6' for CO_2/CH_4 [67]. They concluded that catenated PCNs show higher CO_2/CH_4 selectivity than their noncatenated counterpart since catenation enhances the interaction of PCN atoms with CO_2 . Wenzel et al. performed GCMC simulations on PCN-12-Si to investigate its H_2 uptake capacity at high pressures and concluded that its H_2 storage capacity is about 4.8 wt% at 77 K and 30 bar [29]. Lucena and coworkers studied adsorption behavior of CH_4 in PCN-14 using GCMC simulations and investigated the temperature dependence of the molecular sitting for CH_4 [68]. Parkes et al. investigated adsorption and diffusion of Kr in 16 MOFs including PCN-14 performing GCMC and molecular dynamics simulations and suggested that MOFs are highly promising materials for industrial separation of noble gas from air [69]. Zhuang et al. used GCMC simulations to compute CO_2 , CH_4 , H_2 and N_2 uptakes in PCN-26 and showed that this material can be highly promising for gas storage [31]. Yuan and coworkers performed GCMC simulations to analyze adsorption capacity of PCN-53 for many gases such as N_2 , CO_2 and Ar [42]. They explained the stepwise adsorption behavior of PCN-53 with the existence of both micro and mesopores in the framework. Additionally, Ward et al. predicted N_2 uptake in PCN-53 using GCMC simulations and quantum mechanical based methods [70]. Babarao et al. employed the combination of first-principles calculations and GCMC simulations to investigate the influence of functional groups and flue gas impurities on the post combustion CO_2 capture in PCN-56, PCN-57, PCN-58, PCN-59 and reported that PCN-59 is a good adsorbent candidate to separate CO_2 from a pre-dehydrated flue gas mixture [71]. Jimenez et al. studied the effect

of linker length on the textural properties of *rht*-type PCNs such as surface area, pore size, pore volume and their relation to H₂ adsorption properties using GCMC simulations for PCN-61, PCN-68, PCN-69 and PCN-610 [32]. They concluded that although absolute uptake capacity increases linearly with pore volume, excess uptake capacity maximizes at a certain pore volume. Zheng et al. performed GCMC simulations to compare the gas separation capacity of a *rht*-type MOF with PCN-61 [51]. They studied the effect of acylamide groups for CO₂/N₂ separations and concluded that decoration of a MOF with polar acylamide groups can enhance the CO₂ binding ability and selectivity of the MOF. Li and coworkers synthesized PCN-88 and PCN-88' and reported that these PCNs selectively adsorb CO₂ over CH₄ and N₂ by performing both adsorption experiments and GCMC simulations [72]. Park et al. analyzed PCN-124 using GCMC simulations to show its CO₂ selectivity over CH₄ whereas Wriedt et al. performed GCMC simulations to show CO₂/N₂ adsorption selectivity of PCN-200 [41,73].

As can be comprehended from the literature review, experiments have only examined single-component gas adsorption isotherms in PCNs and computational studies have focused on a single PCN and adsorption-based separation properties of a PCN for a specific gas mixture (generally CO₂/CH₄). There are currently very few studies in the literature that examines the membrane-based gas separation properties of PCNs which requires information on gas transport properties in PCNs' pores. Consequently, the main focus of this study is designated as the investigation of both adsorption and diffusion mechanisms of small gas molecules and their binary mixtures in PCNs from a computational point of view.

Chapter 3: Theoretical Background

In this chapter, adsorption and diffusion phenomena will be briefly discussed. In addition to those, intermolecular interactions, partial atomic charge assignment methods used in the simulations and available codes used in this work to calculate structural properties of PCNs such as surface area and pore volume will be summarized.

3.1. Adsorption and Grand Canonical Monte Carlo Method

The attachment of molecules to the surface of solid by adsorption is immensely broad issue. This chapter is focused on the adsorption of gas molecules in high capacity solid adsorbents such as zeolites and porous coordination networks (PCNs). Thermodynamically, adsorption isotherm gives the amount of adsorbed gas molecules as a function of pressure at a constant temperature [74]. It can be either measured experimentally or calculated using Grand Canonical Monte Carlo (GCMC) simulations. The experimental measurements are based on the fact that the weight of the solid increases and the pressure of the gas decreases as adsorption occurs at the gas-solid interface. Therefore, the amount of gas adsorbed can be measured in two ways: by measuring the change in weight of the solid with a spring balance or the change in pressure of the gas in an accurately known volume if the volume of the adsorbent is also known [75]. These techniques are named as gravimetric and volumetric, respectively. The resulting experimental data, which is collected at constant temperature, are called the equilibrium adsorption isotherm. It is usually plotted as a function of pressure, or in some cases of P/P_0 where P_0 is the saturation vapor pressure[75]. The thermodynamics of adsorption is discussed in more detail in several studies [74,76-79].

For adsorption studies, grand canonical ensemble is a natural ensemble to use [80]. In this ensemble, the chemical potential (μ), temperature (T) and volume (V) are kept constant. For a system in which the equilibrium adsorption isotherm is obtained, the adsorbed gas molecule is in equilibrium with the gas in the reservoir. Also, the chemical potential of the gas inside and outside of the adsorbent are equal [80,81]. In a GCMC simulation of such system, the gas which is contact with the adsorbent can be thought as a reservoir which enforces a chemical potential and temperature on the adsorbed gas.

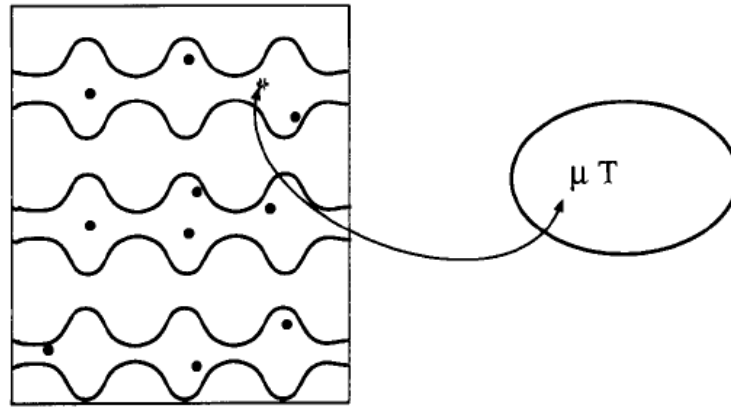


Figure 3.1. Adsorbent in contact with a reservoir which enforces constant chemical potential and temperature by exchanging particles and energy [80].

During a GCMC simulation, the chemical potential and temperature are imposed to the system and the number of particles is allowed to fluctuate. The partition function of a combined system of N interacting particles in volume V and $(M-N)$ ideal gas molecules in volume (V_s-V) , represented in Equation (3.1), can be used to understand the statistical mechanics basis of the GCMC simulation [80].

$$Q(N, M, V, V_s, T) = \frac{V^N (V_s - V)^{M-N}}{\Lambda^{3M} N! (M-N)!} \int d\vec{s}^{M-N} \int d\vec{s}^N \exp[-\beta U(\vec{s}^N)] \quad (3.1)$$

Here, it is assumed that the molecules in the system and reservoir are equal and the molecules in the volume V interact with each other while the ones in the volume $(V_s - V)$ do not interact. During the simulation, if molecule i is transferred from a reduced coordinate $\bar{s}_i$ in the volume $(V_s - V)$ to the same reduced coordinate in volume V , then the potential energy function U changes from $U(\bar{s}^N)$ to $U(\bar{s}^{N+1})$. The total partition function of the system which includes all possible distributions of M particles over two parts of the volume V_s (system volume) is given in Equation (3.2).

$$Q(M, V, V_s, T) = \sum_{N=0}^M \frac{V^N (V_s - V)^{M-N}}{\Lambda^{3M} N! (M-N)!} \int d\bar{s}^{M-N} \int d\bar{s}^N \exp[-\beta U(\bar{s}^N)] \quad (3.2)$$

In a GCMC simulation, there exist three types of moves: particle insertion, particle deletion and particle displacement. For those moves, acceptance rules based on that idea that particles are exchanged with a reservoir containing the same molecules at the same chemical potential are used. A move is performed with a probability which depends on the energy differences of the states. For example, the acceptance of particle displacement is determined by using Equation (3.3).

$$\alpha(\bar{s} \rightarrow \bar{s}') = \min \{1, \exp(-\beta [U(\bar{s}'^N) - U(\bar{s}^N)])\} \quad (3.3)$$

Similarly, the insertion (deletion) of the particle can be decided using Equation (3.4) (Equation (3.5)). For more detailed discussion, Frenkel and Smit's book is an excellent reference [80].

$$\alpha(N \rightarrow N+1) = \min \left\{ 1, \frac{V}{\Lambda^3 (N+1)} \exp(-\beta [\mu - U(N+1) + U(N)]) \right\} \quad (3.4)$$

$$\alpha(N \rightarrow N-1) = \min \left\{ 1, \frac{\Lambda^3 N}{V} \exp(-\beta[\mu + U(N-1) - U(N)]) \right\} \quad (3.5)$$

The average number of adsorbed molecules is the result of a GCMC simulation. Using these data, the adsorption isotherm can be computed directly. To do that, chemical potential (μ) should be converted to the pressure (P). At sufficiently low pressures, the reservoir can be assumed as an ideal gas and therefore, the assumption that the fugacity is equal to the pressure can be made. For higher pressures, Smit stated that either experimental equation of state of the mixture or a simulated equation of state of the model fluid (mixture) can be used for this conversion [79]. In the cases where the equation of state of the system is unknown, a test method can be used to calculate the chemical potential. Test method, commonly known as *widom test particle insertion method*, a particle which does not interact with the system is added to the system. The added particle is a ghost particle which means system does not feel its presence. On the other hand, the ghost particle feels the same energy as a real particle. By calculating the energy change due to the insertion of this ghost particle, the chemical potential of the system can be calculated as shown in Equation (3.6).

$$\mu = k_B T \ln \left\{ \langle \exp(-\beta \Delta U(\bar{s}^{N+1})) \rangle \right\} \quad (3.6)$$

There are two important parameters which can be used to validate GCMC simulation results with the experimental measurements: Henry coefficient and isosteric heat of adsorption. Using widom test particle insertion method, Henry's coefficient (K_H) can be computed [79]. Under the content consideration of this thesis, the calculation of K_H is out of scope. Isosteric heat of adsorption (Q_{st}) is the difference in the partial molar enthalpy of adsorbate between the gas and adsorbed phase and can be defined using Equation (3.7) where U_{ads} is the potential energy of the adsorbed phase and N_{ads} defines the amount of adsorbed molecules in the framework [82].

$$Q_{st} = RT - \left(\frac{\langle U_{ads} \times N_{ads} \rangle - \langle U_{ads} \rangle \times \langle N_{ads} \rangle}{\langle N_{ads}^2 \rangle - \langle N_{ads} \rangle \times \langle N_{ads} \rangle} \right) \quad (3.7)$$

Lastly, one should note the fact that the experimental adsorption isotherm data represent *excess* adsorption while theoretical calculations obtained using GCMC simulations yield *absolute* adsorption [83]. Therefore, the output of GCMC simulations should be expressed in *excess* adsorption units. The conversion from *absolute* adsorption ($n_{absolute}$) to *excess* adsorption (n_{excess}) can be employed using Equation (3.8) is studied in more detailed way by Myers and Monson [83,84]. In GCMC simulations, the adsorption occur on the external surface are also accounted. Therefore, gas molecules which are standing inside the pores of the adsorbent without any interaction are counted as if they were adsorbed. Although, this amount is negligible in the low pressure (smaller than atmospheric pressure), its effect becomes explicit as pressure increases.

$$n_{excess} = n_{absolute} - \frac{PV_{pore}M_{A,gas}}{RT} \quad (3.8)$$

Adsorption studies are essentially prominent since they can lead a proper way to design adsorption applications for gas storage, adsorption and membrane based processes for gas separations or catalysis [79]. As we know more about the adsorption capabilities of nanoporous materials, better equipment can be designed and tailored synthesis studies can be performed. Especially, better understanding of their adsorption capabilities is required for applications for PCNs. Since there is lack of information about the single- or multi-component gas adsorption isotherms of PCNs, both experimental and computational studies of adsorption behavior of gas molecules in PCNs should be performed [14]. For single-component experiments, measuring the weight increase of PCN sample can be related to the adsorbed molecule amount. However, the techniques for multi-component experiments are not only difficult but also very time consuming. Therefore, computational studies related with the adsorption phenomena in PCNs are prominent. In addition, better understanding of mixture adsorption can also result in the discovery of novel separation mechanisms and better interpretation of diffusion coefficients [79,80].

3.2. Diffusion and Equilibrium Molecular Dynamics Method

Diffusion is the process where molecules migrate randomly as a result of their thermal energy [85]. It is related with the tendency of systems to occupy all of the accessible states. To define it in a more simple way, diffusion can be thought as a spontaneous tendency of all systems to equalize concentration, if any external force or effect does not impede this process. Since membrane-based gas separation processes are based on differences in diffusion coefficients of the components and diffusion is also crucial in catalysis and gas chromatography, understanding the diffusion phenomena is vital. Experimentally, diffusion coefficients are very difficult to accurately measure [79,85]. Pulsed Field Gradient Nuclear Magnetic Resonance (PFG-NMR) is a well-established technique to measure diffusion coefficients of gas molecules in microporous solids [86]. In this technique, a particle is labeled and the attenuation of the signal is related to the self-diffusion coefficient of the particle [79]. However, diffusion coefficients may vary by orders of magnitude due to the experimental technique used [79,87,88]. Theoretically, diffusion can be described macroscopically using Fick's law. Fick's law states that there is a linear relation between the matter flux ($\vec{J}$) and the concentration gradient ($\vec{\nabla}c$). This law can be formulated using Equation (3.9) in which D_t is the transport diffusion coefficient, also known as Fickian diffusion coefficient [85]. In Equation (3.8), flux defines the number of species crossing a unit area in the medium per unit of time. Transport diffusion coefficient is a measure of the flow of the material when the concentration difference exists in the system.

$$\vec{J} = -D_t(c)\vec{\nabla}c \quad (3.9)$$

Thermodynamically, the driving force for the diffusion is the gradient in the chemical potential because diffusion is the macroscopic expression of the tendency of a system to move toward equilibrium. In Equation (3.10), D_c represents the corrected diffusion coefficient whereas $L(c)$, μ , k_B and T represent the single-component transport coefficient, chemical potential, Boltzmann constant and temperature, respectively. [79].

$$\vec{J} = -\frac{L(c)}{k_B \times T} \times \vec{\nabla} \mu = -D_c(c) \times \vec{\nabla} \mu \quad (3.10)$$

To link corrected diffusion coefficient to transport diffusion coefficient, the gradient of concentration should be converted to the gradient of chemical potential [79]. This conversion can be performed using thermodynamic correction factor (Γ) defined in Equation (3.11).

$$\Gamma \equiv \frac{1}{k_B \times T \times c} \frac{\partial \mu}{\partial \ln(c)} \quad (3.11)$$

This relation also helps to state the relation between the transport diffusion coefficient and the corrected diffusion coefficient given as Equation (3.12). In the limit of zero loading, ideal gas assumption is valid and therefore, thermodynamic correction factor approaches to unity [79]. In this case, the transport diffusion coefficient is equal to the corrected diffusion coefficient. At higher loading, this approximation is not valid and adsorption isotherm should be known to calculate the thermodynamic correction factor.

$$D_t(c) = \Gamma \times D_c(c) \quad (3.12)$$

It is important to relate the diffusion coefficient to the microscopic properties of the system. Computationally, diffusion coefficient can be calculated using Equilibrium Molecular Dynamics. In Equation (3.13), which can be used to calculate self-diffusion coefficient (D_s), v_i and N describe the velocity of the particle i and number of particles in the system, respectively.

$$D_s(c) = \frac{1}{3N} \sum_{i=1}^N \int_0^\infty \langle v_i(t') v_i(0) \rangle dt' \quad (3.13)$$

Self-diffusion coefficient is a measure of the average mean-square displacement which has made by a single labeled particle in a given time [79,85]. It is a single particle property while the transport diffusion is a collective one. Therefore, self-diffusion coefficient can be efficiently calculated using molecular dynamics simulations. However, transport diffusion

coefficient calculations require more CPU (Central Processing Unit) time. Additionally, the self-diffusion coefficient is also the one which can be measured in NMR experiments [79,80,85].

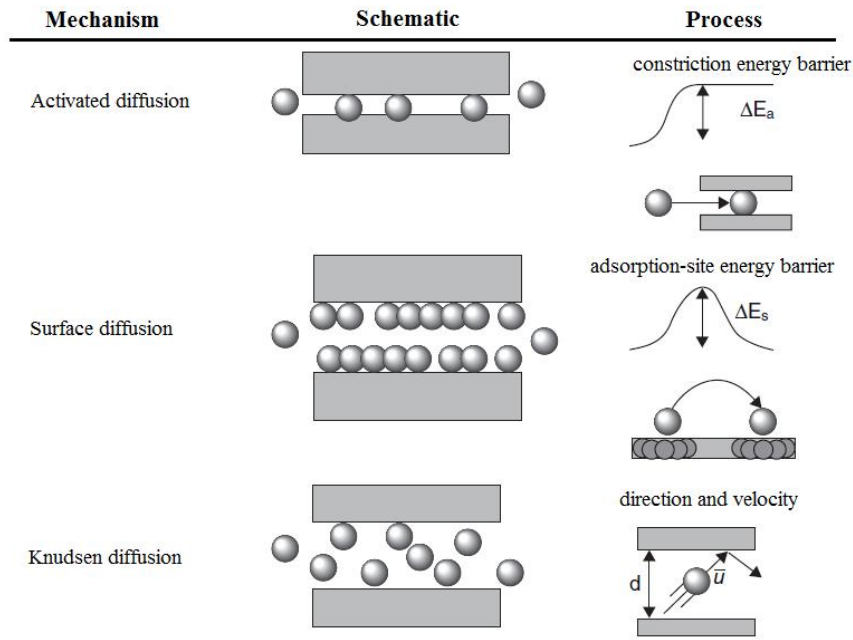


Figure 3.2. Gas diffusion mechanisms in porous and nonporous materials (adapted from [89]).

Gas molecules experience an energy barrier (ΔE_a) when encounter geometric constrictions. Kinetic energy of the diffusing molecules should overcome this energy barrier to make a successful diffusion jump through the membrane's pores [89]. Diffusivity of gas molecules are exponentially dependent to the energy barrier ($D \propto e^{-\Delta E_a/RT}$ where D , R and T describe diffusivity, ideal gas constant and temperature, respectively), also named as activation energy. Gas molecules diffuse within porous materials according to several transport mechanisms depending on their pores [89]. Figure 3.2 represents the scheme and process of these mechanisms. Activated diffusion can be attained when very narrow pores exist. This mechanism is the most commonly studied diffusion mechanism for non-porous polymeric membranes. Surface diffusion is also an activated diffusion process. Differently, in the surface diffusion mechanism, material has wider pores. This mechanism has been shown to be consistent with gas transport in porous membranes [90,91]. Therefore, it is calculated using Equilibrium Molecular Dynamics (EMD) simulations in this work. Surface diffusion

generally occurs simultaneously with Knudsen diffusion but it is the dominant mechanism for a certain pore size region ($< 20 \text{ \AA}$) [85,89]. Surface diffusion is a many body phenomenon which can be attributed to the several lateral interactions developed on the surface. The Van der Waals, dipole-dipole and higher multi-pole interactions are responsible for diffusion of gas molecules. Last mechanism is Knudsen diffusion mechanism which is valid when mean free path length of gas molecules is much larger than pore diameter of the material. It applies to porous materials whose pore sizes are between $10 \text{ \AA}$ and $500 \text{ \AA}$ [89]. As stated earlier, since diffusion of gas molecules in porous coordination networks can be explained using surface diffusion mechanism, the experimental and computational techniques for surface diffusion will be explained.

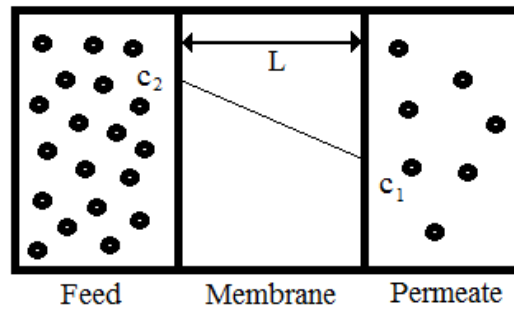


Figure 3.3. Scheme for linear concentration gradient across the membrane (adapted from [89])

Generally, diffusion measurements are based on Fick's law. The diffusion coefficient can be calculated by determining the flux through the membrane for a given concentration difference. Assuming a linear concentration gradient across the membrane, diffusion coefficient can be calculated using Equation (3.14). In Equation (3.14), L defines the thickness of membrane whereas c_1 and c_2 illustrate the concentration in permeate and feed, respectively. Difference between the concentration in the feed and the permeate sides of the membrane can also be expressed as concentration drop across the membrane. It can be estimated from the pressure drop and adsorption isotherm.

$$D = -\frac{|\vec{J}| \times L}{\Delta c} = \frac{|\vec{J}| \times L}{c_2 - c_1} \quad (3.14)$$

After the estimation of concentration drop across the membrane using sorption isotherms and the flux measurement, transport diffusion coefficient can be calculated. Apart from this method, diffusion can also be measured experimentally using different techniques [88]. However, it is out of scope since this study is purely computational.

