SENSING, SEPARATIONS AND ARTIFICIAL PHOTOSYNTHETIC ASSEMBLIES BASED ON THE ARCHITECTURE OF ZEOLITE Y AND ZEOLITE L

DISSERTATION

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By

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ABSTRACT

The growth of zeolite membranes with controlled thicknesses in the sub-micron to micron region is examined, using zeolite L as the example. It was demonstrated that by controlling the concentration of the zeolite solid load and suspension viscosity, dip-coating provided a method to prepare zeolite seed layers of controlled thicknesses. Disk-shaped zeolite L crystals, with size distribution of 0.5-2 microns in diameter, were used as seed crystals for the growth of 2-7 micron thick membranes. By choosing the composition of the secondary growth medium, as well as time and temperature, crystal growth primarily occurred along the xy-plane in these micron plus-thickness membranes, with eventual thickness similar to the originally deposited seed layer. For the synthesis of sub-micron sized membranes, seed crystals from 20-60 nanometers were used and growth was observed along the z-axis. The optimum secondary growth conditions was found to occur at 60 hours of growth time (40 hours for sub-micron membranes) using a temperature of 110ºC with a solution composition of 10K₂O:1Al₂O₃:20SiO₂:2000H₂O. Membranes were characterized by electron microscopy and single gas permeation studies, providing confirmation of membrane densification.

Composite, defect-free membranes consisting of faujasite layers on the surface of microporous α-Al₂O₃ support disks were prepared using a two-step synthesis. Seed layers of externally synthesized nanocrystalline and sub-micron zeolite Y crystals were
deposited on the surface of the support. Polycrystalline layers of zeolite Y were formed by two different hydrothermal secondary growth procedures using growth times of 2 hours for the nano-Y seeded membranes and 7 days for the sub-micron seeded membranes. Nanocrystalline zeolite Y seeded membranes were utilized as chemical sensors for the detection of chemical warfare agents. Parallel electrodes were painted onto the surface of the membranes and impedance spectroscopy was used to monitor the change in resistance across the electrodes upon exposure to DMMP. Due to the interaction of DMMP with the zeolite, charge balancing cations within the zeolite framework can become more mobile, thus decreasing the membrane resistance. Based on this change in resistance, sensor traces were established to show that despite the good membrane sensitivity to DMMP, sensor recovery times were too long for practical applications.

Since the pores of zeolite Y are in the range of 0.74–1.3 nm, small molecules are able to pass one another inside the micropores. Therefore, two different zeolite Y membrane types were prepared from sub-micron crystallites to investigate their gas transport and separation properties. Synthesis #1 membranes were found to have single gas permeances (He) from $9 \times 10^{-10}$–$1 \times 10^{-9}$ kmol m$^{-2}$ s$^{-1}$ kPa$^{-1}$ in the temperature range of 30-130ºC, while synthesis #2 membranes had permeances from $1 \times 10^{-8}$–$1.25 \times 10^{-8}$ kmol m$^{-2}$ s$^{-1}$ kPa$^{-1}$. The separation factors of equimolar mixtures of CO$_2$ and N$_2$ were measured at temperatures ranging from 30-130ºC and at feed pressures from 1.4-4 bar. Membrane #1 was found to provide the best CO$_2$/N$_2$ separation at temperatures lower than 70ºC with separation factors approaching 550. When applying equimolar mixtures to membrane #2, separation factors as high as 250 were obtained at 80ºC, which is due to selective
adsorption of CO₂ in the sub-nanometer micropores of the membrane. For practical applications, it was determined that Synthesis #2 leads to membranes that have good connectivity between the micropores, thus leading to higher permeances and excellent CO₂/N₂ separation properties.

Molecular assemblies in green plants, which upon visible light absorption result in long-lived charge separated states, are critical in the first step for solar to chemical energy conversion in photosynthesis. Motivated by the light and chemical processes that take place in such assemblies, the objective of this research was to develop integrated photochemical molecular assemblies for the conversion of solar to chemical energy. In order to exploit the charge separation, the microstructure of zeolite Y has been utilized to develop hybridized photocatalysts using a variety of combinations of CdS, TiO₂, and Pt. Novel procedures have been developed for synthesizing nanoparticles of these three materials within the microstructure of zeolite Y. Single, binary, and ternary systems were studied for hydrogen production from water containing Na₂S and Na₂SO₃ as a sacrificial reagent under ultraviolet/visible light irradiation.

