GAS-PHASE ADSORPTION IN DEALUMINATED NATURAL CLINOPTILOLITE AND
LIQUID-PHASE ADSORPTION IN COMMERCIAL DAY ZEOLITE AND MODIFIED
AMMONIUM Y ZEOLITE

By

Alba Nydia Costa Hernández

DISSERTATION

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Alba Nydia Costa Hernández

Approved:

Rolando Roque-Malherbe, PhD
Research Advisor

Clariel Báez Félix, PhD
Member

José J Duconge, PhD
Member

Samuel Rosario, PhD
Member

Ángel Rivera Collazo, PhD
Member

Teresa Lipsett, PhD
Dean
Alba Nydia Costa Hernández was born in Humacao, Puerto Rico. She has a Bachelor Degree in Physic Applied to Electronics from University of Puerto Rico, Humacao Campus, Puerto Rico. Also, she has a Master Degree in Environmental Health with a concentration in Occupational Health from University of Puerto Rico, Medical Science Campus, Río Piedras, Puerto Rico.

As Environmental Specialist, she was working in wastewater and water compliance reports, especially in the Consumer Confidence Reports (CCR) or Drinking Water Quality Reports. In 2006 she began to work as an Industrial Hygienist in the Puerto Rico Aqueduct and Sewer Authority (PRASA), responsible to implement safety programs, such as Respiratory Protection, Hazard Communication and Hearing Protection, among others. At present, she is the Director of the Hygiene and Occupational Safety Office in PRASA, responsible of the enforcement of occupational and environmental regulations, such as Process Safety Management and Risk Management Plan, among others.

As a doctoral student she presented her research work “Study of the interaction between dealuminated natural Clinoptilolite and Carbon Dioxide molecule” in poster session at the 43rd IUPAC World Chemistry Congress, August 2011, in San Juan, Puerto Rico. In the year 2013 she was the co-author of the scientific paper “The Study of absorption space in modified clinoptilolite”.

Vita
Dedications

To the angels of my life,

my parents, Tomasita y Rafael Luis.
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Abstract

Alba N. Costa Hernández (PhD Environmental Science)

The Gas-Phase Adsorption in Dealuminated Natural Clinoptilolite and the Liquid-Phase Adsorption in Commercial DAY Zeolite and modified Ammonium Y Zeolite. (April 2013)

Abstract of a doctoral dissertation at the *Universidad del Turabo*.

Dissertation supervised by Professor Rolando Roque-Malherbe, PhD

No. of pages in text: 147

The adsorption of Carbon Dioxide (CO$_2$) is a very important tool for the material characterization. On the other hand, in separation and recovery technology, the adsorption of the CO$_2$ is important to reduce the concentration of this gas considered as one of the greenhouse gases. Natural zeolites, particularly clinoptilolite, are widely applied to eliminate some pollutants from the environment.

One of the goals of this research is to study the structure, composition and morphology of one natural clinoptilolite dealuminated with ammonium hexafluorosilicate (AHFi) and with orthophosphoric acid (H$_3$PO$_4$). Each modified sample was characterized using X-ray Diffraction (XRD), Carbon Dioxide adsorption at 0$^\circ$ C, Thermogravimetric Analysis (TGA), and Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDAX). In addition, the surface chemistry of the modified clinoptilolites was analyzed with Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS).
The adsorption measurements were also used to study of the interaction of CO₂ molecule within the adsorption space of these modified clinoptilolites. It was concluded that one of the modified clinoptilolites, (CSW-HFSi-0.1M), showed a great quality as adsorbent and as catalytic comparable to commercial synthetic zeolites. As far as we know, the modification of clinoptilolite with HFSi to improve their adsorption properties had not been previously attempted.

In the second part of this dissertation, the dynamic adsorption of three isomers of nitrophenols using as adsorbent a commercial DAY zeolite was investigated. Also, the dynamic adsorption of methanol in a less hydrophobic zeolite, Ammonium Y Zeolite was investigated. The obtained breakthrough curves showed that the commercial DAY zeolite could be a suitable adsorbent to the liquid-phase adsorption of the phenolic compounds. Notwithstanding the modified ammonium Y zeolite had a low Si/Al ratio (less hydrophobic) than commercial DAY zeolite; this modified zeolite was useful for the dynamic adsorption of polar compound such as methanol. The obtained results were consistent with those reported in other studies related with the use of zeolites in the removal of organic compounds from the liquid phase.
Resumen

Alba N. Costa Hernández (PhD Ciencias Ambientales)

La Adsorción en Fase-Gaseosa en la Clinoptilolita Natural Dealuminada y la Adsorción Fase-Líquida en la zeolita DAY Comercial y la Zeolita Y Amónica Modificada: (Abril/2013)

Resumén de una disertación doctoral en la Universidad del Turabo.

Disertación supervisada por el profesor Rolando Roque-Malherbe, PhD.

No. de páginas en texto: 147

La adsorción de Dióxido de Carbono (CO₂) es un instrumento importante para la caracterización de materiales. Por otra parte, en la tecnología de separación y recuperación, la adsorción de CO₂ es importante para reducir la concentración de este gas considerado como unos de los gases invernadero. Las zeolitas naturales, particularmente clinoptilolita, son muy aplicadas como adsorbentes para eliminar algunos contaminantes del ambiente.

Uno de los objetivos de esta investigación fue estudiar la estructura, composición y la morfología de una clinoptilolita natural dealuminada con hexafluorosilicato de amonio (HFSi) y con ácido ortofosfórico (H₃PO₄). Cada muestra modificada fue caracterizada con Difracción de Rayos-X (XRD, por sus siglas en inglés), Adsorción de Dióxido de Carbono a 0 °C, Análisis Termogravimétrico, (TGA, por sus siglas en inglés), y Microscopia Electrónica de Barrido acoplado con Análisis por Dispersión de Energía de Rayos X (SEM-EDAX, por sus siglas en inglés). Además, la química de la superficie de las clinoptilolitas modificadas fue analizada con
Espectroscopía Infrarroja por Transformada de Fourier de Reflectancia Difusa (DRIFTS, por sus siglas en inglés).

Las mediciones de adsorción se utilizaron para estudiar la interacción de la molécula de CO$_2$ dentro del espacio de adsorción de estas clinoptilolitas modificadas. Se concluyó que una de las clinoptilolitas modificadas (CSW-HFSi-0.1M), demostró tener una gran calidad como adsorbente y como catalítico comparable con la zeolita sintética comercial. Hasta donde se conoce, la modificación de la clinoptilolita con HFSi para mejorar sus propiedades de adsorción no ha sido anteriormente intentada.

En la segunda parte de esta disertación se investigó la adsorción dinámica de tres isómeros de nitrofenol usando la zeolita DAY comercial como adsorbente. Se investigó, además, la adsorción dinámica de metanol en una zeolita menos hidrofóbica, zeolita Y amónica. Las curvas de ruptura obtenidas demostraron que la zeolita DAY comercial puede ser un adsorbente idóneo para la adsorción en fase líquida de los compuestos fenólicos. A pesar de que la zeolita Y amónica tuvo una baja proporción de Si/Al (menos hidrofóbica) que la zeolita DAY comercial; esta zeolita modificada fue útil para la adsorción dinámica de un compuesto polar como el metanol. Los resultados obtenidos fueron consistentes con aquellos reportados en otros estudios relacionados con el uso de las zeolitas en la remoción de compuestos orgánicos de la fase líquida.
Chapter One

Introduction

1.1 Carbon dioxide emissions

Disposal or other releases of contaminant into the environment generated by anthropogenic sources could ultimately affect the human health. For example, some studies have linked air pollution to a variety of health problems including: aggravation of respiratory and cardiovascular disease; decreased lung function; increased frequency and severity of respiratory symptoms such as difficulty breathing and coughing; increased susceptibility to respiratory infections; effects on the nervous system, including the brain, such as IQ loss and impacts on learning, memory, and behavior; cancer; and premature death (EPA 2010).

Air pollutants can also impact the Earth’s climate. Any pollutant that affects the Earth’s energy balance is known as a “climate forcer”. Some “climate forcers” can absorb energy and lead to climate warming or otherwise can reflect the sun’s rays and prevent that energy from reaching the Earth’s surface, leading to climate cooling (EPA 2010). One “climate forcer” is carbon dioxide (CO$_2$), the main greenhouse gas (GHG) that traps heat in the atmosphere and causes the global warming. The combustion of fossil fuels produces carbon dioxide, with an increasing potential for by-product end-use in the industrial and energy production sectors. The use of CO$_2$ as a by-product would not only have economic benefits but would simultaneously mitigate global climate change concerns (Figueroa et al. 2008). The Energy Information Administration (EIA) within the U.S. Department of Energy (DOE) estimates that consumption of fossil fuels (coal, petroleum and natural gas) will increase by 27% over the next 20 years, thereby
increasing U.S. CO\textsubscript{2} emissions from the current 6000 million tons per year to 8000 million tons per year by 2030 (Figueroa et al. 2008).

Some countries have been major contributors to CO\textsubscript{2} emissions to the atmosphere. For example, Martínez-Zarsozo (2007) indicates that the level of CO\textsubscript{2} emissions from developing countries has been rapidly exceeding that of the developed countries, and actually accounts for almost 50 percent of the world’s CO\textsubscript{2} emissions. This trend is expected to grow if the current path, in terms of energy consumption, is maintained.

1.2 Phenol release in surface water

Human’s activities can also affect the quantity, quality and availability of natural water resources in any given area. The increase in human population leads not only to a greater use of water resources, but also to an increase in wastewater discharges. Water supplies are overloaded with hazardous chemicals and bacteria from domestic, agricultural and industrial waste, where intensive use of pesticides, herbicides, fertilizers, and industrial chemicals are utilized (Bisesi and Koren 2002). A large number of tons of hazardous waste generated in the United States will eventually reach the groundwater and surface water. In the United States, although it is estimated that only 0.5 to 2% of groundwater supplies are contaminated, much of the contamination occurs in areas where this is the only source of drinking water (Bisesi and Koren 2002). In the United States and Puerto Rico most of the groundwater and surface water serves as a Public Water Supply (PWS) whose end-use is as drinking water for human consumption. According to the Environmental Protection Agency (EPA), in the United States the 73.9% of the river and streams that serve as PWS is considered as good, while the 25.3% is considered as impaired. However, in Puerto Rico only the 14.7% of the river and streams that serve as PWS is considered as good (EPA 2010). The other 85.3% is
considered as impaired because it is mostly contaminated with metals (arsenic), toxic inorganic (cyanide) and pathogens (fecal coliform) (EPA 2010).

The Federal Clean Water Act (CWA), an amendment to the Federal Water Pollution Control Act of 1972, establishes the basic structure for regulating discharges of pollutants into the waters of the United States. Section 307 defines a list of priority pollutants for which the U.S. EPA must establish ambient water-quality criteria (the basis of state water-quality standards) and effluent limitations (rules controlling environmental releases from specific industrial categories based on the "best available technology economically achievable"). The EPA list of Priority Pollutants is available through the Code of Federal Regulations 40 CFR - CHAPTER I - PART 423: Appendix A to Part 423 -- 126 Priority Pollutants.

The phenol and phenolic compound are found in the list of priority pollutant because they are extremely dangerous to organisms, even at low concentrations. Phenol is released to the air and water as a result of its manufacture, its use in phenolic resins and organic synthesis. Phenol is found in petroleum products, such as coal tar and creosote, and can be release by combustion of wood and auto exhaust. Phenol is also produced by the natural degradation of organic wastes including benzene.

Phenol has been identified in, at least, 595 of the 1,678 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2008). Of these sites, 589 are located within the United States and four are located in the Commonwealth of Puerto Rico, and two are located in the Virgin Islands.

1.3 Statement of the Problem

Often the implementation of technologies, techniques or methodologies to eliminate or reduce some pollutants from the environment is extremely costly, inefficient and environmentally unfavorable. Some examples are:
1. One of the energy-intensive and expensive technologies of carbon capture and storage (CCS) used for the separation of CO$_2$ from flue gas of coal fired power station can pose environmental hazards derived from accidental spills and from waste processing (Rodríguez-Delgado and Otero-Arean 2011).

2. One of the disadvantages of the technology employing conventional monoethanolamine (MEA) absorption processes that can be used in the recovery of CO$_2$ from flue gas emitted by power plant, steel mills and cement kilns is that the regeneration of the solvent is highly energy intensive. In addition, the process is plagued with corrosion problems and is expensive (Ho et al. 2008). Gas adsorption using alkanolamine solutions generates severe corrosion of the equipment, and the regeneration of amine solutions is highly energy intensive (Sayari et al. 2011).

3. The active carbon is the most frequently used adsorbent in the physicochemical treatment techniques of phenol removal from water, but this turns out to be flammable and requires a high cost for their regeneration.

These disadvantages presented above deserve to conduct studies with naturals and abundant adsorbents. These materials should be low-cost adsorbents and easily modifiable to have the physicochemical properties suitable for the elimination or reduction of some contaminants in the environment.

1.4 Justification of the study

The use of adsorbents in environmental applications deserves a continuous study of some nanoporous materials, such as natural zeolites and related materials, mesoporous molecular sieves, clays, pillared clays, the majority of silica, alumina, active carbon, titanium dioxide, magnesium oxides and the carbon nanotubes and metal-organic framework. Of all these nanoporous materials it is necessary to investigate whether a low cost modified adsorbent, such as dealuminated natural zeolites has the
physicochemical properties suitable for the adsorption of some gases and the adsorption of organic compounds from water.

Through this study we pretend to investigate whether natural clinoptilolite subjected to two simple dealumination treatments, one with ammonium hexafluorosilicate (HFSi) and the other with orthophosphoric acid, has the adequate properties for the adsorption of CO$_2$. Also, in this investigation we pretend to know if the modified natural clinoptilolite, modified molecular sieve ammonium Y zeolite and commercial Dealuminated Y zeolite (DAY) are suitable for the dynamics adsorption in the liquid phase of a phenolic compound such as paranitrophenol (PNP), orthonitrophenol (ONP) and metanitrophenol (MNP). Also, we want to know if the ammonium Y zeolite is suitable for the adsorption of methanol in dynamic condition.

Another justification for this research is to know whether these modified zeolites, especially the dealuminated natural clinoptilolite, have better or similar physicochemical properties of high-silica zeolite as ZSM-5 used in environmental applications.

### 1.5 Research Goal and Objective

#### 1.5.1 Goals

The goal of this research is to demonstrate how a low-cost and most abundant in the world natural zeolite, which has been subjected to a simple treatment of dealumination, has the suitable physical and chemical characteristics for the adsorption of a gas that causes environmental problems such as carbon dioxide.

Another goal is to demonstrate that dealuminated zeolites are suitable to the adsorption of chemical compound derived from phenol. As it was mentioned before, the phenolic compounds are found between the most widespread between dangerous contaminants of the environment.
1.5.2 Specifics Objectives

The first objective is to modify low cost natural clinoptilolite and commercial ammonium zeolite with a simple dealuminated treatment of ammonium hexafluorosilicates (HFSi). The natural clinoptilolite will also be dealuminated with acid treatment using orthophosphoric acid (H₃PO₃). The second objective is to apply some characterization techniques to know if the modified samples have the suitable properties to the adsorption of CO₂ molecule. The carbon dioxide adsorption as a characterization tool will help to determine the micropore volume and the energy characteristic of adsorption. The third objective is to obtain a quantitative measurement to know the interaction of the CO₂ molecules with the adsorption space. The fourth objective is to obtain the breakthrough curve of PNP, ONP, MNP and Methanol in dynamic adsorption with some of the dealuminated zeolites.

1.6 Hypothesis

1. The modified low cost natural clinoptilolite have adequate physicochemical properties which allow the strong interaction of carbon dioxide with the adsorbent porosity.
2. The hydrophobic zeolites used in this study are able to efficiently absorb the nitrophenols isomers and methanol from liquid phase.
Chapter Two

Literature Review

2.1 Carbon Dioxide Emissions

The contamination by anthropogenic sources has an impact on humans, animals and the environment. For example, some studies have established a relationship between air pollution and a variety of health and respiratory problems, cardiovascular diseases, decreased in lung function and cancer, among others (EPA 2010). The contamination by anthropogenic source is also responsible for climatic changes.

The principal greenhouse gases (GHG) affected by anthropogenic activities are carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O), ozone and fluorinated gases (hydrofluorocarbons [HFCs], perfluorocarbons [PFCs] and sulfur hexafluoride [SF$_6$]) (EPA 2010). Figure 2.01 shows the percentage of GHG generated by anthropogenic sources in the year 2004. It shows that the main GHG is CO$_2$, produced especially through the use of fossil fuels. It can be seen in Figure 2.02 that the increased consumption of fossil fuels was mainly in the energy generation sector.

The combustion of fossil fuels produces carbon dioxide (CO$_2$), a GHG with an increasing potential for by-product end-use in the industrial and energy production sectors (Figueroa et al. 2008). Table 2.01 presents the five major fuel consuming sectors contributing to CO$_2$ emissions from fossil fuel combustion.

The emissions of CO$_2$ from fossil fuel combustion increased at an average annual rate of 0.4 percent from 1990 to 2009. The fundamental factors influencing this trend include a generally growing domestic economy over the last 20 years an overall growth in emissions from electricity generation and transportation activities (EPA 2011).
The Energy Information Administration (EIA), within the U.S. Department of Energy (DOE), estimates that consumption of fossil fuels (coal, petroleum and natural gas) will increase by 27% over the next 20 years, thereby increasing U.S. CO$_2$ emissions from the current 6000 million tons per year to 8000 million tons per year by 2030 (Figueroa et al. 2008). Although U.S. CO$_2$ emissions are projected to increase, they will decrease from 23% of the world’s total in 2003 to 19% in 2030.

World energy-related carbon dioxide emissions will rise from 30.2 billion metric tons in 2008 to an estimated 35.2 billion metric tons in 2020 and 43.2 billion metric tons in 2035—an increase of 43% over the projection period (DOE/EIA 2011). With strong economic growth and continued heavy reliance on fossil fuels expected for most non-OECD (countries outside the Organization for Economic Cooperation and Development) economies under current policies, much of the projected increase in carbon dioxide emissions occurs among the developing non-OECD nations. In 2008, non-OECD emissions exceeded OECD emissions by 24% in 2035, they are projected to exceed OECD emissions by more than 100% . Coal continues to account for the largest share of carbon dioxide emissions throughout the projection (DOE/EIA 2011).