Diffusion of gas molecules in porous materials can be computed using Equilibrium Molecular Dynamics (EMD) simulations. Additionally, other methods such as transition state theory can be used to calculate the temperature dependence of diffusion coefficients when the molecular motion is relatively slow and the free energy barriers separating adsorption sites are large [92]. In EMD simulations, the aim is to generate successive configurations of a system by integrating Newton's law of motion [93]. Diffusion coefficients are calculated from the trajectories representing the change in the positions and velocities of particles with respect to time during the simulation. The initial configurations of the gas molecules in pores of the framework are generated by performing a short GCMC simulation whereas the initial velocities of gas molecules are assigned randomly based on Maxwell-Boltzmann velocity distribution [93].

For diffusion studies, canonical ensemble (NVT) is a conventional ensemble to use [80]. In this ensemble, number of molecules (N), volume (V) and temperature (T) are kept constant and the energy of endothermic and exothermic processes is exchanged with a thermostat. Several techniques to control temperature include velocity rescaling, Nosé-Hoover thermostat, Nosé-Hoover chains, Berendsen thermostat, Andersen thermostat and Langevin dynamics [94]. In this study, Nosé-Hoover thermostat is applied to keep the desired temperature and the integration of the system dynamics is based on the explicit NVT chain integrator by Martyna et al [95].

Initially, a NVT-MD simulation is performed to equilibrate the system. Newton's equation is integrated and the positions of each particle in the system are recorded at specified rate after the equilibration [93]. In EMD simulations, force fields which define the interactions between gas molecules and interaction between the gas molecules and the framework atoms are required to measure gas diffusion in the pores of PCNs. After the specification of force field parameters, dynamical properties of the gases in the simulated material can be computed. In section 3.4.1, these force fields will be described in detail.

Understanding the diffusion of gas molecules adsorbed in the pores of PCNs is important for many applications including gas separation and catalysis. For example, separations usually depend on the differences of diffusion coefficients of the components in a mixture. In catalytic applications, diffusion of molecules to the active site may act as a rate limiting feature [79]. Therefore, it is crucial to understand the diffusion mechanisms of gas molecules adsorbed in the pores of PCNs. The most straightforward way to calculate diffusion coefficients of these adsorbed gas molecules is to perform EMD simulations. Since the experiments which aim to measure transport diffusivities and energy barrier to diffusion are challenging, computational calculations gain importance. Especially, measuring diffusivity at different loadings in the pores at extreme conditions such as infinite dilute loading and saturation loading is experimentally difficult [93]. Consequently, EMD simulations can broaden our understanding in gas diffusion in the pores of PCNs under different conditions. As stated in section 2.3, there are a few studies which are related with computational analysis of diffusion of gas molecules in PCNs. This is why the diffusion behaviors of gas molecules and their mixtures are specifically studied performing EMD simulations.

3.3. Intermolecular Interactions

In this study, intermolecular interactions between the atoms are calculated in both GCMC and EMD simulations. In the case of adsorption, dominant forces are the attractive dispersion forces and short-range repulsive forces [75]. These forces are commonly named as van der Waals forces. In addition, electrostatic (Coulombic) forces are responsible for the adsorption of molecules with quadrupole moment.

3.3.1. van der Waals Interactions

Non-bonded interactions including attractive dispersion forces and short-range repulsive forces are generally calculated using Lennard-Jones 12-6 type potentials for all non-bonded pairs of atoms [96,97]. The Lennard-Jones potential can be computed using Equation (3.15) where r represents the distance between two molecules. In order to compute non-bonded interactions between atoms, each atom must be represented using two LJ parameters: σ and ϵ .

σ is the size parameter interpreting distance where intermolecular potential is zero whereas ϵ is the energy parameter describing the size of the potential well, respectively.

$$U_{LJ} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (3.15)$$

The result builds a balance between the long-range attractive van der Waals potential (of order r^{-6}) and the short-range repulsive potential arising from electron orbital overlap (of order r^{-12}), described by the Pauli Exclusion Principle [75]. It approximates empirical data for simple systems with satisfying accuracy. It also has the advantage that it is computationally efficient since r^{-12} is easily calculated as the square of r^{-6} . A representative plot of this potential is shown in Figure 3.4. At large distances ($r \gg r_0$), the magnitude of the interaction potential is negligible. Therefore, the potential is usually truncated at a cut-off distance in the

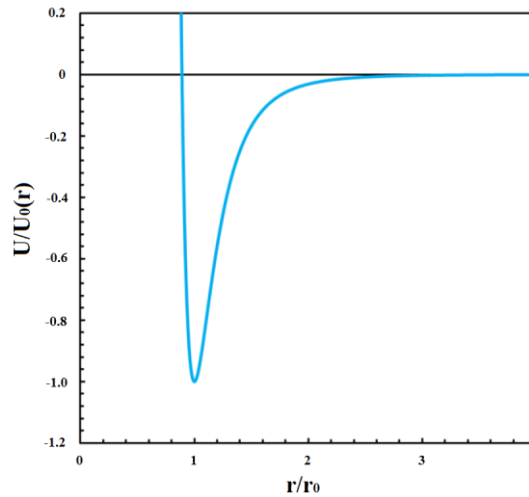


Figure 3.4. The Lennard-Jones 12-6 potential is scaled in units of U_0 , the depth of the well. The equilibrium distance between the interacting molecules is $r = r_0$ (adapted from [75]) simulations. For this work, cut-off distance is set to 13 Å. If the molecules become spontaneously closer together as a result of random collision, it is favorable for them to

remain at a specific distance shown with r_0 , namely equilibrium distance. At very short distance, the Pauli repulsion term dominates and the interacting molecules repel each other.

3.3.2. Electrostatic Interactions

Electrostatic interactions are dominant for electrically charged pairs of atoms. In both GCMC and MD simulations, these interactions are taken into consideration for the interaction calculations of gas molecules which have quadrupole moments such as CO₂ (13.4 C.m²) and N₂ (4.7 C.m²) [98]. Electrostatic interaction potential can be computed using Equation (3.16) where ϵ_0 , q_A and q_B represent the electric constant (permittivity of free space), the partial atomic charges assigned to atom A and B, respectively [96]. Similar to van der Waals potential, the cut-off distance for electrostatic potential is set to 25 Å during the simulations.

$$U_{AB} = \frac{1}{4\pi\epsilon_0} \frac{q_A q_B}{r_{AB}} \quad (3.16)$$

3.4. Computational Details

In this section, computational details including force field parameters used to model PCNs and gas molecules, methods used to assign partial atomic charges to PCN atoms, algorithms used to calculate the structural properties of PCNs will be discussed.

3.4.1. Models to Represent PCNs and Gas Molecules

In this work, the positions of all atoms of PCNs are extracted from X-ray diffraction experiments. To obtain X-ray diffraction files, The Cambridge Crystallographic Data Centre (CCDC) is used. The PCN frameworks are assumed to be rigid during the simulations. The Lennard-Jones (LJ) parameters which are required to calculate the van der Waals interactions between atoms are taken from Dreiding force field [99]. The LJ parameters of the atoms which are not available in the Dreiding force field are taken from Universal Force Field (UFF) [100]. The energetic potential parameters (ϵ) of carbon atom of PCN-26 and PCN-80 are modified to get a better agreement between the experimentally measured gas adsorption data and simulation results. The partial charges of framework atoms are assigned using two

different methods: CBAC (Connectivity Based Atomic Contribution) method and EQeq (Extended Charge Equilibration Method) which will be discussed in section 3.4.2.

Spherical Lennard-Jones (LJ) 12-6 potential is used to model gas molecules. Both H_2 and CH_4 molecules are modeled as single spheres using united atom model. Since they are nonpolar molecules, only van der Waals interactions are taken into account for them. H_2 is modeled using Buch potential whereas TraPPE force field is employed for CH_4 [101,102]. During molecular simulations, CO_2 is represented as a rigid three site molecule with partial point charges located at the center of each site. Potential parameters of CO_2 are taken from TraPPE force field developed by Potoff and Siepmann [103]. Similarly, N_2 molecule is modeled as a three site model with two sites located at two N atoms and the third one located at its center of mass (COM) with partial point charges [104]. For the gas molecules having quadrupole moment (CO_2 and N_2), the electrostatic interactions are computed in addition to van der Waals interactions.

In the air separation study, the O_2 and N_2 molecules are modeled using different potential parameters [105]. The electrostatic interactions are neglected since they induce overestimation of the experimental adsorption data. The potential parameters used in air separation study are given in Table 3.3.

In order to calculate cross-interactions between unlike LJ sites, Lorentz-Berthelot mixing rules are employed as shown in Equation (3.17) [106]. Additionally, periodic boundary conditions are employed during the simulations in order to avoid the surface effects. The simulation box of $2 \times 2 \times 2$ crystallographic unit cells is used in GCMC simulations. During the simulations, 1.5×10^7 steps are performed to guarantee the equilibration and 1.5×10^7 steps are performed to sample the desired properties. Four different types of moves are considered for single-component GCMC simulations including translation, rotation, insertion and deletion of a molecule. In the binary mixture GCMC simulations, another trial move, exchange of molecules is also performed. In the EMD simulations, the initial states with the appropriate adsorbate loadings are obtained from the GCMC simulations and each system is equilibrated for 20 ps prior to taking data. At NVT ensemble, The Nosé-Hoover thermostat is applied to run EMD simulations [80]. At least 20 independent EMD simulations with a length of 16 ns are performed to compute self-diffusivities of gases at a given loading with a time step of

8000 ps. At the lowest loadings, the size of the simulation volume is increased to 4×4×5 to contain enough particles to increase the statistical accuracy of simulations.

Table 3.1 Potential parameters used for PCNs in molecular simulations

Atom	σ (Å)	ϵ/k_B (K)
C	3.47	47.88 ^a
Cl	3.52	142.65
Co ^b	2.55	7.04
Cu ^b	3.11	2.51
Fe ^b	2.59	6.54
H	2.85	7.65
Hf ^b	2.79	36.25
Mn ^b	2.63	6.54
N	3.26	38.97
Ni ^b	2.52	7.55
O	3.03	48.19
Zn	4.04	27.69
Zr ^b	2.78	34.74

^aThis parameter is set to 41.86 for PCN-26 and 23.94 for PCN-80 to get a better agreement with the experimental gas uptake of CO₂.

^bThe potential parameters of metal atoms are taken from UFF since they are not available in Dreiding.

Table 3.2 Potential parameters used for gas molecules in molecular simulations

Molecule	Atom	σ (Å)	ϵ/k_B (K)	q(e)	l(Å)
H ₂	H ₂	2.96	34.20	-	-
CH ₄	CH ₄	3.73	148.20	-	-
CO ₂	C	2.80	27.00	0.70	±1.16
	O	3.05	79.00	-0.35	0
N ₂	N	3.31	36.40	-0.40	±0.55
	COM	0.00	0.00	0.80	0

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad (3.17)$$

Table 3.3 Potential parameters used for O₂ and N₂ molecules [105]

Molecule	Atom	σ (Å)	ε/k_B (K)	l (Å)
O ₂	O	3.12	30.2	±0.48
	COM	0.00	0.00	0
N ₂	N	3.26	34.70	±0.55
	COM	0.00	0.00	0

3.4.2. Charge Assignment Methods (CBAC Method, EQeq Method)

In order to calculate electrostatic interactions, it is required to assign partial charges to each atom in the framework. There are various charge assignment methods in the literature such as Connectivity Based Atom Contribution (CBAC), DDEC (Density Derived Electrostatic and Chemical), DFT (Density Functional Theory), Qeq (Charge Equilibration), EQeq (Extended Charge Equilibration), PQeq (Periodic Charge Equilibration) and REPEAT (Repeating Electrostatic Potential Extracted Atomic) [107]. For charge estimation, the quantum mechanical calculations and the methods requiring iterative approaches are computationally costly. However, it is very useful to have a general method that can be used to quick estimation of the charges with reasonable accuracy for PCNs without requiring the time-expensive quantum mechanical (QM) calculations. Charge estimation method should be simple and easy to apply in order to perform a large scale screening of PCNs for gas storage and separation applications. CBAC and EQeq methods are useful charge assignment methods due to their simplicity and applicability for high-throughput material screening.

Although the number of nanoporous materials such as PCNs is nearly infinite, the atomic types involved are limited. In the CBAC method, the atomic partial charges in the frameworks are calculated using DFT on the basis of the fragmental clusters by Gaussian 03 package [108]. The aim is to estimate charges to framework atoms solely based on the atom type of itself and its neighbors. In other words, the partial charge of a framework atom is determined

by its bonding connectivity environment and the atoms with the same connectivity have identical charges in different PCNs. This assumption allows CBAC method to quickly estimate the atomic partial charges of PCNs without computational cost. However, the same charge is assigned to the same element with same neighbor atoms in different materials. Therefore, an important drawback of this method is the fact that the number of elements whose charge can be assigned using it is very limited.

Another charge estimation method used in this thesis is EQeq method. In the EQeq method, the charges are calculated using all of the measured ionization energies (first, second, third, etc) for every atom in the periodic table. It is the extended version of Qeq method developed by Wilmer and coworkers [109]. The partial charges are determined by simultaneously solving a system of linear equations. This means no iteration is required. Therefore, its computational cost is extremely low with respect to DFT-based calculations. Different from the Qeq method, EQeq method changes the Taylor series expansions for the transition metal atoms to be centered about their oxidation charges and it uses the ionization potentials and electron affinities corresponding to their oxidation states to calculate the partial charges [109]. It is simple, easy to use and rapid general method for charge estimation. In the first part of this thesis, the effect of charge assignment method (CBAC and EQeq) on the adsorption and separation performance of materials is analyzed for PCN-9-Co, PCN-9-Mn and PCN-26.

3.4.3. Calculation of Structural Properties

Recently, a characterization tool to calculate accessible surface area of porous materials was developed by Düren and coworkers [110]. It calculates the accessibility of porous materials with respect to a simple spherical or molecular probe, in this case N_2 atom with a kinetic diameter of 3.31 Å. The accessible surface area is the locus of points which corresponds to the location of the probe particle at a distance, r_c , from an atom of the porous framework and at least r_c from all other atoms in the framework [111]. The distance represented as r_c is usually named as collision diameter. In the algorithm, each atom in the framework is sequentially considered. For each atom, a sphere of diameter $r = r_f + r_p$, where r_f (r_p) is the diameter of the framework atom (probe). The points on the framework surface are randomly generated and at each point, a probe particle is placed. Then the probe is tested for

the overlaps of the other atoms of the framework. The accessible surface area (A_i) can be calculated for atom i in the framework using Equation (3.18).

$$A_i = \pi f r^2 \quad (3.18)$$

In Equation (3.18), f represents the fraction of points which do not overlap between the probe and other framework atoms. Then, total accessible surface area (A_{surface}) becomes the sum of each atom's accessible surface area as shown in Equation (3.19). Here, N is the total number of atoms in the framework.

$$A_{\text{surface}} = \sum_{i=1}^N A_i \quad (3.19)$$

The calculated A_{surface} is in $\text{\AA}^2$ units and should be converted m^2 per gram of the porous material. For a closer approximation with BET surface area, LJ potential minimum distance should be used instead of the collision diameter. Further details can be found in the literature [110]. In this study, surface area of PCNs are calculated using Dürren et al.'s method to develop simple models for adsorption and membrane selectivities of PCNs for CH_4/H_2 and CO_2/H_2 mixtures.

To compute the pore sizes of PCNs, an algorithm developed by Sarkisov and Harrison is used [111]. In this algorithm, pore is considered in a geometric sense as shown in Figure 3.5 in which the grey atoms represent the framework atoms. In the figure, two circles contain the point, P . The red dashed circle shows the largest cavity whereas the black circle is a circle which also contains P , but it is not the largest possible sphere [111]. A Monte Carlo algorithm is used to calculate the pore sizes of the framework. A test point, represented as P in the figure, is randomly located in the simulation cell. If the point is not already inside a framework atom, test to check whether it overlaps with any of the framework atoms or not is performed. If there is no overlap, the second round of Monte Carlo procedure is performed and the porous space is probed to find the largest sphere which contains the randomly-assigned point and does not overlap with any framework atoms [111].

In this work, two important output of this algorithm, namely the limiting pore diameter (LPD) and largest cavity diameter (LCD) are computed for all PCNs. In gas separation

processes, the structural features of porous materials play vital role. In this work, LPD and LCD are calculated using Sarkisov's algorithm and used to develop simple models for diffusion selectivity of CH_4/H_2 and CO_2/H_2 mixtures.

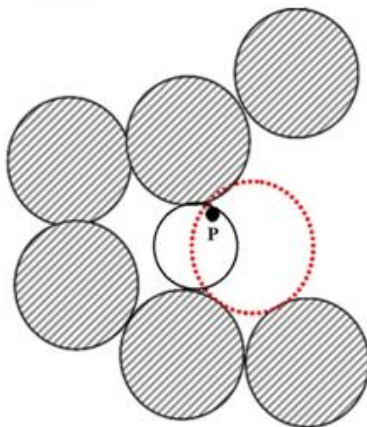


Figure 3.5. Schematic representation of the geometric pore [111].

Another important structural feature of the nanoporous materials is the pore volume (V_{pore}) which can be defined as the sum of volumes of all pores in one gram of adsorbent. In this study, pore volumes of the materials are calculated using Mercury 5.35 software [112]. The structural features of PCNs studied in this thesis are tabulated in Table 3.4.

3.5. Evaluation Criteria for Gas Separation Processes

The adsorbed gas amount and diffusivity of adsorbed gas molecules are computed employing GCMC and EMD simulations, respectively. However, both are not enough to evaluate the gas separation performances of PCNs. In this thesis, several parameters are calculated to specify the good adsorbent and membrane candidates for gas storage and gas separation applications.

Table 3.4. Structural properties of PCNs

PCN	V_{pore} (cm³/g)	A_{surface} (m²/g)	Density (g/cm³)	LPD (Å)	LCD (Å)
PCN-6	1.23	3578.22	0.58	7.11	13.04
PCN-6'	2.96	5253.62	0.29	14.48	22.94
PCN-9-Co	0.68	1382.23	0.86	3.45	15.32
PCN-9-Mn	0.71	1393.41	0.84	3.43	15.20
PCN-9-Fe	0.69	1265.06	0.85	3.03	15.31
PCN-10	0.76	1888.22	0.82	3.08	10.51
PCN-11	0.80	2057.41	0.80	3.48	10.53
PCN-13	0.29	753.69	1.24	4.30	5.18
PCN-14	1.13	2049.94	0.87	4.48	6.66
PCN-16	0.86	2678.73	0.77	4.00	10.66
PCN-16'	0.77	2706.71	0.82	4.42	11.33
PCN-18	0.55	1552.48	0.86	4.31	6.63
PCN-19	0.48	1335.58	1.00	6.69	9.61
PCN-20	1.58	4185.31	0.49	9.13	16.65
PCN-26	0.71	2124.31	0.84	5.02	8.37
PCN-39	0.97	3227.67	0.65	4.53	7.55
PCN-46	1.05	3333.74	0.66	5.56	10.63
PCN-80	1.12	3566.07	0.65	6.44	12.69
PCN-121	0.80	2506.76	0.75	8.29	9.29
PCN-131'	0.15	160.88	1.28	2.59	4.88
PCN-221-Cu	0.91	2942.80	0.75	4.34	15.91
PCN-221-Hf	0.93	2055.28	0.73	3.89	15.57
PCN-222	0.48	3193.78	1.64	15.81	18.00
PCN-224-Ni	1.69	3419.42	0.48	13.63	23.96
PCN-225	0.90	2744.69	0.73	6.47	10.67

3.5.1. Evaluation Criteria for Adsorption-based Separation

In adsorption-based separation processes such as pressure swing adsorption (PSA), adsorption selectivity and working capacity of the adsorbent are the two important parameters that define the efficiency of the process. Adsorption selectivity (S_{ads}) is defined as the ratio of adsorbed amounts of gases in a mixture normalized by the feed composition of the mixture.

$$S_{\text{ads}(i/j)} = \frac{x_i/x_j}{y_i/y_j} \quad (3.20)$$

Here, x stands for the molar fraction of the adsorbed phase obtained from the GCMC simulations while y represents the molar fraction of the bulk gas phase. Equation (3.20) defines the adsorption selectivity of an adsorbent with respect to component i , meaning that if S_{ads} is greater than 1, then the adsorbent is selective for component i . In this study, the adsorption selectivities of PCNs are computed for CH_4/H_2 , CO_2/CH_4 , CO_2/H_2 and CO_2/N_2 separations using the results of binary GCMC simulations. The bulk gas compositions of these mixtures are set to 50/50, 50/50, 15/85 and 15/85, respectively to represent the industrial mixture conditions. Additionally, the adsorption selectivity of O_2/N_2 with 20/80 composition is calculated for PCN-9-Co, PCN-121 and PCN-131'. Working capacity (ΔN) is the difference between the loading amounts of the gas at the corresponding adsorption (N^{ads}) and desorption (N^{des}) pressure and defined in unit of mol gas per kg of adsorbent as shown in Equation (3.21) [14].

$$\Delta N = N^{\text{ads}} - N^{\text{des}} \quad (3.21)$$

The adsorption and desorption pressures are set to 10 and 1 bar, respectively since most adsorption processes in industry are performed under these conditions.

