

STRUCTURAL AND GAS ADSORPTION CHARACTERISTICS OF ZEOLITE
ADSORBENTS

KHAIRUL SOZANA NOR BINTI KAMARUDIN

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy

Faculty of Chemical and Natural Resources Engineering
Universiti Teknologi Malaysia

JULY 2006

To my beloved husband, daughters, and sons....

ACKNOWLEDGEMENT

First and foremost, I thank Allah the Almighty for granting me strength to complete this work. I wish to express my sincere thank to my supervisors, Assoc. Prof. Dr. Hanapi Mat and Prof. Dr. Halimaton Hamdan for their encouragement and guidance. Their valuable comments and suggestions are very much appreciated. I am also grateful to Assoc. Prof. Dr. Zainab Ramli, Assoc. Prof. Dr. Salasiah Endud and the member of Zeolite and Porous Material Group (ZPMG) who offered their assistances during the early stage of my research project. Special thanks to my research colleagues, Chieng Yu Yuan who share the happiness as well as the sorrow during the course of our experimental research, and the undergraduate students, Lim Kai Shin, Lee Miaw Wah, Lim Kim Chuan, and Hafrizal, who show their interest in this research project. I am also grateful to my colleagues and friends who offered encouragement and understanding in the past few years. Our laboratory assistances, Yaakob Sabudin dan Zainab Salleh have given enormous assistances throughout this project and they deserve a lot of thanks. I also thank the staff member in the Faculty of Chemical and Natural Resources Engineering for the assistance and support, and for their availability at a time I needed their help. I also acknowledge the financial support from the Ministry of Science, Technology and Innovation (IRPA Grant No.745 12) and the University Teknologi Malaysia. My deepest gratitude to my husband (Mohd Noor), daughters (Nurin, Maryam, and Najihah), sons (Hanif and Akmal), brother (Lt. Col. Khairul), and sisters (Rozita, Liz, and Gee) for all their supports and encouragement. Finally, I pray to Him to make this work a reason of His pleasure and a benefit to the mankind.

ABSTRACT

Gas adsorption on zeolites gains remarkable attention in this new era of nanotechnology since it has industrial importance in many process industries. New technologies involving catalysis, gas separation, gas purification, gas storage, and high temperature gas sensor hold a great promise for industrial applications. In order to develop and design an efficient and economically feasible process, it is important to understand the adsorption characteristics of gas on zeolite. At present, there are many studies have been carried out in the area of gas adsorption, but the data is fragmented and still far from complete. Therefore, the aim of this study is to address some fundamental aspects of gas adsorption by investigating the structural properties and gas adsorption characteristics of different zeolite structures and cations in the extra-framework zeolites. Commercial zeolites representing channel types (ZSM-5, zeolite beta, mordenite, and ferrierite) and cage types (NaX, NaY, and zeolite A) were used in order to study the effect of structural arrangement on gas adsorption. Synthesized zeolite Y (Na-SZ18) was also used as comparison to NaY commercial, and for modification study. Modification using cation exchange method was carried out on the cage-type zeolite (Na-SZ18) by exchanging Na^+ with other cations namely Li^+ , K^+ , and Rb^+ (alkali metals), Mg^{2+} , Ca^{2+} , and Ba^{2+} (alkaline earth metals), and Mn^{2+} , Ni^{2+} , and Zn^{2+} (transition metals). Methane and carbon dioxide, the main components of natural gas, were used as adsorbates. The physical and chemical properties of zeolite adsorbents were determined using x-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier Transform infra-red (FTIR) spectroscopy techniques, and nitrogen adsorption at 77 K. Gas adsorption measurements were carried out using volumetric and gravimetric methods. Gas adsorption characteristics of zeolites were evaluated based on the adsorption capacity, adsorption isotherms, heat of adsorption, uptake rate of the adsorbates, and FTIR spectra of gas-zeolite interactions. It was found that cage-type zeolites are better adsorbents than channel-type zeolites. The adsorption of methane on Na-SZ18 is 5 times higher while the adsorption of carbon dioxide is 4 times higher than ferrierite. The gas adsorption measurements also revealed that exchanging Na^+ with some metal cations enhanced the adsorption capacity of methane (19.8 %) and carbon dioxide (7.48 %) on modified zeolites. In addition, FTIR spectroscopy results also suggested that the extra-framework cation influenced the interaction between adsorbates and the zeolite surface. Finally, the mechanisms of gas adsorption were proposed based on zeolite of different structures and metal cations. All these results suggests that structural properties and the cations that present in extra-framework zeolites affect the adsorption characteristics of methane and carbon dioxide on zeolites.