Nanoparticle junctions at the interface between CdS and TiO₂ are necessary for achieving an efficient charge separation and electron transfer. Therefore, the order in which these materials were integrated into the zeolite was optimized to provide the highest hydrogen production efficiency. The binary photocatalyst system of CdS/TiO₂-Y was found to improve the hydrogen production over CdS-Y alone by a factor of 9, while platinization was found to improve the hydrogen evolution rate by 13 times. This improvement observed for the zeolite-bound binary system is twice that observed in any previous reports when utilizing the combination of CdS and TiO₂ as photocatalysts. The
significant improvements in hydrogen production can be attributed to the ability of zeolite Y to organize these materials in a manner that provides good particle junctions, thus improved catalytic properties. The theory that the zeolite serves as an ideal host for photocatalytic materials was further demonstrated by using a second binary system consisting of Pt and TiO$_2$ within the zeolite.
To My Wife, Tabitha:

You stood by me like a rock over the last few years, even though I took you a thousand miles away from the ones we love. I thank you for all your unconditional love and support. I only wish that every man had a wife that is as wonderful as you. We are about to start a new chapter in our lives and I cannot wait to share it with you.

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Mom, you have dedicated your life to improving mine. I am excited to spend the rest of my life giving back to you and becoming the best scientist and man that I can be. Dad, even though you are not here to see this dream come true, I know you have been watching me grow into the man you once were. I miss you. I love you Mom and could not have done this without you.

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CHAPTER 1
INTRODUCTION

1.1 Energy Challenge

As the world population and its energy consumption continue to climb, there is not a more serious challenge facing humanity today than finding sources of energy for sustainable development. With the expansion of our energy hungry global economy, more and more energy is being consumed each year. Considering the five main sources of energy shown in Figure 1.1, the global annual energy consumption was near 15 TW (1 TW = $10^{12}$ W) in 2004 [1]. In general, a steady increase has been the trend over the past 40 years and energy consumption is projected to grow globally by 57 percent over the 2004 to 2030 period [2]. Various scenarios for future global annual energy demands have been proposed with estimated usage values of 25-30 TW by 2050 and 40-50 TW by 2100 [2].

The twentieth century saw a rapid twenty fold increase in the use of fossil fuels. Between 1980 and 2004, the worldwide annual growth rate was 2% and according to the US Energy Information Administration's 2006 estimate, 86% of the world’s 15 TW energy consumption in 2004 was supplied by fossil fuels (Figure 1.2) [1]. Despite fossil fuels being our main energy source, it has been realized in recent years that the supply is limited. Coal, which is considered a dirty source of energy, has become the fastest
growing fossil fuel in the last three years. The use of fossil fuels has led to severe air
pollution and increased amounts of carbon dioxide in the atmosphere. Global carbon
dioxide emissions are projected to rise by 1.8% annually between 2004 and 2030, and
despite the possible decline in CO₂ emissions from well-developed countries, these
decreases will be offset by larger increases in developing countries [3]. Records already
indicate that we are in a period of global warming, with a further rise in temperature to be
expected [4]. Therefore, clean and renewable alternative energy sources have been a key
focus in the last few decades. It has been predicted that we will need twice as much
carbon-free power by 2050 than the total power produced from all present global sources.

1.2 Clean and Renewable Energy

Renewable resources are categorized into hydroelectric, wind, biomass,
geothermal, and solar energy resources. Most of earth's available energy resources are
renewable resources and they account for more than 93 percent of total U.S. energy
reserves [5]. Figure 1.3 shows the total amounts globally that may be possible from each
resource; and also includes a proportional comparison with the total global energy
consumption in 2004 [2]. In 2004, renewable energy supplied around 7% of the world's
energy consumption and the renewables sector has been growing significantly since the
last years of the 20th century [6]. Renewable resources are available each year, unlike
non-renewable resources which are eventually depleted. A simple comparison is a coal
mine and a forest. While deforestation could deplete a forest, proper management could
generate a continuous supply of energy, whereas depletion of a coal mine generates no
further supply of energy.
Hydroelectricity is a very attractive renewable resource that should continue to be exploited wherever possible. Not only is hydropower relatively inexpensive because of no fuel costs, but it also produces essentially no carbon dioxide or other harmful emissions, in contrast to burning fossil fuels. Hydroelectricity also avoids the hazards of coal mining and the indirect health effects of coal emissions. Hydro-based plants also tend to have longer economic lives than fuel-fired generation, with some plants now in service for up to 100 years. However, the main drawback to hydroelectricity is that the total hydrological energy potential of the planet, including every river and lake, is approximately 7.2 TW [7]. Even though large dams are still being designed, hydroelectric power is probably not a major option for the future of energy production in developed nations because most major sites within these nations are either already being exploited or are unavailable for other reasons. Therefore, hydroelectric power is probably not a major option for meeting the 10-20 TW global carbon-free power requirements in the mid 21st century.