The excessive emission of CO$_2$ in the atmosphere, not only causes global warming, but also is the cause of health problems. For example, the increase in CO$_2$ emissions to the atmosphere leads to increased pollen and spore production in plants and a fungis, which has been argued that it the cause of increased cases of asthma in children (Maurin et al. 2005).
Table 2.01 CO₂ Emissions from Fossil Fuel Combustion by Fuel Consuming End-Use Sector (Tg or million metric tons CO₂ Equivalent). (US-GSG-inventory 2011)

<table>
<thead>
<tr>
<th>End-Use</th>
<th>1990</th>
<th>2000</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transportation</td>
<td>1489.0</td>
<td>1813.0</td>
<td>1901.3</td>
<td>1882.6</td>
<td>1899.0</td>
<td>1794.6</td>
<td>1724.1</td>
</tr>
<tr>
<td>Industrial</td>
<td>1533.2</td>
<td>1640.8</td>
<td>1560.0</td>
<td>1560.2</td>
<td>1572.0</td>
<td>1517.7</td>
<td>1333.7</td>
</tr>
<tr>
<td>Residential</td>
<td>9931.4</td>
<td>1133.1</td>
<td>1214.7</td>
<td>1152.4</td>
<td>1198.5</td>
<td>1182.2</td>
<td>1123.8</td>
</tr>
<tr>
<td>Commercial</td>
<td>7757.0</td>
<td>972.1</td>
<td>1027.2</td>
<td>1007.6</td>
<td>1041.1</td>
<td>1031.6</td>
<td>985.7</td>
</tr>
<tr>
<td>U.S. Territories</td>
<td>227.9</td>
<td>35.9</td>
<td>50.0</td>
<td>50.3</td>
<td>46.1</td>
<td>39.8</td>
<td>41.7</td>
</tr>
<tr>
<td>Total</td>
<td>44738.4</td>
<td>5594.8</td>
<td>5753.2</td>
<td>5653.1</td>
<td>5756.7</td>
<td>5565.9</td>
<td>5209.0</td>
</tr>
<tr>
<td>Electricity Generation</td>
<td>11820.8</td>
<td>2296.9</td>
<td>2402.1</td>
<td>2346.4</td>
<td>2412.8</td>
<td>2360.9</td>
<td>2154.0</td>
</tr>
</tbody>
</table>

*Fuel consumption by U.S. territories (i.e., American Samoa, Guam, Puerto Rico, U.S. Virgin Islands, Wake Island, and other U.S. Pacific Islands) is included in this report.*
Figure 2.01 Proportional parts representing different anthropogenic GHG regarding total global emissions in 2004 in terms of CO₂ equivalent. (Data obtained from: Cambio Climático 2007: Informe de síntesis. Contribución de los Grupos de trabajo I, II y III al Cuarto Informe de Evaluación del Grupo Intergubernamental de Expertos sobre el Cambio Climático)
1. In the forestry industry include deforestation

Figure 2.02 Proportional part representing different sectors in total emissions of anthropogenic GHG in 2004, in terms of CO₂ equivalent (Data obtained from: Cambio Climático 2007: Informe de síntesis. Contribución de los Grupos de trabajo I, II y III al Cuarto Informe de Evaluación del Grupo Intergubernamental de Expertos sobre el Cambio Climático)
There are several technologies for the separation and capture of CO\(_2\) from the gas stream, although they have not been designed for power-plant scale operations (DOE 2012). Figure 2.03 shows some technologies currently used for the separation and capture of CO\(_2\). The selection of the most suitable technology for the separation and capture of CO\(_2\) depends on the characteristics of the flue gas stream, which mainly depends on the power plant technology. Figure 2.03 shows that one of the technologies for the separation and capture of CO\(_2\) is the adsorption using porous adsorbents, such as activated carbon and zeolite. The use of appropriate adsorbents may potentially reduce the cost associated with CO\(_2\) separation in the overall carbon capture and storage strategy (Sayari et al. 2011). They also mentioned, that some attributes of suitable adsorbents for the CO\(_2\) removal are: high CO\(_2\) selectivity and adsorption capacity, mild condition for regeneration, stability during extensive adsorption and low cost, among others.

The adsorption of gases inside crystalline microporous materials is the basis of many industrial processes for gas purification and separation (Goj et al. 2002). As part of the efforts to reduce emission of greenhouse gases, it has recently been suggested to use microporous adsorbents to selectively remove CO\(_2\) from gas streams (Goj et al. 2002). Zeolites are one of the main microporous materials that are currently under investigation on the separation of CO\(_2\). More recently, a study based on an exhaustive zeolite adsorbent screening reported that the most promising adsorbent for carbon dioxide sequestration area characterized by Si/Al ratio and contain extraframework cations that give strong electrostatic interactions with carbon dioxide (Maurin et al. 2005). The zeolites have the advantage of combining low cost and relatively high stability. Another advantage is the ease ion exchange which facilitates tuning of gas-solid interaction energy, since exchangeable cations constitute the main gas adsorbing centers in zeolites (Rodríguez-Delgado and Otero-Arean 2011).
Figure 2.03  CO₂ Separation and Capture Technologies
2.2 Phenolic Compounds in Water

The surface and groundwater can be contaminated by anthropogenic or natural sources. Some inorganic and organic chemical contaminants coming from some industries can be liberated or deposited in surface or groundwater. For example, the byproducts from various industries can be disposed on land and can eventually enter surface and ground water supplies. It is estimated that about 142,000 tons of hazardous wastes are generated every day in the United States at about 750,000 different locations (Schmidt 2006). Eventually, these hazardous wastes may leach through the soil into the aquifer. Although it is estimated that only 0.5 to 2% of the U.S. groundwater supplies are contaminated, much of the contamination occurs in areas where this is the only source of drinking water (Schmidt 2006).

Phenol is an organic contaminant of surface water that causes great concern due to its toxicity and possible accumulation in the environment (Lin and Juang 2009). Phenol is a colorless, crystalline substance of characteristic odor, soluble in water and organic solvents (Michałowicz and Duda 2007). The most common anthropogenic sources of phenol in natural water include coal tar and wastewater from manufacturing industries, such as resins, plastics, fibers, adhesives, iron, steel, aluminum, leather, rubber and effluents from synthetic fuel manufacturing (ATSDR 2008; Spynskyy et al. 2009). Typically, wastewater from petroleum refineries contains phenol in concentrations that ranges from 5000 mg/L up to 15,000 mg/L (Kaleta 2006). Phenol is also produced by the natural degradation of organic wastes including benzene. Phenol is a major metabolite of benzene which is extensively found in the environment; therefore, phenol may be formed in the environment as a result of the natural degradation of benzene (ATSDR 2008).

Phenol is among the first fifty production volume chemicals generated in the United States. For the year 2005, in the United States, it was estimated that 99,546
pounds (about 45 metric tons) of phenol were released to surface water coming from 677 domestic manufacturing and processing facilities (TRI05 2007). These were about 0.1% of the estimated total environmental releases from facilities required to report to the TRI (ATSDR 2008).

Phenol and its derivatives (alkyl, chloro, and nitro) are widespread pollutants of the environment, especially hydrosphere (Sokhranyaeva 2010). Phenol and its derivatives are found between the most widespread dangerous contaminants to the environment. These compounds are in the list of 11 phenol derivatives that EPA classified as priority organic water pollutant. Six of them are shown in the Figure 2.04. They are priority pollutant because they are extremely dangerous to organisms, even at low concentrations (Ahmaruzzaman, 2008).

The Chlorophenols are the most widespread and the largest group of phenols. Chlorophenols are formed in the environment by chlorination of mono and polyaromatic compounds present in soil and water (Michałowicz and Duda 2007). These compounds are also present in drinking water due to substitution of organic matter and low molecular weight compounds (present in purified water) with chlorine atoms derived from inorganic chlorine oxidants (Michałowicz and Duda 2007). Furthermore, nitrophenols are present in the environment due to natural processes and anthropogenic activity. Nitrophenols, particularly 2-nitrophenol and 4-nitrophenol, are formed by the reaction of phenol with nitrite ions in water.
Figure 2.04  Six phenol structures of the 11 EPA priority pollutant list

- a. Phenol
- b. 4-Nitrophenol
- c. Pentachlorophenol
- d. 2-Nitrophenol
- e. 2-Chlorophenol
- f. 2,4-Dichlorophenol
Some processes that can be used to remove phenolic impurities in water are: extraction with the use of suitable solvents, biological degradation, chemical oxidation, photocatalytic decomposition, enzymatic decomposition, adsorption and ion exchange (Kaleta 2006). Activated carbons are the most widely used adsorbent due to their excellent adsorption abilities for organic pollutants. The high adsorption capacities of these microporous solids are usually related to their high surface area, pore volume and porosity (Ahmaruzzaman 2008). However, its initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent (Ahmaruzzaman 2008).

Recent research has been focused on the production of other adsorbents to replace costly activated carbon and synthetic resins (Lin and Juang 2009). Attention has been focused on various adsorbents, which have absorption capacities and are able to remove, at low cost, the unwanted phenols from contaminated water. Others investigations are focused on a new efficient and recyclable inorganic adsorbents, such as clay materials and zeolites. The zeolites are an important class of aluminosilicates used as catalysts and adsorbents. An important property of zeolites is the capacity to be easily regenerated while keeping their initial properties.

2.3 Natural Zeolites

Actually there are approximately forty natural zeolites; most of them have a high content of aluminum or low ratio of Si/Al (Payra and Dutta 2003). Natural zeolites form a corresponding group of mineral tectosilicates subclass for their specific crystal chemical characteristics. Zeolites are micropores crystalline solids of great interest in pollution abatement and industry as catalysts, adsorbents, ion exchangers and cationic conductors. The estimated global use of natural zeolites is between 3.98 Mt and 5.5 Mt (Wang and Pend 2010). Their relative cheap price is about $0.03-0.12/kg, (Minceva et al. 2008) depending on the quality of the mineral. The use of natural and modified forms
offers as advantages the low cost, the availability in big quantities in many parts of the world, the good mechanical and thermal properties and the combination of high sorption capacity with the ability to adjust the pH of the soil or aqueous system (Misaelides 2011). The natural and modified zeolites are excellent adsorbents due to its high ion-exchange capacity and relatively high specific surface areas. The zeolites, not only offer a great variety of different pore structures, but can also differ in a number of other properties, e.g. the content of aluminum in the framework and the secondary pore structure (Meininghaus and Prins 2000).

Zeolites are microporous solids with molecular structures of hydrated aluminosilicates of alkaline and alkaline-earth metals (Beitollah et al. 2009). The zeolite is a solid with a large surface area, which has been widely used as an adsorbent of gases and as ionic exchanger (Navalon et al. 2009). Zeolites are three dimensions microporous crystalline solids, with tetrahedral of $\text{AlO}_4$ and $\text{SiO}_4$ linked at the corners and sharing all oxygen atoms which cause overall negative structural charge, resulting an high cations exchange capacity (Cheng and Reinhard 2006; Schmidt 2006; Seifi et al 2011; Kaduk 1995). This solid has a rigid structure similar to a honeycomb, consisting of a network of interconnected tunnels and cage. Water moves freely in and out of these pores, but the zeolite framework remains rigid (Beitollah et al. 2009). The structural formula of a zeolite is based on the crystallographic unit cell, the smallest unit of structure, represented by:

$$M_n^z \left[ (\text{AlO}_2)_x (\text{SiO}_2)_y \right] \cdot w\text{H}_2\text{O}$$

Where $n$ is the valence of cation $M$, $w$ is the number of water molecules per unit cell, $x$ and $y$ are the total number of tetrahedral atoms per unit cell.

The channels of the natural zeolites are predominantly occupied by $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$ and $\text{H}_2\text{O}$, as well as traces of $\text{Mg}^{2+}$, $\text{Ti}^{4+}$, $\text{Pd}^{2+}$ and $\text{Ba}^{2+}$. Among these cations, $\text{Na}^+$, $\text{K}^+$,
Ca$^{2+}$ and Mg$^{2+}$ can be exchanged with NH$_4^+$ ions (Ates and Hardacres 2012). The type and density of the exchangeable cations influence the stability of the cavities and the thermal behavior of a zeolite (Ates and Hardacres 2012). The size, charge density and distribution in the porous structure of these exchangeable cations are important in determining the adsorption properties and gas separation. In natural zeolites the relative adsorption capacities in equilibrium pressure range is related to the number of cations available per unit mass of dehydrated zeolites in the limiting volume of the micropore.

The net negative charge of the zeolite is due to the presence of aluminum in the tetrahedral. This negative charge can be balanced by metal cations or other species, which does not belong to the crystal structure such as ammonium. If Al$^{3+}$ replaces a Si$^{4+}$, a negative charge is introduced in the framework that requires the presence of a charge balancing cations in the micropores (Navalon et al. 2009). The silicon (or silica) to aluminum (or alumina) of zeolite ratio determines its surface chemistry. The content and distribution of aluminum affects the structure, shape, crystal size, hydrophilicity and the zeolite acid properties. The presence and distribution of aluminum in the zeolite framework is related to the number and strength of the catalytically active site acid, which affects the effective diffusion path of reactants before they reach an active site (Danilina et al. 2010). The spatial distribution of aluminum or aluminum zoning directly affects the catalytic performance; it also impacts the dealumination (removal of Al atom) and desilication (removal of Si atom) processes that improve the molecular transport through the zeolite crystal.

In the past decade, natural zeolites have found a variety of applications in adsorption, catalysis, building industry agriculture, soil remediation and energy (Wang and Peng 2010). Natural zeolites have been used in environmental and industrial applications. Table 2.02 summarizes some applications of natural zeolites. These solids
have shown to be good adsorbent for $\text{H}_2\text{O}$, $\text{NH}_2$, $\text{NO}$, $\text{NO}_2$, $\text{SO}_2$, $\text{CO}_2$, linear and ábranched hydrocarbons, aromatic hydrocarbons, alcohol, ketones and other molecules (Roque –Malherbe 2000). Hernández-Huesca et al. (1999) studied the ability of natural zeolites to adsorb pure gases such as $\text{CO}_2$, $\text{CH}_4$ and $\text{N}_2$. They explained that the relative adsorption capacities between natural zeolites over the entire equilibrium range was related to two factors one is the number of cations available per unit mass of the hydrated zeolites (cationic density) and the other is the limiting volume of the micropore. For example, they established that the amount of $\text{CO}_2$ adsorbed at low pressure (low degree of coverage) was directly proportional to the number of cations. Furthermore, amount of $\text{CO}_2$ adsorbed at high pressure (high degrees of coverage) was related to the micropore volume.

In natural zeolites the primary porosity or microporosity results of the specific crystal building of the zeolite mineral grains. The secondary porosity (mesopores and macropores) is connected with grain sizes and other minerals in the zeolite rocks, as well as cleavage degrees of zeolites grains (Sprynskyy et al. 2010). These mesopores form the transport channels, active surfaces catalysis and adsorption sites for large molecules.

Natural zeolites having small pores and small pore volumes display strong adsorption at low concentration, resulting in high potential for purification applications (Ackley et al. 2003). For example, six natural zeolites, such as clinoptilolite (HEU), chabazite (CHA), mordenite (MOR), erionite (ERI), ferrierite (FER) and phillipsite (PHI), appear to have the greatest potential for industrial gas separations. In Table 2.03 the structural properties of these natural zeolites are shown. Clinoptilolite appears to be the most favored natural zeolite for gas separations, followed by chabazite and mordenite (Ackley et al. 2003).
<table>
<thead>
<tr>
<th>Applications</th>
<th>Use</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Gas cleaning</td>
<td>Roque-Malherbe (2000)</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Gas separation and Purification</td>
<td>Ackley et al. (2003) and Faghrihan et al. (2008)</td>
</tr>
<tr>
<td>Adsorption in the secondary porosity</td>
<td>Deodorization</td>
<td>Roque-Malherbe (2000)</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Adsorption of some organic pollutant</td>
<td>Sismanoglu and Pura (2001) and Ahmaruzzaman (2008)</td>
</tr>
<tr>
<td></td>
<td>from liquid phase such phenolic compounds</td>
<td></td>
</tr>
<tr>
<td></td>
<td>from municipal wastewater</td>
<td></td>
</tr>
<tr>
<td>Ionic exchange</td>
<td>Removal of toxic heavy metals</td>
<td>Erdem et al. (2004) and Rožic et al. (2005)</td>
</tr>
<tr>
<td>Ionic exchange</td>
<td>Removal of some radionuclide from</td>
<td>Roque-Malherbe (2000)</td>
</tr>
<tr>
<td></td>
<td>radioactive wastewater</td>
<td></td>
</tr>
<tr>
<td></td>
<td>environment</td>
<td></td>
</tr>
<tr>
<td>Ionic exchange</td>
<td>Increase of biogas production in</td>
<td>Roque-Malherbe (2000)</td>
</tr>
<tr>
<td></td>
<td>anaerobic wastewater treatment</td>
<td></td>
</tr>
<tr>
<td>Catalysis</td>
<td>Isomerization of hydrocarbons</td>
<td>Roque-Malherbe (2000)</td>
</tr>
</tbody>
</table>
Clinoptilolite is one of the most abundant among more than 40 natural zeolite species, member of the heulandite group (Kowalczyk et al. 2006; Ahmaruzzaman 2008, Wang and Peng 2110; Cakicioglu-Ozkan and Ulku 2005; García-Besabe et al. 2012). The abundance, low extraction cost and high chemical stability of clinoptilolite make this zeolite a very attractive material for adsorption and environmental applications (García-Basabe et al. 2010).

Each unit cell has an average of 22 water molecules and cations such as Na\(^{+}\), K\(^{+}\), Ca\(^{2+}\) and Mg\(^{2+}\), which are the most common charge-balancing cations (Ünalch 2009; Hernández et al. 2005). Figure 2.05 shows the Heulandites framework type that consists of three channels, the 10-member ring channel A (3.1 x 7.5 Å) which is parallel to 8-member ring channel B (3.6 x 4.6 Å). The 8-member ring channel C (2.8 x 4.7 Å) intersects channels A and B.

Natural clinoptilolite has received extensive attention due to its selectivity for ammonium ions and certain heavy metal cations such as lead, cadmium and nickel (Rožić et al. 2005). This zeolite has also been used in some applications such as natural gas purification, air separation and pre-purification, traces removal of CO\(_2\) and light hydrocarbons, flue gas and ammonia removal and uptake of some gases such as CO\(_2\), CH\(_4\), C\(_2\)H\(_6\), N\(_2\) and C\(_3\)H\(_8\). Faghihian et al. (2008) studied the natural and cation-exchanged clinoptilolite in the kinetics adsorption of pure CO\(_2\), CH\(_4\), O\(_2\) and N\(_2\). Clinoptilolite exchanged with ammonium had good equilibrium selectivity for CH\(_4\). This means that this zeolite can be used to obtain methane as a product from a mixture of methane and nitrogen. Those small cations with a very high charge density, such as H\(^{+}\), caused the zeolite to have more open pore channels which reduces the blockage factor. This allowed the easy diffusion and properly adsorption of larger and more polarizable molecules, such methane and ethane.
Table 2.03 Structural properties of some natural zeolites

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Chemical formula</th>
<th>Structure type from International Zeolite Association (IZA)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clinoptilolite</td>
<td>(Na,K,Ca)$<em>4$Al$<em>6$Si$</em>{30}$O$</em>{72}$·24H$_2$O</td>
<td>HEU</td>
<td>Kowalczyk et al 2006</td>
</tr>
<tr>
<td>Mordenite</td>
<td>Na$<em>8$Al$</em>{18}$Si$<em>{40}$O$</em>{96}$·24H$_2$O</td>
<td>MOR</td>
<td>Mignoni et al. 2008</td>
</tr>
<tr>
<td>Chabazite</td>
<td>Ca$<em>6$(Al$</em>{12}$Si$<em>{24}$O$</em>{72}$)·40H$_2$O</td>
<td>CHA</td>
<td>Roque-Malherbe 2000</td>
</tr>
<tr>
<td>Phillipsite</td>
<td>K$_2$(Ca, Na$_2$)$<em>2$Al$<em>6$Si$</em>{16}$O$</em>{32}$·12H$_2$O</td>
<td>PHI</td>
<td>Wang S and Peng Y (2010)</td>
</tr>
<tr>
<td>Scolecite</td>
<td>(CaAl$_2$Si$<em>3$O$</em>{10}$·3H$_2$O)</td>
<td>NAT</td>
<td>Bosso and Enzweiler 2002</td>
</tr>
<tr>
<td>Stilbite</td>
<td>Na$<em>4$Ca$<em>6$(Al$</em>{20}$Si$</em>{52}$O$_{144}$)·56H$_2$O</td>
<td>STI</td>
<td>Roque-Malherbe 2000</td>
</tr>
<tr>
<td>Analcime</td>
<td>Na$<em>{16}$Al$</em>{16}$Si$<em>{32}$O$</em>{96}$·16H$_2$O</td>
<td>ANA</td>
<td>Wang and Peng 2010</td>
</tr>
<tr>
<td>Laumontite</td>
<td>Ca$<em>4$(Al$<em>6$Si$</em>{16}$O$</em>{48}$)·16H$_2$O</td>
<td>LAU</td>
<td>Roque-Malherbe 2000</td>
</tr>
<tr>
<td>Erionite</td>
<td>K$<em>2$(Na, Ca$</em>{0.5}$)$<em>6$(Al$</em>{10}$Si$<em>{26}$O$</em>{72}$)·30H$_2$O</td>
<td>ERI</td>
<td>Ballirano and Cametti 2012</td>
</tr>
<tr>
<td>Ferrierite</td>
<td>(Na$_2$, K$_2$, Ca, Mg)$<em>3$Al$<em>6$Si$</em>{30}$O$</em>{72}$·20H$_2$O</td>
<td>FER</td>
<td>Wang and Peng 2010</td>
</tr>
</tbody>
</table>
Ünalch et al. (2009) performed a physicochemical characterization of a natural and modified clinoptilolite with cations such as Na\(^+\), K\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\). They concluded that the increase in the specific surface areas of the modified clinoptilolite relative to that of natural forms was possibly related to the entrances available to ions in the structure. They also concluded that the magnitude of the specific surface area could be negatively correlated with the ionic radii of the Na\(^+\), K\(^+\), Ca\(^{2+}\) y Mg\(^{2+}\) cations. The pore sizes in the modified forms were smaller than those in natural forms. The authors concluded that the
decrease in pore size may have been due to the positions of the ions in the structure, which result in the channel blockage.