ABSTRAK

Penjerapan gas pada zeolit mendapat perhatian yang meluas di dalam era teknologi nano kerana ia menawarkan pelbagai kelebihan dalam industri pemprosesan. Teknologi-teknologi baru yang melibatkan pemisahan gas, penulenan gas, penstoran gas, dan penerima gas bersuhu tinggi mempunyai lebih peluang untuk diaplikasi di dalam industri. Untuk membangun dan merekabentuk proses yang cekap dan ekonomi, pengetahuan mengenai sifat-sifat penjerapan gas ke atas zeolit adalah sangat penting. Pada masa kini, terdapat banyak kajian yang telah dijalankan di dalam bidang penjerapan gas, tetapi maklumat yang ada masih lagi belum mencukupi. Oleh itu, kajian ini dijalankan bertujuan untuk menyelidiki aspek-aspek asas penjerapan gas dengan mengkaji sifat-sifat struktur dan ciri-ciri penjerapan zeolit berlainan struktur and berbeza kation di kerangka luar. Zeolit komersil yang mewakili jenis sesalur (ZSM-5, zeolit beta, mordenite, dan ferrierite) dan jenis sesangkar (NaX, NaY dan zeolit A) digunakan untuk mengkaji kesan susunan struktur terhadap penjerapan gas. Zeolit Y yang disintesis (Na-SZ18) juga digunakan sebagai perbandingan kepada NaY komersil, and kajian pengubahsuaian zeolit. Pengubahsuaian menggunakan kaedah pertukaran kation dijalankan terhadap zeolit jenis sesangkar (Na-SZ18) dengan menukarkan Na^+ dengan kation lain, iaitu Li^+ , K^+ , and Rb^+ (logam alkali), Mg^{2+} , Ca^{2+} , and Ba^{2+} (logam bumi alkali), and Mn^{2+} , Ni^{2+} , and Zn^{2+} (logam peralihan). Gas metana dan karbon dioksida, komponen utama di dalam gas asli, digunakan digunakan sebagai zat terjerap dalam kajian ini. Ciri-ciri fizikal dan kimia zat penjerap zeolit ditentukan menggunakan teknik pembelauan sinar-X (XRD), imbasan elektron mikroskopi (SEM), dan infra-merah pengubahan Fourier (FTIR) spektroskopi, dan penjerapan nitrogen pada suhu 77 K. Pengukuran penjerapan gas dijalankan menggunakan kaedah volumetrik dan gravimetrik. Ciri-ciri penjerapan gas dinilai berdasarkan kepada kapasiti penjerapan, penjerapan isotherma, haba penjerapan, kadar penjerapan zat terjerap, dan spektra FTIR interaksi gas-zeolit. Hasil kajian ini mendapati zeolit jenis-sesangkar mampu menjerap dengan lebih baik berbanding zeolit jenis-sesalur. Penjerapan keatas Na-SZ18 5 kali lebih tinggi, manakala penjarapan carbon dioksida pula adalah 4 kali ganda melebihi penjerapan ferrierite. Pengukuran penjerapan gas juga menunjukkan pertukaran Na^+ dalam zeolit dengan beberapa jenis kation logam boleh meningkatkan kapasiti penjerapan metana (19.8 %) dan karbon dioksida (7.48 %) keatas zeolit. Keputusan spektroskopi FTIR juga menunjukkan kation tersebut mempengaruhi interaksi antara zat terjerap dan permukaan zeolit. Akhir sekali, mekanisma penjerapan gas dicadangkan berdasarkan hasil kajian zeolit berlainan struktur dan kation logam. Keputusan-keputusan kajian ini menunjukkan bahawa sifat-sifat struktur dan kation di luar kerangka zeolit mempengaruhi ciri-ciri penjerapan gas metana dan karbon dioksida pada zeolit.