Wind is another renewable energy source which has been used by humans for thousands years. The available global wind energy estimates range from 300 to 870 TW, but a total electrical power of only 2 TW can be provided from terrestrial wind power with the use wind mills [8]. Most of this wind energy is available over the open ocean because of fewer obstructions, thus making it very difficult to harvest. Until the end of the nineteenth century, biomass was the predominant fuel. However, today it has only a small share of the overall energy supply. Based on the current production of power from biomass and its land requirements, 600 million hectares of land would be needed to
produce 3 TW from biomass [9]. This would require 31% of the total land area on earth to be covered by energy farms devoted solely to producing biomass to meet the carbon-free energy demand requirement. Given these requirements and not including the significant amount of land needed to house our expanding world population, the highest amount of energy from biomass is estimated to be 7-10 TW from the entire agricultural land mass of the planet. Other renewable energy sources, such as tidal and geothermal, are restricted to certain geographic areas of the world.

Clearly, the combination of renewable energy sources described above cannot satisfy the requirement for 10-20 TW of carbon-free power. However, in theory, renewable energy sources can easily supply the world's energy needs with the help of solar energy. Solar energy is, in fact, the only renewable resource that has enough terrestrial energy potential to satisfy a 10-20 TW carbon-free supply constraint in the future. Because of its existence for at least several billion more years, solar energy is an inexhaustible and freely available energy source. As shown in Figure 1.4, 89 PW (1 PW = 10^{15} W) of solar power falls on the planet's surface. While it is not possible to capture all, or even most, of this energy, capturing less than 0.02% would be enough to meet the current energy needs [10]. To put this into perspective, the energy that the earth receives in just one hour is more than that used by all humankind activities in a whole year. Advances in technology, growing environmental concerns and fears that conventional fuels may run out, all contribute to a steady interest in solar power as a mainstream energy source. The ultimate goal is to capture and utilize solar energy for sustainable development on a grand scale.
1.3 Solar Energy Conversion

Figure 1.5 illustrates the different strategies of solar energy conversion. On the far right, light can be directly converted into electrical energy when light shines on a photovoltaic solar cell. When light strikes a photovoltaic cell, it may be reflected, passed or be absorbed. Only the absorbed light can provide energy to generate electricity. When enough solar energy is absorbed by the material (a semiconductor, (SC)), electrons are dislodged from the material's atoms. When the electrons leave their position, they travel with a negative charge toward the front surface of the cell, which is a metal electrode (M). The resulting imbalance of charge between the cell's front and back surfaces creates a voltage potential, thus when the two surfaces are connected, electricity flows. Known for their extensive use in space programs, photovoltaic devices have been around for decades. Historically, photovoltaic cells have been used at remote sites to provide electricity in which cheaper electricity is not available, but their cost of production and their efficiency of operation have limited their utilization.

Dye-Sensitized solar cells (DSSC) have emerged as an alternative approach to the photovoltaic device for the direct conversion of sunlight to electrical energy (Figure 1.6) [11]. In a DSSC, the bulk of the semiconductor is used solely for charge transport and the photoelectrons are provided from a separate photosensitive dye. Charge separation occurs at the surfaces between the dye and the semiconductor when light is absorbed by the dye, thus leading to a photocurrent. The hole left behind on the dye is then regenerated using a solution redox couple that also serves to accept electrons from the external circuit [12]. As shown in the middle of Figure 1.5, light can also be converted to electrical and chemical energy using a photoelectrochemical cell [13]. When irradiated, the
combination of a SC and M electrode immersed in water gives rise to photoexcited electrons that are capable of reducing water to give H₂, whereas the electron vacancies oxidize water to O₂. The third approach for solar energy conversion is direct conversion into stored chemical energy in the form of carbohydrates or fuel (Figure 1.5, left). Plants use solar radiation to produce sugars (the fuel) and O₂ from CO₂ and water in a process known as photosynthesis. Even though there is still much that remains to be understood about natural photosynthesis, one can only be inspired by the elaborate construction of light harvesting assemblies and photosynthetic reaction centers of green plants that lead to the conversion of CO₂ and H₂O into carbohydrates and O₂.

1.4 Natural Photosynthesis

The sun, via photosynthesis, is the source of energy, either directly or indirectly, for all life on earth. There are two major photosynthetic organisms found in nature. Anaerobic bacteria can photochemically reduce CO₂ to carbohydrates, but are not capable of using water as an electron source for the formation of O₂. Therefore, they are not of great interest for our present purpose. Aerobic cyanobacteria, algae and green plants not only have the ability to reduce CO₂ by photosynthesis, but also oxidize water to oxygen [14].