Using the combination of these two criteria, adsorption selectivity and working capacity, another important parameter named as sorbent selection parameter (S_{sp}) can be computed and used to compare the performances of different nanoporous material in adsorption-based separation of gas mixtures.

$$S_{sp} = \frac{S_{ads(i/j)}^2}{S_{des(i/j)}} \times \frac{\Delta N_i}{\Delta N_j} \quad (3.22)$$

Similarly, regenerability (R), the ratio of working capacity to the adsorbed amount at adsorption pressure, is also an important parameter to evaluate adsorbent for cyclic PSA and VSA processes [14]. Regenerability expresses the fraction of adsorption sites regenerated during desorption steps. In this study, S_{sp} and R are computed using binary GCMC simulations at the adsorption pressure of 10 bar and desorption pressure of 1 bar.

$$R(\%) = \frac{\Delta N_1}{N_1^{ads}} \times 100 \quad (3.23)$$

In this work, the plot of working capacity versus adsorption selectivity is used for quick evaluation of the performances of PCNs for adsorption-based gas separation applications. A good adsorbent candidate should possess high adsorption selectivity due to the fact that the purity of the product increases as selectivity increases. Furthermore, high working capacity is also required for PCNs to be good adsorbent candidates since it represents the storage capability for the strongly adsorbed gas molecule in the working conditions. Apart from these conditions, PCNs should exhibit high S_{sp} and R. The former should be large since it is the combination of working capacity and adsorption selectivity. The latter is related with the efficiency of the adsorbent at each PSA or VSA cycle.

3.5.2. Evaluation Criteria for Diffusion-based Separation

In order to examine the membrane-based separation performances of PCNs combining the results of GCMC and EMD simulations, both adsorption and diffusion of gas mixtures in the pores of PCNs must be known. Diffusion selectivity (S_{diff}) is the ratio of the self-diffusivities (D_s) of each gas component in the binary mixture. In Equation (3.24), c represents the corresponding adsorbed loading calculated from GCMC simulations.

$$S_{\text{diff}(i/j)} = \frac{D_{s,i}(c_i, c_j)}{D_{s,j}(c_i, c_j)} \quad (3.24)$$

In most nanoporous materials, adsorption selectivity favors the more strongly adsorbed component whereas diffusion selectivity favors the weakly adsorbed component since strongly adsorbed species diffuse more slowly than the weakly adsorbed species. In other words, high adsorption selectivities are generally compensated by low diffusion selectivities. This situation makes most materials promising for adsorption-based gas separations and much less efficient for membrane-based gas separations since the permeation selectivity (membrane selectivity) is calculated by multiplication of adsorption and diffusion selectivity. It would be very useful to identify materials where both adsorption and diffusion selectivities favor the same component and hence high membrane selectivities can be obtained. Therefore, in this study, diffusion selectivity is calculated to evaluate the diffusion-based performances of PCNs and to compute the membrane selectivity of PCNs.

3.5.3. Evaluation Criteria for Membrane-based Separation

Once the adsorption and diffusion-based selectivities of the material for a given gas mixture are calculated from molecular simulations, the permeation selectivity (S_{perm}) also known as membrane selectivity can be defined as the multiplication of adsorption and diffusion selectivity.

$$S_{\text{perm}} = S_{\text{ads}} \times S_{\text{diff}} \quad (3.25)$$

Permeation selectivity and permeability of membranes are calculated at a membrane feed pressure of 10 bar and permeate pressure of vacuum. More details about derivation of this expression can be found in the literature [113]. Besides selectivity, the gas permeability through PCNs is also important because both high selectivity and high permeability are desired in a membrane process. Membrane materials that suffer from low gas permeability require large surface areas and cause a high capital cost. Therefore, gas permeability of the PCNs is calculated using Equation (3.26).

$$P_i = \frac{\phi \times D_{s,i} \times c_i}{f_i} \quad (3.26)$$

In Equation (3.26), P_i , ϕ , $D_{s,i}$, c_i , and f_i represent the permeability of the component i (mol/m/s/Pa), the fractional pore volume of PCN materials, the self-diffusivity of the component i , the concentration of component i at the upstream face of the membrane (mol/m³) and the bulk phase fugacity of the component i (Pa), respectively. The gas permeability is reported in the unit of Barrer since it is more widely used in the membrane community.

In this work, the plot of permeability versus permeation selectivity is used to evaluate the performances of PCNs for membrane-based gas separation applications. A good membrane candidate should possess high membrane selectivity since high permeation selectivity leads to purer products and increases the efficiency of separation. Additionally, high permeability is also required for PCNs to be good membrane candidates because the required amount of surface area of membrane candidate decreases as permeability increases. Consequently, capital cost of gas separation unit also decreases. Therefore, the good membrane candidates should be at the right-upper part of the permeability versus permeation selectivity figure.

3.6. Mixed Matrix Membrane Calculations

Mixed matrix membranes (MMM) consist of inorganic fillers (dispersed phase) that are embedded into a continuous phase including a polymer matrix. The aim of MMM study in this thesis is to analyze the performances of PCN-filled MMMs for air separation. The O₂ and N₂ permeations in PCN-filled MMMs are predicted using Maxwell model for air separation applications. Maxwell model considers ideal morphology by assuming that the dispersed phase is embedded into polymer matrix perfectly and there is no rigidification on matrix chain layer around the dispersed particles [114]. It is important to note that there is no available experimental study related with the performances of PCN-filled mixed matrix membranes in the literature.

In order to perform MMM calculations, experimental gas permeability data for pure polymers are taken from the literature. The O₂ and N₂ permeabilities of pure PCNs are also required to determine the performance of PCN-filled MMMs for air separation processes. Since this data is not available from the literature, molecular simulations are performed to estimate gas permeabilities of PCNs. At the same conditions with polymer experiments, GCMC simulations are employed to compute single component adsorption amount of gas molecules in pure PCNs. The corrected diffusivities (D_c) are then calculated performing EMD simulations at the gas loading taken from GCMC simulations. The transport diffusivity is calculated using the corrected diffusivity and the thermodynamic correction factor as shown Equation (3.12). Flux of gas molecules are computed using Equation (3.9) and then converted to permeability via Equation (3.27). In Equation (3.27), P , J , L and p represent gas permeability in PCN, flux, membrane thickness and pressure, respectively. After the gas permeabilities of PCNs are computed as explained using molecular simulations, this data is used to estimate permeability of MMMs using Maxwell model [7].

$$P = \frac{J \times L}{\Delta p} \quad (3.27)$$

Equation (3.28) represents the Maxwell model. Here, P_{MMM} , $P_{polymer}$, ϕ and λ stand for permeability of MMM, permeability of pure polymer, volume fraction of PCNs in MMM and the ratio of permeability of pure PCN to permeability of pure polymer, respectively.

$$P_{\text{MMM}} = P_{\text{polymer}} \times \left[\frac{2(1-\phi) + (1+2\phi)\lambda}{(2+\phi) + (1-\phi)\lambda} \right] \quad (3.28)$$

Chapter 4: Initial Analysis of Adsorption and Diffusion in PCNs

4.1. Validation of Accuracy of the Simulations

This section will briefly validate the accuracy of potential parameters used in the simulations performed in this work. Before performing detailed analysis about the separation performances of PCNs, the results of our simulations are compared with the available experimental data of the single-component gas adsorption of several PCNs in order to validate the accuracy of the molecular simulation parameters. GCMC simulations are performed exactly at the same pressure and temperature with the experimental data to be consistent. Figure 4.1 and 4.2 show the simulated and experimental data for excess uptake of H₂, CH₄, CO₂ and N₂ in various PCNs [21-23,25,26,28,30,31,34,41,62,65]. There is a reasonable agreement between experiments and simulations for all four gases and all PCNs both at low and high pressures although there are some simulation results that deviate from experimental measurements by 10-20%, which is acceptable for the purpose of this work. For example, experiments measure H₂ uptake of PCN-10 (PCN-11) as 2.4 wt% (2.7 wt%) at 1 bar and 298 K, while our simulations predict a value of 2.3 wt% (2.5 wt%) under the same conditions [28]. The quantity of adsorbed CH₄ is measured as 179.1 cm³ STP/cm³ by experiments at 110 bar and 298 K in PCN-46 and our GCMC simulations predict this value as 178 cm³ STP/cm³ under the same conditions [30]. Similarly, a good agreement is obtained for CO₂, although simulations slightly overestimate the experimental CO₂ adsorption isotherms at high pressures. For example, our simulations calculate the adsorbed quantity of CO₂ as 13.4 mmol/g in PCN-80 at 10 bar and 296 K whereas experiments report this value as 11.4 mmol/g [23]. In PCN-26, our simulations predict N₂ uptake of 13.3 cm³STP/g at 1 bar and 298 K

whereas the N_2 uptake is measured as $9.2 \text{ cm}^3\text{STP/g}$ in experiment performed under the same conditions [31]. Motivated from the good agreement between experiments and simulations for single-component gas uptakes, the same potential parameters are used to perform binary mixture GCMC and EMD simulations for detailed analysis of separation performances of PCNs.

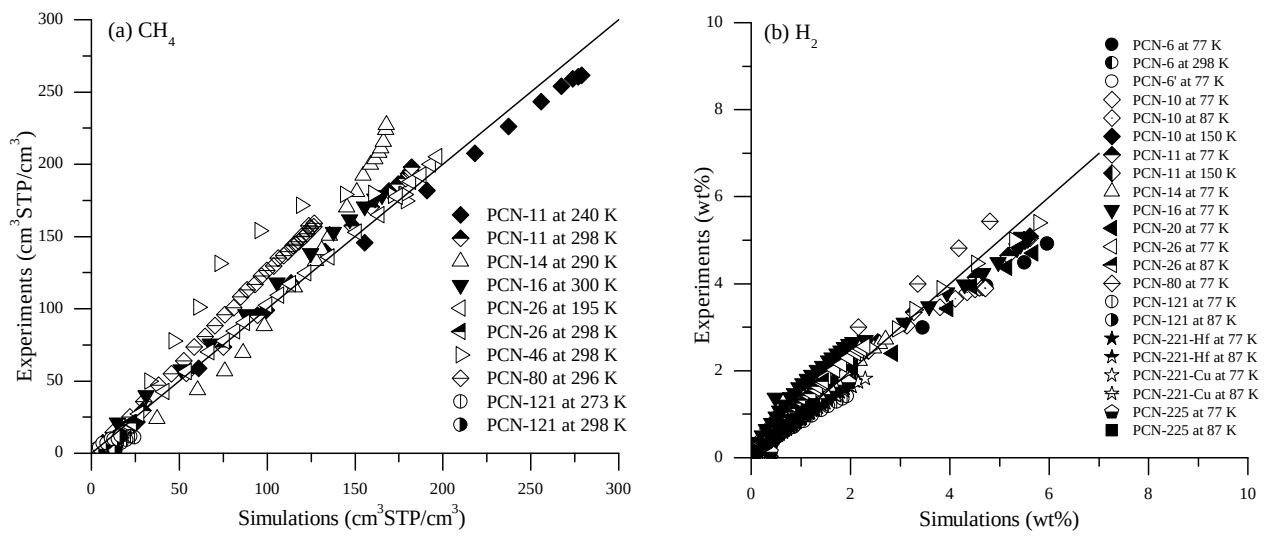


Figure 4.1. Comparison of our simulation data with the experimental gas uptake data of PCNs for (a) CH_4 and (b) H_2 . Experimental data are collected at 1-50 bar in (a) and 1-65 bar in (b) from the literature [21-23,25,26,28,30,31,34,41,62,65].

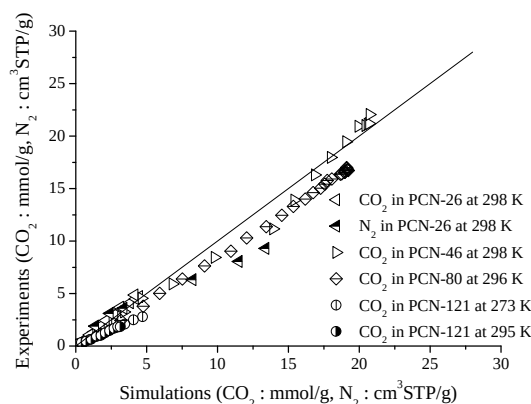


Figure 4.2. Comparison of our simulation data with the experimental gas uptake data of PCNs for CO₂ and N₂. Experimental data are collected at 1-50 bar for CO₂ and up to 1 bar for N₂ from the literature [23,30,31,41].

4.2. Gas Storage and Separation Performance Analysis of PCNs

In this work, atomically detailed simulations are used to predict the performance of PCN materials both in adsorption-based and membrane-based separations of CH₄/H₂, CO₂/CH₄, CO₂/H₂ and CO₂/N₂ mixtures. The adsorption-based selectivity, working capacity, regenerability, sorbent selection parameter, diffusion-based selectivity, membrane-based selectivity and gas permeability of various PCNs are predicted. Additionally, the effect of charge assignment method on this type of separation analysis is studied.

In order to compute adsorption-based separation performances of PCNs for CH₄/H₂, CO₂/CH₄, CO₂/H₂ and CO₂/N₂ mixtures, mixture GCMC simulations are performed at 298 K up to 50 bar. Binary adsorption isotherms of each mixture for PCN-9-Co, PCN-9-Fe, PCN-9-Mn and PCN-26 are given in Figures A1-A4 of Appendix-A, respectively. Adsorption selectivities of PCN-9-Co, PCN-9-Fe, PCN-9-Mn and PCN-26 for CH₄/H₂, CO₂/CH₄, CO₂/H₂ and CO₂/N₂ mixtures are shown in Figure 4.3. Adsorption of CH₄ is favored over H₂ for the equimolar CH₄/H₂ mixture since H₂ has weak interactions with PCN atoms. All PCNs are CH₄ selective (~14-36) for CH₄/H₂ separation and adsorption selectivity for CH₄ shows a decrease with increasing pressure. The reason of this decrease can be explained by the interplay of energetic and entropic effects. At low pressures energetic effects favor CH₄ adsorption over H₂ and lead to high CH₄ selectivity whereas at higher pressures, most of the adsorption sites are full and only small H₂ molecules can find adsorption sites in contrast to large CH₄ molecules. Therefore, CH₄/H₂ selectivity decreases at high loadings. Adsorption of

CO₂ is strongly favored over the second component (CH₄, H₂, N₂) in all mixtures due to the electrostatic interactions of CO₂ molecules with the framework atoms which is absent for CH₄ and H₂ molecules. N₂ has also electrostatic interactions with the framework atoms but the quadrupole moment of CO₂ (13.4 C.m²) is larger than that of N₂ (4.7 C.m²) [98]. Figure 4.3 shows that adsorption selectivity of PCN-26 for CO₂ over H₂, CH₄ and N₂ increases with increasing pressure. This can be attributed to the collaborative electrostatic interactions between the CO₂ molecules as well as interactions between CO₂ molecules and framework atoms. These interactions enhance the CO₂ selectivity. In contrast to PCN-26, CO₂/CH₄, CO₂/N₂ and CO₂/H₂ selectivities of PCN-9 series are almost constant at high pressures after a sharp decrease at low loadings which can be explained by the available pore volumes of materials. PCN-26 has a large pore volume (0.84 cm³/g) compared to PCN-9 materials (0.33-0.51 cm³/g). Therefore, saturation is reached in PCN-9 series and the CO₂ selectivities become almost constant at high pressures. The CO₂/CH₄ selectivities (6-115) of all PCNs are lower than the CO₂/N₂ (15-700) and CO₂/H₂ (170-7000) selectivities due to the stronger competition between CO₂ and CH₄ molecules for available adsorption sites. The highest CO₂ selectivities are observed for CO₂/H₂ mixture since CO₂ is the most strongly adsorbed component and H₂ is the weakly adsorbed molecule as the single-component adsorption isotherms shown in section 4.1 suggests.

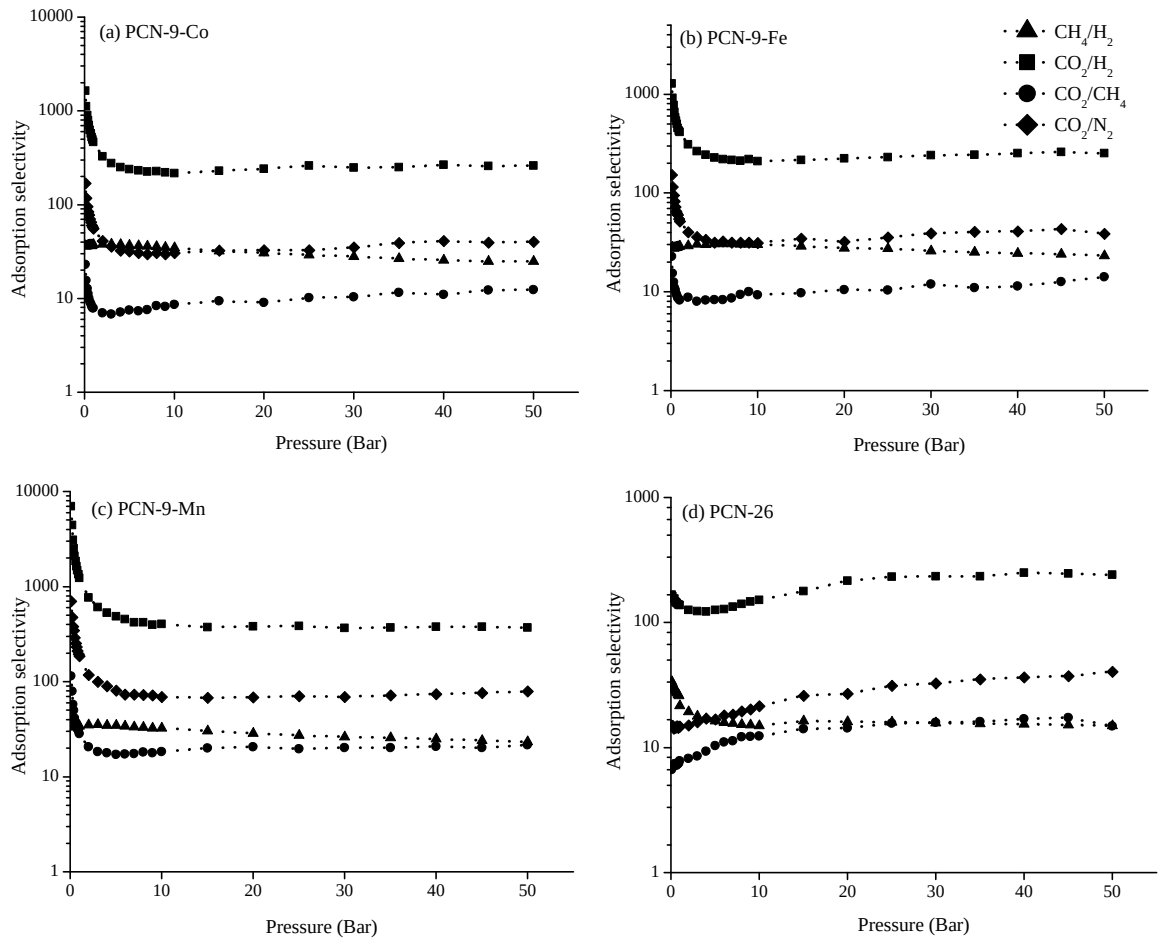


Figure 4.3. Predicted adsorption selectivities of PCNs for CH_4/H_2 , CO_2/CH_4 , CO_2/H_2 and CO_2/N_2 mixtures at 298 K. Compositions of the bulk gas mixtures are 50/50, 50/50, 15/85 and 15/85, respectively. Lines are to guide the eye.

In addition to adsorption selectivity, working capacity (ΔN), regenerability ($R(\%)$) and sorbent selection parameter (S_{sp}) of PCNs are calculated. The adsorption-based separation performances of PCNs are compared with other adsorbent materials for an industrially important process, natural gas purification in Table 4.1. Two S_{sp} values are calculated for PCN materials, one from mixture GCMC and one from single-component GCMC simulations. The S_{sp} values and adsorption selectivity calculated from mixture GCMC simulations (given in parentheses in Table 4.1) are higher than the ones predicted from single-component GCMC simulations. This is expected, since more strongly adsorbed component (CO_2) decreases adsorption of the other component (CH_4 , N_2 , H_2) in the mixture. Data for

other materials are taken from the literature and represent the top adsorbent candidates for natural gas purification [115]. HKUST-1 (also known as CuBTC), 35% Li-reduced diimide-POP and MOF-508b were recently reported as the strongest candidates for landfill gas separation due to their high S_{sp} values which are 21, 11.5 and 10.9, respectively. Table 4.1 suggests that PCN-26 exhibits better performance than these top adsorbent candidates due to its higher S_{sp} value of 37.3 and adsorption selectivity of 5.7. Although PCN-9 series have lower S_{sp} values compared to PCN-26 and other MOFs, they all exhibit higher CO_2 working capacity and CO_2 uptake.

Table 4.1 Separation performance of PCN materials for natural gas purification using PSA. The bulk composition of gas mixture is $CO_2/CH_4:50/50$. Adsorption and desorption pressures are 5 and 1 bar, respectively at 298 K unless otherwise specified. Numbers in parentheses show the data calculated from mixture GCMC simulations. Materials except PCNs represent the top adsorbent candidates for which data is taken from the literature [115].