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LIST OF SYMBOLS

β	-	affinity coefficient
ε	-	potential field
a	-	partial molar area
a_o	-	lattice constant
B	-	Langmuir adsorption equilibrium constant
C	-	Polanyi constant
D, D_m	-	diffusivity, bulk diffusivity
D	-	Polanyi constant
D_k	-	Knudsen diffusivity
d	-	pore diameter
D/r^2	-	diffusional time constant
E	-	interaction energy
h, k, l	-	-lattice point positions
k	-	Henry's constant
K	-	Freundlich equilibrium constant
$k_{p\infty}$	-	equilibrium constant
m	-	mass of adsorbent
M_A, M_B	-	molecular weight of element A and B
M_∞	-	saturated amount of adsorbate adsorbed
M_t	-	average amount of adsorbate adsorbed as a function of time
n	-	Toth isotherm parameter
N_A	-	Avogadro number
n_s	-	total amount of adsorbate in the adsorbed state
n_v	-	no. of molecules per unit volume
P	-	partial pressure

P_o	-	atmospheric pressure
P_r	-	relative pressure
q	-	amount of adsorbate adsorbed per unit area
q_m	-	amount adsorbed by monolayer coverage
q_s	-	saturation limit
Q_{s-s}	-	integrated heat evolved due to sorbate-sorbate interactions
R	-	gas constant
r	-	radius of adsorbate
$R_{Si/Al}$	-	framework Si/Al ratio
S	-	specific surface area
T	-	temperature
t	-	constant
T_{AV}	-	average temperature
V	-	volume of the gas
V_N	-	net retention volume
W	-	volume adsorbed above the surface
W_o	-	limiting volume at the adsorbed space
α	-	Freundlich
ΔG	-	Gibbs free energy
ΔH_o	-	enthalpy change
ΔH_{ST}	-	isosteric enthalpy change
ΔS	-	entropy change
θ	-	angle
θ_r	-	fraction of surface coverage
λ	-	mean free path of gas molecules
$\Omega_{D,AB}$	-	collision integral based on the Lennard-Jones potentials
σ_{AB}	-	average collision diameter

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Adsorption is a process in which material accumulates at the interface. In the case of gas adsorption, solid and gas are called as adsorbent and adsorbate respectively. According to Dabrowski (2001), this adsorption process is a result of intermolecular forces attraction between adsorbate and adsorbent. The adsorbates attract to the surface of adsorbent through van der Waal forces (physical adsorption) and chemical bond formation (chemical adsorption). When the intermolecular attractive forces between a solid and a gas are greater than those existing between molecules of the gas itself, the gas will condense upon the surface of the solid even though its pressure may be lower than the vapor pressure corresponding to the prevailing temperature. The adsorption phenomenon is accompanied by an evolution of heat (Suzuki, 1990; Dabrowski, 2001).

A tremendous growth of gas adsorption processes has made adsorption system a key separation and purification tool in chemical and petrochemical industries (Padin *et al.*, 2000; Barbosa *et al.*, 2000; Da Silva and Rodrigues, 2001; Hasegawa *et al.*, 2001; Rege and Yang, 2002; Hincapie *et al.*, 2004). Hence, it

generates intense interest in porous material (adsorbents) such as activated carbon, zeolite, silica, and alumina since the choice of potential adsorbent can be crucial in determining the performance of any adsorption process (Rakoczy and Traa, 2003; Bae and Lee, 2005). Although, in principle, porous material can provide all the basic requirements for adsorption, in practice the best adsorbent needs to fulfill requirements for specific adsorption system. Current development shows that zeolite has gained broad academic and industrial interest stemming from its unique combination of properties (Mohamed and Mekkawy, 2003; Clausse *et al.*, 2004; Berthomieu *et al.*, 2005). Furthermore, the fine-tuning of the zeolite structure by all sorts of modification methods while maintaining its topology makes zeolite more attractive than any other adsorbents (Langmi *et al.*, 2005; Garcia *et al.*, 2005).

So far, adsorption was used in many fields mainly separation and purification processes such as gas dehydration, separation and purification of hydrogen from steam reformer, separation and purification of air, separation of paraffins, and removal of pollutants from the flue gases (Harlfinger *et al.*, 1983; Stelzer *et al.*, 1998; Tatlier and Erdem-Senatalar, 2004; Chang *et al.*, 2004; Koriabkina *et al.*, 2005). However, extensive studies on the zeolitic materials may lead to other potential applications in adsorptive natural storage, hydrogen gas storage, high temperature gas sensor and semiconductor materials (Langmi *et al.*, 2005; Biloe and Goetz, 2001; Nijkamp *et al.*, 2001; Mintova and Bein, 2001; Matranga *et al.*, 1992).