In green plants, the formation of one molecule of O₂ from two molecules of water requires the transfer of four electrons, as does the reduction of one molecule of CO₂ to the level of glucose (eq. 1.1-2) [15]:

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad (1.1) \]

\[ 4\text{e}^- + 4\text{H}^+ + \text{CO}_2 \rightarrow 1/6(\text{C}_6\text{H}_{12}\text{O}_6) + \text{H}_2\text{O} \quad (1.2) \]
The total process of photosynthesis can be written as a catalytic reduction of carbon dioxide by water accompanied by a considerable storage of free energy (eq. 1.3):

\[ \text{H}_2\text{O} + \text{CO}_2 \rightarrow \frac{1}{6}(\text{C}_6\text{H}_{12}\text{O}_6) + \text{O}_2 \quad \Delta G^\circ = 502 \text{ KJ mol}^{-1} \quad (1.3) \]

The electron transfers occur in two different reaction systems: The interaction of Photosystem I (PS I) and Photosystem II (PS II) was suggested by Hill and Bendall in 1960 and the energetic Z scheme that they proposed is shown in Figure 1.7 \[16,17\].

The process of photosynthesis is as follows: Each photosystem contains an array of antenna pigments whose function is to harvest the absorbed light and transfer the energy to the primary photoelectron donor, a chlorophyll dimer (P₆₈₀ for PS II and P₇₀₀ for PS I). After the absorption of quantum of light, the chlorophyll dimer is excited, and a very rapid “down hill” electron transfer chain starts with high quantum efficiency. The electron vacancy left behind in the chlorophyll can extract an electron from a somewhat higher electron donor molecule. To ensure fast forward electron transfer and prevent energy wasting back reactions, a special arrangement of electron carriers are placed at specific distances in a phospholipid chloroplast membrane (Figure 1.8) \[18\]. The efficiency of the electron transfer is almost 100% with negligible back electron transfer. Finally, the oxidized manganese cluster is formed at one end of the chain and the reduced nicotinamide adenine dinucleotide phosphate (NADPH) is formed at the other. The oxidation of water and reduction of CO₂ occur at the both ends of the membrane.

1.5 Water Splitting

In his 1874 science fiction tale The Mysterious Island, Jules Verne predicted, "Water will be the coal of the future." It is a vision of infinite clean energy available for
people to use. Solar powered water splitting, if made practical, would combine two of the most abundant resources in the world, namely water and sunlight. There are several potential reactions that involve water to produce energy rich fuels; however, hydrogen involves the fewest number of electrons, has the highest energy stored per gram of fuel and for our purposes is of greatest importance. Therefore, using natural photosynthesis as a model for photochemical solar energy conversion, the concept of artificial photosynthesis has been proposed to make high-energy chemicals by using sunlight [19-24]. The light-driven splitting of water into hydrogen and oxygen is one such example and the energetics of this reaction are shown below in eq. 1.4.

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2 \quad \Delta G^\circ = 237.2 \text{ KJ mol}^{-1} \quad E^\circ = 1.23 \text{ V} \quad (1.4)
\]

Hydrogen by itself is only a means of storing energy and not a primary source of energy, but the combination of hydrogen and oxygen in a fuel cell can provide electrical energy with great efficiency. However, water does not absorb visible light and there are various other scientific hurdles to overcome. Finding a cost-effective method for photochemical water splitting to generate hydrogen would be a major advance in energy production and the critical breakthrough in moving the hydrogen economy toward reality. The accomplishment of light driven water splitting can be guided by the key steps and requirements of natural photosynthesis and in our attempts to emulate photosynthesis, it would be prudent to look at how nature has perfected it.
1.6 Artificial Photosynthetic Systems

1.6.1 Requirements for Artificial Photosynthesis

During the past two decades, significant efforts have been devoted to the study of artificial systems that mimic portions of the natural photosynthetic machinery. The construction of a biomimetic supramolecular system that consists of various elements that can carry out the function of natural photosynthesis is a long-term goal in this area of research. This is a challenging goal because success requires integration of multiple chemical functions in a stable chemical architecture. As in natural photosynthesis, separate half-reactions can be addressed separately and combined at a later stage into a single device. Complexity is unavoidable because of multifunctional requirements such as light absorption, energy transfer, electron transport, and redox catalysis. There is a need to arrange and integrate functional groups and to provide an overall structural hierarchy.

1.6.2 Photochemical Systems

From our present understanding, emulating nature is possible as far as light harvesting, oxygen evolution, electron propagation and the general architecture. However, for hydrogen production, we have to rely on our ingenuity, whereas plants produce NADPH instead. Natural photosynthesis is ideally compartmentalized to keep the charge separated species spatially isolated. The three important components of the reaction center are chlorophyll, the light absorbing sensitizer, pheophytin, the electron acceptor and tyrosine, the electron relay. Therefore, an artificial photosynthetic system needs a light collecting and energy propagating component, a redox unit, the means for
propagating electrons and catalysts with the components arranged in the appropriate spatial orientation. Figure 1.9 illustrates the minimal number of elements and processes required in a molecular assembly for artificial photosynthesis. The multifunctional requirements of artificial photosynthesis lead to the concept of the “integrated modular assembly” as described by Meyer et al [19,25]. In the integrated modular approach, reaction “modules” are linked together to construct reactive molecular assemblies. Energy conversion is based on light absorption and electron transfer.