Modified form of HEU-type zeolites, such as natural clinoptilolite, are obtained by ion exchange, either with NH$_4^+$ or by leaching with inorganic acids (H-form zeolites). It was believed that with this modification the extra-framework cations are replaced with H$_3$O$^+$ and the tetrahedral framework is altered by loss of Al$^{3+}$ (Radosavljević et al. 2004). Kurama et al. (2002) investigated the conversion on a natural clinoptilolite to hydrogen form (H-form) by ammonium exchange followed by calcination and direct treatment with hydrochloric (HCl) acid. The researcher found that the ion exchange with H$^+$ had a great influence on the effective pore volume and surface area of clinoptilolite, both parameters increased after the treatment.

2.4 Faujasite

Faujasite structure crystallizes in the cubic space group Fd3m with a lattice constant ranging from about 24.2 to 25.1 Å. This depends on the concentration of aluminum in the framework, the cations and hydration status. (Kaduk and Faber 1995; Kaduc 2005). The chemical composition and some crystallographic composition are shown in Table 2.04.

This zeolite has 192 tetrahedral sites per unit cell and is composed of 24 tetrahedral cuboctahedral units (sodalite cage) linked through a prism or double 6-ring (Kaduc 2005). Figure 2.06 shows the faujasite framework. The three-dimensional structure of zeolite Y is formed by connecting sodalite units via hexagonal prisms to give a framework characterized by big, empty cavities (supercages) with a diameter of about 13 Å. Most of the extraframework cations are located at a few well-defined extraframework sites. Site I is in the center of the hexagonal prism, closely surrounded by the six oxygen’s of the two bases of the prism. Site I’ is located on the external base of the hexagonal prisms, just inside the sodalite cage. These cations are surrounded by
three oxygen atoms from the base of the prisms. Sites II’ and III’ are located in the middle of the six membered ring forming the boundary between the supercage and the sodalite cage, just inside the sodalite cage and the supercage, respectively.

The cages and pores on the structure make faujasite act as a catalyst because they allow access of rather large molecules. Faujasite zeolites are commonly separated into two classes, zeolite X having a Si/Al ratio between 1 and 1.5 and zeolite Y having a Si/Al ratio above 1.5. The zeolite Y, generally, has 54 to 56 atoms of aluminum and 136 to 138 atoms of silicon in the framework (Frizt 1989). More recently, low silica X (LSX) zeolite, with a Si/Al ratio of 1.0, has been encountered in the literature (Frising and Leflaive 2008). Both X and Y zeolites belong to the FAU family, and consist of β cages and hexagonal prism, connected in such way that large internal supercages (α-cage) are created (Daems et al. 2006). The α-cage permits the entrance of hydrocarbons through 12 membered ring (12 MR) window with a diameter of 7.4 Å.
Table 2.04  Information of Faujasite from Collection of Simulated XRD Power Patterns for Zeolite

<table>
<thead>
<tr>
<th>Zeolite Framework type</th>
<th>FAU</th>
<th>Recognized by the IUPAC Commission on Zeolite Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition</td>
<td>$\text{Na}<em>{28.8}\text{Ca}</em>{14.4}(\text{H}<em>2\text{O})</em>{263}/[\text{Si}<em>{134.4}\text{Al}</em>{57.8}\text{O}_{384}]$</td>
<td>Kaiserstuhl, Germany</td>
</tr>
<tr>
<td>Refined composition</td>
<td>$\text{Na}<em>{16}\text{Ca}</em>{16}(\text{H}<em>2\text{O})</em>{42.7}/[\text{Si}<em>{134.4}\text{Al}</em>{57.8}\text{O}_{384}]$</td>
<td>Derived from the structure refinement</td>
</tr>
<tr>
<td>Cristal data</td>
<td>$Fd\bar{3}m$ (No. 227) origin at centre $(3m)$ $a = 24.74$ Å $b = 24.74$ Å $c = 24.74$ Å $\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$</td>
<td>Lattice parameter and space group information from the International Tables for Crystallography, 4th revised edition 1995</td>
</tr>
</tbody>
</table>


The chemical composition of zeolite Y is:

\[ \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4.8\text{SiO}_2 \cdot 8.9\text{H}_2\text{O} \]

The physicochemical properties in the faujasite have been studied based in the difference of Si/Al ratio. For example, Sato et al. (2003) studied the structural change in NaY zeolite during ion exchange treatments. Three starting NaY zeolites (different Si/Al ratio) were subjected to three cycles of ion exchange treatment using \((\text{NH}_4)_2\text{SO}_4\) and subsequent calcinations. During the study, the structural changes of starting material with low Si/Al ratio differed from those materials with medium and high Si/Al ratio. They found that the stability of the zeolitic framework during ion exchange treatments decreased with the increasing number of Al in the framework. The framework of the starting zeolite with a low Si/Al ratio was not stable under the ion exchange treatment. In those samples with low Si/Al ratio, during the second and third cycles, the zeolitic
framework structure was deteriorated as evidence of loss crystallinity and decrease in micropore surface area.

Other effects on faujasite (X and Y zeolites) have been related to the change in the Si/Al ratio. For example, Canet et al. (2007) mentioned in a study about X and Y zeolites that the decrease in Si/Al ratio causes an increase in the number of compensating cations or adsorption sites. Then if the number of adsorption sites increases, the negative charge of oxygen atoms in the zeolitic framework increases; therefore, interactions between the porous media and the adsorbate are more important. They also mentioned that the greater the number of adsorption sites, the more attracted will be the adsorbate by the zeolite, so the adsorption heat at zero coverage is high.

The adsorption selectivity of adsorbate molecules has been related to the Si/Al ratio of X and Y zeolites. Deams et al. (2006) investigated the relation of Si/Al ratio on the adsorption of alkanes, alkenes and aromatics compounds in X and Y zeolites. They explained that the higher adsorption selectivity for benzene on NaY (Si:Al 2.79) compared to NaX (Si:Al 1.23) was related to the cation distribution in both zeolites. The researcher explained that the NaX zeolite contains about four additional cations per supercage compared to NaY. These extra cations are located in some specific site through the structure (III or III’) which are unoccupied in Y-type zeolite. Guillemot et al. (2007) established a relationship between the adsorption capacity and the number of adsorption site in both NaX and NaY zeolites. The researcher mentioned that the NaX zeolite exhibits a higher adsorption capacity because it has a higher number of adsorption sites (88 cations per supercage) than NaY zeolite (56 cations per supercage). However, lower micropore volume in NaX zeolite was a limiting factor for the dynamic adsorption of tetrachloroethylene (PCE) in dry conditions. They established in the study that the micropore volume decreases with the increasing of the number of no-framework cations.
2.5 Zeolites Dealumination

The modifications of zeolites by dealumination (removal of Al atoms) or desilication (removal of Si atoms) change the structural composition and the acid characteristic of the structure (Zhao 2007). Different types of dealumination procedure has been applied in the past, such as treatment with steam at elevated temperature, with silicon tetrachloride (\(\text{SiCl}_4\)) vapor at moderate temperature, with ammonium hexafluorosilicate (HFSi) and with chelating agent such as ethylenediaminetetraacetic acid (EDTA) (Triantafillidis et al. 2000). The dealumination produces a high-silica zeolite; at the same time mesoporous are created as a result of the removal of aluminum. They also have good hydrothermal stability and excellent catalytic activity and fair hydrocarbon isomerization rates (Hernández et al. 2005). This imparts a hydrophobic property to zeolite for the adsorption of non-polar molecules. In the literature it is well documented that a decrease in the framework aluminum content decreases the hydrophilicity of the internal voids, increasing their adsorption capacity towards hydrophobic compounds (Navalon et al. 2009). The partially dealuminated zeolites has improved pore volume better than the natural precursor.

In dealumination two processes affecting the chemical composition and phase as well as the structural characteristic of the final product occur. These processes are the breaking of the structure and the formation of extraframework aluminum species (EFAI) in monomeric or polymeric structures of aluminates or aluminosilicates (Triantafillidis et al. 2000). Depending on the method of dealumination, hydrothermal/thermal treatment, acid leaching or chemical treatments, the extraframework aluminum (EFAI) species are often formed inside the zeolite structure (Kao and Chang 2006).

The hydrothermal treatment involves contact of the zeolite with steam at high temperature. In hydrothermal treatment at elevated temperature the zeolitic water can become steam while the dealumination occurs (Fritz 1989). However, at elevated
temperature the zeolite framework undergoes a structural damage under hydrothermal conditions. The steam may facilitate the transport and filling of vacancies left by the aluminum atoms which increases the stability of the zeolite. With this technique highly crystalline zeolites with aluminum content in the framework of 21 to 38 per unit cell can be synthesized. The dealumination ratio in the zeolite depends on the steaming time, flow rate and temperature for example, the increase of steaming time will cause that aluminum be removed from the framework.

During hydrothermal treatment hydrolysis or breakdown of Al-O-Si bonds occurs, where aluminum is removed from the framework leaving a vacancy (hydroxyl nest) or a partial amorphization of the framework. However, this treatment does not remove all the aluminum available in the framework; it remains as extraframework aluminum (EFAI) in the zeolitic material (Fritz 1989). The extraframework species may be in the form of cationic species: \( \text{Al}^{3+}, \text{AlO}^+, \text{Al(OH)}^{2+}, \text{Al(OH)}_2^+, \) and neutral or polymeric species: \( \text{AlOOH}, \text{Al(OH)}_3 \) and \( \text{Al}_2\text{O}_3 \) (Kao and Chang 2006). These cationic or neutral form and can be located in the channels or cavities of the zeolite.

The dehydration of zeolites exchanged with metal cations results in the formation of Brønsted acid sites in the pore and cavities of the zeolite. Water molecules dissociate in the local electrostatic fields of multivalent metal cations leading to the formation of OH groups at the metal cations, and the hydroxyl protons bound to oxygen bridges between framework silicon and aluminum atoms in the form of \( [\text{Al(OH)}(\text{H}_2\text{O})_{n-1}]^{2+} \) as seen in Figure 2.07 (Huang et al. 2008).

The Lewis acid sites, acting as electron pair acceptors, are extraframework species. These acid sites are formed, for example, by cations exchange or by steaming to create lattices defects and extraframework aluminum clusters (Huang et al. 2008). Only aluminum extraframework cationic species \( \text{Al}^{3+}, \text{Al(OH)}^{2+} \) and \( \text{Al(OH)}_2^+ \) act as strong Lewis acid sites. In many cases, the species of EFAI interact with the framework
aluminum (Brønsted acidity) of the zeolitic structure causing an increase in the catalytic activity of the zeolite.

![Figure 2.07 Formation of Brønsted acid sites](image)

The increase of the Si/Al ratio of the framework by steaming requires two steps: the first is the elimination of Al from the framework, and the second is the healing of these lattice faults by silicate units. According to Salman et al. (2006), this healing occurs via the formation and migration of silicic acid leaving mesopores behind. This process is promoted by protons formed in situ or by careful pre-thermal decomposition of NH$_4^+$ ions introduced before by ion exchange. These authors explained that without the exchange of Na$^+$ by NH$_4^+$ ions the healing process does not occur under the same condition.
The zeolite Y dealuminated (DAY) has high thermal and hydrothermal stability and high catalytic activity (Fritz 1989). For example, many applications of zeolite faujasite are mainly attributed to its acid-catalyzed activity. This zeolite is important in the catalytic cracking, hydrocracking and isomerization reactions in the petrochemical industry (Li et al. 2007).

The dealumination by chemical treatment includes the technique with steam of SiCl$_4$ at moderate temperature, the treatment with ammonium hexafluorosilicate (AHFS) or the treatment with a chelating agent ethylenediaminetetraacetic acid (EDTA) at a relatively low temperature (Triantafillidis et al. 2000). According to Cherif et al. (2003), the dealumination by silicate derivate, such as Ammonium Hexafluorosilicate, does not create secondary porosity (mesopore and macropore), but it leads to the formation of extraframework silica. The dealumination with SiCl$_4$ is more direct than the hydrothermal treatment since the SiCl$_4$ replaces aluminum in the framework, leading also to the formation of aluminum chloride (AlCl$_2$). The zeolites synthesized with the use of SiCl$_4$ have less extraframework aluminum (EFAl) than the zeolites prepared with hydrothermal treatment. However, there is always a minimum amount of extraframework aluminum that remains in the zeolite. Meininghaus and Prins (2000), in a study of several hydrophobic zeolites, established that faujasite treated with SiCl$_4$ differ substantially from those faujasite treated hydrothermally. The faujasite treated with SiCl$_4$ does not have mesoporous; however, this zeolite has a lower content of non-framework aluminum and more silanol groups. However, the high concentration in silanol groups in the dealuminated faujasite was drastically reduced by additional steaming treatment. With this additional treatment, the researcher obtained dealuminated faujasite with a low content of non aluminum and small numbers of silanol groups, properties that helped in the sorption of some volatile compound.
In contrast to the other chemical treatment, the use of ammonium hexafluorosilicate or HFSi completely eliminated the non-framework aluminum in the zeolite. It was reported a modification in the technique consisted in the thermal treatment of ground mixture zeolite NH₄Y and use of AHFS. The chemical reaction proposed for this technique was the following (Kao and Chang 2006):

\[
\{\text{AlO}_{4}\}^\times (\text{NH}_4)^\times + (\text{NH}_4)_2\text{SiF}_6 \rightarrow \{\text{SiO}_{4}\} + \text{NH}_4\text{AlF}_4 + \text{NH}_4\text{HF}_2 + \text{NH}_3
\]

A high degree of dealumination by different treatments may result in loss of microporosity and the formation of mesopores in the crystalline material. A high degree of dealumination can also cause the breakdown of the structure. For example, the breakdown of the structure of the parent Y zeolite was mainly dependent on the degree or percentage of dealumination (Triantafillidis et al. 2000). Some research has shown that, under controlled conditions, dealumination of zeolite X with HFSi results in pore size enlargement which range in average pore size from 3 to 5 nm (Zhao 2007). This pore size enlargement creates mesoporous aluminosilicates with slightly lower surface than their parent zeolites. Also, these materials have unique pore structure, with pore size of nanoscale range. It has been shown that the pore size enlargement occurs only in dealumination of zeolites with high aluminum content, such as zeolite A and zeolite X.

### 2.6 Adsorption in modified zeolites

#### 2.6.1 Gas Adsorption

The adsorption is defined as an increase in concentration of gas molecules over a solid surface, or an increase in the concentration of a dissolved substance at the interface of a solid and a liquid phase (Roque-Malherbe 2007). The adsorption phenomena is classified as physical or chemical adsorption. In physical adsorption the attractive forces between adsorbate molecules and atoms or ions of the solid surface result in a van der Waals force. The adsorbate molecules may also be under the
influence of dispersion force and orientation force of permanent and induced dipole (Chikazawa and Takei 2006). If the solid surface consists of ions of polar groups, they will produce an electric field that induces dipoles in the adsorbed molecules. On the other side, the chemical adsorption occurs in vapor-solid and liquid-solid systems where adsorbate molecules are adsorbed by chemicals bonds.

The adsorption process in zeolites is considered as a physisorption process, this is because the hydroxyl group's interactions of zeolite can be considered as of van der Waals type interactions (Roque-Malherbe 2000). In zeolite, the interactions of adsorbed molecules (sorbate-sorbate interactions) are also of van der Waals type interactions. Some factors affecting the adsorption process are temperature, adsorbent quantity and particle size, including other chemical properties of the adsorbent and adsorbate (Prabha Dubey et al. 2009).

During the adsorption process a molecule which contacts the surface of a solid adsorbent, like zeolite, is subjected to diverse energy fields with different potentials. The potentials are: dispersion energy, repulsion energy, polarization energy, field dipole energy, field gradient quadrupole energy, adsorbate-adsorbate interaction energy and acid-base interaction with the active site, if the zeolite surface contains hydroxyl bridge sites (Roque-Malherbe et al. 2003). Dispersion and repulsion interactions are present in all adsorption gas-solid systems; therefore, they are nonspecific interactions (Roque-Malherbe 2010). The electrostatic interactions between the adsorbed molecules and the adsorbent framework, such as polarization energy, field dipole energy and field gradient quadrupole energy depend on the structure and composition of the adsorbed molecule and the adsorbent itself (Roque-Malherbe 2010).

The adsorption properties of zeolites strongly depend on pore structure and chemical properties (Tien Tsai et al. 2009; Wang and Peng 2010). Some parameters
that particularly influence the adsorption in zeolites are Si/Al ratio and the type, number
and locations of cations in its structure (Ackley et al. 2003). The cations type, size,
charge density, location and the extent to which it is exposed to the adsorbate molecules
have a strong effect in both selectivity and adsorption capacity (Ackley et al. 2003). The
adsorbed molecules can interact with the surface of the zeolite through lattice oxygen
atoms, through accessible extra framework cations, and through with Al and Si atoms
(Sethia et al. 2010). However, Al and Si atoms are not directly exposed to the adsorbate
molecules. The principal interactions of these molecules with the zeolite surface are with
lattice oxygen atoms and extra framework cations. The electrostatic interactions
between the adsorbate molecules and the extra framework cations of the zeolite depend
on the quadrupole moments, the polarizability, and the dipole moment of the adsorbate
molecules (Sethia et al. 2010).