1.2 Research Background

The earliest applications of zeolite adsorbents were the drying of refrigerant gas and natural gas (van Bekkum *et al.*, 1991). An exciting new scientific direction has emerged through introduction of various zeolites structural frameworks aiming to produce highly efficient process. Thus, the understanding of zeolite structure and

structure-properties relationship becomes the basic interest and the most challenging task in zeolite research.

There are numerous types of natural and synthetic zeolites that could be used in catalysis and gas adsorption applications. Natural zeolites have not gained much industrial importance due to some limitations in availability and variation in chemical composition and physicochemical properties. However, due to great demand of zeolites for industrial applications, synthetic zeolites are produced in large quantities. According to the International Zeolite Association - Structure Commission, more than 150 distinct framework structures of zeolite have been synthesized. At the same time, various techniques evolved for identifying and characterizing these materials accelerate the development of zeolite as potential adsorbent. In the presence of various structural frameworks, the selection of suitable adsorbent would depend on the adsorption capacity and selectivity of zeolite. Consequently, this would depend on the properties of adsorbent and adsorbate. Other factors such as temperature and pressure should also be considered. As reported in literatures, there are several parameters used in order to evaluate the performance of zeolites as gas adsorbents (Bellat *et al.*, 1995; Triebe *et al.*, 1996; Armor, 1998; Hernandez-Huesca *et al.*, 1999; Pires *et al.*, 2001; Rege and Yang, 2002; Khelifa *et al.*, 2004). The measurements of gas adsorption isotherm, gas adsorption capacity, and gas uptake rate could also be used to determine the characteristics of gas adsorption on zeolite adsorbent.

In many cases, the adsorbent was further improved by carrying out post-synthesis treatment (modification) that could change the properties of zeolites at molecular level (Vansant, 1987; Bellat *et al.*, 1995; Siantar *et al.*, 1995; Armor, 1998; Choi *et al.*, 2000; Qian and Yan, 2001; Nery *et al.*, 2003). The modification of internal zeolite pore structure for example, is a way of “engineering” the structure of zeolites. Cation exchange and dealumination are the most common methods used to modify the physical and chemical properties of zeolites. However, the selection of modification method also depends on the gas adsorption system. Different adsorbates that adsorbed at different temperature and pressure may require different methods of

modification. In general, the modification should be able to overcome any discrepancies related to structural and physicochemical properties of the zeolite. Furthermore, the method should be simple and caused minimum damage to the structure.

1.3 Research Motivation and Aims

Research in the area of gas adsorption is continuously expanding with the use of zeolites in several important applications such as catalysis, natural gas storage, natural gas purification and hydrocarbon separation (Wegrzyn and Gurevich, 1996; Mota, 1999; Biloe *et al.*, 2001; Anpo *et al.*, 2002; Stefanis *et al.*, 2004; Cavenati *et al.*, 2004). However, to be more competitive, the adsorptive capability of zeolite adsorbent should be improved. With more than 150 zeolites structures that have been synthesized (International Zeolite Association (IZA)-Structure Commission), it is very important to understand the characteristics of gas adsorption on zeolite adsorbent for the selection of suitable adsorbent for the system. Zeolite was chosen due to the fact that it has high porosity and can be employed as selective adsorbent (Dabrowski, 2001; Holmberg *et al.*, 2004). However, current developments show the diversification in zeolite compositions and structures (IZA -Structure Commission), thus it requires detailed explanation on adsorption phenomena on of gases on zeolite adsorbent.