Material	N_1^{ads} (mol/kg)	ΔN_1 (mol/kg)	R(%)	S_{ads}	S_{sp}
PCN-9-Co	9.86(8.85)	4.87(4.05)	49.46(45.83)	2.50 (7.47)	2.23(49.60)
PCN-9-Fe	9.77(8.81)	4.87(4.18)	49.92(47.50)	2.92(8.34)	2.60(71.56)
PCN-9-Mn	12.02(11.39)	3.93(3.44)	32.75(30.21)	3.18 (17.19)	1.72(93.53)
PCN-26	10.77(10.13)	7.81(7.18)	72.52(70.88)	5.71(10.31)	37.31(161.88)
HKUST-1	8.01	5.34	66.7	4.9	21.0
35%Li-reduced diimide-POP	2.93	1.44	49.2	3.6	11.5
MOF-508b (at 303 K)	3.60	2.58	71.7	2.9	10.9
MIL-101c (at 303 K)	6.70	3.20	47.8	5.0	9.5
$[Zn_3(OH)(p-cdc)_{2.5}(dmf)_4]$	0.94	0.66	70.6	3.3	8.3
55% Li-reduced diimide-POP	2.12	1.01	47.5	4.6	7.7
Zeolite-13X	5.37	1.40	26.1	4.2	2.0

Landfill gas separation can also be achieved by a VSA process which typically operates between adsorption pressure of 1 bar and desorption pressure of 0.1 bar. CUK-1, Mg-MOF-74 and $[Zn_3(OH)(p-cdc)_{2.5}]$ are reported as the best candidates for landfill gas separation using VSA as shown in Table 4.2. None of the PCNs considered in this work can outperform CUK-

1 since this MOF shows a particularly high S_{sp} value due to its low working capacity of CH_4 [115]. PCN-26 can be a strong adsorbent since it has a similar (higher) S_{sp} value to Mg-MOF-74 and Ni-MOF-74 (than HKUST-1, ZIF-82, zeolite-13X).

Table 4.2 Separation performance of PCN materials for natural gas purification using VSA. The bulk composition of gas mixture is $CO_2/CH_4:50/50$. Adsorption and desorption pressures are 1 and 0.1 bar, respectively at 298 K unless otherwise specified. Numbers in parentheses show the data calculated from mixture GCMC simulations. Materials except PCNs represent the top adsorbent candidates for which data is taken from the literature [115].

Material	N_1^{ads} (mol/kg)	ΔN_1 (mol/kg)	R (%)	S_{ads}	S_{sp}
PCN-9-Co	4.98(4.79)	2.78(2.59)	55.98(54.03)	4.75(7.90)	3.34(13.79)
PCN-9-Fe	4.89(4.62)	3.06(2.81)	62.60(40.75)	6.28(8.24)	7.36(17.45)
PCN-9-Mn	8.08(7.95)	2.60(2.56)	32.15(32.22)	8.25(28.43)	3.74(77.75)
PCN-26	2.95(2.95)	2.50(2.50)	84.64(84.98)	5.19(7.81)	20.99(73.83)
CUK-1	2.76	2.33	84.4	14.0	359.0
Mg-MOF-74	7.23	2.32	32.1	12.5	23.5
$[Zn_3(OH)(p-cdc)_{2.5}]$	0.59	0.49	83.1	7.8	21.4
Ni-MOF-74	6.23	3.16	50.7	8.5	21.0
ZIF-82	1.42	1.20	84.9	5.6	20.5
HKUST-1	2.81	1.90	67.5	5.5	19.8
Zeolite-13X	3.97	1.97	49.6	13.2	19.1

Other than natural gas purification, the performances of PCNs in flue gas separation are also examined. The typical composition of flue gas (CO_2/N_2) is assumed to be 10/90 whereas the typical adsorption and desorption pressures of a VSA process are assumed to be 1 bar and 0.1 bar, respectively in Table 4.3. Single-component adsorption isotherm-based calculations of Snurr and Bae identifies ZIF-78 as the strongest candidate for flue gas separation with an S_{sp} value of 396 [115]. Adsorption selectivity of ZIF-78 (34.5) is comparable with the selectivity of PCNs (13-60) considered in this work. The CO_2 uptake, working capacity and regenerability values for PCNs slightly change when the mixture isotherms are used instead of single-component isotherms. On the other hand, adsorption selectivity and S_{sp} values dramatically change when the mixture isotherms are used. The reason of change in adsorption selectivity is the sharp decrease of N_2 uptake due to the strong adsorption of CO_2 in the mixture. The reason of change in S_{sp} is the increase of adsorption selectivity (due to decrease

Table 4.3 Separation performance of PCN materials for flue gas separation using VSA. The bulk composition of gas mixture is CO₂/N₂:10/90. Adsorption and desorption pressures are 1 and 0.1 bar, respectively at 298 K unless otherwise specified. Numbers in parentheses show the data calculated from mixture GCMC simulations. Materials except PCNs represent the top adsorbent candidates for which data is taken from the literature [115].

Material	N_1^{ads} (mol/kg)	ΔN_1 (mol/kg)	R(%)	S_{ads}	S_{sp}
PCN-9-Co	2.81(2.78)	1.65(1.61)	58.94(58.15)	47.71(68.59)	42.97(113.53)
PCN-9-Fe	2.39(2.38)	1.63(1.61)	68.23(67.86)	52.06(63.99)	74.06(130.52)
PCN-9-Mn	6.03(5.94)	1.95(1.87)	32.33(31.57)	60.30(244.39)	24.96(736.00)
PCN-26	0.81(0.73)	0.71(0.62)	87.48(85.98)	13.43(14.14)	18.62(21.27)
ZIF-78	0.60	0.58	96.3	34.5	396
Zeolite-5A	3.50	2.36	67.4	61.8	163
Zeolite-13X	2.49	1.35	54.2	86.2	128
ZIF-82	0.41	0.38	92.5	26.4	105
Co-carborane MOF-4b	0.07	0.06	83.8	154	104
ZIF-81	0.27	0.25	93.4	22.7	101
Ni-MOF-74	4.34	3.20	73.7	41.1	83.5
ZIF-79	0.26	0.24	92.90	21.30	83.0
ethylenediamine- H ₃ [(Cu ₄ Cl) ₃ (BTtri) ₈]	0.45	0.26	57.60	58.40	77.2
[Zn ₂ (tcpb)(p-(CF ₃)NC ₅ H ₄) ₂]	0.16	0.13	80.7	43.9	57.9

of N₂ uptake) and the decrease of working capacity of second component, N₂. One important outcome from these tables is that materials that exhibit high S_{sp} may have low regenerability and this type of materials may not be useful in practical applications. For example, PCN-9-Mn is the strongest candidate for adsorption-based separation of CO₂/H₂ due to its high adsorbed loading of CO₂, high adsorption selectivity and high S_{sp} , however it has the lowest regenerability among other materials. This result underlines the importance of choosing materials by considering several criteria for adsorption-based gas separations.

Figure 4.4 compares adsorption selectivity and working capacity of PCNs for CH₄/H₂, CO₂/CH₄, CO₂/H₂ and CO₂/N₂ separations at 10 bar and 298 K. In order to compare adsorption-based separation performances of PCNs with other materials, data for well-known MOFs and zeolites are taken from the literature and shown in Figure 4.4 [116]. A promising adsorbent material should have both high adsorption selectivity and high working capacity. In other words, the best adsorbent materials are expected to be at the right upper corner of Figure

4.4. Figure 4.4(a) shows that PCN-9 series are very promising for CH₄/H₂ separation since they have higher CH₄ selectivities (>25) and higher working capacities (4 mol CH₄/kg PCN) than several widely studied MOFs and zeolites such as Mg-MOF-74, CuBTC, ZIF-8, CHA. Both selectivities and working capacities of PCN-9 series are similar to each other suggesting that the identity of metal center in the material is not very important for CH₄/H₂ separation performance of materials. Separation performance of PCN-26 is similar to Mg-MOF-74 and it has higher working capacity than traditional zeolites, ITQ-29 and CHA. These results suggest that PCNs considered in this work can be good adsorbents for CH₄/H₂ separation.

Figure 4.4(b) shows that adsorption-based separation performances of PCNs for CO₂/CH₄ mixtures are similar to Zn-MOF-74 and CHA. Although PCNs considered in this work are not able to exhibit the high CO₂ selectivity of AFX or NaX, they have higher working capacities (5-9 mol CO₂/kg PCN) than most of the MOFs and zeolites. The CO₂/CH₄ selectivities of PCNs are around 10 and this is higher than the selectivities of widely examined MOFs such as CuBTC, MIL-53, ZIF-8, IRMOF-1.

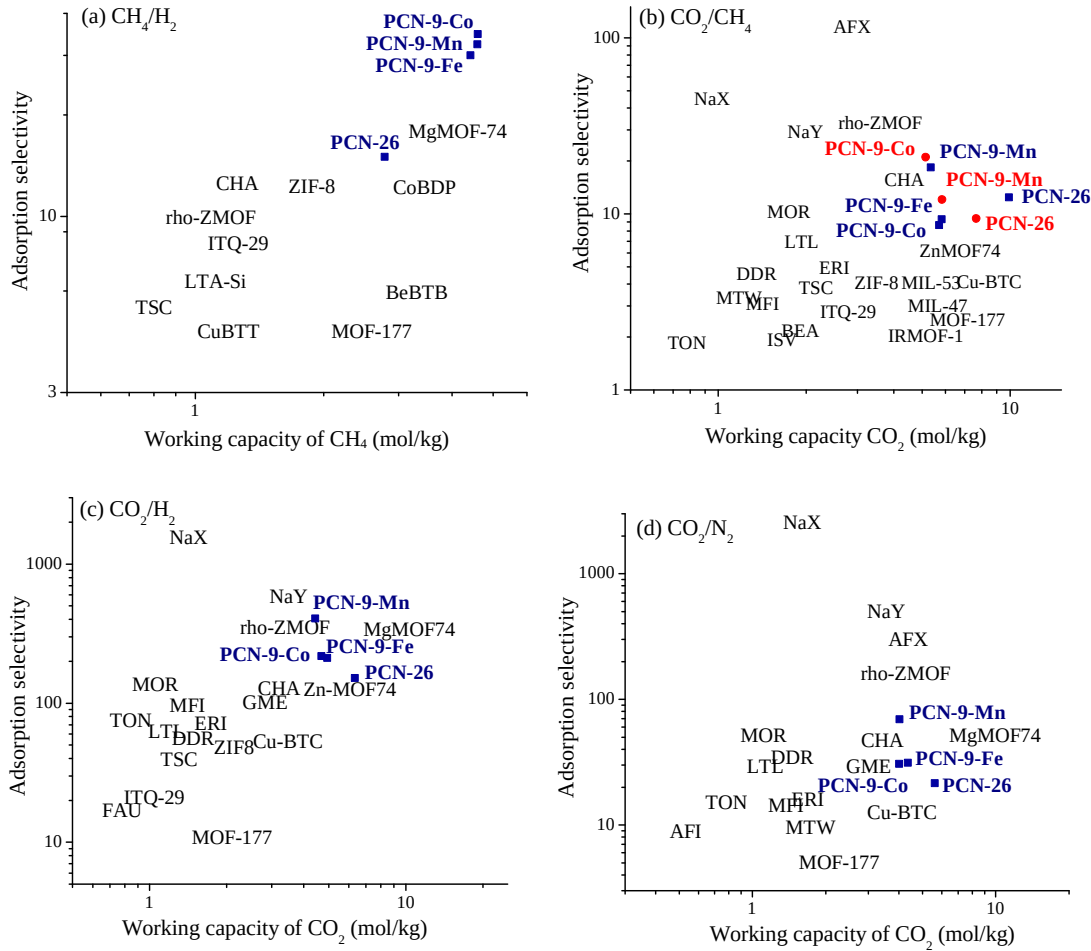


Figure 4.4. Adsorption-based separation performance of PCNs for (a)CH₄/H₂, (b)CO₂/CH₄, (c)CO₂/H₂ and (d)CO₂/N₂ mixtures. The compositions of the bulk gas mixtures are (a)50/50, (b)50/50, (c)15/85 and (d)15/85 at 298 K. The adsorption and desorption pressure are set to 10 bar and 1 bar, respectively. For other materials data is taken at 300 K from the literature [116]. Red colors in Figure 4.4(b) represent the results from atomic simulations where EEq charges are used instead of CBAC charges.

The data of PCNs shown in blue color are calculated by atomic simulations in which the CBAC method is used to assign partial charges to PCN atoms for accounting electrostatic interactions between PCN atoms and CO₂. In order to understand the effect of atomic charge assignment method on the predicted adsorption selectivities and working capacities of the materials, our simulations are repeated using the charges obtained from EEq method [109]. The predictions based on EEq method are shown in red color in Figure 4.4(b). The atomic charges of the PCN-9-Fe are assigned using only the EEq method since there is no data for the atom configuration of this PCN in CBAC method. Figure 4.4(b) shows that predicted

adsorption selectivity and working capacity of PCNs change when the EQeq method is used instead of CBAC method, although this change is not significant. Changing the charge assignment method alters the binary adsorption isotherms obtained from GCMC simulations. The CO_2 and CH_4 adsorption isotherms calculated using CBAC charges with the ones calculated using EQeq charges are compared and the results can be shown in Figure A5 of Appendix-A. Figure A5(a) shows that at low pressures, simulations based on CBAC and EQeq methods agree well with each other and also with the experimentally reported CO_2 adsorption isotherm of PCN-26. Figure A5(b) represents that adsorbed amount of CO_2 in PCN-26 obtained from CBAC method (~52 molecules/unit cell) is higher than the one obtained from EQeq method (~41 molecules/unit cell) at 10 bar whereas the adsorbed amounts of CH_4 obtained from these methods are almost same (~4 molecules/unit cell). Therefore, at 10 bar, CO_2/CH_4 adsorption selectivity (12.37) calculated using CBAC method is higher than the one calculated using EQeq method (9.40) for PCN-26. The same discussion is valid for PCN-9-Mn as can be seen from Figure A5(d). On the other hand, adsorption isotherms of PCN-9-Co show a different trend. When the charge assignment method is changed from CBAC to EQeq, the adsorbed amount of CO_2 in equimolar CO_2/CH_4 mixture changes from 89 to 103 molecules/unit cell in PCN-9-Co at 10 bar as shown in Figure A5(c). The adsorbed amount of CH_4 in equimolar CO_2/CH_4 mixture, on the other hand, decreases from 10 to 4 molecules/unit cell in PCN-9-Co under the same conditions. In other word, EQeq method predicts higher adsorbed amount for CO_2 and lower adsorbed amount for CH_4 compared to CBAC method. Therefore, adsorption selectivity (21.0) obtained from EQeq method is a lot higher than the selectivity (8.6) obtained from CBAC method under the same conditions as shown in Figure 4.4(b). So far, the effects of charge assignment method on predicted separation performance of PCNs for CO_2/CH_4 mixtures are represented and discussed. The same type of calculations is repeated for CO_2/H_2 and CO_2/N_2 mixtures and the same discussion is also valid for these mixtures. However, the predictions based on EQeq method are not shown in Figure 4.4(c) and (d) for clarity of the figures.

Figure 4.4(c) shows predicted adsorption selectivity and working capacity of the PCNs for CO_2/H_2 separation. The CO_2/H_2 selectivities are in the range of 151-405 and the working capacity of CO_2 is in the range of 4-6 mol CO_2/kg material. All PCNs show better performances than the widely studied MOFs and zeolites such as CuBTC, ZIF-8, MFI and

CHA. One can conclude that the four PCNs investigated in this work are highly promising materials for adsorption-based separation of CO_2/H_2 mixtures. Figure 4.4(d) presents the performances of the PCNs for CO_2/N_2 separation. All PCNs exhibit similar performances with adsorption selectivities in the range of 21-69, which are lower than MOFs such as NaX, NaY, AFX and *rho*-ZMOF. The high CO_2/N_2 adsorption selectivity of NaX and NaY can be attributed to the strong electrostatic interactions between the CO_2 and extra non-framework cations of these zeolites [116]. The working capacities of PCNs for CO_2/N_2 separations are similar to that of CO_2/H_2 separations, 4-5 mol CO_2/kg PCN. This high working capacity make them better candidates than materials such as CHA, MOR, GME and CuBTC in CO_2/N_2 separations. In summary, PCN materials are potential candidates for separation of CO_2 from CH_4 , H_2 , N_2 mixtures specifically due to their high CO_2 working capacities.

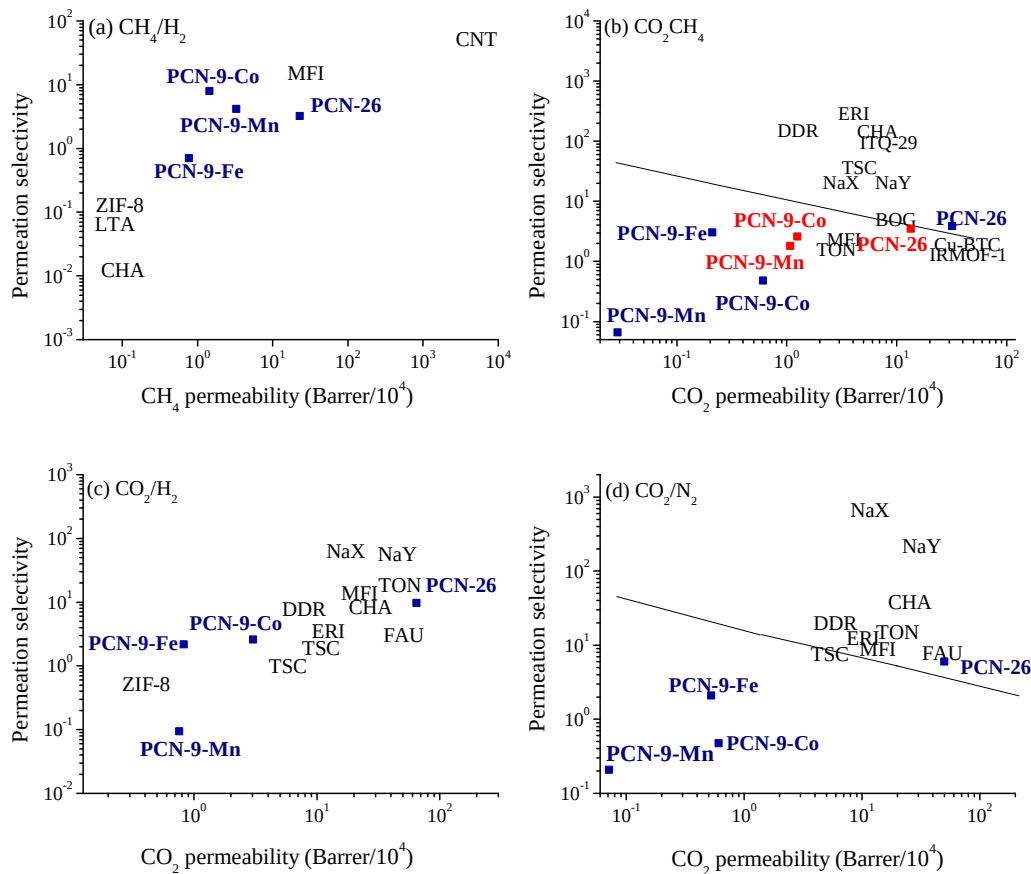


Figure 4.5. Comparison of separation performances of PCN membranes with other nanoporous membranes for (a) CH_4/H_2 , (b) CO_2/CH_4 , (c) CO_2/H_2 and (d) CO_2/N_2 mixtures at 298 K. The compositions of the bulk gas mixtures are (a) 50/50, (b) 50/50, (c) 15/85 and (d) 15/85 at 298 K. Composition of the CO_2/H_2 mixture is set to 1/99 only for PCN-9-Mn. The

feed and permeate pressures are set to 10 bar and vacuum, respectively. For other materials data is taken at 300 K from the literature [116]. Red colors in Figure 4.5(b) represent the results from atomic simulations where EQeq charges are used instead of CBAC charges.

The potential of PCNs as membranes for the same type of gas separations are also investigated. For an efficient membrane-based separation, both high permeation selectivity and permeability are required. Membranes having high selectivity and low permeability are not economic, since they require large surface areas and high capital costs. In order to assess membrane-based separation performance of PCNs in CH_4/H_2 , CO_2/CH_4 , CO_2/H_2 and CO_2/N_2 separations, permeation selectivity and permeability of PCNs are compared with other nanoporous membranes in Figure 4.5. Figure 4.5(a) suggests that LTA, CHA and ZIF-8 which have narrow windows separating their large cages exhibit H_2 selective permeation due to their molecular sieving properties. These materials also have very low CH_4 permeability, around 0.1 Barrer. Permeabilities of PCN membranes are higher than ZIF-8, LTA and CHA due to their larger pore openings. PCN-26, PCN-9-Co and PCN-9-Mn are CH_4 selective whereas PCN-9-Fe is found to be slightly H_2 selective (1.43). PCN-9-Fe favors CH_4 over H_2 in adsorption (selectivity of ~ 30 at 10 bar) however, H_2 diffuses almost 50 times faster than CH_4 and this makes PCN-9-Fe slightly H_2 selective in permeation.