Since water itself does not absorb solar radiation, except for infrared radiation, a photosensitizer molecule (P) is needed that would absorb photons of light of appropriate energy to generate a high energy state (P*). A suitable electron acceptor (A) is needed to undergo a fast electron-transfer quenching reaction of the donor- photosensitizer-acceptor (D-P-A) array. The quenching is driven by a favorable free-energy change with $\Delta G^o < 0$, either oxidatively, $D-P^*-A \rightarrow D-P^+-A^-$, or reductively, $D-P^*-A \rightarrow D^+-P^-A$.

The spatially separated oxidative and reductive redox equivalents ($D^+$ and $A^-$) are achieved by electron transfer, $D-P^+-A^- \rightarrow D^+-P^-A^-$ or $D^+-P^-A \rightarrow D^+-P^-A^-$, also driven by $\Delta G^o > 0$. Finally, the separated charges are used in redox reactions to yield the final energy conversion products such as $H_2$ and $O_2$. The latter process can be slow because of its multi-electron nature, whereas the competing and energy wasting back electron transfer is typically very fast. In most systems, a catalyst is required to help speed up the generation of fuel.

Two approaches have dominated research in this area. One has been based on the metal-to-ligand charge transfer (MLCT) excited states of metal polypyridyl complexes [26-28]. A second is based on electron propagation from the coupling of inorganic
semiconductor nanoparticles and their incorporation into molecular assemblies. Both approaches utilize the same underlying physical principles—systematic molecular assembly strategies. Only the later case will be discussed.

1.6.3 Photosensitizers (Electron Donor)

Cadmium sulfide, CdS, is an n-type, direct bandgap, II-VI semiconductor that has been primarily used in photocell applications. Bulk CdS crystallizes into two different forms, the more stable hexagonal structure and the zinc blende or cubic phase, depending on the synthesis conditions and temperature. The bandgap of CdS at room temperature is approximately 2.4 eV, which corresponds to 520 nm, thus giving the solid an orange appearance [29]. The absorption spectrum of CdS in the ultraviolet/visible region is dominated by an increasing absorption to the blue of its bandgap, which is due to increasing energy levels. Irradiation of CdS with light exceeding the bandgap energy promotes an electron from the valence band (VB) to the conduction band (CB), thus leaving a positively charged hole behind, as shown in Figure 1.10 [30]. The spatial separation of this electron-hole pair (also known as an "exciton") can be calculated using the Bohr formula (eq. 1.5):

\[ r = \frac{\varepsilon h^2}{4\pi^2 m_r e^2} \]  

(1.5)

where \( r \) is the radius of the sphere defined by the 3-dimensional separation of the electron-hole pair, \( \varepsilon \) is the dielectric constant of the semiconductor and \( m_r \) is the reduced mass of the electron-hole pair. For CdS, the Bohr excitonic radius is roughly 3 nm. If the
physical size of the semiconductor approaches that of the excitonic Bohr radius, unusual quantum confinement effects are observed, which are manifested as quantization of the energy levels in the semiconductor and as an increase in the bandgap of the semiconductor particle. Alternatively, quantum confinement can be viewed as the electronic intermediate between bulk solid (bands) and molecule (bonds). Semiconductor nanoclusters in this size regime are therefore also known as "quantum dots."

The most recent work on CdS has dealt primarily with the photophysics of quantum confined nanoparticles. Using ultrafast time-resolved spectroscopy, it has been shown that light induced electronic transitions from the valence band to the conduction band of CdS occur on a timescale faster than 500 femtoseconds [31,32]. Depending on the size and quality of the CdS nanoparticles, the excited state of CdS can have a lifetime ranging from a few hundred picoseconds up to a few nanoseconds. This is long enough for the excited state of CdS to efficiently transfer its energy to another molecule (a quencher), by either energy transfer or electron transfer. In the absence of a quencher, the excited state undergoes deactivation through both non-radiative and radiative decay pathways. The photocatalytic action of colloidal or suspended semiconductor particles is based on the generation of electrons and positive holes which rapidly move to the surface of the particles and initiate redox processes. Because of its visible region light absorption, CdS has a suitable conduction band potential (-1.1 V vs. NHE) to reduce the H^+ ion effectively. Therefore, CdS is has been shown to generate H_2 as a standalone photocatalyst [33-36]. However, the utility of CdS as a photocatalyst has been limited because photogenerated holes in the valence band tend to react with CdS itself, thus causing anodic decomposition or photocorrosion. To prevent the deleterious
photocorrosion of the semiconductor, Scheme 1.1 shows that a sacrificial donor such as sulfide can be added to scavenge the valence band holes [37-45]. The product of this oxidation reaction (disulfide or polysulfide), however, has an absorption that overlaps and interferes with the light absorption of CdS. This can be avoided by conducting the experiment in the presence of sulfite, which undergoes a spontaneous reaction with disulfide, yielding optically transparent thiosulfate and sulfide.