To date, there are limited types of zeolites being used in gas adsorption applications (Eldridge, 1993; Choudhary and Mayadevi, 1996; Sakuth *et al.*, 1998; Hernandez-Huesca *et al.*, 1999; Jayaraman *et al.*, 2004; Olson *et al.*, 2004; Stefanis *et al.*, 2004; Diaz *et al.*, 2004). One of the reasons that limit the use of various zeolites is due to lack of understanding on the characteristics of adsorption especially related to structural and physicochemical properties of the zeolitic materials. Hence, it requires extensive studies on zeolite adsorbents in order to expand the selection of

the material for adsorption application. Even though it is known that structural framework of zeolite would influence the diffusivity of adsorbate, and thus influence the adsorption capacity and selectivity, properties that affect the adsorption capacity are still not clearly identified since the studies only involve limited number of zeolites (Werner and Mersmann, 1994; Exter *et al.*, 1997; Keller *et al.*, 1999; Weireld *et al.*, 1999; Yang *et al.*, 2001; Czaplelewski *et al.*, 2002; Langmi *et al.*, 2003; Kubanek *et al.*, 2005; Maurin *et al.*, 2005). Therefore, the **first objective** of this research is to study gas adsorption characteristics of structurally different zeolites.

In order to achieve this objective, several types of zeolite were selected namely A, X, Y, Na-SZ18, ZSM-5, mordenite, ferrierite, and beta. These zeolites were selected to represent different zeolite properties such as pore network system, pore size, surface area, pore volume, and zeolite compositions (Si, Al, and Na). Except for zeolite X, Y, and Na-SZ18, each zeolite has different structural framework arrangement that represent different pore network system (one-, two-, three-dimensional pore network system, straight and zig-zag channel system). Zeolite X, Y, and Na-SZ18 belong to faujasite structure, with the difference in the ratio of Si/Al. In this study, zeolites are divided into two main categories, interconnected cage-like voids and uniform channel-like systems in which the channel is connected either in one-, two- or three-dimensional system. Adsorbates used in this study are methane and carbon dioxide, main component in natural gas. The adsorbates represent small gas molecules with different characteristics; methane is non-polar molecules whereas carbon dioxide appears to have a quadrupole moment. Based on the gas adsorption capacity and gas uptake rate, the gas adsorption performance of different structural framework was investigated.

However, structural framework is not the only factors that affect the adsorption capacity and selectivity of zeolites. This is due to the fact that, apart from the diffusion of adsorbate, the interaction of adsorbate-adsorbent is equally important in the adsorption process. Hence, this investigation was extended to the physicochemical properties of zeolites that include zeolite crystallinity, porosity, and

chemical composition. The samples are initially characterized using methods such as x-ray diffraction (XRD) spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy, and surface analysis based on nitrogen adsorption (NA). The relationship between these properties and adsorption isotherm, adsorption capacity, and gas adsorption uptake provide a fundamental understanding on the effect of zeolite physicochemical properties of adsorbent on gas adsorption characteristics. In addition, several equation models were used to determine the thermodynamic and kinetic parameters of the material understudied.

Since the adsorption involves evolving of heat, heat of adsorption was calculated in order to determine type of adsorption occurred on the zeolite surface, either chemical adsorption or physical adsorption. Finally, to complete the first objective, gas-zeolite interaction were carried out using FTIR spectroscopy method. The spectra relatively show the amount adsorbed and the strength of interaction between the adsorbate and the adsorbent. The results reveal some important characteristics of adsorption on zeolite adsorbent, which lead to development of mechanistic model of gas adsorption on zeolite adsorbent. After completing the first objective, to study gas adsorption characteristic different zeolite structures, one of the zeolite understudied was selected for zeolite modification. The selection was made based on the adsorption capacity, thermodynamic and kinetic properties, and gas-zeolite interaction of different zeolite structures.

As the adsorption involves the interaction between adsorbate and adsorbent, the charge balancing cation (usually sodium) has important roles in the adsorption process (Bellat *et al.*, 1995; Armor, 1998; Barbosa *et al.*, 2000; Khelifa *et al.*, 2004; Maurin *et al.*, 2005b). However, there is apparent discrepancy between the results obtained since those studies were carried out using different cations, different zeolites, different adsorbates, and at different experimental conditions. Other studies on cation exchange only focused on the physical and chemical changes of the zeolitic material (Siantar *et al.*, 1995; Huang *et al.*, 1998; Albert and Cheetham, 2000; Trigueiro *et al.*, 2002; Öhman *et al.*, 2002; Nery *et al.*, 2003). Therefore, the **second objective** of this research is to study the effect of different cations on gas adsorption

characteristics of zeolite adsorbent. It was carried out by cation exchange method in which, sodium that present as charge balancing cations in the extra-framework of zeolite of the selected zeolite was replaced by other cations.