The CO_2/CH_4 permeation selectivity and CO_2 permeability of PCNs and other nanoporous membranes are shown in Figure 4.5(b) together with Robeson's upper bound established for CO_2/CH_4 separations using polymeric membranes [116]. Materials that can exceed this upper bound are highly promising candidates for membrane-based CO_2/CH_4 separation. Among the PCN materials considered in this study, only PCN-26 is located above the Robeson's upper bound mainly due to its high CO_2 permeability. Similar to Figure 4.5(b), the calculations using the EQeq charge assignment method are repeated. The results can be found in Figure 4.5(b). As discussed earlier, CO_2/CH_4 adsorption selectivity predicted from CBAC method is higher than the one predicted from EQeq method. On the other hand, CO_2/CH_4 diffusion selectivity does not significantly change with the charge method. As a result, predicted permeation selectivity of PCN-26 from CBAC method is slightly higher than the one calculated from EQeq method. The most significant change in predicted permeation selectivity is observed for PCN-9-Mn. When the EQeq method is used to assign partial point charges to PCN-9-Mn, permeation selectivity of PCN-9-Mn is increased from 0.06 to 1.7. This can be explained with the following discussion: CO_2 adsorption significantly decreases

and diffusion of CO₂ molecules increases from $\sim 10^{-7}$ to 5×10^{-6} cm²/s when the EQeq method is used instead of CBAC. The diffusion coefficient of CH₄ molecules remains almost constant. Therefore, CO₂/CH₄ diffusion selectivity of PCN-9-Mn increases from 0.003 (CBAC) to 0.14 (EQeq). As a result, both CO₂/CH₄ permeation selectivity and CO₂ permeability increase when the charge method is switched from CBAC to EQeq. PCN-9-Mn is a good example that electrostatic interactions hence the charge assignment method may significantly affect the predictions about the separation performance of materials that have high affinity for CO₂. The atomic simulations are performed by turning off the electrostatic interactions between CO₂ molecules and PCN atoms to understand for which materials these interactions are important. Results shown in Figure A5 suggest that electrostatic interactions are responsible for 18% of the CO₂ adsorption in PCN-9-Mn whereas this number is only 8% in PCN-9-Co at 10 bar and 298 K.

Figure 4.5(c) shows that all PCNs except PCN-9-Mn are CO₂ selective membranes, since high adsorption selectivities of these materials towards CO₂ dominated diffusion selectivities towards H₂. Although PCN-9-Mn exhibits the highest adsorption selectivity of CO₂/H₂ among other PCNs, the diffusion selectivity very strongly favors H₂ and makes PCN-9-Mn a H₂ selective membrane. EMD simulations of PCN-9-Mn are performed at the bulk gas composition of CO₂/H₂:1/99 rather than 15/85. PCN-9-Mn has a very high adsorption affinity for CO₂ over H₂ (405 at 10 bar) and the amount of adsorbed H₂ molecules in CO₂/H₂ mixture is very low even for a bulk gas composition of 15/85. Therefore, the bulk gas composition is set to 1/99 for CO₂/H₂ to include more of the weakly adsorbed component for statistic accuracy of EMD simulations. Figure 4.5(c) also shows that PCN-26 is the strongest membrane candidate for CO₂/H₂ separations due to its high CO₂ permeability and selectivity.

In Figure 4.5(d), separation performances of PCNs for CO₂/N₂ gas mixtures are shown. Similar to the results of CO₂/CH₄ separation, PCN-26 is above the upper bound for CO₂/N₂ separation. The high permeation selectivity (~ 5.9) of PCN-26 can be attributed to its adsorption selectivity for CO₂ (~ 21.5) which dominates over its low diffusion selectivity (~ 0.27). PCN-9 materials show weak performances for separation of CO₂/N₂ gas mixtures under the conditions studied in this work. PCN-9-Co and PCN-9-Mn are weakly N₂ selective membranes due to their diffusion selectivities towards N₂. PCN-9-Fe is CO₂ selective membrane since its adsorption selectivity towards CO₂ dominates the diffusion selectivity

towards N_2 . PCN materials considered in this work do not show higher selectivity than traditional zeolites NaX and NaY. However, recent molecular simulations clearly demonstrated the drawbacks of these materials, low working capacities as adsorbents and low gas permeabilities as membranes [116].

To conclude, the adsorption-based and membrane-based separation performances of PCNs using atomic simulations are examined for the first time in the literature. Additionally, the importance of partial charge assignment method on the selectivity predictions are tested since electrostatic interactions may be significant for mixtures including CO_2 and N_2 . Results show that using CBAC or EQeq method may significantly affect the judgment about the material's selectivity if the contribution of electrostatic interactions between CO_2 molecules and framework is high [14].

Chapter 5: Adsorption-based and Membrane-based Gas Separation Performances of PCNs

This chapter includes an extended analysis of the adsorption-based and membrane-based separation performances of twenty five different PCNs CH_4/H_2 , CO_2/H_2 , CO_2/CH_4 and CO_2/N_2 mixtures using molecular simulations. As stated in Chapter 4, PCNs are identified to show higher selectivity than traditional zeolites and polymers in membrane-based CO_2 separations. In addition to PCN-9 series and PCN-26, various PCNs including PCN-6, PCN-6', PCN-10, PCN-11, PCN-13, PCN-14, PCN-16, PCN-16', PCN-18, PCN-19, PCN-20, PCN-39, PCN-46, PCN-80, PCN-121, PCN-131', PCN-221-Cu, PCN-221-Hf, PCN-222, PCN-224-Ni and PCN-225 are investigated as adsorbent and membrane candidates for gas separation applications.

5.1. Adsorption-based Separation Performances of PCNs

In Chapter 4, the adsorption selectivity and working capacity of four PCNs for CH_4/H_2 , CO_2/H_2 , CO_2/CH_4 and CO_2/N_2 mixtures are examined and it is concluded that these four PCNs can be promising materials for adsorption-based gas separations [14]. In this work, our molecular simulations are extended for twenty five new PCNs whose adsorption selectivity and working capacity in Figure 5.1 together with the data of well-known zeolites and MOFs. Figure 5.1(a) suggests that PCN-13 is one of the best candidates to separate CH_4/H_2 mixtures among the materials considered in this work since it outperforms other PCNs, traditional zeolites and MOFs due to its high CH_4 selectivity (77) and high working capacity (2.2 mol CH_4/kg PCN). PCN-131' has the second highest CH_4 selectivity, 61, among the materials

high CO₂ selectivity of these three materials is due to the strong electrostatic interactions between CO₂ and extra framework cations [116]. Although PCN-225 does not possess very high CO₂ working capacity compared to several PCNs, it exhibits higher adsorption selectivity (79) towards CO₂ with respect to NaX, NaY and rho-ZMOF. Zr atoms in the framework of PCN-225 strongly interact with CO₂. Additionally, PCN-222 show comparable adsorption selectivity of CO₂/CH₄ (26) and very high CO₂ working capacity (12.4 mol CO₂/kg PCN) compared to NaX, NaY and rho-ZMOF (~29-43 and 0.8-2.7 mol CO₂/kg PCN). PCN-9-Co and PCN-13 are the best candidates to separate CO₂ from CH₄ in terms of selectivity (21 and 22, respectively). PCN-9-Co also exhibits high working capacity (5.4 mol CO₂/kg PCN) but PCN-13 exhibits significantly lower working capacity (1.1 mol CO₂/kg PCN) due to its smaller pore volume. Several PCNs such as PCN-10, PCN-11, PCN-16, PCN-16', PCN-46, PCN-224-Ni show high CO₂ working capacity (~7-14 mol CO₂/kg PCN) and similar adsorption selectivity (~5-15) compared to zeolites. CO₂/CH₄ adsorption selectivity of PCN-6 and PCN-6' are calculated as ~4.4 and 3.9 at 10 bar, 298 K whereas Babarao and coworkers computed selectivities as ~3.6 and 2.5 at 10 bar, 300 K, respectively [67]. The slight difference between selectivities can be attributed to the different force fields and different partial charge assignment methods used in simulations.

Figure 5.1(c) represents adsorption-based separation performances of PCNs for CO₂/H₂ mixture. The selectivity values for CO₂/H₂ mixture are higher than the other mixtures since CO₂ is the most strongly adsorbed component whereas H₂ is the most weakly adsorbed one in PCNs' pores. This is due to the three-site representation of CO₂ compared to single-site representation of H₂ and electrostatic interactions between CO₂ and PCN atoms which are absent for H₂ [14]. PCN-9-Co and PCN-9-Mn exhibit very high CO₂ selectivity (~2300 and ~1660, respectively) and high working capacity (5.5 mol CO₂/kg PCN and 6.1 mol CO₂/kg PCN, respectively) compared to other materials. In fact, performances of these PCNs are found to be similar to zeolite NaX, one of the most promising adsorbent for CO₂/H₂ separation due to the strong electrostatic interactions between the CO₂ molecules and extra framework cations of NaX [115]. Similar to PCN-9-Co and PCN-9-Mn, PCN-225 also exhibits high adsorption selectivity (~105) and working capacity (~4.2 mol CO₂/kg PCN) towards CO₂. Adsorption selectivity of PCN-13 is also high (~1030) but its working capacity is similar to zeolites (1.7 mol CO₂/kg PCN). Several PCNs (PCN-9-Fe, PCN-11, PCN-14,

PCN16', PCN-18, PCN-19, PCN-26, PCN-39 and PCN-224-Ni) exhibit good adsorption selectivity (~ 65 -285) and high working capacities for CO_2 (~ 5 -8.5 mol CO_2/kg PCN) compared to other nanoporous materials.

Figure 5.1(d) represents that PCN-9-Co and PCN-9-Mn are the best candidates for separation of CO_2/N_2 mixtures since they show high adsorption selectivity (~ 470 and 280, respectively) and high working capacity (5.6 and 6.3 mol CO_2/kg PCN, respectively). PCN-13 and PCN-221-Cu are other good adsorbent candidates for this separation due to high adsorption selectivity (~ 115) and large working capacity (7.7 mol CO_2/kg PCN), respectively.

Other important parameters to evaluate new adsorbent materials are S_{sp} and R%. In Appendix-B, Tables B1-B4 represent the calculated S_{sp} and R% values of all PCNs for CH_4/H_2 , CO_2/CH_4 , CO_2/H_2 and CO_2/N_2 separations. Results show that PCN-9-Co, PCN-9-Fe, PCN-9-Mn, PCN-13 and PCN-131' are potential candidates for CH_4/H_2 separations due to their high S_{sp} values (~ 940 -3400). PCN-9-Co, PCN-9-Mn and PCN-13 also exhibit high performances (S_{sp} values of 6×10^4 - 5×10^5) for CO_2/H_2 separation although they suffer from low regenerability (~ 35 -50%). PCN-19 can be an ideal adsorbent for CO_2/CH_4 separation since it exhibits optimum S_{sp} and R% values as 226 and 75%, respectively. These values are higher than the values of widely used MOF, HKUST-1 (CuBTC) for which S_{sp} and R% values are reported as 21 and 66.7% at the adsorption (desorption) pressure of 1 bar (0.1 bar) using single-component adsorption data [115]. For capturing CO_2 from CO_2/N_2 mixture, performances of PCN-9-Co and PCN-9-Mn are found to be better (S_{sp} of $\sim 10^4$) than ZIF-78, zeolite-5A and zeolite-13X for which the S_{sp} values were computed as 396, 163 and 128, respectively at the adsorption (desorption) pressure of 1 bar (0.1 bar) using single-component adsorption data [115].

5.2. Membrane-based Separation Performances of PCNs

Membrane-based separation performances of PCNs are investigated by comparing permeation selectivity and permeability of PCNs with zeolites and other MOFs. Permeation selectivity is simply defined as the multiplication of adsorption selectivity (calculated from GCMC results) and diffusion selectivity (calculated from EMD results) [113]. In most nanoporous materials, adsorption selectivity favors the more strongly adsorbed component whereas diffusion selectivity favors the weakly adsorbed component since strongly adsorbed

species diffuse more slowly than the weakly adsorbed species [113]. In other words, high adsorption selectivities are generally compensated by low diffusion selectivities and therefore membrane selectivities of materials are found to be much lower than their adsorption selectivities. This situation makes most materials promising for adsorption-based gas separations and much less efficient for membrane-based gas separations. It would be very useful to identify materials where both adsorption and diffusion selectivities favor the same component and hence high membrane selectivities can be obtained.

Figure 5.2(a) shows that some PCNs are CH₄ selective membranes (PCN-6, PCN-9-Co, PCN-9-Mn, PCN-13, PCN-14, PCN-16', PCN-18, PCN-19, PCN-26, PCN-39, PCN-46, PCN-80, PCN-121, PCN-221-Cu, PCN-221-Hf, PCN-225) whereas some others are H₂ selective (PCN-6', PCN-9-Fe, PCN-10, PCN-11, PCN-16, PCN-20, PCN-131', PCN-222, PCN-224-Ni). All CH₄ selective PCNs exhibit strong adsorption selectivity towards CH₄ although their diffusion selectivity favors fast H₂ molecules. Since the CH₄/H₂ adsorption selectivity values are higher (~ 10 -77) than CH₄/H₂ diffusion selectivity values (~ 0.08 -0.48), these PCNs become CH₄ selective membranes. On the other hand, H₂ selective PCN membranes exhibit low CH₄ adsorption selectivities and very high diffusion selectivities towards H₂. Two PCNs, PCN-10 and PCN-11 are identified as strongly H₂ selective membranes (25 and 7, respectively) because their narrow pore sizes limit the diffusion of large CH₄ molecules (1×10^{-6} cm²/s in PCN-10 and 3×10^{-6} cm²/s in PCN-11) compared to small H₂ molecules (4×10^{-4} cm²/s in PCN-10 and 7×10^{-4} cm²/s in PCN-11). PCN-131' is also identified as a strongly H₂ selective membrane with a very low CH₄ permeability due to its small pore volume and narrow pore sizes as discussed below.

In Figures 5.2(b) and (d), the Robeson's upper line which represents the selectivity/permeability trade-off of polymeric membranes is included for CO₂/CH₄ and CO₂/N₂ separations [116]. Materials that can exceed these lines are highly promising for membrane-based gas separations and they can replace the traditional polymeric membranes in CO₂ separations. Figure 5.2(b) shows that several PCNs (PCN-10, PCN-11, PCN-16, PCN-16', PCN-19 and PCN-131') are located above the Robeson's upper bound due to their high CO₂ selectivities. PCN-131' exhibits significantly high permeation selectivity ($\sim 10^5$) for CO₂/CH₄ since diffusion selectivity strongly favors CO₂ over CH₄. Our classical EMD simulations of adsorbed CH₄ in PCN-131' indicated that CH₄ cannot move along the pores on

the nanosecond time scales ($<10^{-8}$ cm²/s). The reason for this behavior is clear from the potential energy surface of adsorbed CH₄ in PCN-131' as shown in Figure B1. A large energy barrier, $\Delta E \cong 71$ kJ/mol, exists for CH₄ to move through the narrow pores of PCN-131'. This value corresponds to a diffusion coefficient ($\sim 10^{-15}$ cm²/s) that is far too slow to be directly observed with EMD. Unlike CH₄, diffusion of CO₂ in PCN-131' is rapid enough that can readily be characterized by EMD ($\sim 2 \times 10^{-6}$ cm²/s). In a previous study, it is shown that energy barrier computed using quantum chemistry calculations with flexibility effects can be ~ 20 kJ/mol less than the energy barrier computed from classical EMD calculations without flexibility effects [117]. In the case of PCN-131', the energy barrier for CH₄ at the pore edges is very high and it is reasonable to think that even if the flexibility of the pore was taken into account, this barrier would not decrease to a value of 24 kJ/mol at which diffusivities in the order of 10^{-7} cm²/s can be observed. Therefore, it can be concluded that PCN-131' is a CO₂ selective membrane since both adsorption and diffusion selectivity strongly favors CO₂ over CH₄. Similar to PCN-131', PCN-10 and PCN-11 are strong candidates for separating CO₂ from CH₄ due to their high CO₂ selectivities. Diffusivities of CH₄ in these materials are accessible by EMD simulations ($\sim 1 \times 10^{-6}$ cm²/s in PCN-10 and $\sim 4 \times 10^{-6}$ cm²/s in PCN-11) and diffusion selectivity favored CO₂ but not as strongly as in the case of PCN-131'.

Figure 5.2(c) suggests that all PCNs are CO₂ selective membranes except PCN-6', PCN-20, PCN-221-Hf, PCN-222 and PCN-224-Ni which are weakly H₂ selective. These PCNs are CO₂ selective in adsorption but slow diffusion of CO₂ compared to H₂ compensated their adsorption selectivities. For example, in PCN-20, the strongly adsorbed CO₂ molecules diffuse slowly ($\sim 10^{-5}$ cm²/s) compared to weakly adsorbed, light and small H₂ molecules ($\sim 10^{-3}$ cm²/s). Therefore, diffusion selectivity favors H₂. Among CO₂ selective PCNs, PCN-11, PCN-14, PCN-16 and PCN-16' are strong candidates for CO₂/H₂ separation due to their large CO₂ permeabilities ($\sim 50\text{--}70 \times 10^4$ Barrer).

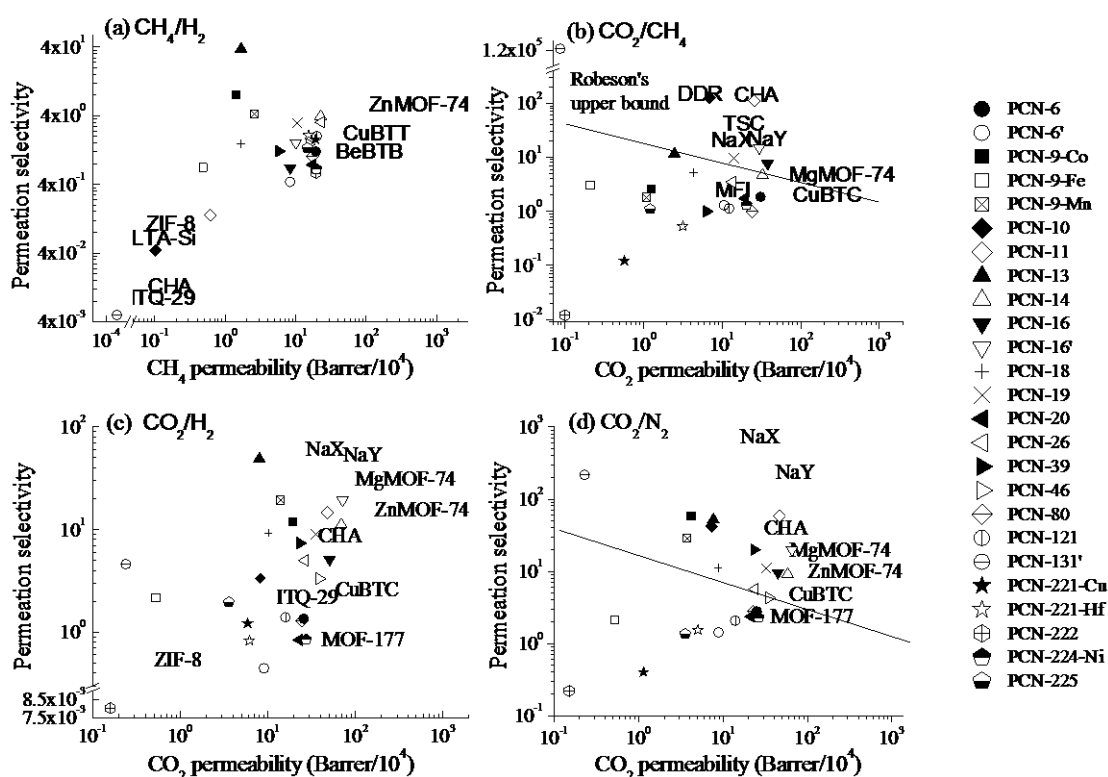


Figure 5.2. Comparison of separation performances of PCN membranes with other nanoporous membranes for (a)CH₄/H₂, (b)CO₂/CH₄, (c)CO₂/H₂ and (d)CO₂/N₂ mixtures at 298 K. The compositions of the bulk gas mixtures are (a)50/50, (b)50/50, (c)15/85 and (d)15/85 at 298 K. Composition of the CO₂/H₂ mixture is set to 1/99 only for PCN-9-Mn. The feed and permeate pressures are set to 10 bar and vacuum, respectively. For other materials data is taken at 300 K from the literature [116].

Figure 5.2(d) represents that fifteen PCNs (PCN-9-Co, PCN-9-Mn, PCN-10, PCN-11, PCN-13, PCN-14, PCN-16, PCN-16', PCN-18, PCN-19, PCN-39, PCN-121, PCN-131', PCN-221-Hf, PCN-225) are located above the upper bound for CO₂/N₂ gas mixtures. Although PCN-14, PCN-16, PCN-19 exhibit relatively weaker adsorption selectivities (~10) towards CO₂ compared to other PCNs, their CO₂ permeabilities (~30-60×10⁴ Barrer) allow them to be above the upper bound. The pore sizes of PCN-10, PCN-11 and PCN-131' limit the diffusion of large N₂ molecules (6×10⁻⁶ cm²/s in PCN-10, 2×10⁻⁵ cm²/s in PCN-11 and 3×10⁻⁷ cm²/s in PCN-131') therefore, both adsorption and diffusion selectivity favor CO₂ in these materials. The CO₂ permeability of PCN-131' is low both in CO₂/N₂ (2.3×10³ Barrer) and CO₂/CH₄ (0.8×10³ Barrer) separations compared to PCN-10 and PCN-11. This can be attributed to the lower pore volume of PCN-131' (0.14 cm³/g) compared to PCN-10 and PCN-11 (0.75 and

0.79 cm³/g, respectively). The results represented in Figure 5.2 suggest that there are several PCNs that can show higher selectivity and permeability than traditional zeolite and polymer membranes, especially in CO₂ separations.