The other disadvantage of using semiconductors, such as CdS, for photocatalytic reactions is their lower quantum efficiency. It is understood that the low quantum efficiency mainly results from the poor charge separation efficiency due to a very fast recombination of photo-produced electrons and holes on the semiconductor particles. Another contribution to the lowered efficiency in semiconductors is the presence of low lying surface states can act as electron traps or sinks. Therefore, to suppress the recombination and consequently improve the charge separation efficiency, electron acceptors are commonly utilized.

1.6.4 Electron Acceptors

In 1972, Fujishima and Honda discovered the phenomenon of photocatalytic splitting of water on a titanium dioxide (TiO₂ or titania) electrode under ultraviolet light [46]. Since then, enormous efforts have been devoted to the research of this inorganic semiconductor, which has led to many promising applications. Titania as a photocatalyst is regarded as the most efficient and environmentally-benign and it has been widely used for the photodegradation of various pollutants. The principle of the titania photocatalytic reaction is the same as that described for CdS. Upon absorption of photons with energy
larger than the bandgap of TiO$_2$, electrons are excited from the valence band to the conduction band, creating electron-hole pairs. These charge carriers migrate to the surface and react with the chemicals adsorbed on the surface.

Since its commercial production in the early twentieth century, TiO$_2$ has been widely used as a pigment in sunscreens, paints, ointments, toothpaste, etc [47]. Titanium dioxide occurs in nature as the well-known naturally occurring minerals rutile, anatase and brookite. The most common form is rutile, while anatase and brookite both convert to rutile upon heating [48]. These three structural forms or titania all contain six coordinate titanium. The bandgap of TiO$_2$ at room temperature is 3.2 eV, which corresponds to 388 nm, thus giving the solid its white color. However, only about 3–5% of the solar spectrum falls in the wavelength range for titania, thus limiting the efficient utilization of solar energy for TiO$_2$.

The efficient use of sunlight has thus become an appealing challenge for developing photocatalytic technologies using TiO$_2$. Therefore, TiO$_2$ has been used as an electron acceptor in light harvesting chromophore-quencher systems due to its electronic structure and location of the conduction band. To improve the response of titania to visible light, it has been sensitized by coupling it to a narrow bandgap semiconductor with a higher CB than that of TiO$_2$. In this sensitized TiO$_2$, charge injection from the CB of the narrow bandgap semiconductor to that of TiO$_2$ can lead to efficient and longer charge separation by minimizing the electron–hole recombination. For water splitting applications, it has been shown experimentally that the anatase form is the more active phase, despite the rutile crystalline structure being the most stable.
1.6.5 Photo-Induced Electron Transfer

It is well-known that electron acceptors adsorbed onto or physically attached to the surface of CdS nanoparticles quench the exciton emission by an electron-transfer process upon irradiation [49-55]. Excited-state electron transfer of CdS to electron-transfer acceptors, such as titanium dioxide (TiO$_2$) and metallic platinum (Pt) have been well studied. Upon absorption of light, CdS generates a high-energy excited state CdS* (eq. 1.6). An excited electron can then be transferred to Pt or TiO$_2$, resulting in a reduced acceptor and oxidized donor (eq. 1.7). The charge recombination of the electron and the electron hole is a thermodynamically favorable reaction; therefore, the rate of the back electron transfer (BET) is comparable or faster to that of the forward electron transfer. To prevent BET, electron donors such as alcohols or sulfides, can be used to remove the hole from CdS (eq. 1.8).

\[
\begin{align*}
\text{CdS} & \rightarrow \text{CdS}^* \\
\text{CdS}^* + \text{TiO}_2 \text{ or (Pt)} & \rightarrow \text{CdS}^+ + \text{TiO}_2^- \text{ or (Pt)} \\
\text{S}^{2-} + \text{CdS} & \rightarrow \text{CdS} + \text{S}
\end{align*}
\]

Previous investigations have indicated that the inter-particle electron transfer between CdS and TiO$_2$ semiconductor nanoclusters is influenced by changing the particle size of the two components [56]. The relative energy difference between the conduction bands of CdS and TiO$_2$ provides the driving force for the electron transfer between these two semiconductors. For larger particles, the bottom of the conduction band for TiO$_2$ is lower than that of CdS by about 0.5 eV, favoring injection from photoexcited CdS into TiO$_2$, as depicted in Figure 1.11. However, upon quantization of TiO$_2$, photo-induced electron transfer is far less efficient due to changes in the energy levels of the
semiconductor materials. Coupling of two such semiconductor systems has a beneficial role in improving charge separation and thus provides an early conceptual basis for artificial photosynthesis.