This modification method is simple, however it results in some variations to the properties of adsorbent without create much defect on the structure. Cations were selected to represent three groups of metals; alkali metal, alkaline earth metal and transition metal groups. Apart from the size and the charge of cation, the amount and the locations of cation in three dimensional zeolite matrixes might influence the adsorption characteristics of zeolite. The characterizations were also carried out on the modified zeolites to provide useful information on the structure and properties of zeolite after modification. Gas adsorption measurements were carried out to determine gas adsorption isotherm, gas adsorption capacity, the uptake rate of methane and carbon dioxide.

The data obtained were used to evaluate the thermodynamic and kinetic parameters of gas adsorption on metal cation exchanged zeolites. The relationship between gas adsorption capacity and physicochemical properties of modified zeolite were further evaluated in the presence of different cations. In addition, FTIR spectroscopy was used to study the interaction between adsorbates and modified adsorbent. The results would give some indications the effect of cations on physicochemical properties and the characteristics of adsorption. By using methane and carbon dioxide, the study would demonstrate the effect of adsorbate properties on gas adsorption characteristics. Finally, the mechanistic model based on the presence of different cations in zeolite adsorbent was proposed to provide a better insight on the role of cation in gas adsorption.

In general, the experimental approach of this study as given in Figure 1.1 which involves synthesis of zeolite, characterization of zeolites, gas adsorption studies using methane and carbon dioxide as adsorbates, selection of potential adsorbent, and modification by metal cation exchange method. The characterization

and gas adsorption studies were also carried out on modified zeolites. Investigation on gas adsorption characteristics was carried out based on the properties of zeolites, the adsorption capacity, adsorption isotherm and the gas uptake rate of the zeolites.

1.4 Thesis Outline

The earlier section of this chapter provides brief introduction to the adsorption process and its applications. The research background presents an overview of zeolite as an adsorbent and gas adsorption system. This leads to the study on the characteristics of gas adsorption on zeolite adsorbent, which are specifically presented in the research motivation and aims.

Chapter 2 presents the basic theory of gas adsorption and summarizes the state-of-art of the related study; zeolite structure and properties, methods of modification, and fundamental aspect of gas adsorption on zeolites. It also gives brief description on thermodynamics and kinetics of adsorption that have been used as a tool to describe adsorption phenomena in zeolites. **Chapter 3** outlines the experimental work of the research. It consists of list of materials and experimental methods used in this study. It outlines method of zeolite synthesis, basic theory on structural and physical characterization and methods to characterize the zeolites samples. In addition, the experimental procedures in gas adsorption study and gas-zeolite interaction study are depicted in this chapter.