Chapter 6: Prediction of Adsorption, Diffusion and Membrane Selectivities of PCNs

Adsorption, diffusion and permeation selectivities can be calculated using the results of molecular simulations as described in Chapter 4 and 5. Since these simulations are carried out for binary gas mixtures, they are computationally demanding. Especially calculating the self-diffusivities of mixtures using EMD simulations require significant computational resources to collect data from several independent trajectories. In this work, the aim is to develop simple models that can predict PCNs' selectivities based on the material's structural properties without performing extensive molecular simulations. Furthermore, several PCNs have been synthesized and these materials are very rich in the variety of topology, pore size and composition. This type of modeling effort will be useful to quantitatively understand the structure-performance relationships of PCNs. First, the correlations between adsorption selectivity of CH₄/H₂, CO₂/H₂, CO₂/CH₄ and CO₂/N₂ mixtures at different pressures with three parameters, pore volume (V_{pore}), surface area (A_{surface}) and the inverse of difference of isosteric heats of adsorption of components in the mixture ($1/\Delta Q$) are examined. The first two parameters are chosen since they represent structural properties of PCNs that can be easily computed or measured from experiments and the last parameter is considered based on the study of Wu et al. which shows that limiting adsorption selectivity correlates with $1/\Delta Q$ calculated at infinite dilution [118]. It is important to note that only focus is not infinite dilution case (low pressure), the correlation of adsorption selectivity calculated at various pressures with $1/\Delta Q$ values calculated exactly at the same pressures are also examined.

In this study, twenty PCNs including PCN-6, PCN-6', PCN-9-Co, PCN-9-Fe, PCN-9-Mn, PCN-10, PCN-11, PCN-13, PCN-14, PCN-16, PCN-16', PCN-18, PCN-19, PCN-20, PCN-26, PCN-39, PCN-46, PCN-80, PCN-131', PCN-224-Ni are used. Adsorption selectivity values of each PCN for CH₄/H₂, CO₂/H₂, CO₂/CH₄ and CO₂/N₂ mixtures at 0.1, 1, 10, 50 bar are plotted

against V_{pore} , A_{surface} , $1/\Delta Q$ and resulting correlation coefficients, R^2 , are shown in Figure C1 (See Appendix C). A good correlation between adsorption selectivity and three parameters are found for CH_4/H_2 mixture at all pressures whereas no meaningful correlation is found for other mixtures. Figure 6.1 shows the correlations between CH_4/H_2 adsorption selectivity and V_{pore} , A_{surface} , $1/\Delta Q$. Based on these results, a simple model is developed to predict the CH_4/H_2 adsorption selectivity of PCNs as a function of three parameters. In Equation (6.1), a, b, c, d, e, f represent the model coefficients and listed in Table 6.1.

$$S_{\text{ads}} = a \times V_{\text{pore}}^b + c \times A_{\text{surface}}^d + e \times (1/\Delta Q)^f + 1 \quad (6.1)$$

Table 6.1 The coefficients of equations (6.1) and (6.2) for CH_4/H_2 and CO_2/H_2 mixtures

Coefficients	CH_4/H_2	CO_2/H_2
a	7.19	0.001
b	-0.58	-0.74
c	734.36	3.06
d	-1.75	-19.91
e	1.76×10^{-5}	4.17×10^{-4}
f	-5.54	-4.56
A	0.34	0.19
m	3.00	-0.94
n	7.39	-0.73

$$S_{\text{diff}(i/j)} = A \times \left(\sqrt{\frac{M_j}{M_i}} \right) \times \frac{\exp\left(\frac{-m \times \sigma_i}{\text{LPD}}\right)}{\exp\left(\frac{-n \times \sigma_j}{\text{LCD}}\right)} \quad (6.2)$$

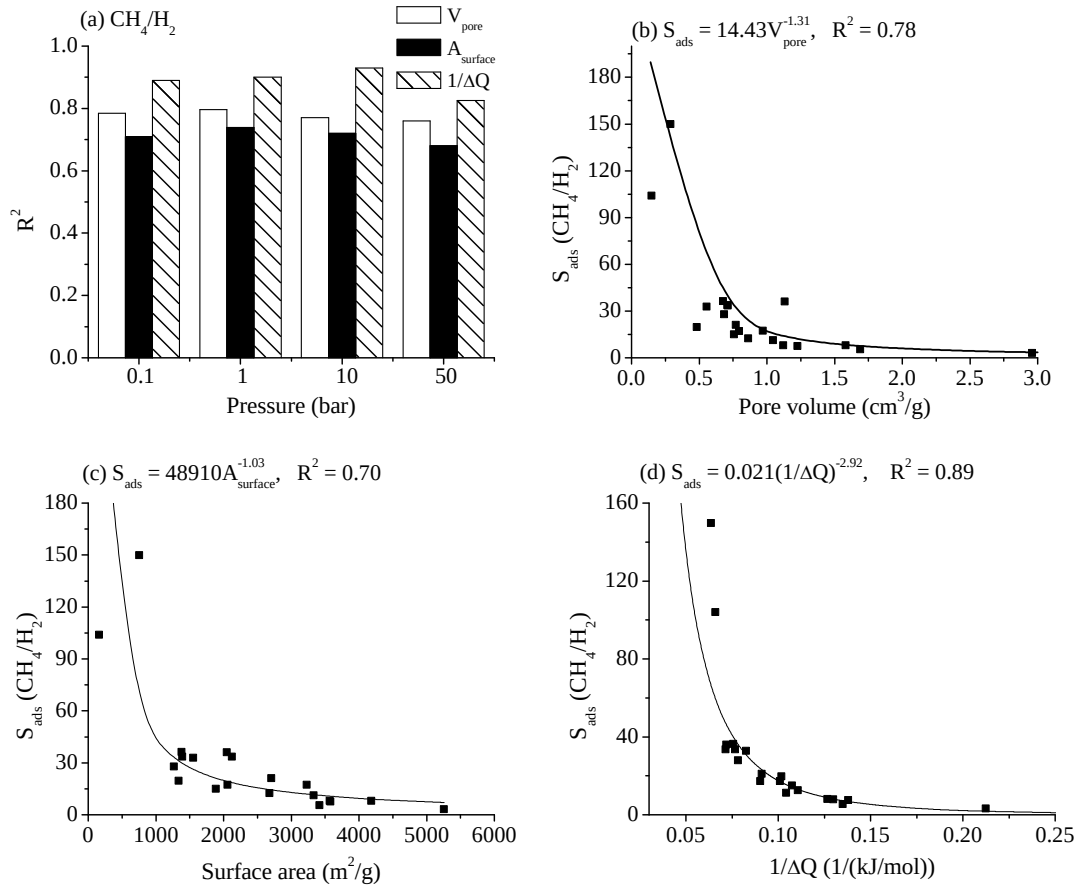


Figure 6.1. (a) Coefficient of correlation, R^2 , of CH_4/H_2 adsorption selectivity with V_{pore} , A_{surface} and $1/\Delta Q$ at different pressures. Correlation between CH_4/H_2 adsorption selectivity and (b) V_{pore} , (c) A_{surface} and (d) $1/\Delta Q$ at 0.1 bar.

Figure 6.2(c) compares diffusion selectivities predicted using Equation (6.2) with the ones obtained from EMD simulations. It is important to note that this model is used only for materials in which diffusion of both gas molecules are fast enough to be captured by classical EMD simulations. As discussed earlier in here and literature, diffusion of CH_4 is very slow in materials which have narrow pore sizes that are close to the kinetic diameter of CH_4 [117]. Therefore, results shown in Figure 6.2(c) includes PCNs that have limiting pore diameter >4 Å. Figure 6.2(c) suggests that Equation (6.2) can be used to make accurate estimates for CH_4/H_2 diffusion selectivity of PCNs. Permeation selectivity ($S_{\text{perm}} = S_{\text{ads}} \times S_{\text{diff}}$) of PCNs is then estimated by multiplication of two models, adsorption selectivity predicted from Equation (6.1) and diffusion selectivity predicted from Equation (6.2). The results shown in Figure 6.2(d) indicate that predictions of the model are in a good agreement with the results of molecular simulations. The discrepancy between the model and simulations can be attributed to the weak prediction of the models either for adsorption selectivity or diffusion selectivity.

For example, adsorption selectivity of PCN-13, which exhibits the highest permeation selectivity for CH_4 over H_2 , is underestimated and therefore its permeation selectivity is also underestimated by the model (28) compared to simulation results (37). Selectivities of PCN-14 and PCN-26 are calculated as 3.9 and 3.2 from the simulations and predicted as 3.5 and 1.8 by our model. Another important aspect of the permeation model is that its predictions are qualitatively accurate i.e. the model accurately estimates which component is preferred in membrane permeation. For example, PCN-6' is not a CH_4 selective but a H_2 selective membrane with a permeation selectivity of 2.3. Our model also identifies the PCN-6' as a H_2 selective membrane with a permeation selectivity of 1.5. The good agreement between the model predictions and simulation results suggest that reasonable *initial* estimates can be made about membrane selectivity of PCNs using these simple selectivity models.

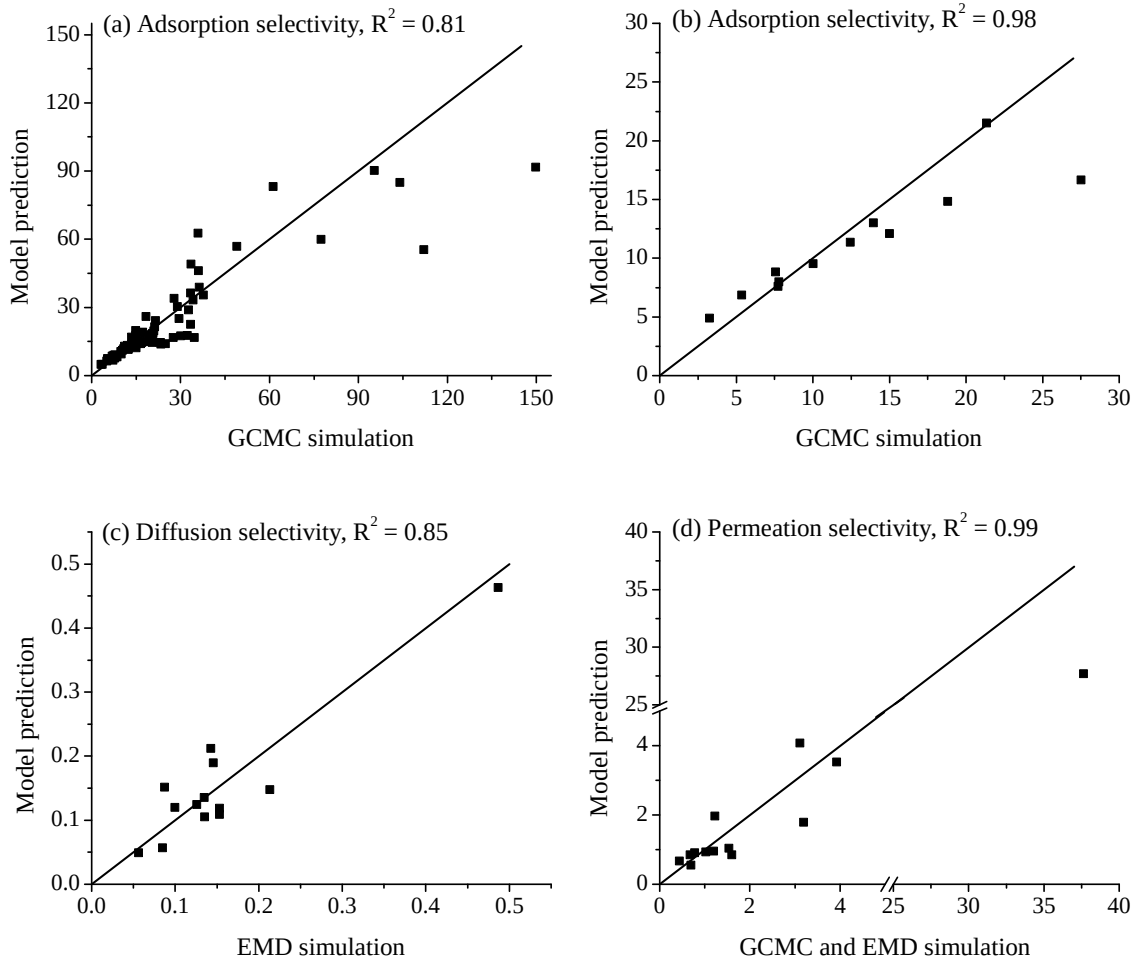


Figure 6.2. Comparison of model predictions and simulation results for (a) CH_4/H_2 adsorption selectivity at 0.1, 1, 10 and 50 bar, (b) CH_4/H_2 adsorption selectivity at 10 bar, (c) CH_4/H_2 diffusion selectivity at 10 bar and (d) CH_4/H_2 permeation selectivity at 10 bar.

There is not a good correlation between adsorption selectivity and structural properties of PCNs for other mixtures as shown in Figure C1 in Appendix C but the R^2 values of CO_2/H_2 mixture are higher than the ones obtained for other CO_2 -related mixtures. The same models, Equation (6.1) and (6.2) with different sets of parameters as tabulated in Table 6.1 are used to predict adsorption, diffusion and membrane selectivity of PCNs for CO_2/H_2 mixtures. Figure C2 shows that there is a reasonable agreement between model predictions and simulation results both for adsorption and permeation selectivities of CO_2/H_2 mixture. The model slightly underestimates permeation selectivity for PCN-11 (10) and PCN-19 (8) compared to the simulation results (15 and 9, respectively). This discrepancy is mainly caused by the diffusion selectivity model, which generally underestimates the EMD results. On the other hand, the model overestimates the permeation selectivity of PCN-13 (59) and PCN-18 (12) compared to the simulations results (49 and 9, respectively). Overall, considering the high computational demand of molecular simulations, especially binary EMD simulations, it will be very useful to apply these simple models for identification of highly selective materials.

Approximate models which can predict adsorption, diffusion and permeation selectivities of PCNs for CH_4/H_2 and CO_2/H_2 mixtures are developed. These models are mainly based on the structural properties of the materials which can be simply measured or computed such as pore volume, surface area and pore diameter. Model predictions for adsorbent and membrane selectivities are found to be in a good agreement with the direct results of detailed molecular simulations. For example, adsorption selectivity model suggests that in order to obtain a high selectivity, the differences in the interactions between two gases and PCN must be as large as possible whereas the porosity and surface area of PCN must be as small as possible. Supporting this idea, simulations show that two PCNs which exhibit the highest CH_4/H_2 selectivity, PCN-13 and PCN-131', have the lowest porosity and surface area. It is also important to note that selectivity of a material is determined by the interplay of various factors and cannot be correlated to only three properties. For example, chemical composition and topology of PCNs should strongly affect the affinity of materials for specific gas molecules but these as parameters are not considered in the simple models developed in this thesis. Therefore, models suggested in this study can only be used to get an initial estimate of the material's selectivity prior to more extensive studies. The picture that one can get from recent high-throughput studies is that the correlations between structure and property of materials are very complex and simply not captured by sets of 20-100 materials [119,120]. For example,

the adsorption selectivity model that is developed considering twenty PCNs in this work are used to predict CH₄/H₂ selectivity of widely studied MOFs (MOF-5, CuBTC, COF-6, COF-10, ZnATZ, ZnBDC, ZIF-69, ZIF-90). Model predictions are compared with the direct molecular simulation results in Figure C3. These results suggest that the adsorption selectivity model developed for PCNs can make good predictions for the adsorption selectivity of other MOFs at various pressures. However, one can expect that as the number and variety of materials increase, the accuracy of predictions may get worse. Of course, it would be much more useful to carry out a systematic study on a very large number of materials to gain further insight into structure-performance relationships. Therefore, models suggested in this study can only be used to get an initial estimate of the material's selectivity prior to more extensive studies. Large scale computational screening studies on PCNs will be highly useful for identifying the most promising materials for adsorption-based and membrane-based gas separations. Time, resources and efforts can be then directed to more detailed examination of these promising materials using experimental manners.

Chapter 7: Performances of PCNs and PCN-filled MMMs for Air Separation

In this chapter, the performances of PCN-9-Co, PCN-121 and PCN-131' as pure membranes and as fillers in mixed matrix membranes (MMMs) are examined to separate O₂ from O₂/N₂ which is commonly named as air separation. Force field parameters to model O₂ and N₂ molecules are given in Table 3.3 (See Section 3.4.1). In this study, the accuracy of potential parameter sets for both adsorbate and adsorbent atoms are validated by comparing single gas uptake data obtained from simulations with the ones from experiments as shown in Figure 7.1 [40,41,58]. There is a good agreement between the simulation results and experimental data. At 0.9 bar and 77 K, simulations predicted the adsorbed amount of O₂ (N₂) as 621.3 cm³STP/g (551.3 cm³STP/g) in PCN-121 and 113.7 cm³STP/g (99.7 cm³STP/g) in PCN-131'. However, experiments measure these values as 670.4 cm³STP/g (602.2 cm³STP/g) for PCN-121 and 155.2 cm³STP/g (115.1 cm³STP/g) for PCN-131'. Especially as temperature increases, the agreement between the simulations and experiments get better. For example, the measured adsorbed amount of O₂ is 199.2 cm³STP/g at 1 bar and 143 K whereas simulation result slightly overestimates it as 210.1 cm³STP/g under the same conditions. Overall, the agreement between the simulation and experiment results is reasonable for the aim of this study.

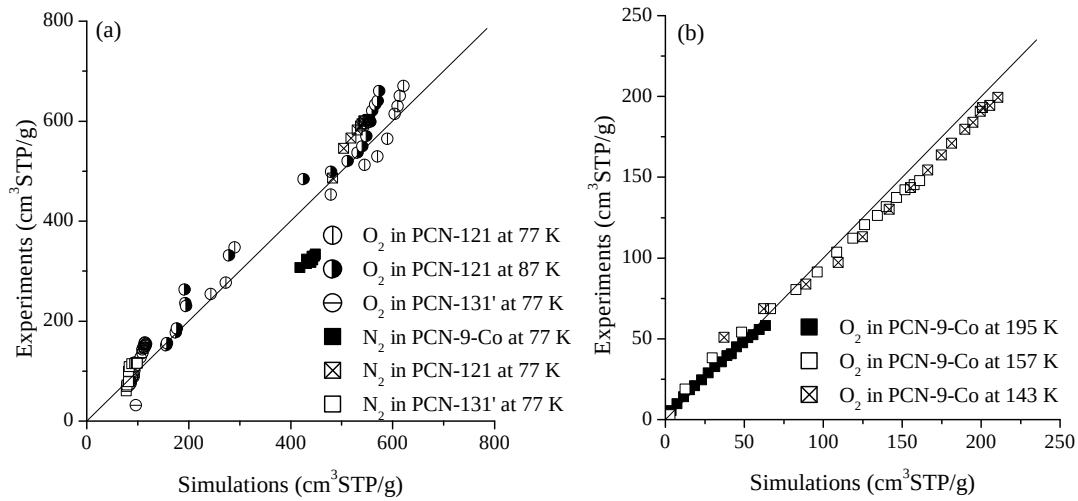


Figure 7.1. The comparison between simulation results and experiments for O₂ and N₂ uptakes in PCNs at the specified temperatures. In (a), the low temperature scale is represented whereas in (b) temperature is higher. Data is between 0-1 bar.

In the first part of this study, binary component GCMC and EMD simulations are performed at the conditions as described for other mixtures. The mixture composition is set to 20/80 at 308 K. The results are given in Table 7.1. As expected, the selectivities are very low. The reason comes from the fact that air separation is difficult since O₂ and N₂ are similar molecules in terms of physical and chemical properties. Both PCN-9-Co and PCN-121 are slightly N₂ selective membranes whereas PCN-131' is O₂ selective. The adsorption and diffusion selectivities of PCN-131' favor different components in O₂/N₂ mixture. However, resulting permeation selectivity favors O₂ since magnitude of the diffusion selectivity is larger. Additionally, the O₂ permeabilities of PCNs are calculated. PCN-9-Co and PCN-121 exhibit very high permeabilities towards O₂. On the other hand, PCN-131' shows much lower O₂ permeability compared to PCN-9-Co and PCN-121 as a result of its low pore volume.

Table 7.1 Adsorption, diffusion and membrane selectivities of PCNs for O₂/N₂ and O₂ permeabilities of PCNs

PCN	S _{ads}	S _{diff}	S _{perm}	P _{O₂} (Barrer)
PCN-9-Co	0.68	1.28	0.87	2.31×10 ⁴
PCN-121	0.74	1.07	0.79	5.91×10 ⁴
PCN-131'	0.63	2.28	1.44	86.62

In the second part of this study, the aim is to analyze the separation performances of PCNs as fillers in MMMs to separate O₂ from N₂. The O₂ permeabilities and permeation selectivities are calculated as described in section 3.6. As the continuous phases of MMMs, polymers such as Matrimid, Polydimethylsiloxane (PDMS), Polysulfone (PSF), Polyvinyl acetate (PVAc) are used. For these polymers, the conditions at which experiments were performed, the permeabilities and the ideal selectivity defined as the ratio between permeabilities of components are listed in Table 7.2. The GCMC and EMD simulations for PCNs are performed under the same conditions with polymers. The gas permeabilities are computed as described in section 3.6. Since there is no available experimental gas permeability data for PCN-filled MMM in the literature, Maxwell Model is used to predict gas permeabilities of each PCN-filled MMM in this study. The reason for choosing Maxwell Model is the fact that it can accurately reproduce the experimental gas permeabilities of MMMs as explained by Erucar and Keskin in detailed [7]. The ideal selectivities of MMMs are calculated by the ratio of the permeabilities of O₂ to the permeabilities of N₂. The calculations are repeated for 4 times. In the first round, the volume fraction of PCN fillers is set to 10% whereas it is set to 50% in the last round of calculations.