In the zeolite framework, adsorption in cavities and channels (first porosity) is
considered as a volume filling of microporous zeolite adsorption space and not as a
layer by layer surface coverage. In zeolites, the adsorption process occurs as follows:
first, the micropore filling, where the adsorption occurs in the first porosity; second, the
surface coverage at high pressure, consisting in monolayer and multilayer adsorption
and capillary condensation that occur in the second porosity formed by mesopores and
macropores (Roque-Malherbe 2000). Ghezini et al. (2008) explained that a CO$_2$
molecule with a kinetic diameter of $\sigma = 0.33$ nm can easily penetrate through the zeolites
cavities and channels, which have approximately $0.51 \times 0.55 \times 0.66$ nm (Site I), $0.54 \times$
$0.56 \times 0.45$ nm (Site II) and a diameter in order $0.89$ to $0.90$ nm (Site III). This means
that the intensity of the adsorption field inside these pores and cavities is high over the
whole primary porosity. The authors also agree in the fact that if the intensity of the
adsorption field is high in the adsorption it space, implies that the adsorption in zeolite is not a surface process, but rather a volume filling.

### 2.6.1.1 Gas adsorption application

Gas adsorption can be used for the characterization of zeolites and related materials. Some parameters that can be obtained in the characterization of porous adsorbent are: $S$, the specific surface area ($m^2$/$g$); $W^{MP}$, the micropore volume ($cm^3$/$g$); $W$, total volume, which is the sum of micropore and mesopores volume; PSD, the pore size distribution (cc-STP/g-$Å$).

The physical adsorption of nitrogen ($N_2$), argon (Ar) or carbon dioxide ($CO_2$) is a technique used to study the pore characteristics of some porous solids, especially after post synthesis treatment (Groen et al. 2003). The amount of adsorbed gas is a direct measure of the properties and porous structure of solids. Nitrogen adsorption at 77K is widely used in the characterization of solids because this gas is cheaper than other noble gases. In terms of the adsorption properties, nitrogen is something specific because of its quadrupole and favors strong adsorption sites, such as functional groups that carry partial charge (Do et al. 2008). Carbon dioxide is rarely used as adsorbate to study the porous texture of the solids. However, this gas possesses a high kinetic energy at ambient temperature which ensure that its molecules can easily penetrates through the narrowest pores of zeolites (Ghezini et al. 2008).

One method widely used to characterize the adsorbent and the specific adsorbate-adsorbent interactions is the calorimetric method. This method is used to study the heat of adsorption in the gas-adsorbent system. The heat of adsorption profile obtained may indicate the degree of energetic heterogeneity of gas-solid interactions. An increase in the heat of adsorption with gas loading is characteristic of adsorbents with non-heterogeneous gas-solid constant energy. This increase is due to the interactions
between adsorbed molecules. By contrast, a decrease in the heat of adsorption with the
gas loading is characteristic of highly heterogeneous adsorbents with a wide distribution
of gas-solid interaction energy. When the heat of adsorption is kept constant with the
gas loading, a balance between the strength of adsorbate-adsorbate interactions and the
degree of heterogeneity of gas-solid interactions exists (Dunne et al. 1996).

There are a lot of studies related to the characterization of natural and modified
zeolites. López-Fonseca et al. (2003) characterized some zeolites dealuminated with
ammonium hexafluorosilicate (HFSi). Adsorption isotherms with $N_2$ at 196º C (469 K) of
typical for crystalline microporous materials were obtained in those zeolites treated at
low degree of dealumination (less and equal to 50%). This means that the microporous
character of the modified zeolites was retained and these samples did not possess any
appreciable mesopores volume. In contrast, for those zeolites with a high degree of
dealumination (64%) the values of surface area and pore volume were severely affected.
The authors explained that this was probably due to the collapse of the crystal structure
and to the blockage of the zeolite pore system to a very large extent.

García-Basabe et al. (2010) conducted a study using a natural clinoptilolite
dealuminated with a low concentration of hydrochloric acid. The $N_2$ adsorption
measurement on the different zeolitic materials revealed a significant increase in surface
area, micropore volume and external surface area in dealuminated samples (acid form).
The authors explained that the abrupt increase of this parameter in dealuminated
samples compared with parent zeolite can be due to the almost complete replacement of
the metal cations by $H^+$, together with the elimination of some impurities, also resulting in
more available space within the zeolite. The acid treatment of high-silica natural
clinoptilolite can render adsorbents of enhanced accessible pore volumes via the
mechanism of decationation and dealumination, and also by dissolution of any
amorphous materials blocking the A-C channels of the clinoptilolite structure. The adsorption uptake capacity in the clinoptilolite increased with the degree of dealumination due to the displacement of blocking material from the void entrance (Hernández et al. 2005). The elimination of polyvalent or large cations decreases cations blocking effect and allows the participation of a greater number of adsorption (cationic) centers along zeolitic channels that are forming the microporous structure in dealuminated samples (Hernández et al. 2007).

Ates and Hardacre (2012) obtained a considerable increase in surface area, micropore volume and total volume for a natural zeolite after an ion exchange with NH$_4^+$. The samples subjected to acid treatment had similar results to those exchanged with NH$_4^+$. The increase in surface area, micropore volume and total volume was due to the dealumination and elution phase. Sprynskyy et al. (2010) also obtained a significant increased micropore volume in a natural clinoptilolite treated with 2M hydrochloric acid solutions. The micropore volume of raw zeolite evaluated by t-plot method was 0.0031 cm$^3$/g. However, the contribution of the micropore volume for the treated clinoptilolite increased more than eleven times, and was evaluated as 0.0342 cm$^3$/g by also t-plot method.

In addition to the characterization of dealuminated zeolites, adsorption methods help to know the interaction of adsorbed molecules with the surface of natural or modified zeolites. For example, with the adsorption the interaction between hydrophilic or hydrophobic zeolites surface with polar molecules can be studied. After dealumination treatment, zeolites with high content of silicon become hydrophobic. In hydrophobic pore space, the water-surface interactions are weak, and water only forms weak hydrogen bonds with the hydrophobic siloxane surface. Figure 2.08 shows the hydrophobic zeolite surface. On the other hand, in zeolites with low silicon content, the silanol group or
cations (hydrophilic center) are associated with the tetrahedrally coordinated aluminum and dominate the water adsorption in zeolite micropores. Cations located at the surface of the zeolite pores form coordinated covalent bond with water, this is known as coordinated water. The hydrogen that is bonded to either silanol group or coordinated water molecules is known as “zeolitic water” (Chen and Reinhard 2006).

Zeolites with highly hydrophobic surface has a good thermal and chemical stability, unique pore structures and easy regeneration, which make them a good adsorbent, one that can be widely used in some applications, such as catalysis and gas separation. Some studies have been conducted to know the enhancement effect of gas adsorption in hydrophobic zeolites. Sumin et al. (2010) studied the effect of hydrophobic modification of ZSM-5 on the CO$_2$ adsorption in water, cyclohexane and soy bean oil. The zeolite was modified by hydrothermal synthesis combined with acid treatment. They found that the polar solvent molecules of water and soy bean oil did not allow the CO$_2$ gas adsorption on unmodified zeolite. The authors explained that the polar groups on the surface of unmodified zeolite particles can strongly interact with polar solvent molecules of water and soy bean oil and, therefore, the particles hardly adsorb the CO$_2$ molecules any more. They also explained that modified zeolites with a strong hydrophobicity have large non-polar zones on their surface.

The weak interaction between non-polar groups of modified zeolite and polar solvent molecules results in a strong adsorbing effect for CO$_2$ in water. In relation to non-polar solvent such as cyclohexane, they explained that cyclohexane molecules may have a strong interaction with the non-polar groups on the surface of modified zeolite particles. Most surface active sites of modified zeolite were covered by cyclohexane molecules, leading to the loss of adsorption capacity for CO$_2$. 
Figure 2.08 Structure of water molecule in hydrophobic zeolite micropore
Some methods have been studied in order to determine the adsorption capacity in hydrophobic zeolites. Sumin et al. (2009) investigated the CO$_2$ adsorption in zeolites subjected to hydrophobic treatment, such as framework element and the surface modification coating methods. In the framework element method, the hydrophobic zeolites were obtained by altering the silica-aluminum ratio. On the other hand, the surface modification coating method was based on the incorporation of organic molecules in the zeolites structure. This method was used only with the intention of modifying the zeolite surface. The researchers showed that with the framework element modification method, the complete lattice structure, adsorption capability and the good hydrophobic property in the zeolite were maintained. However, the incorporation of organic molecules produces a partial blockage of the channel, which greatly decreases the surface area preventing at the same time the zeolite adsorption capability of CO$_2$.

Halasz et al. (2002) compared the hydrophobic Y and the ZSM-5 zeolites in the adsorption of methanol. The differences in the isotherms of aluminum free Y zeolite and the ZSM-5 zeolites were explained based on differences between the size and the negative potential of their pores. The authors explained that overall potential in the micropores is determined by the sum of van der Waals and Coulomb potentials generated by small of Si$^{4+}$ and large O$^{2-}$ ions that pave walls of the microchannels of these zeolites. They explained that the framework electrostatic potential was negative along the centre of the large micropores in the hydrophobic Y zeolite. This was the reason to explain the repulsion of strongly polar water molecules and the adsorption of less polar methanol molecule in the channels of Y zeolite. On the other hand, the electrostatic potential changed dramatically in the channels of ZSM-5. They explained that the change in the potential was due to the proximity of the Si$^{4+}$ and O$^{2-}$ ions to the centre of the narrow zeolite channels. The change in electrostatic potential caused a
difference of array of molecules on the channels of ZSM-5. They also explained that those molecules entering the centre of ZSM-5 channel are not closer to the walls than in the large pore of Y zeolite, and that the unbalanced potential field helps to retard the adsorbate molecules in the zeolite pores.

In addition to studying the behavior of hydrophobic surface in modified zeolites, the gas adsorption helps us to determine a quantitative measure of the interaction between the adsorbed gas molecules and the zeolite porosity. This quantitative measure that determines the interaction between adsorbed gas molecules and the zeolite porosity is known as isosteric heat of adsorption ($q_{\text{ISO}}$). The isosteric heat of adsorption decreases with increasing quantities of adsorbed substances. This occurs if the adsorbent surface is energetically heterogeneous due to the presence of several types of adsorption site. However, the isosteric heat of adsorption may increase with increasing quantities of adsorbate if there are strong lateral interactions between adsorbed molecules (Domínguez et al. 2010). The energetic heterogeneity in the adsorbent depends on the distribution of micropores and mesopores with different shapes and sizes. This parameter depends also on the distribution of the adsorption sites inside the pores with different polarities.

Some researchers have studied the isosteric heat of adsorptions in dealuminated zeolites or high silica zeolites. For example, Hernández et al. (2005) investigated the adsorption of benzene, toluene and $p$-xylene (BTX) by several clinoptilolite dealuminated with various acid treatments. After the treatment the large and blocking cations at zeolite pore entrance were substituted by protons ($H^+$) providing access to aromatic molecules into the channels of clinoptilolite. They concluded that the difference between the heats of adsorption of BTX on natural and acid-treated clinoptilolites indicated that the nature of the adsorptive molecules significantly affected the degree of interaction between
atoms of hydrogen of adsorptive and oxygen atoms of zeolites. This means that the presence or absence of methyl groups in the adsorptive molecules was a significant factor in determining heats of adsorption of natural and treated samples. It was concluded that the difference in magnitudes of isosteric heat of adsorption only in the treated sample was also due to the effect of the molecular sieve displayed by each adsorbent. Fleys and Thopmson (2004) measured the isosteric heat of adsorption in silicalite-1 and all-silica zeolite DAY. The isosteric heat of adsorption was slightly higher in silicalite-1 than in all-silica zeolite DAY. It was explained that probably the silicalite-1 has higher adsorbate-wall interaction energy than all-silica zeolite DAY. The author mentioned that in silicalite the pore diameters are smaller and the water molecules are more confined in the small pore of silicalite, compared to all-silica zeolite DAY. In this study the researcher mentioned that the cations can also influence significantly the isosteric heat of adsorption. At low loading, cations act like a pump, the water molecules adsorb at cations sites, and the isosteric heat is high. They also mentioned that at intermediate loading, a monolayer, and then multilayer, water molecules cover the walls of DAY zeolite, leading to a decrease of the isosteric heat as the stronger sites were already occupied.

2.6.2 Liquid phase adsorption on dealuminated zeolites

The fundamental principles and methodology of the liquid-phase adsorption is different from the gas-phase adsorption. The pH, type of adsorbent, the solubility of adsorbate in the solvent, temperature and adsorptive concentration are some important factors to consider in the liquid-phase adsorption. That makes this technique less studied than the adsorption from gas phase.

Liquid phase adsorption using adsorbents such as activated carbon, silica, resins and zeolites is a technique widely used in the removal of organic pollutants from
industrial wastewater (Roque-Malherbe 2007). Liquid phase adsorption using zeolites as adsorbent has been a very studied technique by many researchers. For example, the use of zeolites in the removal of trace quantities of pollutants, such as heavy metal ions and phenols, has been studied (Ahmaruzzaman 2008). The potential use of zeolites in the removal of recalcitrant pollutant and environmental remediation has taken a great interest mainly for their synergetic adsorption strength, controllable pore structure, excellent chemical stability and its ability to remove organic and inorganic pollutants in the environment (Foo and Hameed 2011).

The adsorption capacity of organic compounds by some dealuminated zeolites has also been investigated. For example, Dealuminated Y Zeolite (DAY) with a low content of aluminum, has been studied in the adsorption of organic compounds dissolved in water. The synthetic zeolite DAY has the same structure as faujasite (FAU) zeolite, but without aluminum atoms. DAY zeolite has an open structure with a pore volume of 0.38 cm$^3$/g and a high symmetry (cubic Fd-3) (Fleys et al. 2004). The framework is composed of sodalite units interconnected through six-membered oxygen bridges. These units form supercages that are connected to neighboring cages through four tetrahedrally directed twelve-membered rings with a free diameter equal to 7.5 Å. A unit cell of the zeolite DAY comprises 192 tetrahedral units of SiO$_2$ (Fleys et al. 2004). A highly dealuminated zeolite (DAY) has also been used in the recovery of organic solvents (Bae Kim et al. 2005; Ki Ryu et al. 2002).

Some studies have been conducted on liquid phase adsorption which compares two or more microporous materials in the adsorption of organic compounds. For example, Muñiz-López et al. (2009) investigated the dynamics adsorption of paranitrophenol (PNP) in liquid phase using as adsorbents granular activated carbon (GAC) and the zeolite DAY. The dynamics adsorption was carried out in a packed bed
adsorption reactor (PBAR) filled with each adsorbent. With the experimental data obtained, they were able to calculate the parameters related to the morphology of each adsorbent and PBAR operational parameters. The calculated parameters were used to explain the profile of breakthrough curves obtained for each adsorbent. It was concluded that the reactor filled with the zeolite DAY operated more efficiently than the reactor filled with GAC because the adsorbent-adsorbate interaction was higher for the zeolite DAY. This conclusion was based in the fact that the pore diameter of DAY was smaller than the pore diameter of GAC. With this argument they explained that a molecule within the DAY adsorption space is closer to adsorbent framework and, therefore, the interaction field (e.g. adsorbate-adsorbent interaction) will be high in this adsorption space.

Koubaissy et al. (2011) investigated the adsorptive removal of aromatic compound in dealuminated faujasite zeolite. The adsorption capacity of several compounds on dealuminated faujasite was evaluated considering pH and the solubility in water of the aromatic compounds. They found that the adsorption capacity for a family of compounds increases with decreasing water solubility. In the dynamic adsorption analysis the breakthrough curves of 2,4- dichlorophenol (2,4-DCP) and 2,4-dinitrophenol (2,4-DNP) were obtained with same concentration and pH=3. The breakthrough curves of 2,4-DCP indicate that this compound was less favorably adsorbed than 2,4-DNP over HFAU zeolite. It was found that the adsorption capacity of 2,4-DNP was higher, despite the slightly lower solubility of 2,4-DCP. The researcher explained that this result seems to be related to the electron donation of –Cl substituent compared to electron withdrawing group such as –NO2. According to the researcher, the mesomeric effect (effect used in a qualitative way, and describes the electron withdrawing or releasing groups) of –Cl increases the electronic density of the aromatic ring structure. They were able to corroborate what other studies have shown, that an
increase in electronegativity of aromatic structure reduces significantly the adsorption capacity of the compounds. They also concluded that the adsorption capacity decreases when the hydroxyl group acidic character and the acidity of hydrogen of aromatic ring decreases. Thereby, the aromatic compound whose acidity is strong (smaller pKa) will be better adsorbed. Koubaissy et al. (2008) investigated the adsorption on several nitrophenolic compounds from aqueous solution using hydrophobic FAU zeolite. They studied the effect of pH (4,7 and 9) and water solubility on the adsorption of ortho-nitrophenol (ONP), para-nitrophenol (PNP), meta-nitrophenol (MNP) and 2,4-dinitrophenol (2,4-DNP). They also compared the adsorption capacity for different water solubility compounds. The adsorption isotherm showed that ONP was less adsorbed from a solution with pH=7 than from a solution with pH=4. The researcher explained that in a neutral solution (pH =7), the phenolic compounds partially dissociate in water and form a dissociate species (X-PHO); and that in an acid solution (pH =4) only occurs the formation of a molecular specie (XPHOH). They explained that the dissociated species are more polar than molecular species, and they interact preferentially with water rather than with zeolite. They explained that, in the case of ionic compound (dissociate species), the repulsion occurs between the oxygen sites of zeolites and the negative group of the molecule. The breakthrough curves obtained from the flow reactor showed that ONP was better adsorbed than PNP and MNP. They explained that less-soluble molecule such as ONP, will be more adsorbed than other molecule with larger solubilities, such as PNP and MNP. They concluded that the decrease of the pollutant interactions with water causes an increase in interaction with the adsorbent.

2.7 ZSM-5

It has been established that the dealumination in natural zeolites improves its adsorption capability and its hydrophobic property. Perhaps these modified natural
zeolites may have some physicochemical characteristics similar to other zeolites widely used in industrial processes or petrochemical industries, such as ZSM-5. The zeolite ZSM-5 is perhaps the most versatile solid-acid catalyst known (Lobo 2003). Medium pore size ZSM-5 zeolite plays an important role in petrochemicals and fluid catalytic cracking processing (Aly et al. 2011). This molecular sieve with MFI structure is synthesized from hydro-gels containing precursors of silicon and aluminum at autogenously pressure and temperature above 100 °C (Aly et al. 2011). Even though the Al content is low, the acidity manifested by these zeolites is adequate for hydrocarbon catalysis reactions (Lobo 2003). The ZSM-5 is considered the catalyst of choice when shape selectivity influences the preferential formation of light olefins (Petrik 2009). Some authors mentioned that mesoporous ZSM-5 has shown improved catalytic performance in the cracking of model compounds due to the hierarchical porosity of the walls and to the easier transport and access to the acid sites. Bari Siddiqui et al. (2010) investigated the enhanced production of light olefin from catalytic cracking of FCC (fluid catalytic cracking) naphtha over mesoporous ZSM-5. They compared these mesoporous zeolite with three conventional ZSM-5 catalysts having different Si/Al ratio. They found that the mesoporosity of ZSM-5 significantly enhanced the production of light olefin and aromatics, compared with the conventional ZSM-5. It was concluded that the mesopores, low acidity and small crystal were important parameters to enhance light olefin yield from FCC naphtha cracking.