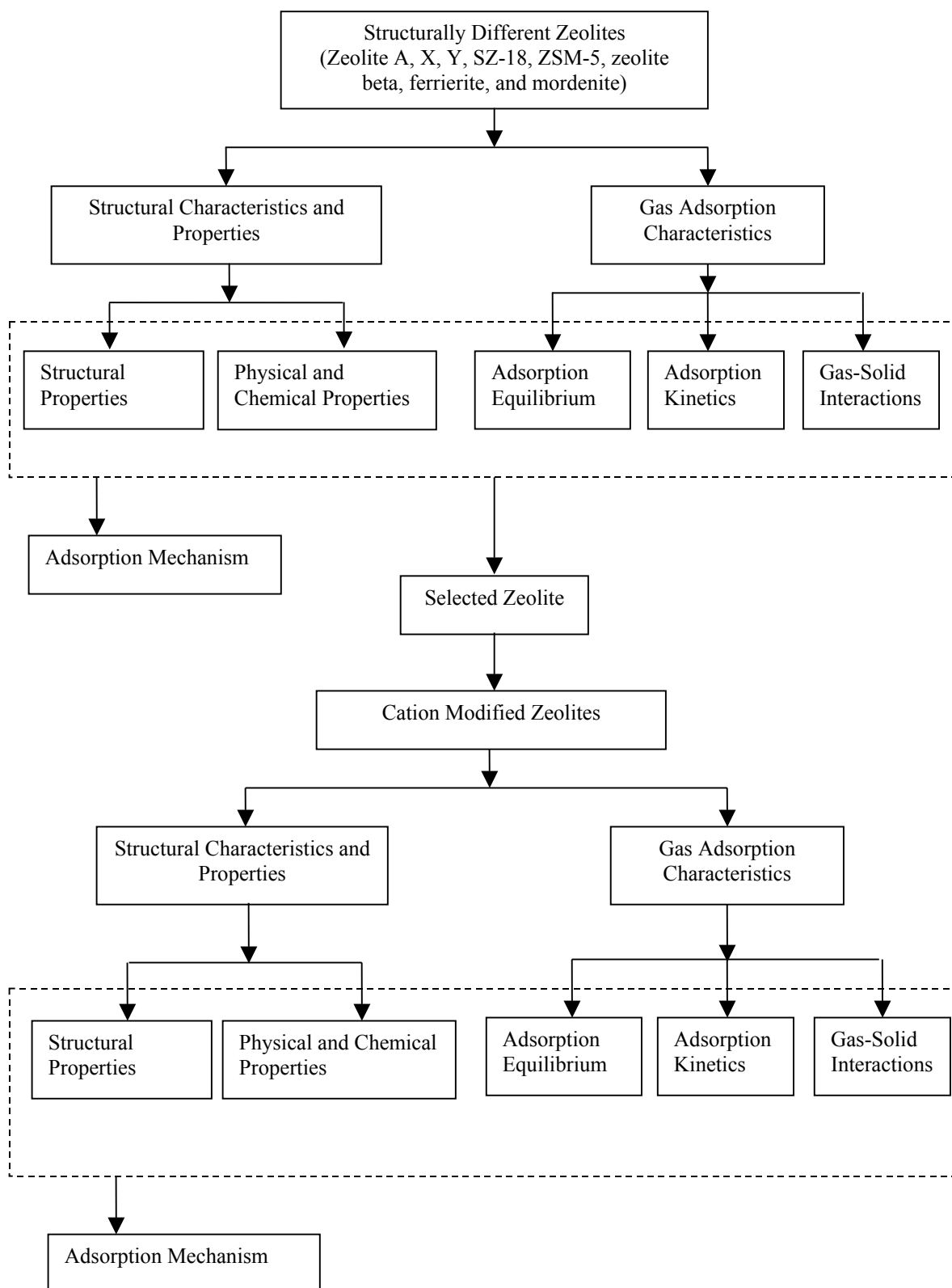


Figure 1.1: An experimental approach adopted for the study.

Results and discussion are divided into two chapters. **Chapter 4** focuses on structurally different zeolites, discusses the physical and chemical properties of different zeolites and its effect on adsorption capacity. In order to understand adsorption characteristics of gases, data on gas adsorption isotherm and gas uptake rate were used to obtain the thermodynamic and kinetic parameters of gas adsorption. Heat adsorption of a given adsorbate-adsorbent system was calculated in order to determine type of adsorption occurred. The data were also fitted into several equation models and the validity and the applicability of models were thoroughly discussed. The gas - zeolite interaction are also discussed in this chapter. Finally, based on the properties and adsorption study of structurally different zeolites, the gas adsorption mechanism on zeolite was presented in this chapter.

Extending the findings in Chapter 4, zeolite modification was carried out using cation exchange technique on the selected sample. The effects of different cation on zeolite physical and chemical properties are discussed in the **Chapter 5**. Again, adsorptive characteristics of modified exchanged zeolites are discussed and evaluations of thermodynamic and kinetic parameters of modified exchanged zeolites are presented in this chapter. In the presence of different cations, gas-zeolite interactions are thoroughly evaluated. Subsequently, the adsorption mechanism dependency of metal cations is proposed.

Chapter 6 states some general conclusions, implications of this work and directions on future work. The experimental studies reported in this work provide useful information on gas adsorption characteristics of zeolite adsorbent. Evaluation of physical and chemical properties of structurally different zeolites and modified exchanged zeolites give a good understanding about zeolite as an adsorbent.

1.5 Summary

Unique physical and chemical properties of zeolite and its ability to maintain microporosity behavior after modification is the main reason for every study carried out on zeolites especially in the area of gas adsorption. The emergence of new applications requires extensive studies on the potential adsorbent such zeolites. However, insufficient knowledge about physical and chemical properties of zeolite and modified zeolites as well as their effect on gas adsorption characteristics may limit the usage of the zeolite. Therefore, this work will address the effect of zeolite properties on gas adsorption characteristics in order to get better understanding and hence, to be able to engineer those properties to enhance gas adsorption capacity and selectivity.

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