Table 7.2. Gas permeabilities, ideal selectivities and experiment conditions of polymers for O₂/N₂ separation

Polymer	P _{O2} (Barrer)	P _{N2} (Barrer)	$\alpha(O_2/N_2)$	P _{feed} and P _{permeate} (bar)	T (K)
Matrimid ^a	1.46	0.22	6.64	4.00 and vacuum	308
PDMS ^b	32.24	11.99	2.68	4.00 and vacuum	308
PSF ^a	1.16	0.34	4.70	3.10 and 1.24	308
PSF ^b	0.98	0.18	5.47	4.00 and vacuum	308
PVAc ^a	0.51	0.07	6.57	4.48 and vacuum	308

^a Taken from [121] and ^b Taken from [122]

Figure 7.2 represents the performances of pure PCNs, pure polymers and PCN-filled MMMs to separate O₂ from N₂. Although PCN-9-Co exhibits low O₂ selectivity, its O₂ permeability is very high. Similarly, PCN-121 also shows high O₂ permeability. Since its selectivity is slightly larger compared to PCN-9-Co, PCN-121 is located much closer to Robeson's upper bound representing the upper limit in the performances of polymers for air separation applications. PCN-131' is located above Robeson's upper bound. However, its O₂ permeability is relatively lower than PCN-9-Co and PCN-121 due to its low pore volume. It exhibits moderate O₂ selectivity which is larger than other pure PCNs. Pure polymers exhibit

high O_2 selectivity compared to pure PCNs. On the other hand, their O_2 permeability values are significantly smaller with respect to O_2 permeabilities of PCNs. Therefore, PCN-filled MMM exhibit better separation performances in terms of O_2 permeabilities. Unfortunately, PCNs do not possess high O_2 selectivities to enhance the polymers' selectivities. Consequently, the resulting MMMs exhibit better O_2 permeabilities as the volume fraction of fillers increases from 10% to 50% and moderate selectivity towards O_2 compared to pure polymers.

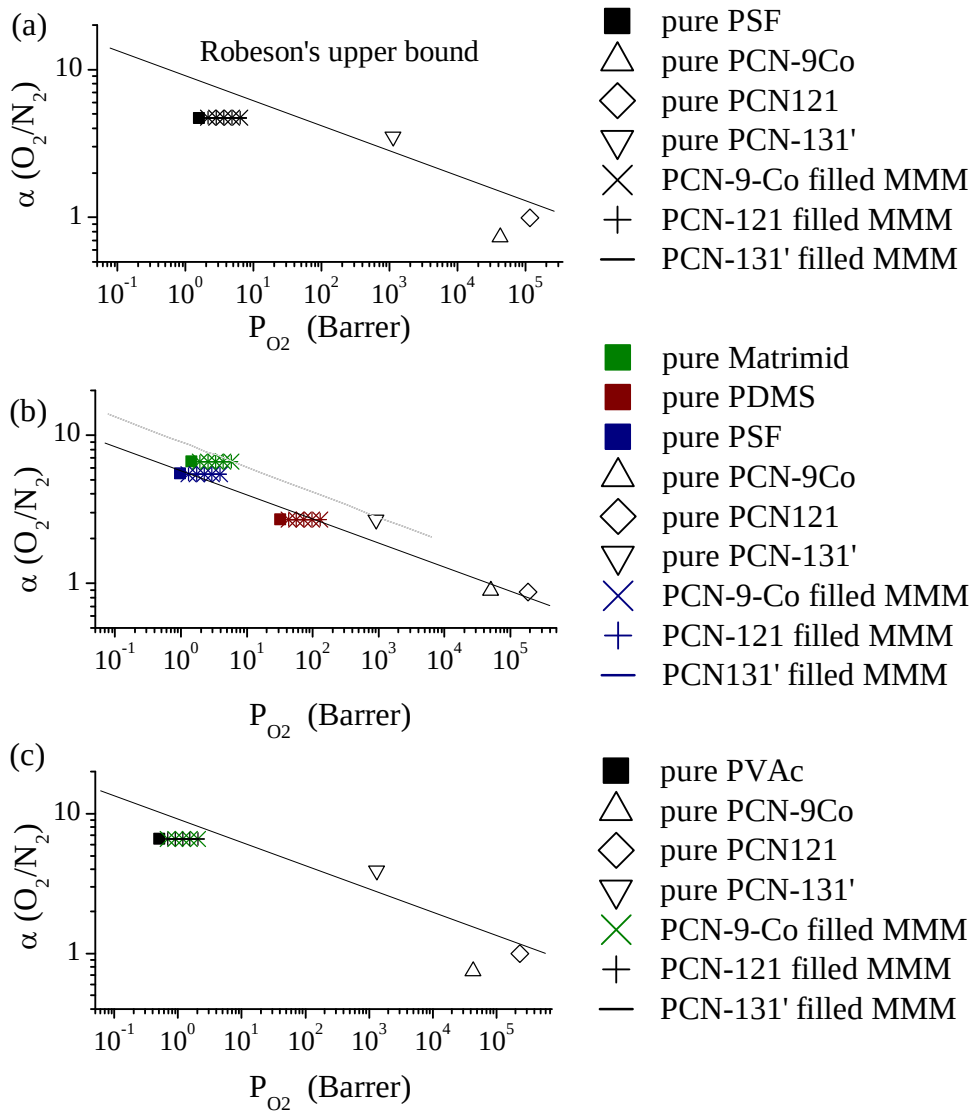


Figure 7.2. O_2 selectivity and O_2 permeability of pure PCNs, pure polymers and PCN-filled MMMs. The temperature is 308 K. The feed (permeate) pressure is set to 3.10 (1.24) in (a), 4 (vacuum) in (b) and 4.48 (vacuum) in (c). Lines represent Robeson's upper bound [121]. Each $\times$, + and - symbols represent increment of 10% in volume fraction of PCN in PCN-filled MMMs.

Chapter 8: Conclusion

Porous Coordination Networks (PCNs) are a new and developing class of nanoporous materials which offer considerable potential for applications such as gas storage, gas separation and catalysis. PCNs can be promising adsorbent and membrane candidates for gas separation applications due to their tunable pore sizes, large surface areas, high pore volumes, good thermal and mechanical stabilities. Predicting the performances of PCNs as adsorbents and membranes using computational methods can play important roles in selecting ideal materials for specific applications and tailoring the synthesis of new materials. Atomic simulations are helpful to provide a detailed understanding on the molecular scale which is not easily accessible from experiments.

Although a large number of PCNs have been synthesized to date, the potential performance of PCNs for adsorption-based and/or membrane-based gas separation applications is not known. In this thesis, the adsorption-based and membrane-based separation performances of PCN-9 series and PCN-26 are examined using atomic simulations for the first time in the literature. The results suggest that PCNs considered in this work exhibit higher adsorption selectivity and working capacity than widely studied zeolites and MOFs in adsorption-based separation of gas mixtures. PCN-26 is identified as a strong candidate for membrane-based separation of CO_2/CH_4 and CO_2/N_2 mixtures. This PCN can even exceed the upper bound established for polymeric membranes due to its high CO_2 permeability. The importance of partial charge assignment method on the selectivity predictions is also tested because electrostatic interactions may be significant for mixtures including CO_2 and N_2 . Results show that using Connectivity-based Atom Contribution Method (CBAC) or Extended Charge Equilibration Method (EQeq) may significantly affect the judgment about the

material's selectivity if the contribution of electrostatic interactions between CO₂ molecules and framework is high.

Since PCNs are predicted to outperform traditional zeolites and widely studied metal organic frameworks in CO₂ separation processes. The adsorption-based and membrane-based separation performance study is extended to twenty five PCNs. PCN-9 series and PCN-26 are identified to show higher selectivity than traditional zeolites and polymers in membrane-based CO₂ separations. In addition to these PCNs, various others including PCN-6, PCN-6', PCN-10, PCN-11, PCN-13, PCN-14, PCN-16, PCN-16', PCN-18, PCN-19, PCN-20, PCN-39, PCN-46, PCN-80, PCN-121, PCN-131', PCN-221-Cu, PCN-221-Hf, PCN-222, PCN-224-Ni and PCN-225 are investigated as adsorbent and membrane candidates for gas separation applications. Several PCNs such as PCN-9 series and PCN-14 are identified as promising candidates for adsorption-based CH₄/H₂ separations since they exhibit both high adsorption selectivity and working capacity towards CH₄. PCN-9-Co, PCN-9-Mn, PCN-14 and PCN-16 are found to be strong adsorbents for CO₂ capture from CO₂/H₂, CO₂/CH₄ and CO₂/N₂ mixtures because of their high CO₂ working capacities. Several PCNs membranes are shown to exceed Robeson's upper bound established for CO₂/CH₄ and CO₂/N₂ separations. It is concluded that both adsorption and diffusion favor the same component CO₂ over CH₄ (N₂) in PCN-10, PCN-11, PCN-131' and make these PCNs highly CO₂ selective in membrane-based CO₂/CH₄ (CO₂/N₂) separations. Additionally, simple models that can predict adsorption, diffusion and permeation selectivities of PCNs are developed for CH₄/H₂ and CO₂/H₂ mixtures based on the structural properties of materials such as pore volume, surface area and pore diameter. Predictions of the models for adsorbent and membrane selectivities are found to be in a good agreement with the direct results of detailed molecular simulations. For example, adsorption selectivity model suggests that in order to obtain a high selectivity, the differences in the interactions between two gases and PCN must be as large as possible whereas the porosity and surface area of PCN must be as small as possible. Supporting this idea, simulations show that two PCNs which exhibit the highest CH₄/H₂ selectivity, PCN-13 and PCN-131', have the lowest porosity and surface areas. Since these models are developed by studying 20 different PCNs, the models suggested in this study can only be used to get an initial estimate of the material's selectivity prior to more intensive studies. Of course, it would be much more useful to carry out a systematic study on a very large PCN database to gain further insight into structure-performance relationships for PCNs. This type of models will be

highly useful for large scale screening of PCNs for gas separation applications to identify the promising materials.

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APPENDIX A: Binary Adsorption Isotherms of PCNs

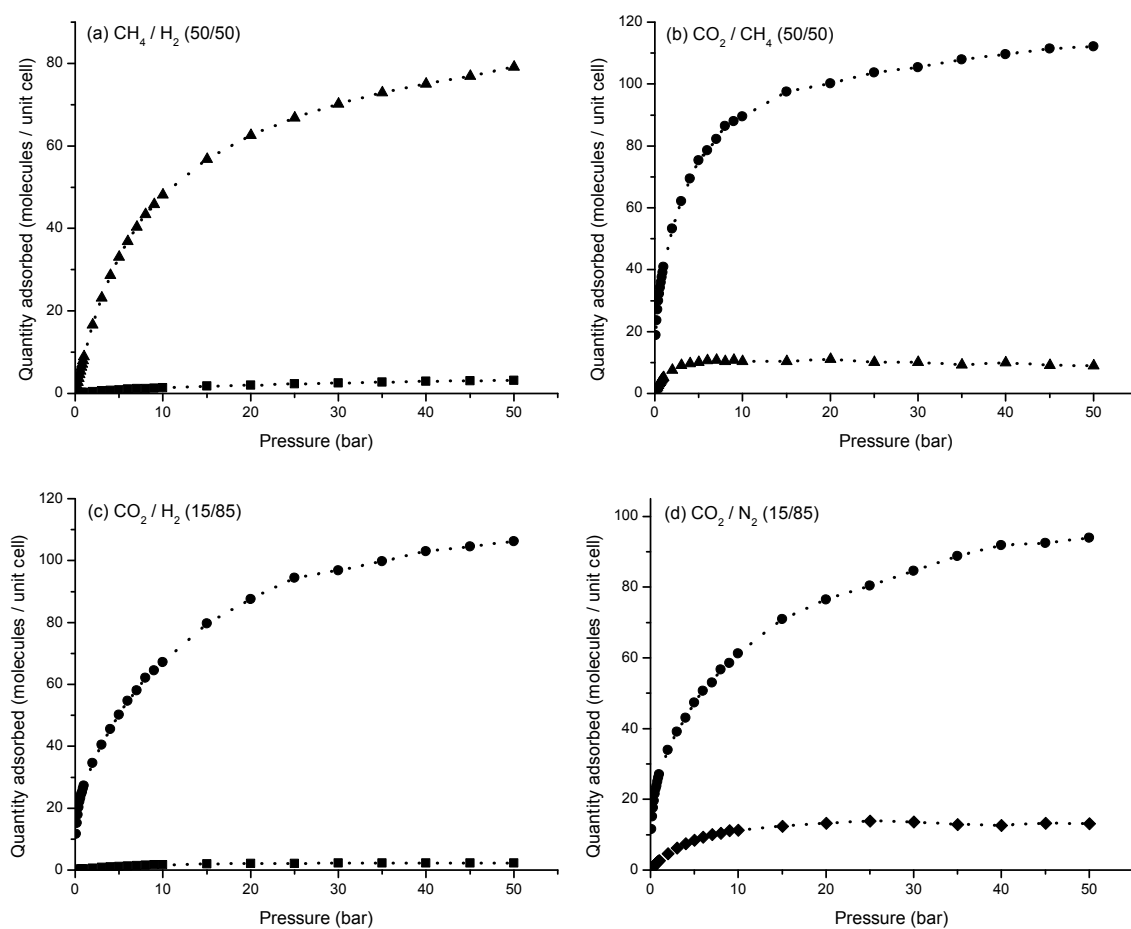


Figure A1. Binary GCMC adsorption isotherms at 298 K for PCN-9-Co. Circles: CO₂, triangles: CH₄, squares: H₂, diamonds: N₂.

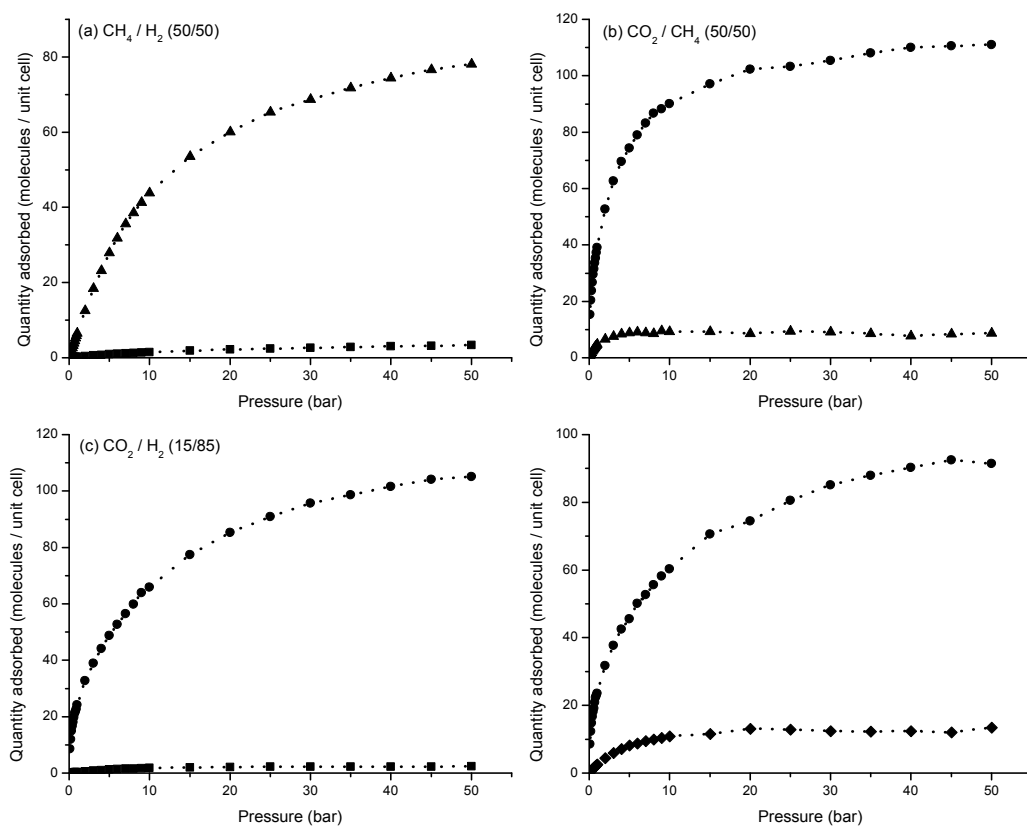


Figure A2. Binary GCMC adsorption isotherms at 298 K for PCN-9-Fe. Circles: CO₂, triangles: CH₄, squares: H₂, diamonds: N₂.

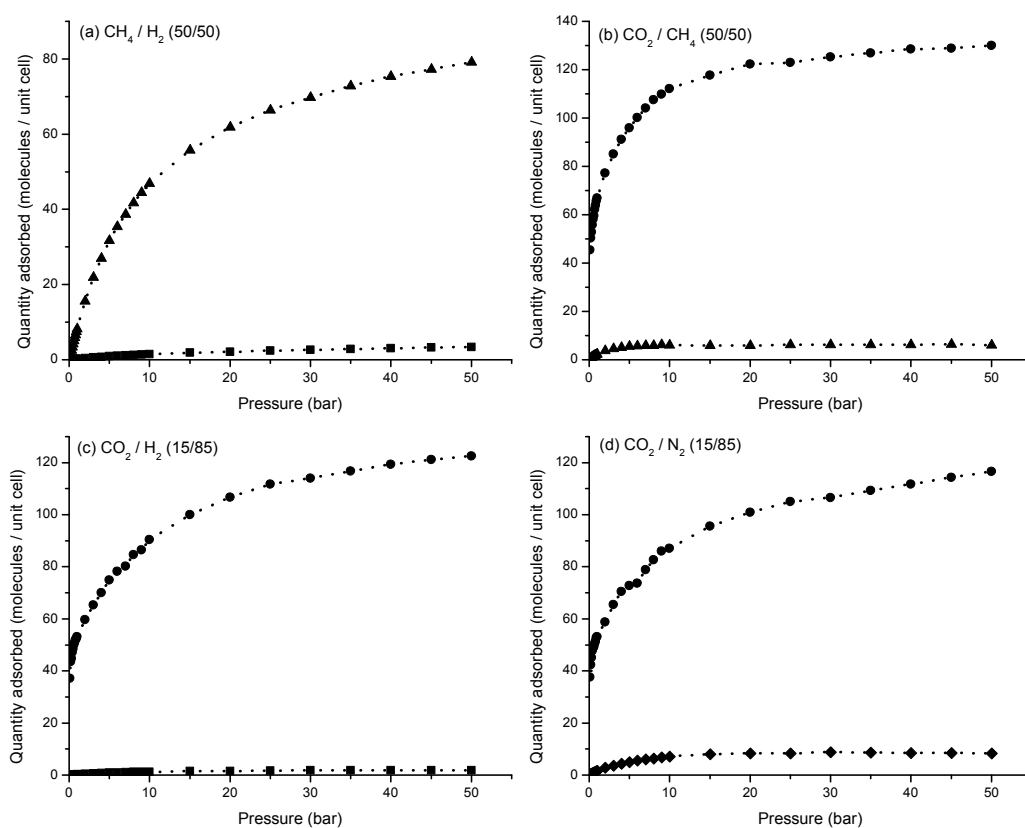


Figure A3. Binary GCMC adsorption isotherms at 298 K for PCN-9-Mn. Circles: CO₂, triangles: CH₄, squares: H₂, diamonds: N₂.

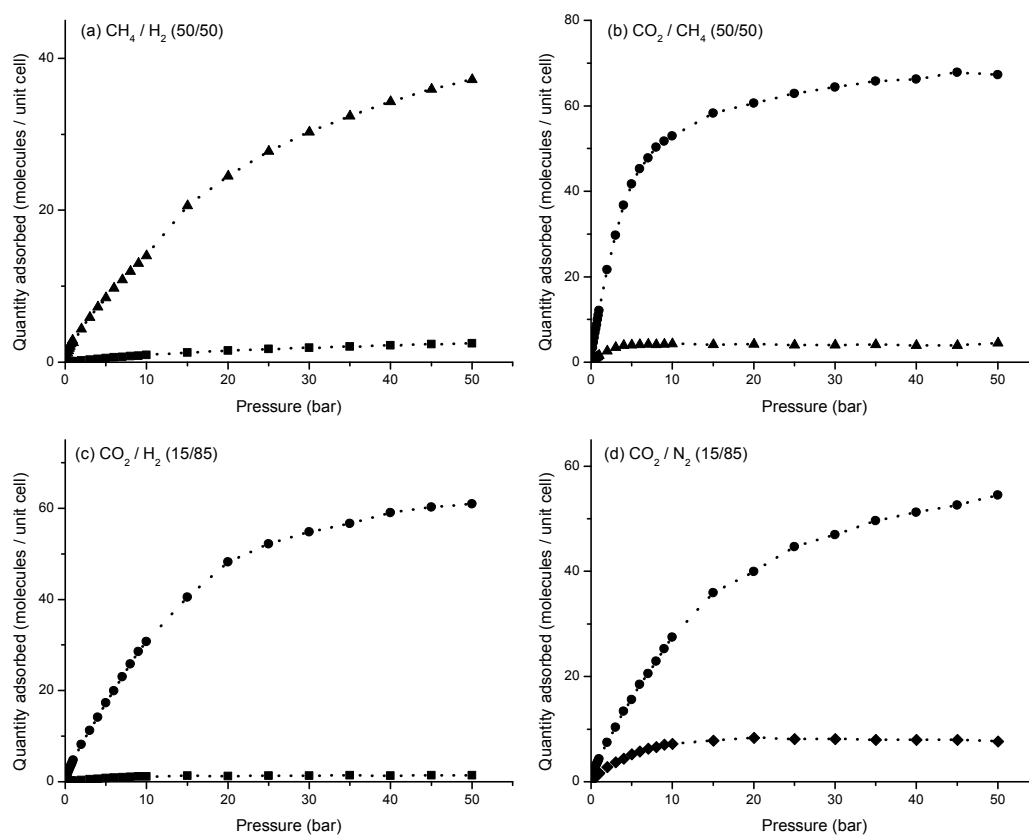


Figure A4. Binary GCMC adsorption isotherms at 298 K for PCN-26. Circles: CO₂, triangles: CH₄, squares: H₂, diamonds: N₂.