ZSM-5 is among the zeolites that have been more extensively studied in recent studies carried out on adsorbents. For example, Zukal et al. (2010) studied the adsorption isotherms of carbon dioxide using six high silica zeolites, including ZSM-5. According to adsorption capacities and isosteric adsorption heat related to the amount of
CO\textsubscript{2} adsorbed, they obtained detailed insight into the carbon dioxide interaction with zeolites of different framework topology.

ZSM-5 has been widely used in research about the adsorption of some gases, like carbon dioxide (CO\textsubscript{2}), methane (CH\textsubscript{4}) and nitrogen (N\textsubscript{2}). Sethia et al. (2010) investigated the effect of SiO\textsubscript{2}/AlO\textsubscript{3} ratio in the adsorption properties of some gases, such as carbon monoxide (CO) and nitrogen, in zeolite ZSM-5. It was demonstrated that the selectivity of CO over N\textsubscript{2} decreased with increasing the SiO\textsubscript{2}/AlO\textsubscript{3} ratio of the ZSM-5. They explained that the decrease in selectivity was due to the strong interaction of CO with sodium ions, which also decreased with the increase in the SiO\textsubscript{2}/AlO\textsubscript{3} ratio. It was established that the strong interaction with sodium ions was due to the higher quadrupole moment and polarizability of CO. Among the adsorbents studied, the ZSM-5 with the highest number per unit cell cations in the framework was shown to have the maximum adsorption capacities and heat of adsorption.

Ghezini et al (2008) used the H-ZSM-5 zeolite to study the carbon dioxide adsorption at high pressure and temperatures of 273 and 293 K. They used Dubinin-Radushkevich (D-R) method and "t-plot method" of De Boer for the analysis of experimental adsorption data that allowed the determination of the micropore volume (W\textsubscript{0}). The value of W\textsubscript{0} obtained through D-R method for the CO\textsubscript{2} adsorption at 293 K was similar to those reported in the literature for N\textsubscript{2} adsorption at 77K by t-plot method. The difference in the value of micropore volume resulted from the different Si/Al ratio of the H-ZSM-5 zeolites used in each methodology. Once again it was demonstrated that the micropore volume is a function of Si/Al ratio. Furthermore, the equilibrium pressure was rapidly reached because at elevated temperature the adsorption favored the gas whose molecules have a higher kinetic energy. As mentioned previously, at
high temperatures the molecules of CO$_2$ have more kinetic energy than N$_2$ so they can quickly reach the narrower pores.

Considering how important is the use of ZSM-5, is worth knowing if this zeolite may be replaced by a natural zeolite whose low cost is an important factor to justify its use in many industrial and environmental applications. In Chapter Four, the physicochemical characteristics of the tested natural Clinoptilolite will be determined. Also in that chapter, the interaction between a CO$_2$ molecule, the modified natural zeolite, a ZSM-5 zeolite and other microporous materials will be compared.
Chapter Three
Methodology

3.1 Gas adsorption in dealuminated natural clinoptilolite

The methodology describes the process of modification or dealumination and the characterization of the tested samples. The experimental data obtained from adsorption isotherms was used to study the interaction of CO₂ molecules with the adsorbent surface.

3.1.1 Materials

All the chemicals used in this research were analytical grade without additional purification. The Ammonium Hexafluorosilicate (98%) was supplied by Aldrich Chemistry Company. The water used in the synthesis process and in the preparation of the solutions was bi-distilled.

The natural clinoptilolite studied came from a deposit located in Sweetwater, Wyoming, USA. The sample was provided by ZeoponiX Inc., Louisville, Colorado. For purposes of this investigation, the natural zeolite was labeled Clinoptilolite Sweetwater (CSW). The measured mineralogical composition of this material was clinoptilolite, (90 ± 5 wt.%), and the rest, montmorillonite (2 wt.%), quartz (2 wt%), calcite (2 wt %), feldspars (1 wt. %), magnetite (1wt %) and volcanic glass (2 wt %).

3.1.2 Sample preparation

Clinoptilolite Sweetwater (CSW) of 30 to 40 meshes was exchanged with a 1M ammonium chloride solution (NH₄Cl). This solution was prepared with 13.40 g of ammonium chloride in 250 ml of deionized water (DDW). Twenty-five grams of natural zeolite were exchanged in reflux five times with 1M NH₄Cl solution at 100°C, each exchange had a duration of three hours. This treatment produced an ammonium
clinoptilolite that was identified as NH$_4$-CSW. This zeolite was thereafter filtered, washed exhaustively with bi-distilled water and dried in an oven at 70$^\circ$ C.

The ammonium clinoptilolite was dealuminated with a 0.1M solution of (NH$_4$)$_6$SiF$_6$ or ammonium hexafluorosilicate (HFSi). This solution was prepared with 0.05 g of HFSi in 500 ml of DDW. Another 0.4M solution was prepared with 0.20 g of HFSi in 500 ml of DDW. A sample of 10 g of ammonium zeolite was refluxed for four hours with 500 ml of 0.1M HFSi at 80$^\circ$ C. The equipment used in the dealumination procedure can be seen in Figure 3.01. The same treatment was given to another 10 g of ammonium zeolite, but with 0.4M solution of HFSi. Following this treatment, each sample was filtered, washed exhaustively and dried in an oven at 70$^\circ$ C. Finally, each sample was calcined at 500$^\circ$ C for a period of two hours. The calcined sample prepared with 0.1M HFSi was identified as CSW-HFSi-0.1M and the calcined sample prepared with 0.4M of HFSi was identified as CSW-HFSi-0.4M.

The natural clinoptilolite was also dealuminated with orthophosphoric acid. The dealumination was carried out by 20 and 40 minutes reflux of 20 g of natural clinoptilolite with a 4M solution of orthophosphoric acid (H$_3$PO$_4$) at 373K. After, the treatment with H$_3$PO$_4$ sample was washed and dried in an oven at 70$^\circ$ C. This treatment resulted in the clinoptilolite dealumination by isomorphous replacement of aluminum atoms by phosphorus atoms. The dealuminated samples were identified as CSW-H$_3$PO$_4$-20 and CSW-H$_3$PO$_4$-40. Figure 3.01 shows the equipment used during the dealumination treatment.
Figure 3.01 Equipment used in dealumination treatment with HFSi and Orthophosphoric acid
3.1.3 Characterization Method

All dealuminated natural clinoptilolite samples will be characterized by Carbon Dioxide Adsorption at 273 K, Thermogravimetric Analysis (TGA), Diffuse Reflectance Infrared Fourier Transform Spectra (DRIFTS), X-ray Diffraction (XRD), and SEM and EDAX Analysis.

3.1.3.1 Thermogravimetric Analysis

The study of hydrated state in the modified zeolites was carried out with thermogravimetric analysis (TGA). The TGA testing process will carry out with a TA, Q-500 instrument. The equipment used in TGA analysis can be seen in Figure 3.02. Samples will be place onto a ceramic sample holder suspended from an analytical balance. The sample and holder were heated according to a predetermined thermal cycle: the temperature was linearly scanned, from 25 to 300 °C, at a heating rate of 5 °C/min under a pure N₂ flow of 100 ml/min. The instrument software automatically controlled data collection, temperature control, heating rate and gas flow. The TGA data will be collected as a \( W_t \% \) versus \( T \) (°C) profile, where \( W_t \% = (M_t/M_0) \times 100 \) is the percent ratio of the sample mass during the thermal treatment, \( M_t \), and the initial mass of the sample \( M_0 \).

Figure 3.02 TA, Q-500 instrument
3.1.3.2 Diffuse Reflectance Infrared Fourier Transform Spectra

The Diffuse Reflectance Infrared Fourier Transform Spectra (DRIFTS) will be used to obtain some information about the chemistry of the tested samples. With the help of this analysis, the different hydroxyl groups bounded in modified zeolites surface can be known. The DRIFTS will be obtained using a Thermo Scientific Nicolet iS10 FTIR spectrometer shown in Figure 3.03. The data of the hydrated and dehydrated samples will be collected at a resolution of 4 cm⁻¹ employing 100 scans per sample. A background, with pure KBr, provided by Nicolet, applying the same conditions will always be obtained prior to sample collection. Both the hydrated and dehydrated samples spectra will be obtained at room temperature under N₂ (Praxair, 99.99%) flowing at a rate of 50 cm³/min. Before the analysis, the dehydrated samples will be previously treated at 100 °C, for 2 h under a N₂ flow applying the previously reported conditions. For gathering of the DRIFTS spectra for the dealuminated natural clinoptilolite with adsorbed carbon dioxide, the background will be carefully measured using the dehydrated sample at room temperature. It will allow the CO₂ (Praxair, 99.99%) into the sample chamber of the IR high temperature cell at flow at a rate of 50 cc/min rate for three minutes followed by purging under N₂ (Praxair, 99.99%) at the same flow rate for one minute. Spectra of the carbon dioxide molecule adsorbed on the clinoptilolite framework will be obtained at room temperature under N₂ flow (Roque-Malherbe 2010).
3.1.3.3 X-Ray Diffraction

With the help of the X-ray diffraction (XRD) method some qualitative and quantitative information from XRD profile of the modified samples will be obtained. The qualitative analysis will consist in the comparison of the obtained profile of the modified samples with the profile of the same zeolite available in an existing database. The obtained profile will also help to obtain some quantitative measurement, such as cell parameter and crystallite size. This measurement will be compared with simulated XRD powder samples of zeolites. The comparison of the obtained result with the existing data will give an idea of the effect of dealumination on the crystalline solid under study.

The XRD tests will be carry out using a Bruker D8 Advance System in a Bragg-Brentano vertical goniometer configuration. The equipment used in the XRD test can be seen in Figure 3.04. The angular measurements will be made with a (Theta/2Theta) of +/- 0.00001 reproducibility, applying steps of 0.01° from 5° to 60° to obtain XRD profiles that
could be accurately resolved by least square methods. The X-ray radiation source is a ceramic X-ray diffraction Cu anode tube type KFL C 2 K of 2.2 kW, with long fine focus. A variable computer-controlled motor driven divergence slit with 2.51 Soller slit will be included to allow keeping the irradiated area on the sample surface constant. A Ni filter will be placed, prior to the detector, to eliminate CuKα radiation. A LynxEye™ one-dimensional detector will be employed. This detector is based on a Bruker AXS compound silicon strip technology and increases measured intensities, without sacrificing resolution and peak shape. All together, with the use of small scanning step, resulted in high quality XRD profiles suitable for mathematical treatment. High temperature measurements in vacuum were performed using an Anton Paar HTK-1200N stage. This high vacuum chamber was designed to be used in the range from room temperature up to 1200 °C. The sample will be mounted on an alumina sample holder with temperature sensor located just below the sample.

Figure 3.04 Bruker D8 Advance System
3.1.3.4 Scanning Electron Microscope and Energy Dispersive X-Ray Analysis

The Scanning Electron Microscope (SEM) will help to study the morphology of the modified samples. The Energy Dispersive X-Ray Analysis (EDAX) will provide an elemental chemical analysis of the tested samples. This will give us an idea of the chemical composition of the samples after they were subjected to ionic exchange. This analysis was performed using an Energy Dispersive X-ray (EDAX) spectrometer coupled to a JEOL JSM-6010LA SEM and EDAX analysis. In both cases, the acceleration of the electron beam was 20 kV. The sample grains were placed on a carbon tape, and then introduced into the sample holder. Different spots were analyzed in order to guarantee that we were testing a homogeneous distribution within the sample. Together with the EDAX analysis, scanning electron micrographs of the tested samples were obtained. Figure 3.05 shows the SEM and EDAX analysis system.

Figure 3.05   JEOL JSM-6010LA SEM and EDAX analysis system.
3.1.3.5 Carbon Dioxide Adsorption Study

The carbon dioxide adsorption study, as a characterization tool, will help to obtain some calculated parameter from Dubinin-Radushkevitch plot of the adsorption isotherm of carbon dioxide. This study will also be used to calculate a quantitative measurement to know the interaction of the carbon dioxide molecule with the adsorption space.

The adsorption isotherms of CO$_2$ at 273 K in samples degassed at 573 K during 3 hours in high vacuum (10^-6 Torr) will be obtained, in upgraded Quantachrome Autoadsorb-1 automatic physisorption analyzer. The relative pressure range that will be use is: 0.00003<P/P$_o$<0.03. The micropore volume ($W_{MP}$) and the characteristic energy of adsorption (E) will be obtained with the help of CO$_2$ adsorption isotherm and the Dubinin-Radushkevich (DR) equation. Figure 3.06 shows the Quantachrome Autoadsorb-1 automatic physisorption analyzer.

Carbon dioxide adsorption at 273 K can be used in order to apply a Dubinin adsorption isotherm to describe the carbon dioxide adsorption and to determinate the correspondent adsorption parameter. Carbon dioxide adsorption can also be used to determinate the micropore volume ($W_{MP}$), characteristic energy of adsorption (E) and isosteric heat of adsorption ($q_{ISO}$).

The Dubinin-Astakhov (D-A) adsorption isotherm equation can be represented in a log-log scale as follows (Bearing et al. 1972):

$$\ln (n_a) = \ln (N_a) - \left(\frac{RT}{E}\right)^n \ln \left(\frac{P_o}{P}\right)^n$$

Where $n_a$ is the amount adsorbed, $\frac{P_o}{P}$ is the inverse of relative pressure, $P_o$ is the vapor pressure, $P$ is the equilibrium adsorption pressure, $E$ is the characteristic energy of adsorption, $N_a$ is the maximum adsorbed in the volume of the micropore, and $n$ is a
heterogeneity and empirical parameter. This equation is very important in the description of the experimental data of adsorption in microporous material (Roque-Malherbe et al 2010). The fitting process of this equation can be used to calculate the best fitting parameter such as $N_a$, $E$ and $n$. With $n = 2$ we have the well-know Dubinin-Radushkevich (DR) equation. With the Dubinin plots of the adsorption isotherms of carbon dioxide at 273 K we have:

$$y = \ln (n_a), \quad b = \ln (N_a), \quad m = \left(\frac{RT}{E}\right)^2 \quad \text{and} \quad x = \left(\ln \frac{P_0}{P}\right)^2$$

Thereby the micropore volume ($W_{MP}$) and the characteristic energy of adsorption ($E$) can be calculated. The micropore volume is $W_{MP} = N_aV_L$, (where $V_L$ is the molar volume of CO$_2$ at 273K), and the characteristic energy of adsorption ($E$) is obtained in KJ/mol.

![Figure 3.06](image_url) Quantachrome Autoadsorb-1 automatic physisorption analyzer
3.2 Liquid-phase adsorption on dealuminated zeolites

In this part of the investigation, the hydrophobic zeolites were used to study the liquid phase adsorption of organic compounds. This study will be carried out with the help of the breakthrough curves obtained at the output of a Packet Bed Adsorption Reactor or PBAR. The operational parameters will be calculated from the obtained breakthrough curve.

3.2.1 Materials

The molecular sieves catalyst support, ammonium Y zeolite powder of 100 mesh used in this research was supplied by the company Sigma-Aldrich. Twenty-grams of this commercial zeolite were dealuminated with 0.1M solution of HFSi and another twenty-gram were dealuminated with 0.4 M solution of HFSi. Following this treatment, each sample was filtered, washed exhaustively, and dried in an oven at 70°C. Finally, each sample was calcined at 300°C for a period of two hours. The calcined sample prepared with 0.1M HFSi was identified as DAY-HFSi-0.1, and the calcined sample prepared with 0.4M of HFSi was identified as DAY-HFSi-0.4.

The commercial Dealuminated Y zeolite (DAY) was also used in the dynamic adsorption study. The DAY-20F (Si/Al = 20) was provided by Degussa AG, Germany. The paranitrophenol (PNP), orthonitrophenol (ONP) and methanitrophenol (MNP) was provided by VMR International Inc.

3.2.2 Dynamic Adsorption Study

The dynamic adsorption study was carried out in a laboratory made set-up consisting of an analyte (PNP, ONP, MNP or methanol) container to supply the aqueous solution fluid to a high performance liquid chromatography (HPLC) double piston KNAUER-K-501 pump, which feeds the packed bed adsorption reactor (PBAR). The equipment used for this study can be seen in Figure 3.07. With this equipment the
breakthrough curves can be obtained, resulting from the dynamic adsorption of analyte in DAY adsorbent beds. Figure 3.08 shows an example of a breakthrough curve. The input and output concentration of the analyte aqueous solution fluid was measured with a Shimadzu UV/VIS 1800 recording spectrophotometer.

The PBAR consisted of a Phenomenex cylindrical stainless steel column exhibiting an internal diameter, \( d = 4.6 \times 10^{-3} \) m, and a total length, \( L = 0.15 \) m. The reactor has cross sectional area, \( S = 1.662 \times 10^{-5} \) m\(^2\), the bed length (D) was measured for each adsorbent, and the adsorbent mass in the bed was \( M = 0.5 \) g. This PBAR was fed with an input flow, \( F = \Delta V / \Delta t \), of an aqueous solution with a PNP, ONP, MNP or methanol concentration through the input section of the reactor. The initial concentration (\( C_0 \)) of PNP, ONP or MNP was 1400 ppm and the initial concentration of the methanol solution was 2800 ppm.

Figure 3.09 shows an example of packed bed adsorption reactor (PBAR). Two of the operational parameter are the interstitial fluid velocity, \( \upsilon \), and the rate coefficient, \( k \). The other operational parameters of the PBAR, that can be obtained from measured breakthrough curves, are: the length of the mass transference zone (MTZ), \( D_o \); the column breakthrough capacity, \( B_c \); the estimated breakthrough time, \( (t_b) \); and the breakthrough curve with \( (\Delta t) \) in minutes. The \( D_o \) has the following expression (Roque-Malherbe 2010):

\[
D_o = 2D \frac{V_b - V_e}{V_b + V_e}
\]

Where \( V_b \) is the fed volume up to breakthrough, and \( V_e \) is the fed volume up to bed saturation. The \( V_b \) and \( V_e \) can be calculated with the input flow \( F \), the estimated breakthrough time \( (t_b) \) and the estimated saturation time.
The column breakthrough capacity ($B_C$) has the following expression:

$$B_C = \frac{C_0V_e}{M}$$

The interstitial fluid velocity $u$ has the following expression:  

$$u = \frac{F}{S}$$

Figure 3.07  High performance liquid chromatography (HPLC) double piston KNAUER-K-501 pump
\[ \frac{C}{C_0} = 1 \]

Initial concentration

Fed Volume

Breakthrough concentration \( (C_0) \)

Fed volume to breakthrough \( (V_e) \)

Fed volume to saturation \( (V_b) \)

Figure 3.08 Breakthrough Curve
Figure 3.09  Packed Bed Adsorption Reactor (PBAR)
4.1 Characterization of modified natural clinoptilolite

The profiles obtained during the XRD analysis were compared with some existing pattern in the Collection of Simulated XRD Power Patterns for Zeolite, Powder Diffractions File (PDF) of the International Center for Diffraction Data (ICDD) (Leng 2008). The Collection of Simulated XRD Power Patterns for zeolite has information such as Zeolite Framework Types, Chemical Composition, Refined Composition, Crystal Data, Reference, Powder Pattern Identification Table, Calculated Diffraction Powder Diffraction Data and the Simulated Powder Pattern. Table 4.01 presents some information of clinoptilolite.

Table 4.02 presents the cell parameters of the modified clinoptilolite samples that were calculated by fitting the XRD profiles of these materials with mathematical functions simulating XRD patterns using the Pawley method. The calculations of the cell parameter were performed assuming the C12/m1 (No. 12) space group. Also, in Table 4.02 the calculated cell parameters for this space group, along with the Gaussian crystallite size (Φ), are presented. The information presented in this table was calculated with the use of TOPAZ software. This program made the corrections to separate instrumental and strain effects from the crystallite size by applying the Williamson-Hall. The calculated parameters for the modified samples are similar to those reported for a typical clinoptilolite in Table 4.01.
Table 4.01  Some parameter of Clinoptilolite

<table>
<thead>
<tr>
<th>Zeolite Framework type</th>
<th>HEU</th>
<th>Recognized by the IUPAC Commission on Zeolite Nomenclature</th>
</tr>
</thead>
</table>

Chemical Composition  
\[ \text{Na}_{1.84}\text{K}_{1.76}\text{Mg}_{0.2}\text{Ca}_{1.24}(\text{H}_2\text{O})_{21.36}\]  
\[\text{[Si}_{29.84}\text{Al}_{6.16}\text{O}_{72}]\]  
Agoura, California, U.S.A.

Refined Composition  
\[\text{/Na}_{1.84}\text{K}_{1.76}\text{Mg}_{0.2}\text{Ca}_{1.24}(\text{H}_2\text{O})_{21.36}/\]  
\[\text{[Si}_{29.84}\text{Al}_{6.16}\text{O}_{72}]\]  
Derived from the structure refinement

Crystal data  
\( C\ 2/m\ 1\) (No. 12) unique axis \( b \), cell choice 1  
\( a = 17.662\ \text{Å} \)  
\( b = 17.911\ \text{Å} \)  
\( c = 7.407\ \text{Å} \)  
\( \alpha = 90^\circ \)  
\( \beta = 116.40^\circ \)  
\( \gamma = 90^\circ \)  
Lattice parameter and space group information from the International Tables for Crystallography, 4th revised edition 1995

Reference  
K. Koyama and Y. Takeuchi,  
*Z. Kristallogr.* 145 pag 216–239 (1977)

Source: Treacy and Higging (2007)
Table 4.02 Obtained cell parameters for the modified clinoptilolite samples calculated with the Pawley method assuming the \textit{C2/m} space group and Gaussian crystallite size ($\Phi$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>b(Å)</th>
<th>c (Å)</th>
<th>$\beta$(degree)</th>
<th>$V$(Å$^3$)</th>
<th>$\Phi$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSW-NH$_4$</td>
<td>17.693(4)</td>
<td>17.959(4)</td>
<td>7.404(6)</td>
<td>116.01(1)</td>
<td>2114(1)</td>
<td>40(1)</td>
</tr>
<tr>
<td>CSW-HFSi-0.1</td>
<td>17.659(4)</td>
<td>17.858(3)</td>
<td>7.394(5)</td>
<td>116.34(1)</td>
<td>2089(1)</td>
<td>39(1)</td>
</tr>
<tr>
<td>CSW-HFSi-0.4</td>
<td>17.688(5)</td>
<td>17.965(3)</td>
<td>7.403(1)</td>
<td>116.31(1)</td>
<td>2108(1)</td>
<td>39(1)</td>
</tr>
<tr>
<td>CSW-H$_3$PO$_4$-20</td>
<td>17.672(4)</td>
<td>17.975(6)</td>
<td>7.416(6)</td>
<td>116.33(1)</td>
<td>2111(1)</td>
<td>37(1)</td>
</tr>
<tr>
<td>CSW-H$_3$PO$_4$-40</td>
<td>17.695(8)</td>
<td>17.990(1)</td>
<td>7.411(2)</td>
<td>116.180(1)</td>
<td>2116(1)</td>
<td>29(1)</td>
</tr>
</tbody>
</table>

Figures 4.01 and 4.02 show the XRD profiles and details obtained for all the modified samples. Figure 4.01 shows that all the modified samples are crystalline. In Figure 4.02 it can be seen how the dealumination treatment had an impact in the sample crystallinity. The modified sample with orthophosphoric acid had a low crystallinity (49%), whereas one sample modified with ammonium hexafluorosilicate remained with high crystallinity (92%). This means that dealumination with orthophosphoric acid was more effective in the removal of aluminum atoms from the framework. However, the removal of large amount of framework aluminum can lead to loss crystallinity and the collapse of the structure.
It was found that the XRD profile obtained for the modified samples produces a match with the profile of the clinoptilolite available in the PDF-2, 2009 release database, created by the International Center for Diffraction Data.

Figure 4.03 shows one of the fitted profiles. The differences could be related to the ionic radius of Al\(^{3+}\) (0.39 Å) and Si\(^{4+}\) (0.26 Å) in tetragonal coordination. A difference in the values of these parameters was observed throughout the dealumination process.

Figure 4.01 XRD profiles of the modified natural clinoptilolite
Figure 4.02 XRD profile detail of samples NH$_4$-CSW, CSW-HFSi-0.1, CSW-HFSi-0.4 and CSW-H$_3$PO$_4$-20

NH$_4$-CSW (100% Crystallinity)

CSW-HFSi-0.1 (92%)

CSW-HFSi-0.4 (79%)

CSW-H$_3$PO$_4$-20 (49%)
Figure 4.03  XRD profile of the CSW-HFSi-0.1 sample fitted with Pawley method for the \textit{C2/m} space group
The Thermogravimetric technique is effective for assessing thermal stability and chemical reactions by monitoring mass change in materials (Leng 2008). The reactions involving mass change are dehydration, desorption, decomposition and oxidation. The TG profile is useful for the study of hydrated state in porous materials such as zeolites. During the TG analysis, the process of water thermo-desorption occurs by the release of water adsorbed in different sites of the zeolite tunnels. In a typical TGA curve for a sample heated under vacuum, the low temperature portion (< 50°C) of a curve represents desorption of water from the surface of grains in the powdered sample. The portion of the curve at temperature between 50°C to 200°C represents desorption of "loosely bond zeolite water". The portion of a curve at temperature between 200°C to 700°C represents the slow desorption of water from clinoptilolite component of a sample (Knowlton and White 1981). This water is referred to as "tightly bound water". Otherwise, Ates and Hardacre (2012) classified the water molecules in the zeolites, based in the obtained results of the effect of various treatment conditions on natural zeolites. They classified the water molecules in three forms: physisorbed water (<100°C), water associated with extra-framework cations (100°C – 400°C) and water associated with silanol nests (>400°C).

Figures 4.04 and 4.05 show the water thermo-desorption profile for a modified samples at temperature between 30°C to 300°C. The form of the curves shows the sudden loss of mass in both samples. The slope change of a TG curve is the main characteristic used to analyze a sample, despite that sometimes the slope change is uncertain. To remove the uncertainty of the TG curve the derivative TG curve (DTG) which represents a plot of \( \frac{dw}{dt} \) vs temperature can be used. A peak in the DTG curve represents a maximum of mass change rate, that is, this plot identifies the temperature at which mass loss is at maximum. Figure 4.06 and figure 4.07 show TGA derivative
profiles corresponding to the modified clinoptilolite CSW-HFSi-0.1, CSW-HFSi-0.4, CSW-H$_3$PO$_4$-20 and to the ZSM-5 (CBV-3020). These profiles were resolved by fitting a theoretical profile, which is computed with the sum of two Lorentzian functions to the experimental data. This has been performed by applying the peak separation and the analysis software PeakFit (Seasolve Software Inc., Framingham, Massachusetts) based on the least square procedure. Figure 4.06 and figure 4.07 show that the experimental profile is the continuous line which is fitted by the theoretical function illustrated by the dashed line. The two peaks used for the computation of calculated profile are also displayed as dashed curves.

The analysis of the TGA derivative profiles shows the presence of two steps for water release. In the first step, the loss of zeolitic water or the mostly water present in micropores occurred. This thermal effect was demonstrated with the broad peak centered approximately at 50 °C for the samples ZSM-5 (CBV-3020) and CSW-HFSi-0.1. The same thermal effect occurred for the samples CSW-HFSi-0.4 and CSW-H$_3$PO$_4$-20 at approximately 100 °C. The release of physically adsorbed water at different temperature is typical for the energetically heterogeneous adsorbent as a zeolite. This may be related to the different adsorption energies to the framework. The second step of water release occurred approximately at 75 °C for the sample ZSM-5 (CBV-3020), at 125 °C for CSW-HFSi-0.1, at 150 °C for CSW-HFSi-0.4 and at 175 °C for CSW-H$_3$PO$_4$-20. This second process was related to the removal of coordinated water known as “loosely bound water” and “tightly bound water”.
Figure 4.04 TGA profiles of the ZSM-5 (CBV-3020) and the CSW $\text{H}_3\text{PO}_4$-20
Figure 4.05 TGA profiles of the modified natural clinoptilolites:

CSW-HFSi-0.4 and CSW-HFSi-0.1
Figure 4.06 TGA derivative profiles of the ZSM-5 (CBV-3020) and the CSW-H₃PO₄-20
Figure 4.07 TGA derivative profiles of the modified natural clinoptilolites:
CSW-HFSi-0.4, CSW-HFSi-0.1
The morphology of the modified sample was analyzed with the help of scanning electron microscope or SEM. Figure 4.08 shows the SEM micrographs of the modified clinoptilolites, CSW-NH$_4$, CSW-HFSi-0.1 and CSW-HFSi-0.4. From this micrograph it was evidenced that the natural zeolite (CSW) has a primary clinoptilolite crystallite which size ($\Phi$) is 40 nm. This primary crystallites form secondary particles with diameters from 3 to 40 $\mu$m. Figure 4.09 shows the SEM micrographs at higher magnification, in which the lath morphology of these primary clinoptilolite crystallites of the modified samples can be observed.

Table 4.03 presents the EDAX elemental analysis of the modified clinoptilolite CSW-NH$_4$, CSW-HFSi-0.1, CSW-HFSi-0.4 and CSW-H$_3$PO$_4$-20 and of the previously reported samples Na-CSW and Na-HC. The obtained results demonstrated that with the ionic exchange process it was possible to replace approximately the 85% of the compensating ions present in natural clinoptilolite. That is, the compensating ions Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$ present in natural clinoptilolite were replaced by Na$^+$ and NH$_4^+$ to produce the CSW-Na and CSW-NH$_4$ samples. In the samples treated with orthophosphoric acid the compensating cations were replaced with protons. Other authors mentioned that the treatment with orthophosphoric acid assists in the elimination of impurities, such as carbonate or Fe (De las Posas et al. 1996). The obtained results also show the reduction of aluminum atom from the framework causing a slight increase in the Si/Al ratio for the CSW-HFSi-0.1 and CSW-HFSi-0.4 samples and a moderate increase in CSW-H$_3$PO$_4$-20.
Figure 4.08 SEM micrographs corresponding to the samples CSW-NH₄, CSW-HFSi-0.1 (bar = 5 μm) and CSW-HFSi-0.4 (bar = 10 μm).
Figure 4.09 SEM micrographs of tested samples CSW-NH₄, CSW-HFSi-0.1, CSW-HFSi-0.4 and CSW-H₃PO₄-20 (bar = 2 μm).
Table 4.03  EDAX elemental analysis of the natural and modified samples in wt. %.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>Al</th>
<th>O</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-CSW</td>
<td>37.4</td>
<td>9.3</td>
<td>45.2</td>
<td>5.5</td>
<td>0.9</td>
<td>0.0</td>
<td>0.7</td>
<td>1.1</td>
<td>4.0</td>
</tr>
<tr>
<td>Na-HC</td>
<td>37.5</td>
<td>9.4</td>
<td>45.4</td>
<td>5.8</td>
<td>1.0</td>
<td>0.0</td>
<td>0.4</td>
<td>0.5</td>
<td>4.0</td>
</tr>
<tr>
<td>CSW-NH₄</td>
<td>40.8</td>
<td>10.3</td>
<td>45.5</td>
<td>0.3</td>
<td>1.0</td>
<td>0.0</td>
<td>0.7</td>
<td>1.4</td>
<td>4.0</td>
</tr>
<tr>
<td>CSW-HFSi-0.1</td>
<td>41.4</td>
<td>9.6</td>
<td>46.3</td>
<td>0.1</td>
<td>0.9</td>
<td>0.0</td>
<td>0.3</td>
<td>1.0</td>
<td>4.3</td>
</tr>
<tr>
<td>CSW-HFSi-0.4</td>
<td>45.4</td>
<td>9.5</td>
<td>43.1</td>
<td>0.1</td>
<td>0.8</td>
<td>0.0</td>
<td>0.3</td>
<td>0.8</td>
<td>4.8</td>
</tr>
<tr>
<td>CSW-H₃PO₄-20</td>
<td>40.1</td>
<td>6.6</td>
<td>50.8</td>
<td>0.6</td>
<td>0.9</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0</td>
<td>6.1</td>
</tr>
</tbody>
</table>

The IR spectroscopy was used for the chemical and structural zeolite characterization. The vibrational spectrum obtained from zeolites characterization arises from the framework and charge-balancing cations vibrations and from isolated groups, such as surface OH groups. The lattice vibrational frequencies, referred as lattice mode of aluminosilicates zeolites, refer to stretching and bending modes of the T-O (tetrahedral-oxygen) linkages, as well as specific vibrations form discrete structural units.

In the IR spectra, the band in the range from 3000 to 3800 cm⁻¹ is associated to the most important OH stretching vibrations related to the hydroxyl functionalities.

The hydroxyl groups bound to the zeolite surface are the most important groups and can provide information about the material chemistry. These groups are associated
with the acidity and are responsible for the catalytic activities of the zeolite. The different
groups that can be found attached to the zeolite structure are: the lattice terminations
silanol group (3740 cm⁻¹), which are terminal hydroxyl groups showing low acidity; the
hydroxyl groups occurring at defect sites or hydroxyl nest (3720 cm⁻¹); the OH group
attached to the positively charged extra-framework aluminum (3680 cm⁻¹); and the OH
group attached to multivalent cations, which compensates the negative charge of the
framework (band from 3580 to 3520 cm⁻¹) (Li and Wu 2003). The most important group
found from 3600 to 3650 cm⁻¹ is the bridging OH group (Si-OH-Al) in which the proton
shows Brönsted acid character.

Figure 4.10 shows the Diffuse Reflectance IR Fourier Transform Spectroscopy
(DRIFT) spectrum for the previously reported ZSM-5 and for some modified samples. In
the ZSM-5 spectra, evidence of three bands caused by the O-H stretching vibrations are
observed: the first band is around 3590 cm⁻¹, corresponding to the Brönsted acid sites
(Al-OH-Si); the second is around 3660 cm⁻¹, corresponding to the positively charged
extra-framework aluminum (Al-OH); and the third band is around 3740 cm⁻¹,
corresponding to terminal silanol groups (Si-OH). The spectra of the modified sample
CSW-HFSi-0.1 presents a narrow band around 3740 cm⁻¹, corresponding to terminal
silanol groups. These spectra present another band from 3600 to 3650 cm⁻¹,
corresponding to positively charged extra-framework aluminum. Similar results were
obtained in a study by García-Basabe et al. (2010), where natural clinoptilolite was
subjected to step-wise dealumination with Hydrochloric Acid. In that study, the band
corresponding to bridging OH groups (3625 cm⁻¹) decreases during elimination of
aluminum from the framework.

The sample CSW-H₃PO₄-20 DRIFTS spectra did not present any band in the
range between 3200 to 3800 cm⁻¹. The absence of band in the sample spectra should be
related to the dehydroxylation process, which is the loss of structural hydroxyl ions as water molecules on heating. Generally in zeolites, the dehydroxylation process can occur at high temperatures (up to 500°C), in which the bridging hydroxyl groups undergo condensation to produce water and to left the zeolite negatively charged. The surface dehydroxylation and dehydratation was also the reason of the clinoptilolite weight loss (10.83 wt%) during thermal treatment in the range between 33 °C and 1000 °C (Sprynskyy et al. 2010).

In contrast to the sample CSW-H₃PO₄-20, the treatment to which the sample CSW-HFSi-0.1 was subjected created a framework with positive and negative charges. Also, the removal of the charge compensating cations from this modified zeolite will allow an open adsorption space where adsorbed molecules are subjected to electrostatic interactions with the framework. In other words, in the open adsorption space there will be electrostatic interactions between the adsorbed molecule and the adsorbent as a result of the electrostatic field created by the negative a positive charge of the zeolite framework.
Fig. 4.10 DRIFTS spectra of the modified natural clinoptilolites: ZSM-5 (CBV-5020) and the CSW-HFSi-0.1 and CSWH₃PO₄-20
Dubinin plots of the adsorption isotherms of carbon dioxide at 0°C on the modified zeolites and the previously reported ZSM-5 (CBV-5020) zeolite are shown in Figure 4.11.

Table 4.04 the result for the micropore volume, $W_{MP}^{CO2}$, and other parameter calculated for these samples can be seen. The micropore volume was obtained with the help of carbon dioxide adsorption and by fitting the Dubinin-Astakhov (D-A) adsorption isotherm equation in a log scale (see Chapter Three) with $n = 2$ to the reported adsorption data. If $n = 2$, then we use the Dubinin-Radushkevich (D-R) isotherm equation for the calculation of the micropore volume. The precision of the measured micropore volumes was related, first, to the excellent fitting of the adsorption data by the D-R isotherm equation, second, to the appropriate relative pressure range tested ($0.00003 < P/P_0 < 0.003$) and third, to the great amount of adsorption points obtained in the adsorption test. With these arguments it can be affirmed that carbon dioxide adsorption was carried out in the micropore region of the material. In other words, with the help of carbon dioxide adsorption at 0°C, the micropore volume of the studied samples was evaluated. Cakicioglu-Ozkan and Ulku (2005) evaluated the micropore volume using also the D-R method in the water vapor adsorption data of clinoptilolite treated with HCl acid. In this study, neither of the obtained results for micropore volume was higher than the micropore volume of our tested modified samples.

Table 4.04 also shows the zeolitic phase concentration ($f$) in wt% calculated with the help of the micropore volume ($W_{MP}$) of the zeolite present in the natural zeolite rock or in a bound form of a commercial zeolite and the micropore volume of the corresponding pure phase ($W_{phase}^{pure}$).
The zeolitic phase concentration \( (f) \) in wt% was calculated with the following equation (Roque-Malherbe et al. 1995):

\[
f = \frac{W_{MP}^{CO_2}}{W_{phase}^{pure}}
\]

The zeolitic phase concentration \( (f) \) present in the modified clinoptilolites can be calculated with the micropore volume for the HEU framework of the pure clinoptilolite \((\approx 0.16 \text{ cm}^3/\text{g})\) and the micropore volume for the MFI framework of the pure H-ZSM-5 \((0.18 \text{ cm}^3/\text{g})\). In Table 4.04 the zeolitic phase concentration calculated for the modified clinoptilolite can be seen. The result shows that CSW-HFSi-0.1 was the sample that had a higher zeolite phase. Also, this sample was the one which maintained a high crystallinity percentage.