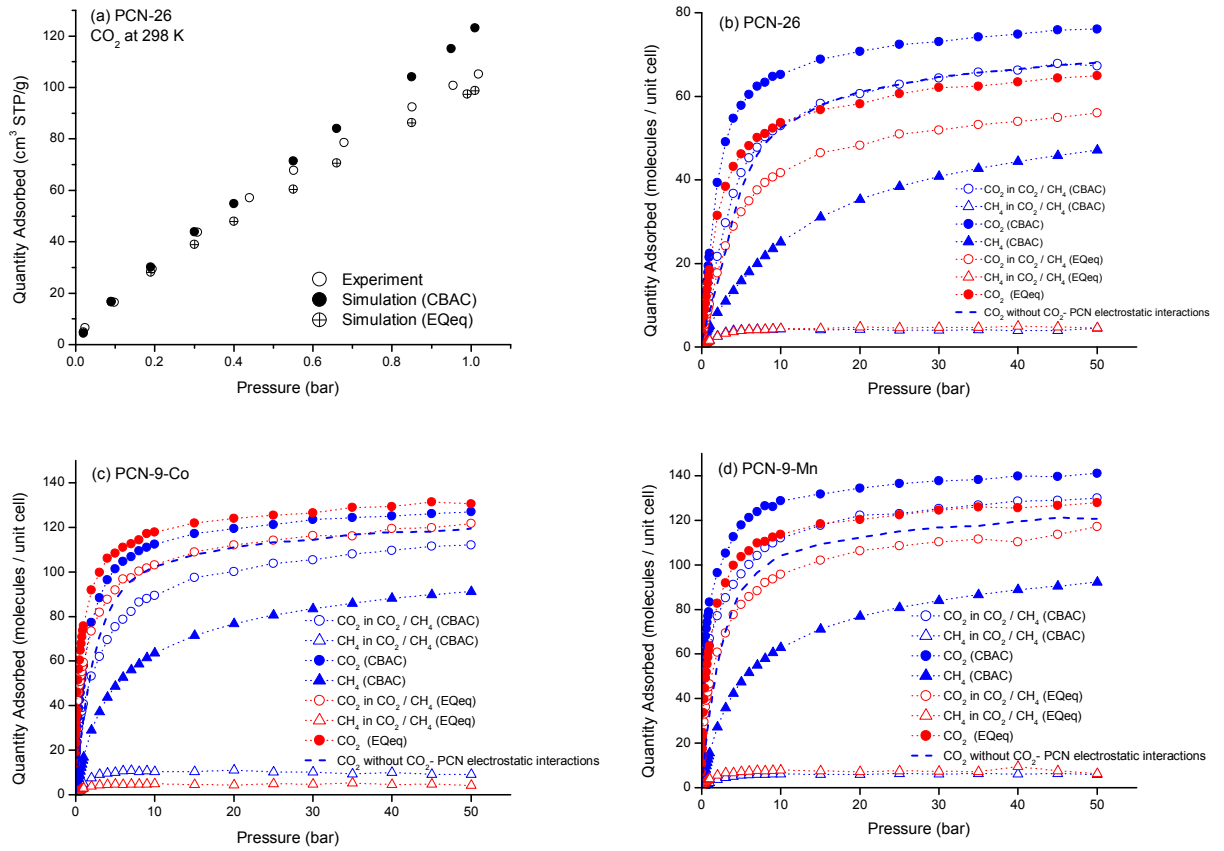


Figure A5. (a) Comparison of experimental CO_2 adsorption data with the atomic simulations based on CBAC and EQeq methods for PCN-26. (b-d) Effects of CBAC and EQeq methods on single-component and binary gas adsorption isotherms of PCNs. Open (closed) symbols represent data obtained from binary (single-component) GCMC simulations. Dash lines represent simulation results without electrostatic interactions between CO_2 molecules and PCN frameworks.

APPENDIX B: S_{sp} and Regenerability Calculations of PCNs**Table B1.** Sorbent selection parameter (S_{sp}) and per cent regenerability (R%) values of PCNs for CH₄/H₂:50/50 mixture at 298 K. The adsorption and desorption pressures are set to 10 and 1 bar, respectively.

Material	S_{sp}	R(%)	Material	S_{sp}	R(%)
PCN-6	63.12	89.22	PCN-20	57.94	88.40
PCN-6'	11.03	90.00	PCN-26	146.11	81.67
PCN-9-Co	1083.98	81.36	PCN-39	155.48	84.51
PCN-9-Mn	978.59	82.54	PCN-46	91.94	87.33
PCN-9-Fe	943.45	85.03	PCN-80	54.87	88.37
PCN-10	223.67	87.24	PCN-121	183.22	87.12
PCN-11	265.71	86.52	PCN-131'	1984.67	62.63
PCN-13	3403.76	59.05	PCN-221-Cu	188.58	86.72
PCN-14	599.02	80.86	PCN-221-Hf	182.71	84.79
PCN-16	154.91	80.87	PCN-222	40.71	88.75
PCN-16'	318.53	84.97	PCN-224-Ni	28.67	89.20
PCN-18	280.03	79.44	PCN-225	145.99	83.32
PCN-19	486.39	86.54			

Table B2. Sorbent selection parameter (S_{sp}) and per cent regenerability (R%) values of PCNs for CO₂/H₂:15/85 mixture at 298 K. The adsorption and desorption pressures are set to 10 and 1 bar, respectively.

Material	S_{sp}	R(%)	Material	S_{sp}	R(%)
PCN-6	112.94	90.48	PCN-20	132.33	90.83
PCN-6'	24.51	90.38	PCN-26	2855.44	82.12
PCN-9-Co	579309.20	43.51	PCN-39	8062.55	81.55
PCN-9-Mn	408861.67	53.16	PCN-46	373.09	85.66
PCN-9-Fe	3084.33	63.36	PCN-80	80.12	89.88
PCN-10	557.05	90.55	PCN-121	391.32	85.90
PCN-11	4433.49	88.99	PCN-131'	9609.80	67.31
PCN-13	65966.20	34.32	PCN-221-Cu	10031.79	64.85
PCN-14	4039.83	87.35	PCN-221-Hf	1599.77	72.02
PCN-16	610.36	90.81	PCN-222	1286.12	42.05
PCN-16'	19588.97	82.08	PCN-224-Ni	623.96	85.47
PCN-18	6092.70	85.08	PCN-225	66695.67	25.77
PCN-19	11141.43	89.07			

Table 5. Sorbent selection parameter (S_{sp}) and per cent regenerability (R%) values of PCNs for CO₂/CH₄:50/50 mixture at 298 K. The adsorption and desorption pressures are set to 10 and 1bar, respectively.

Material	S_{sp}	R(%)	Material	S_{sp}	R(%)
PCN-6	32.57	92.33	PCN-20	19.84	89.25
PCN-6'	18.08	91.85	PCN-26	148.28	75.57
PCN-9-Co	492.24	42.46	PCN-39	12.89	79.97
PCN-9-Mn	164.27	51.45	PCN-46	51.96	85.96
PCN-9-Fe	131.80	56.67	PCN-80	14.38	89.48
PCN-10	43.21	88.01	PCN-121	29.23	83.92
PCN-11	54.04	77.68	PCN-131'	24.59	44.66
PCN-13	8096.68	20.66	PCN-221-Cu	244.79	52.46
PCN-14	76.17	76.32	PCN-221-Hf	74.54	69.27
PCN-16	52.89	88.60	PCN-222	155.31	47.27
PCN-16'	416.43	66.36	PCN-224-Ni	67.60	81.44
PCN-18	81.67	69.94	PCN-225	3067.42	18.59
PCN-19	226.58	74.75			

Table B4. Sorbent selection parameter (S_{sp}) and per cent regenerability (R%) values of PCNs for CO₂/N₂:15/85 mixture at 298 K. The adsorption and desorption pressures are set to 10 and 1 bar, respectively.

Material	S_{sp}	R(%)	Material	S_{sp}	R(%)
PCN-6	10.53	90.46	PCN-20	12.05	90.25
PCN-6'	6.18	90.48	PCN-26	106.27	81.36
PCN-9-Co	58563.44	43.88	PCN-39	731.43	81.00
PCN-9-Mn	18893.12	52.58	PCN-46	15.56	85.17
PCN-9-Fe	83.63	60.94	PCN-80	7.95	89.44
PCN-10	21.46	89.49	PCN-121	19.80	85.14
PCN-11	106.45	88.11	PCN-131'	155.80	64.13
PCN-13	6423.37	35.50	PCN-221-Cu	434.37	63.80
PCN-14	70.24	85.50	PCN-221-Hf	75.05	70.53
PCN-16	28.23	90.26	PCN-222	143.84	41.73
PCN-16'	286.82	80.54	PCN-224-Ni	79.69	85.32
PCN-18	144.87	83.73	PCN-225	477.27	24.38
PCN-19	244.28	88.21			

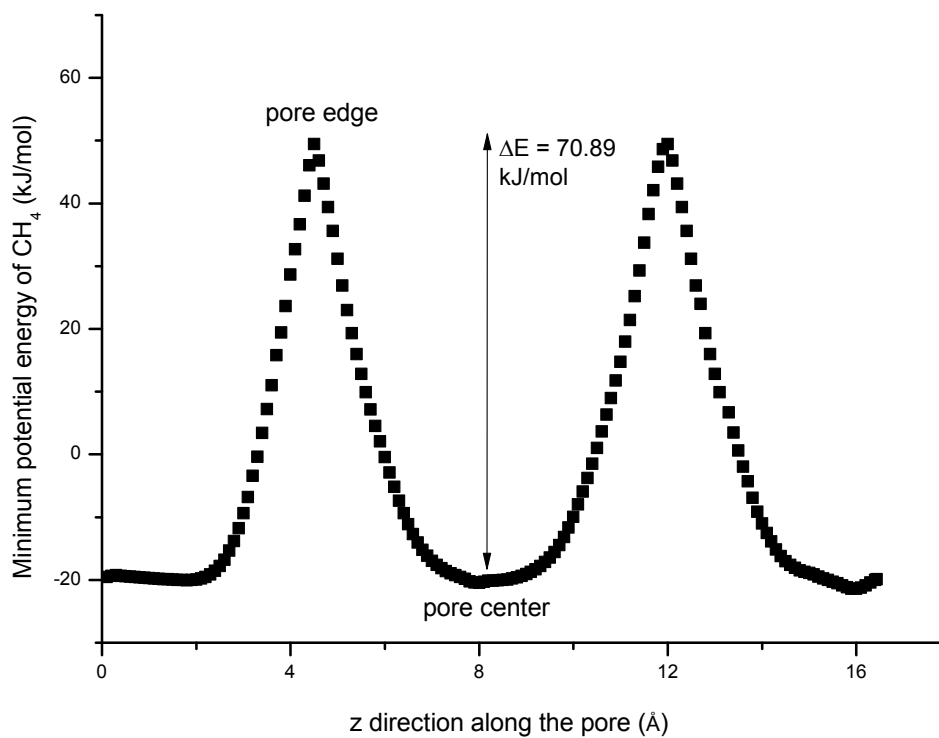


Figure B1. Minimum potential energy of CH_4 as a function of position along the pore axis in PCN-131'.

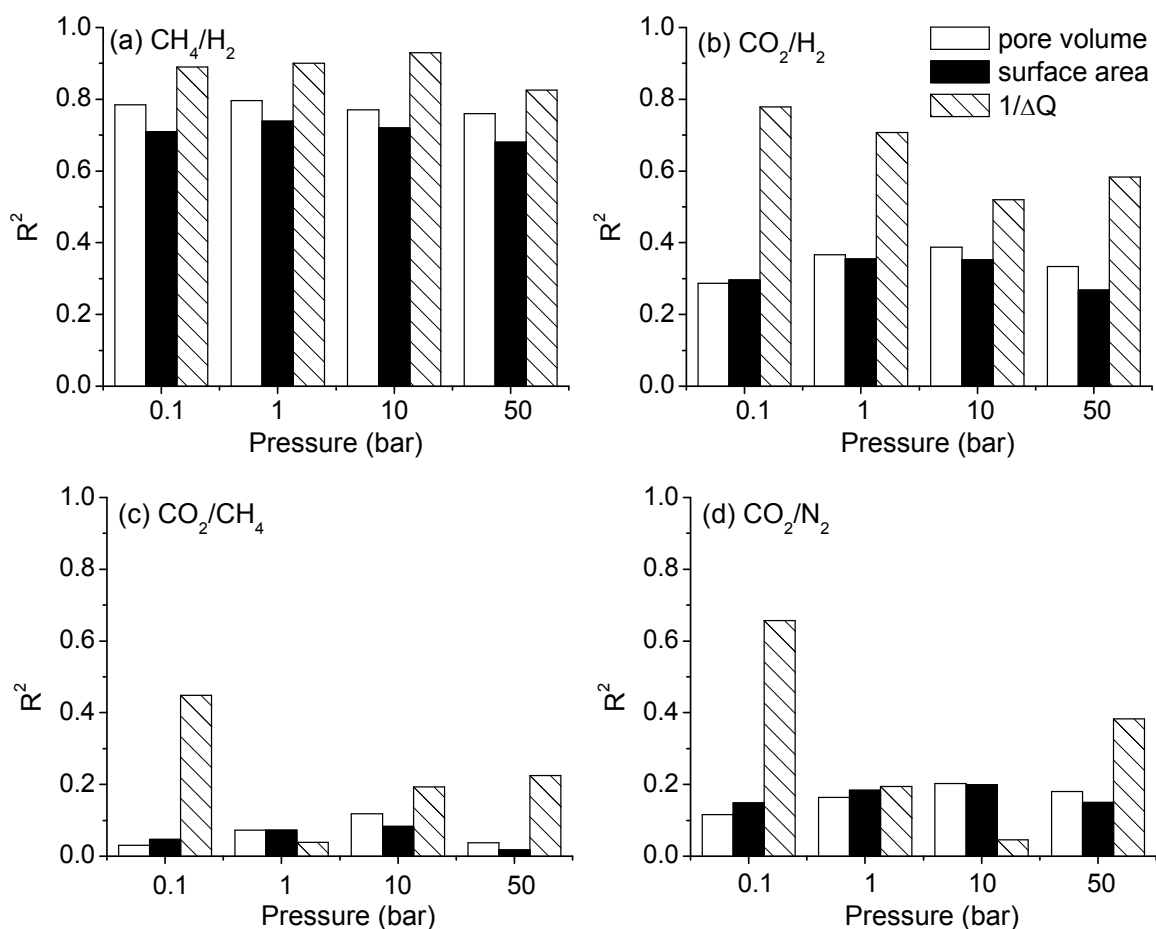
APPENDIX C: Selectivity Prediction Comparison between Models and Simulations

Figure C1. Coefficient of correlation (R^2) of adsorption selectivity with pore volume, surface area and the inverse of the difference between components' isosteric heats of adsorption values for (a) CH_4/H_2 , (b) CO_2/H_2 , (c) CO_2/CH_4 and (d) CO_2/N_2 mixtures at various pressures, 298 K.

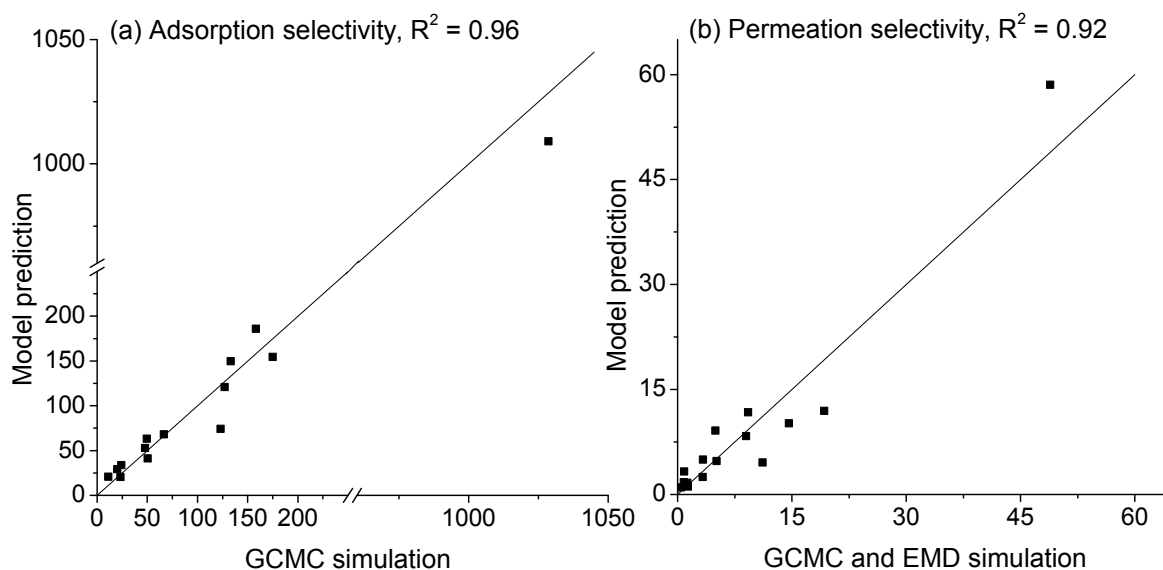


Figure C2. Comparison of model predictions and simulation results for (a)adsorption selectivity and (b)permeation selectivity of PCNs for CO₂/H₂ separation. The composition of the bulk gas mixture is 15/85 and temperature is 298 K. Adsorption selectivity and permeation selectivity data is presented at 10 bar.

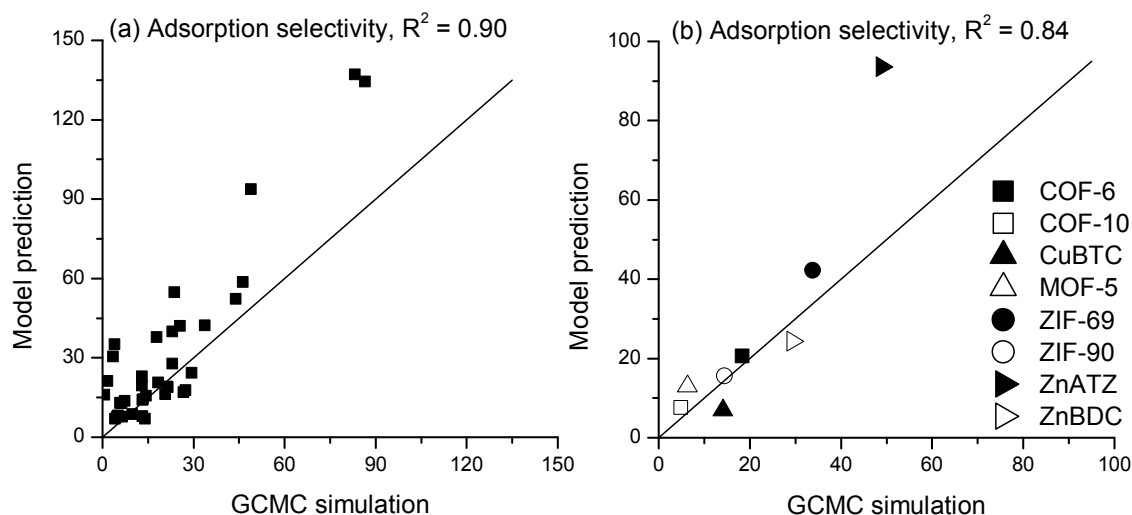


Figure C3. Comparison of model predictions and GCMC simulation results for CH₄/H₂ adsorption selectivity of different nanoporous materials. The composition of the bulk gas mixture is 50/50 and temperature is 298 K. Adsorption selectivity data is presented at 0.1, 1, 10 and 50 bar in (a), only at 10 bar in (b).

VITA

T. Nur Ozturk was born in Artvin, on May 11, 1989. She received her BS degree in Physics Engineering from Istanbul Technical University in 2011. In 2011, she was accepted to the Master of Science program in Physics Engineering at Istanbul Technical University. After completing her first year in the graduate program in ITU, she transferred to Computational Science and Engineering at Koç University. Her research interests include statistical thermodynamics, adsorption and diffusion phenomena in chemical and biological systems and computational investigation of physical chemistry related problems. She will continue her Ph.D. work at Department of Physics in Concordia University.

Publications

- T. N. Ozturk and S. Keskin, "Predicting Gas Separation Performances of Porous Coordination Networks using Atomistic Simulations," *Industrial & Engineering Chemistry Research* 52, 17627-17639 (2013).
- T. N. Ozturk and S. Keskin, "Computational Screening of PCNs for Adsorption and Membrane-based Gas Separations" *Journal of Physical Chemistry C* 118 (25), 13988-13997 (2014).