Table 4.05 shows the phase composition of the modified samples obtained from the X-ray data (Figure 4.01). Using the sample CSW-NH\(_4\) as the standard, it can be seen that the amount of clinoptilolite increases in those sample treated with 0.1 mg/L of hexafluorosilicate (CSW-HFSi-0.1). However, the amount of clinoptilolite decreases in the sample treated with 0.4 mg/L of hexafluorosilicate (CSW-HFSi-0.4) and more significantly, in the sample treated with orthophosphoric acid (CSW-H\(_3\)PO\(_4\)-20). With these results it can be stated that the increase in the concentration of hexafluorosilicate (to 0.4 g/ml) and the treatment with orthophosphoric acid are not recommended to produce an adsorbent comparable with commercial zeolites.
Figure 4.11 Dubinin-Radushkevitch (D-R) plots of the adsorption isotherms of carbon dioxide at 273 K on: CSW-HFSi-0.1, CSW-HFSi-0.4 and the ZSM-5 (CBV-5020).
Table 4.04  Micro pore volume and zeolitic phase amount calculated with Dubining-Radushkevish isotherm equation

<table>
<thead>
<tr>
<th>Samples</th>
<th>$N_a$ [mmol/g]</th>
<th>$W_{CO_2}^{Mg}$ [cm$^3$/g]</th>
<th>Zeolitic phase Concentration (f) [wt %]</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5-3020</td>
<td>3.55 ± 0.01</td>
<td>0.169 ± 0.001</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CSW-HFSi-0.1</td>
<td>3.13 ± 0.01</td>
<td>0.149 ± 0.001</td>
<td>93</td>
<td>92</td>
</tr>
<tr>
<td>CSW-HFSi-0.4</td>
<td>2.81 ± 0.01</td>
<td>0.134 ± 0.001</td>
<td>84</td>
<td>79</td>
</tr>
</tbody>
</table>

Table 4.05  Phase composition of the modified clinoptilolite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clinoptilolite [wt %]</th>
<th>Others [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSW-NH$_4$</td>
<td>91(5)</td>
<td>9(5)</td>
</tr>
<tr>
<td>CSW-HFSi-0.1</td>
<td>95(5)</td>
<td>5(5)</td>
</tr>
<tr>
<td>CSW-HFSi-0.4</td>
<td>72(5)</td>
<td>28(5)</td>
</tr>
<tr>
<td>CSW-H$_3$PO$_4$-20</td>
<td>41(5)</td>
<td>59(5)</td>
</tr>
</tbody>
</table>
4.2 Interaction of Carbon Dioxide with the modified Clinoptilolite

As mentioned before, during the adsorption process a molecule which contacts the surface of a solid adsorbent like zeolite, is subjected to diverse energy fields distinguished by different potentials. These potentials are: dispersion energy ($\phi_D$), repulsion energy ($\phi_R$), polarization energy ($\phi_P$), field dipole energy ($\phi_E\mu$), field gradient quadrupole energy ($\phi_{EQ}$), adsorbate-adsorbate interaction energy ($\phi_{AA}$) and acid-base interaction with the active site ($\phi_{AB}$), if the zeolite surface contains hydroxyl bridge sites (Roque-Malherbe et al. 2003). Dispersion and repulsion interactions are present in all adsorption gas-solid systems; therefore, they are nonspecific interactions (Roque-Malherbe 2010). The electrostatic interactions between the adsorbed molecules and the adsorbent framework such as polarization energy, field dipole energy and field gradient quadrupole energy depend on the structure and composition of the adsorbed molecule and the adsorbent itself (Roque-Malherbe 2010). The interaction between the adsorbent and adsorbed molecules with a noticeable quadrupole moment, such carbon dioxide molecule ($Q_{CO2} = -4.3 \times 10^{-42} \text{ C/m}^2$), leads to specific interactions in which the combination of the dispersive and electrostatic attractive interactions are stronger than the dispersion interactions. This means that a carbon dioxide molecule interacts with adsorbent surface through their dispersive and quadrupole moment.

The adsorption interaction between adsorbate and the adsorbent can also be determined with parameters calculated from the D-R adsorption sootherm equation. For example, the characteristic energy of adsorption, $E$, calculated by fitting the Dubinin-Radushkevitch (D-R) adsorption isotherm equation in a log scale with $n = 2$ to the reported adsorption data, as shown in Figure 4.11. This quantitative measurement that determines the interaction between adsorbed carbon dioxide molecules and the zeolite
Porosity is known as isosteric heat of adsorption \( q_{iso} \). The isosteric heat of adsorption can be calculated with the following equation (Bearing et al. 1972):

\[
q_{iso} (\theta) = -\Delta G + EF(T, \theta)
\]

Where:

\[
\Delta G = RT \ln \left( \frac{P}{P_0} \right) \quad \quad F(T, \theta) = \frac{\alpha T}{2} \ln[1/\theta] \left( \frac{1}{n} \right)^{1/2}
\]

\[
\alpha = -d \ln N_{a}/dT \]

\[
\theta = n_a/N_a
\]

In which \( E \) and \( n \) are parameters of the Dubinin adsorption equation. Table 4.06 shows the parameter \( E \) calculated with the D-R adsorption isotherm equation (with \( n=2 \)). For the parameter \( E \) it can be also affirmed that:

\[
E = \Delta G(1/e)
\]

where: \( \theta = 1/e \), if \( e \approx 2.71828183 \) (base of the Napierian logarithm system), then \( \theta = 1/e = 0.37 \).

With the help of this information the following equation for the isosteric heat of adsorption can be established (Roque-Malherbe et al. 2010):

\[
q_{iso} (0.37) = -\Delta G(0.37) + EF(T,0.37) = E[F(T,0.37) – 1]
\]

The \( F (T,0.37) \) using experimental calorimetric data previously reported for the carbon dioxide adsorption at 27°C on MCM-41 can be calculated. For this material it has been previously reported a \( q_{iso} = 22 \) KJ/mol for the carbon dioxide adsorption at 27°C in the range of 0.1 < \( n_a < 0.7 \) mmol/g. Also, it has been reported a characteristic energy of adsorption, \( E = 19 \) KJ/mol by fitting the Dubinin-Astakhov (D-A) adsorption isotherm equation in a log scale with \( n = 2 \) to the reported adsorption data. With this information it was able to estimate the following:

\[
F(T,0.37) \approx 2.16
\]
Therefore:

\[ q_{iso} = (0.37) = 1.16E \]

Table 4.06 shows the calculated \( q_{iso} \) for the modified zeolites. The obtained results of \( q_{iso} \) for the samples CSW-HFSi-0.4 and CSW-HFSi-0.1 were very similar. However, those results are greater than the \( q_{iso} \) of the previously reported ZSM-5-3020. Those results are also greater than other samples previously reported, as it can be seen in Table 4.07. With the adsorption data obtained it can be argued that there is a strong interaction between carbon dioxide molecule and the tested modified samples.

Table 4.06 Parameter calculated with Dubinin-Radushkevish isotherm equation

<table>
<thead>
<tr>
<th>Sample</th>
<th>( N_a ) [mmol/g]</th>
<th>( E_{CO_2}^{o} ) [KJ/mol]</th>
<th>( q_{iso}^{CO_2} ) [KJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5-3020</td>
<td>3.55 ± 0.01</td>
<td>33 ± 1</td>
<td>38 ± 2</td>
</tr>
<tr>
<td>CSW-HFSi-0.1</td>
<td>3.13 ± 0.01</td>
<td>40 ± 1</td>
<td>46 ± 2</td>
</tr>
<tr>
<td>CSW-HFSi-0.4</td>
<td>2.81 ± 0.01</td>
<td>43 ± 1</td>
<td>50 ± 2</td>
</tr>
</tbody>
</table>
Table 4.07  Parameter calculated with the Dubinin-Radushkevish equation for a particle packing silica, Cd, Zn, Cu and Ni-nitroprusside (NPs), dealuminated Y zeolite (DAY) and Ni MOF

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{CO2}^{[KJ/mol]}$</th>
<th>$q_{iso}^{CO2} [KJ/mol]$</th>
<th>$N_a [mmol/g]$</th>
<th>$W_{MP}^{CO2} [cm^3/g]$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-68-Silica</td>
<td>24 ±1</td>
<td>28 ±1</td>
<td>3.57 ± 0.01</td>
<td>0.170 ± 0.001</td>
<td>Farneth and Gorte, 1995</td>
</tr>
<tr>
<td>Cd-NP</td>
<td>21 ±1</td>
<td>25 ±1</td>
<td>2.67 ± 0.01</td>
<td>0.127 ± 0.001</td>
<td>Roque-Malherbe et al. 2011b</td>
</tr>
<tr>
<td>Cu-NP</td>
<td>20 ±1</td>
<td>24 ±1</td>
<td>3.23 ± 0.01</td>
<td>0.154 ± 0.001</td>
<td>Roque-Malherbe et al. 2011a</td>
</tr>
<tr>
<td>DAY</td>
<td>17 ±1</td>
<td>20 ±1</td>
<td>6.93 ± 0.01</td>
<td>0.331 ± 0.001</td>
<td>Farneth and Gorte, 1995</td>
</tr>
<tr>
<td>Ni-MOF</td>
<td>16 ±1</td>
<td>18 ±1</td>
<td>1.68 ± 0.01</td>
<td>0.080 ± 0.001</td>
<td>Cazorl-Amorós et al. 1998</td>
</tr>
<tr>
<td>Zn-NP</td>
<td>12 ±1</td>
<td>14 ±1</td>
<td>5.08 ± 0.01</td>
<td>0.242 ± 0.001</td>
<td>Roque-Malherbe et al. 2011b</td>
</tr>
<tr>
<td>Ni-NP</td>
<td>9 ±1</td>
<td>11 ±1</td>
<td>5.78 ± 0.01</td>
<td>0.275 ± 0.001</td>
<td>Roque-Malherbe et al. 2011b</td>
</tr>
</tbody>
</table>
When comparing the results presented in Tables 4.06 and 4.07, it can be noticed that the isosteric heat of adsorption of the tested samples (CSW-HFSi-0.1 and CSW-HFSi-0.4) is greater than the isosteric heat of adsorption of the other microporous materials. With this, it can be concluded that the use of this modified clinoptilolite is very favorable for the adsorption of gases such as CO$_2$. That is, this modified clinoptilolite could be used in technology for the separation or purification of gases, and thereby eliminates or reduce those gases that are not environmentally favorable.

### 4.3 Liquid-phase adsorption on dealuminated zeolites

Table 4.08 shows the result of EDAX elemental analysis of the modified Ammonium Y Zeolite and the previously reported DAY zeolite. The obtained results also show that removal of aluminum atom from the framework for the DAY-HFSi-0.1 and DAY-HFSi-0.4 samples was not significant. The low Si/Al ratio obtained of the modified Ammonium Y Zeolite shows that the dealumination treatment with HFSi was no effective as in the natural Clinoptilolite. Otherwise, the commercial DAY has greater Si/Al ratio than the modified Ammonium Y Zeolite, from which it can be concluded that the former is more hydrophobic than the latter.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Si [at%]</th>
<th>Al [at%]</th>
<th>O [at%]</th>
<th>Si/Al</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial DAY</td>
<td>58</td>
<td>2</td>
<td>39</td>
<td>29</td>
<td>(Muñiz-López et al. 2010)</td>
</tr>
<tr>
<td>DAY-HFSi-0.1</td>
<td>40</td>
<td>15</td>
<td>43</td>
<td>3</td>
<td>This study</td>
</tr>
<tr>
<td>DAY-HFSi-0.4</td>
<td>37</td>
<td>13</td>
<td>12</td>
<td>3</td>
<td>This study</td>
</tr>
</tbody>
</table>
Figure 4.12 shows the breakthrough curves, each of them obtained from the dynamic adsorption of PNP, MNP or ONP in adsorption reactor packed with commercial DAY. The breakthrough curve of PNP was obtained from a study previously reported (Muñiz-López et al. 2010). Figure 4.13 shows the breakthrough curve for 2800 ppm of methanol using the tested samples DAY-HFSi-0.4M. All the obtained breakthrough curves are an evidence of the adsorption of polar and non-polar compounds in hydrophobic zeolites.

Figure 4.12  Breakthrough curves of 1400 ppm of Orthonitrophenol (ONP), Metanitrophenol (MNP) and Paranitrophenol (PNP) samples in commercial DAY zeolite.
The obtained breakthrough curves from the adsorption of nitrophenols isomers in commercial DAY show that the breakthrough volume of ONP was greater than the MNP and PNP. Similar results have been reported by Koabaissy et al. (2008) where a solution of 3.6 mmol/L of each isomer was adsorbed in a flow reactor using FAU zeolites at pH of 4. With this result it can be stated that the less soluble compound (ONP) will be better adsorbed by DAY zeolite. The authors concluded that the decrease pollutant interaction with water causes an increase in interaction with the adsorbent. Table 4.09 shows the water solubility of each compound used in this investigation.

Table 4.10 shows the Operational Parameter of modified zeolites. The interstitial fluid velocity ($\upsilon$) was calculated from the data provided by the HPLC pump. The breakthrough time ($t_0$), the breakthrough with ($\Delta t$) and the column breakthrough capacity (Bc) were estimated from each breakthrough curve obtained. The mass transfer zone ($D_0$) was calculated from the breakthrough data.

### Table 4.09 Water solubility for each adsorbate used in this investigation

<table>
<thead>
<tr>
<th>Compound</th>
<th>Symbol</th>
<th>Water Solubility (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Nitrophenol (Orthonitrophenol)</td>
<td>ONP</td>
<td>1.26</td>
</tr>
<tr>
<td>4-Nitrophenol (Paranitrophenol)</td>
<td>PNP</td>
<td>12.6</td>
</tr>
<tr>
<td>3-Nitrophenol (Metanitrophenol)</td>
<td>MNP</td>
<td>13.5</td>
</tr>
<tr>
<td>Methyl Alcohol (Methanol)</td>
<td>MeOH</td>
<td>Miscible in water</td>
</tr>
</tbody>
</table>
Table 4.10  Operational Parameter for the DAY and for the modified zeolite DAY-HFSi-0.4M

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>F (ml/min)</th>
<th>u [mm/s]</th>
<th>t₀ [seg]</th>
<th>Δt [seg]</th>
<th>Bc [g/g]</th>
<th>D₀ [Cm]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAY</td>
<td>2 ml/min</td>
<td>2.006</td>
<td>1800</td>
<td>190</td>
<td>0.17</td>
<td>0.43</td>
<td>(Muñiz-López et al. 2010)</td>
</tr>
<tr>
<td></td>
<td>PNP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAY</td>
<td>2 ml/min</td>
<td>1.98</td>
<td>3180</td>
<td>780</td>
<td>0.29</td>
<td>0.654</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>ONP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAY</td>
<td>1.5 ml/min</td>
<td>1.5</td>
<td>2340</td>
<td>5580</td>
<td>0.16</td>
<td>4.678</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>MNP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAY</td>
<td>1.0 ml/min</td>
<td>1.0</td>
<td>1800</td>
<td>1080</td>
<td>0.084</td>
<td>1.985</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>MNP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAY-HFSi-0.4M</td>
<td>2.0 ml/min</td>
<td>1.98</td>
<td>3840</td>
<td>780</td>
<td>0.71</td>
<td>0.791</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
One of the operational parameter obtained from breakthrough curve is the breakthrough capacity (Bc), which is defined as the mass of sorbate removed by the sorbent at break point concentration. The breakthrough capacity is also termed as maximum acceptable concentration of the sorbates. From this definition it can be concluded that the mass of the ONP (higher Bc) was the adsorbate more efficiently removed by the DAY. Also, from the Figure 4.12 it can be noticed that the ONP breakthrough curve broke up later (higher estimated breakthrough point, \( t_0 \)) than the curve of MNP and PNP.

The breakthrough curve of methanol in practically hydrophilic zeolite, modified ammonium Y zeolite (DAY-HFSi-0.4M) is shown in the Figure 4.13. This sample turned out to have lower Si/Al ratio than commercial DAY. Therefore, in this sample only the small and hydrophobic molecules, such as methanol and water, could diffuse into pores fast enough and were taken up. The faujasite framework consists of sodalite cages which are connected through hexagonal prisms. The pores structures are arranged perpendicular to each other. Each pore is formed by a 12-membered ring, has a relatively large diameter of 7.4 Å. The inner cavity has a diameter of 12 Å and is surrounded by 10 sodalite cages. This means that a molecule of methanol, with a kinetic diameter of 3.8 to 4.1 Å, can diffuse within the faujasite framework without any problem.

The breakthrough capacity (Bc) obtained from the methanol breakthrough curve (Table 4.10) was greater than the breakthrough capacity (in g/g) obtained in the study realized by Meininghaus et al. (2000). In this study, the breakthrough capacity was determined from the breakthrough curve of methanol on two different zeolites, Dealuminated Y Zeolite and Mordenite.
It can be concluded that our tested zeolite (DAY-HFSi-0.4M) had a greater concentration of the sorbate at the breakthrough point; therefore, it would be recommended to use this sample with other polar solvent similar to methanol.

Figure 4.13  Breakthrough curve of 2800 ppm methanol in Dealuminated Y Zeolite  (DAY-HFSi-0.4M).
Chapter Five
Discussion and Conclusion

5.1 CO$_2$ adsorption in dealuminated clinoptilolite

In Chapter Two it was mentioned that CO$_2$ emissions has been increasing in the last years, where the burning of fossil fuel is the greatest contributor of CO$_2$ emission in the atmosphere (Figure 2.01). The electricity generation and transportation are the two sectors where the combustion of fossil fuels generates a million of metric tons of CO$_2$ to the atmosphere (see Table 2.01).

Some methodologies have been applied to the elimination or reduction of CO$_2$ emission to the environment. Figure 2.03, shows some methodologies used for the separation and capture of CO$_2$, among which are included the adsorption using microporous materials, such as zeolites and activated carbon. Sayari et al. (2011) asserts that the most suitable adsorbent for the CO$_2$ removal from flue gas has the following characteristics: high CO$_2$ adsorption capacity, fast kinetics, high CO$_2$ selectivity, mild conditions for regeneration, stability during extensive adsorption-desorption cycling, tolerance to the presence of moisture and other impurities in feed and low cost.

It has been reported in the literature that the use of natural zeolites and their modified forms offers a great advantage due to its low cost, to its great abundance in many parts of the world, to its excellent thermal and mechanical properties and to its high adsorption capacity. The use of zeolites in the separation technology and in the capture or sequestration of carbon dioxide is due to its ease ionic exchange which
facilitates tuning of gas-solid interaction energy and to the availability of extraframework cations that give strong electrostatic interactions with carbon dioxide molecule.

Hernández-Huesca et al. (1999) and Faghihian et al. (2008) are some authors cited in this work who mentioned the use of natural zeolites, such as clinoptilolite, in the gas purification of natural gas with a high content of CO$_2$. Table 5.01 shows some patents related to the use of clinoptilolite in gas separation.

Table 5.01 Survey of some patents related to the use of Clinoptilolite in gas separation

<table>
<thead>
<tr>
<th>Application</th>
<th>Gas 1 (less adsorbing)</th>
<th>Gas 2 (more adsorbing)</th>
<th>Material</th>
<th>Patent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Separation</td>
<td>CH$_4$</td>
<td>CO$_2$</td>
<td>Na-Clinoptilolite</td>
<td>US 5,938,819</td>
</tr>
<tr>
<td>(Natural gas upgrading)</td>
<td></td>
<td></td>
<td></td>
<td>US 4,935,580</td>
</tr>
<tr>
<td>Purification (Air pre-purification)</td>
<td>Air (N$_2$, O$_2$)</td>
<td>CO$_2$</td>
<td>Ca-Clinoptilolite</td>
<td>US 5,587,003</td>
</tr>
<tr>
<td>Purification (Natural gas purification)</td>
<td>CH$_4$, C$_2$’s, C$_3$’s</td>
<td>CO$_2$</td>
<td>Na-Clinoptilolite</td>
<td>US 4,935,580</td>
</tr>
</tbody>
</table>

Source: Ackley et al. 2003
Alonso-Vicario et al. (2010) noted that despite many commercially available zeolites are synthetically produced, there is a great demand for the use of natural zeolites in gas separation. Some of the natural zeolites used in gas separation are Clinoptilolite, Mordenite, Erionite, Ferrierite and Phillipsite. This author also mentioned that natural zeolites usually require activation prior to their use and a packaging process that makes their use not profitable. For the above reason, natural zeolites must have better properties that allow them to overcome synthetic zeolites in commercial gas separation.

According to the revised literature, the adsorption of some gases is dependent on the chemical and structural composition of the zeolite. Some factors which can be modified to improve the adsorption in natural zeolites are the Si/Al ratio, the type, and the number and location of the cations available in zeolite framework. For example, the Si/Al ratio in zeolites can be altered by dealumination (removal of Al atom) or desilication (removal of Si atoms) causing a change in the structural composition and the acid characteristic of the structure (Zhao 2007). Some studies have shown that the type and level of dealumination will have an impact on the structural composition of the zeolite. Table 5.02 shows a summary of some recent studies related to dealuminated clinoptilolites that were cited in this work.

In this work, the treatment applied in the dealumination of natural clinoptilolite was the use of 0.1M and 0.4 M solutions of \((\text{NH}_4) \text{SiF}_6\) or ammonium hexafluorosilicate (HFSi) and the use of 4M solution of orthophosphoric acid \((\text{H}_3\text{PO}_4)\). After these treatments, a determination of the chemical and structural properties of the tested samples took place to know if these materials were appropriate for CO\(_2\) adsorption.
Table 5.02 Some recent investigation with dealuminated clinoptilolites

<table>
<thead>
<tr>
<th>Type of zeolite</th>
<th>Treatment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural zeolites</td>
<td>Dealumination with ammonium hexafluorosilicate</td>
<td>López-Fonseca et al. (2003)</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Dealumination with hydrochloric acid</td>
<td>García-Basabe et al. (2010)</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Dealumination with 2M hydrochloric acid solutions</td>
<td>Sprynskyy et al. (2010)</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Dealumination with acid treatment</td>
<td>Hernández et al. (2005)</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Dealumination with hydrochloric acid</td>
<td>Hernández et al. (2007)</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Dealumination with metal exchange</td>
<td>García-Basabe et al. (2012)</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>Dealumination with hydrochloric acid</td>
<td>Rožić et al (2005)</td>
</tr>
</tbody>
</table>
The obtained results of the characterization showed that some of the tested samples had the suitable properties for the CO$_2$ adsorption, so they were comparable to the widely used commercial zeolites.

The result obtained in the XRD analysis showed that the modified clinoptilolites did not lose their crystalline phase, even after being subjected to different treatments such as ionic exchange with ammonium chloride (NH$_4$Cl) and dealumination with Ammonium Hexafluorosilicate and orthophosphoric acid. It was demonstrated that the structure was not destroyed, even though the clinoptilolite was subjected to high temperature (500 °C) and to acid treatment (dealumination with orthophosphoric acid). This confirms its great properties of thermal and chemistry stability.

The XRD profile obtained from the modified samples, shown in Figure 4.01, produced a match with the profile of the clinoptilolite available in the PDF-2, 2009 release database, created by the International Center for Diffraction Data. Also, the cell parameters of the modified samples, shown in Table 4.02, were similar to the cell parameters of clinoptilolite reported by Treacy and Higging (2007) presented in Table 4.01.

The thermal analysis of modified samples was evaluated from TGA derivative profiles shown in Figures 4.06 and 4.07. These profiles show the presence of two steps for water release: first step is due to the lost of mostly water, present in micropore; and the second step was related to the coordinated water known as “loosely bound water” and “tightly bound water”. It is worth mentioning that the profile of the sample was very similar to the profile of synthetic zeolite ZSM-5, classified as a very versatile catalytic.

The release of physically adsorbed water at a different temperature is typical for the energetically heterogeneous adsorbent as a zeolite. This may be related to the different adsorption energies to the framework. Roque-Malherbe (2007) explains that
most adsorbent have heterogeneous surface, that is, the heat evolved during the adsorption is dependent on the adsorption amount. He explains that a heterogeneous surface can be characterized by different surface sections, which have different adsorption energies.

The morphology of the modified clinoptilolite was analyzed with SEM micrograph. The obtained micrograph of modified clinoptilolites, shown in Figures 4.08 and 4.09, in helped to confirm the natural zeolite (CSW) primary clinoptilolite crystallite size.

The chemical composition of the modified samples, presented in Table 4.03, was evaluated with EDAX elemental analysis. With this result was demonstrated that chemical composition of modified sample was successfully altered. The ionic exchange treatment used in this work helps to replace approximately the 85% of the compensating ions present in natural clinoptilolite. With the ionic exchange with ammonium chloride, acidic zeolite (CSW-NH₄) having a form H-HEU whose acidity is comparable to H-ZSM-5, the most commercialized synthetic zeolite, could be obtained.

The presence of the compensating cations in zeolites framework is a very important factor that has been well cited in the literature. Some authors have mentioned that these cations play a very important role in determining the adsorption and gas-separation properties of zeolites. For example, Hernández et al. (2005) mentioned that the selectivity and uptake rate of gases by clinoptilolite zeolites are influenced by the type, number and location of the charge-balancing cations residing in the A-C channels. Hernández-Huesca and Aguilar-Armenta et al. (2001) mentioned that different cationic forms of a given zeolite may lead to significant differences in the selective adsorption of a given gas, due to both the location and size of the interchangeable cations, which affect the local electrostatic field and the polarization of the adsorbate. It has been shown that the presence of some cations can be a limiting factor for the adsorption of
certain gases. For example, Aguilar-Armenta et al. (2001) concluded that the slow adsorption of CH$_4$ was probably due to diffusive restrictions in zeolite channels, which was principally the result of channel blockage by Na$^+$ cations. The influence of this blockage on the adsorption rate decreased with decreasing kinetic diameter of the gas molecules.

Table 4.03 shows an increase in Si/Al ratio for the modified samples. The dealumination helped to reduce the aluminum atom from the framework causing a slight increase in the Si/Al ratio, mainly in those sample dealuminated with ammonium hexafluorosilicate (HFSi), and a moderate increase in the sample dealuminated with orthophosphoric acid (H$_3$PO$_4$). As found in the literature, the dealuminated zeolites have good hydrothermal stability, excellent catalytic activity and better adsorption capacity towards hydrophobic compounds than non-dealuminated zeolites. Also, the zeolites partially dealuminated have improved pore volume than the natural precursor.

The chemistry of the zeolites surface was analyzed with Diffuse Reflectance IR Fourier Transform Spectroscopy (DRIFTS). The DRIFT spectrum was utilized to identify the hydroxyl groups bound to the zeolite surface. As has been mentioned in the literature, the hydroxyl groups bound to the zeolite surface are the most important groups and can provide information about the chemistry of the materials. These groups are associated with the acidity and are responsible for the catalytic activities of the zeolite. The DRIFT spectrum of the CSW-HFSi-0.1, shown in Figure 4.10, presents two bands corresponding to two hydroxyl groups bound to the zeolite surface. One narrow band, corresponding to terminal silanol groups, and another band, corresponding to positively charged extra-framework aluminum, are observed in the spectrum. The presence of terminal silanol groups and extra-framework aluminum in both samples clearly shows the removal of aluminum from the framework. In the spectrum of this
sample, a band corresponding to bridging OH group could not be identified. One reason found in the literature review was that the absence of the Brønsted acid sites in the modified sample could be due to the dehydroxylation process or degradation of the Brønsted acid sites. According to Weitkamp (2000), the degradation of the Brønsted acid sites occurs when the sample is subjected to a severe heat treatment equal to or greater than 500 °C. On the other hand, García-Basabe et al. (2010) found that the reduction of bridging OH group (Brønsted acid sites) in dealuminated clinoptilolites was due to the increase in level or degree of dealumination. This affirmation was also used to explain the formation of silanol nest defects due to the of Al vacancy present in the zeolite framework.

Furthermore, in the previously reported data of ZSM-5, it was evident the presence of three bands corresponding to Brønsted acid sites, positively charged extra-framework aluminum and terminal silanol groups. In contrast to modified sample CSW-HFSi-0.1, the ZSM-5 has a noticeable band in the DRIFT spectrum corresponding to the most important hydroxyl groups, the bridging OH group with Brønsted acidic character.

It is worth mentioning that the spectrum of the modified sample, CSW- HFSi-0.1, is very similar to the spectrum of the ZSM-5 used as reference in this study. It can be concluded that the CSW-HFSi-0.1 has an acidity comparable with synthetic zeolite ZSM-5.

The study of CO₂ adsorption was utilized in this work, first, to measure the micropore volume and others parameters, and second, to study the interaction of CO₂ molecule with zeolite porosity. The micropore volume and other calculated parameter are shown in Table 4.04. In this test, the precision of the measured micropore volumes was achieved and this led us to affirm that carbon dioxide adsorption was carried out in the micropore region.
The zeolitic phase concentration \( (f) \) present in modified clinoptilolites was calculated with the help of micropore volume measured and with the micropore volume for the HEU framework of the pure clinoptilolite. The zeolitic phase concentration was high in the sample treated with lowest concentration of HFSi. However, it can be stated that the increase in the concentration of dealumination resulted in the reduction of the zeolitic phase concentration in the modified clinoptilolite. A similar result was found in the literature where natural clinoptilolite was dealuminated with HCl, producing an important loss of zeolite phase (Arcoya et al.1994).

The face composition, shown in Table 4.05, was also reduced with the increase of HFSi concentration and with the use of orthophosphoric acid. According to these results, it can be stated that the increase in the concentration of hexafluorosilicate and the dealumination with orthophosphoric acid was not favorable to produce an adsorbent comparable with commercial zeolites. On the other hand, it is noteworthy that with the treatment of 0.1 M ammonium hexafluorosilicate was possible to increase the amount of clinoptilolite in the sample. It can be concluded that the modified sample CWS-HFSi-0.1 showed a higher degree of purity than commercial zeolite ZSM-5.

The interaction of CO\(_2\) molecule with zeolite porosity was also investigated with the help of adsorption isotherm. It has been mentioned before that the quantitative measure that determines the interaction between adsorbed carbon dioxide molecules and the zeolite porosity is known as isosteric heat of adsorption \( (q_{\text{iso}}) \). The isosteric heat of adsorption, shown in Table 4.06, was calculated for the tested zeolites. The obtained results demonstrated that interaction of the CO\(_2\) molecule in dealuminated clinoptilolite porosity is stronger than other samples previously reported, as shown in Table 4.07. This strong interaction allows the modified samples to have adsorption selectivity for the carbon dioxide molecule. Therefore, the tested sample could be used in gas separation.
The adsorption selectivity of the adsorbent is strongly associated to the electrostatic interactions between the adsorbed gas molecules and the adsorbent framework. For example, in aluminosilicates zeolites, such as modified clinoptilolites, the electrostatic interactions are stronger than the sum of dispersion and repulsion interactions during the adsorption of gases with a high dipole moment, such as H$_2$O, H$_2$S, SO$_2$, and NH$_3$, or with a high quadrupole moment, such as CO$_2$. Therefore, the modified clinoptilolite has strong adsorption selectivity for H$_2$O, H$_2$S, SO$_2$, NH$_3$, and CO$_2$. Other gases with zero dipole moment and low quadrupole moment, such as H$_2$, Ar, CH$_4$, N$_2$, and O$_2$, are less strongly adsorbed in these types of aluminosilicates zeolites. The only interaction present in the adsorption of these gases is the dispersion force. Therefore, in a gas separation process, the modified clinoptilolites will selectively adsorb some gases, such as H$_2$O, H$_2$S, SO$_2$, NH$_3$, and CO$_2$, of the mixture of gases.

Aside from the above, other factors that could be considered to explain the strong adsorption of the CO$_2$ molecule by modified samples are the geometrical factor. As mentioned in Chapter Two, the framework structure of the clinoptilolite (HEU framework type) consists of three channels, a 10-member ring channel A (3.0 x 7.6 Å) which is parallel to 8-member ring channel B (3.3 x 4.6 Å). The 8-member ring channel C (4.0 x 5.5 Å) intersects channels A and B. According to Cobzaru and Oprea (2005), the effective diameter of the access windows to the clinoptilolite channels and cavities are of the size 4.4 x 3 Å and 7.9 x 3.5 Å, respectively. The clinoptilolite and other natural zeolite adsorb molecules with kinetic diameter (σ) do not exceed 4.3, 3.9, and 3.5 Å. According to Hernández–Huesca (1999), σ for CO$_2$ is 3.3 Å. It is evident that the adsorption of this gas in the clinoptilolite is not limited by steric factor. This means that the CO$_2$ molecules freely penetrate the entrance windows towards the micropore. Table 5.03 shows the kinetic diameter of CO$_2$ and other gases. From this information it can be assumed that
a molecule of hydrogen sulfide (H$_2$S) and water can be fitted into modified clinoptilolite micropore. However, a molecule of other gases, such as nitrogen, oxygen and methane, cannot be fitted into clinoptilolite micropore.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\sigma$ (Å)</th>
<th>Gas</th>
<th>$\sigma$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>3.64</td>
<td>H$_2$O</td>
<td>2.64</td>
</tr>
<tr>
<td>O$_2$</td>
<td>3.46</td>
<td>N$_2$O</td>
<td>3.17</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.30</td>
<td>H$_2$S</td>
<td>3.4</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>3.76</td>
<td>NH$_3$</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Some researchers had been using natural clinoptilolite in gas purification and separation studies (Aguilar-Armenta, 2001; Alonso-Vicario, 2010; Hernández-Huesca et al., 1999; Ackley et al. 2003). Several of these researchers concluded that natural clinoptilolite is a suitable adsorbent for the adsorption-based process, know as Pressure Swing Adsorption (PSA), used in the separation and capture of carbon dioxide. The PSA is a process based in preferential adsorption of the undesired gas on a porous adsorbent at high pressure and recovery of the gas at low pressure.

In summary, two important aspects can be mentioned from this study: the use of the low-cost and more abundant natural zeolites and the treatment used to produce great quality adsorbent and catalytic comparable to commercial synthetic zeolites. The great quality is based in its thermal, chemical and mechanical stability, in their acidity
comparable with the most commercialized synthetic zeolite (H-ZSM-5) and in their high purity, which surpasses the purity of the commercial synthetic zeolite (ZSM-5). It is also important to state that with the treatment used, an adsorbent highly selective to CO₂ gas was produced.

It was concluded that this modified clinoptilolite is a suitable adsorbent for the adsorption-based process used in the capture of carbon dioxide. Therefore, this can be used in bio-gas and natural gas cleaning, carbon dioxide recovery and gas drying. This modified clinoptilolite could be successfully applied for removing H₂O, NH₃, NO₂, SO₂, H₂S, CO₂ and other impurities from gas streams.

5.2 Liquid-phase adsorption in dealuminated zeolites

In Table 2.02 several environmental applications of natural zeolites were presented. As ion exchangers, natural zeolites have been used in the removal of some contaminants from wastewater. According to Wang and Peng (2010), the property of natural zeolites as ion exchangers depends on many factors, such as framework structure, ion size and shape, charge density of the anionic framework, ionic charge and concentration of the external electrolyte solution.

Also, the zeolites have been used as adsorbents in the removal of water pollutant. Several authors, some of them cited in this dissertation, conducted investigations on the adsorption of organic compounds from the liquid phase using natural and synthetic zeolites (Muñiz-López et al. 2009; Koubaiussy et al. 2011; Koubaiissy et al. 2008; Kaleta 2006; Khalid et al. 2004). Zeolites as adsorbent are strongly dependent on pore structure and chemical properties (Tien Tsai et al. 2009; Wang and Peng 2010). Some parameters that particularly influence the adsorption in zeolites are Si/Al ratio and the type, number and locations of cations in its structure (Ackley et al. 2003). In this part of this work we only take into consideration the Si/Al
ratio to determine the hydrophobicity of the tested samples. This was because it has been well documented in the zeolite literature that decreasing framework aluminum content (increase of Si/Al ratio) reduces the hydrophilicity of the internal void, increasing their adsorption capacity towards hydrophobic compound (Navalon et al. 2009).

Considering the slight increase of the Si/Al ratio of the modified natural clinoptilolite, this zeolite was used in the PNP adsorption in dynamic condition. However, from the results obtained, it cannot be stated that the PNP was favorably absorbed by the modified clinoptilolite. An explanation for this is that the PNP molecule cannot access the micropore of the modified natural clinoptilolite. As mentioned previously, the effective diameter of the access windows to the clinoptilolite channels and cavities are of the size 4.4 x 3 Å and 7.9 x 3.5 Å, respectively. The clinoptilolite and other natural zeolite adsorb molecules with kinetic diameter (σ) not exceeding 4.3, 3.9 and 3.5 Å. According to Koubaissy et al. (2008), the molecular size of PNP is calculated to be 6.7 Å; therefore, it can be concluded that the adsorption of the molecule of PNP in the clinoptilolite was limited by geometric factor.

The modified Ammonium Y Zeolite was also used in the PNP adsorption in dynamic conditions. The experimental variables of temperature, adsorbent mass, input flow and PBAR dimensions used before were maintained in this part of the investigation. The results obtained were not favorable to justify the adsorption of PNP by this modified zeolite under dynamic conditions. Justification for these results is based on the low hydrophobicity of the sample due to the not significant increase in the Si/Al ratio for those samples treated with ammonium hexafluorosilicate. In the literature it can be found that in faujasite, the Si/Al ratio is about 2.4. In this research, the Y zeolites which was subjected to treatment with HFSi, a Si/Al ratio of 3.0 was obtained, so it can be concluded that the treatment was not appropriate to obtain a highly hydrophobic zeolite.
In the case of commercial DAY zeolite, the molecular size of PNP was not a limiting factor to the adsorption of this organic compound. In Table 4.08 the difference of Si/Al ratio between DAY zeolite and the others modified samples can be seen. Thus, it can be concluded that, for the DAY, the geometric factor and hydrophobicity were not limiting factors for the adsorption of PNP. In the adsorption of other nitrophenols isomers, the polarity and solubility in water was a significant factor to determine the effectiveness of the adsorption capacity. In Table 4.10, it can be seen that the Breakthrough Capacity of the ONP was higher than the Breakthrough Capacity of the MNP and PNP. These results were similar to those presented by Koubaissy et al. (2008), where the lower water solubility and less polar compound was better adsorbed by FAU zeolite. The ONP has a dipole moment of 3.74, while the PNP and MNP has a dipole moment of 5.7 and 5.1, respectively (Xiaohong et. Al 2011). From this information it can be stated that ONP is less polar than PNP and MNP. Moreover, from Table 4.09 it can be stated that the ONP is the less soluble compound in water. Therefore, it can be also concluded that the smaller the interaction of the compound with water, the interaction with the adsorbent will be greater.

With the information presented above we reaffirm the importance of the use of zeolites, especially dealuminated zeolites, in the removal of organic compounds present in water. Therefore, we recommend the application of this dealuminated zeolite (DAY) in that technology, such as Packed Bed Reactor, used in the removal of water pollutant. I also recommend further research on the use of modified natural zeolites for the removal of those organic and inorganic water contaminants, especially those who are included in the National Drinking Water Regulations, of the Environmental Protection Agency.


Cairon O. 2010. Evidencing the three cationic coordination vacancies of S_{II} Na⁺ in NaY zeolite: additional insights from IR surface species. Physical Chemistry Chemical Physics. 12 (42): 14217-14216.