1.6.6 Kinetics of Electron Transfer Reactions

The electron transfer reaction between CdS and TiO₂ can be considered an outer sphere or non-bonded electron transfer, which refers to an electron transfer event that occurs between chemical moieties that remain separate species before, during, and after the transfer event. This is opposed to inner sphere electron transfer in which the two sites undergoing ET are connected by a chemical bridge. Because the ET in outer sphere electron transfer occurs between two non-connected species, the electron is forced to move through space from one redox center to the other. Outer sphere electron transfer is generally enthalpically less favorable than inner sphere electron transfer, but by the same token, outer sphere electron transfer is usually entropically more favorable than inner sphere electron transfer because the two sites involved do not have to go through the ordering processes associated with the formation of a bridge [57].

Classical or Marcus theory is the most widely accepted theory of outer-sphere electron transfer, and according to recent work by Kamat et al., can be applied to charge transfer between two semiconductors [58]. Outer sphere electron has been used to describe a number of important processes in chemistry and biology, including photosynthesis. The electron transfer rate constant, according to the classical model, is given by eq. 1.9,

\[ k_{ET} = \kappa \nu_n \exp \left( -\frac{\Delta G^*}{RT} \right) \]  

(1.9)
where $\kappa v_n$ is the frequency factor and $\Delta G^*$ is the free energy of activation required for the electron transfer between the sensitizer and the acceptor to occur the Franck-Condon principle (Figure 1.12) [59,60]. The activation energy barrier ($\Delta G^*$) can be calculated from eq. 1.10 according to Marcus theory.

$$\Delta G^* = \frac{\lambda}{4} \left[ 1 + \left( \frac{\Delta G^o}{\lambda} \right)^2 \right]$$  (1.10)

Eq. 1.14 expresses the barrier height or the free energy activation in terms of the overall free energy of reaction $\Delta G^o$ and the reorganization energy, $\lambda$, which is composed of solvational ($\lambda_0$) and vibrational components ($\lambda_i$) (eq. 1.11).

$$\lambda = \lambda_0 + \lambda_i$$  (1.11)

Therefore, based on Marcus theory, the rate of electron transfer can be written as the following (eq. 1.12):

$$k_{ET} = \kappa v_n \exp \left\{ - \left[ \frac{(\lambda + \Delta G^o)^2}{4\lambda RT} \right] \right\}$$  (1.12)

Eq. 1.12 describes the relationship between the rate constant ($k_{ET}$) and the driving force of the reaction ($\Delta G^o$). According to the Marcus theory, the electron transfer barrier decreases as $-\Delta G^o$ increases until $-\Delta G^o = \lambda$, at which point classical electron transfer becomes barrierless. As illustrated in Figure 1.12, the barrier then increases as $-\Delta G^o$ increases further. Figure 1.12 shows the changes in the electron-transfer barrier in the classical limit at fixed $\lambda$ according to eq. 1.12 for three cases: (A) in the normal region with $-\Delta G^o < \lambda$, (B) at the barrierless point, where $-\Delta G^o = \lambda$ and $k_{ET} = v_{ET}$, and (C) in the inverted region, where $-\Delta G^o > \lambda$. The inverted region was initially predicted by Marcus,
and has been observed experimentally [61-69]. From Marcus’s theory, it is clear that for an efficient artificial photosynthetic system, it would be advantageous to have the forward ET in the normal region and the back electron transfer in the inverted region, thereby maximizing the charge separation.

In order to fully understand how Marcus theory can be applied to electron transfer between semiconductors, careful charge transfer studies involving size-controlled cadmium selenide (CdSe) and TiO₂ nanoparticles were carried out by Kamat et al [70]. Through the coupling of CdSe and TiO₂ nanoparticles, electron injection from CdSe into TiO₂ was studied by ultrafast time-resolved spectroscopy. It was determined that the rate of electron transfer was dependent upon the size of the CdSe nanoparticles due to increasing bandgap energies and a conduction band shift to more negative potentials.

The driving force (ΔG°) for the electron transfer between CdSe and TiO₂ is dictated by the fact even the largest CdSe particles studied have a conduction band potential that is 0.3 V more negative than that of TiO₂. The smallest CdSe nanoparticles examined were determined to be 0.8 V more negative than the conduction band for titania. Figure 1.13 shows the energy gap dependence on the electron transfer rate, in which an enhanced transfer rate was observed as the particle size decreased [58]. The driving force of 0.8 eV is at or close to the reorganization energy (λ); therefore, a normal Marcus region was expected in which the rate of electron transfer increases with the driving force. This small energy difference obtained by decreasing the particle size was sufficient to increase the electron transfer rate by nearly 3 orders of magnitude.
1.7 Zeolites

Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves." The term molecular sieve refers to a particular property of these materials in which they can selectively sort molecules based primarily on a size exclusion process. This is due to a well-defined crystalline pore structure of molecular dimensions. Their three-dimensional frameworks generally contain silicon, aluminum and oxygen in a corner-shared SiO$_4$ and AlO$_4$ tetrahedral arrangement [71]. The presence of Al in the zeolite framework leads to a charged framework and cation-exchange capabilities [72]. A wide variety of cations, such as Na$^+$, K$^+$, Cd$^{2+}$, Mg$^{2+}$ and others, can be accommodated into the porous structure of zeolites. These positively charged ions can readily be exchanged for others in solution. Under ambient conditions, the zeolite will fill its void volume with water giving it the following formula for a unit cell,

$$M_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot w\text{H}_2\text{O}$$

where $n$ = cation valence, $y/x$ = a ratio usually in the range of 1-5, and $w$ = number of water molecules.

As of January 2008, 175 unique zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known [73]. A selection of different zeolites with their framework codes are shown in Figure 1.14. The vertices in these structures represent the tetrahedral atoms and the lines represent bridging oxygen atoms. As illustrated in Figure 1.14, these zeolite structures are built by the same secondary building units (SBUs), but via different connections. Traditionally, zeolites have found extensive applications in petroleum processing and heterogeneous catalysts because of chemical reactions that take place within their internal cavities. Recent developments
have seen a dramatic expansion in their use for the synthesis of fine chemicals [74].
Because of their well-defined microporosity, zeolites have been used as host materials
that have been developed into new nanocomposites with optical, magnetic, or electrical
properties [75-80].

1.7.1 Linde Type L

The structure of Linde Type L (LTL or zeolite L) is illustrated in Figure 1.15 [81].
As shown in Figure 1.15a, LTL consists of cancrinite cages linked by double 6-rings
(D6R). These units form columns in the c-direction, which are connected by oxygen
bridges and thus give rise to 12-membered rings with a free diameter of 7.1 Å (Figure
1.15b). As a consequence, zeolite L consists of one dimensional channels running
through the whole crystal, with a largest free diameter of about 12.6 Å and a unit cell
length of 7.5 Å. When all of the SBUs are properly arranged, the main channels become
linked and give rise to the cylindrical morphology illustrated in Figure 1.15c. The Si/Al
ratio for LTL is typically 3.0 and the number of one-dimensional channels lying parallel
to the c-axis is equal to \(0.265(d_c)^2\), where \(d_c\) is the diameter of the cylindrical shaped
zeolite in nanometers [81].

Fine tuning of the size and morphology of zeolite L crystals in the range of 30 nm
to 3000 nm is possible by either changing the composition of the starting gel for
otherwise constant reaction conditions or by modifying the synthesis conditions [81-85].
Figure 1.16 shows four of the possible morphology types for zeolite L. Nanocrystalline
LTL cylinders are shown Figure 1.16a, which have an average particle size of 30-60 nm.
Figure 1.16b represents the most common LTL crystal shape, which are cylindrical rods
ranging from 1-6 µm in length. The disk-like LTL crystallites shown in Figure 1.16c-d can vary in thickness from 0.1-1 µm and can have thicknesses up to 2 µm. The synthesis procedure for obtaining these various types of LTL is detailed in Chapter 2, where the emphasis is focused on nanocrystalline and disk-like zeolite L.

1.7.2 Faujasite Zeolite Y

Zeolite Y exhibits the FAU (faujasite) structure. Figure 1.17a shows that the zeolite Y structure is made up of sodalite cages (β-cages) connected by double 6-rings (D6R). These units give rise to a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes (Figure 1.17b). Due to the tetrahedral arrangement of 10 sodalite cages, zeolite Y is defined as having a window diameter of 7.4 Å, since the aperture is defined by a 12 member oxygen ring. These windows lead into a larger cavity known as the supercage, which has a diameter of 13 Å. The unit cell of zeolite Y is cubic with Fd-3m symmetry [86-88]. The Si/Al ratio for zeolite Y can be quite broad because it can exist at low aluminum contents; however, it is typically around 2.5. Unlike zeolite L, only the crystal size of zeolite Y can be modified. The size of zeolite Y can be tuned between 25 nm to 1.5 µm, depending on the composition of the starting gel, as well as the presence of templating agents upon which the zeolites are built.

1.8 Zeolite Based Molecular Assemblies

Zeolites have played an important role in the construction of multifunctional molecular assemblies to mimic natural photosynthesis [89]. In natural photosynthesis, the
multiple chemical functions including the oxidative and reductive parts of the photochemical chains are integrated in a stable chemical architecture. Zeolites, as a result of their ability to compartmentalize reactants and products, provide an ideal platform for these assemblies since spatial separation of charge is an obvious means to prevent energy wasting back electron transfer [90,91]. The ion-exchange ability of zeolites and their microporosity make it possible to introduce molecules into the structure. Electron donors (CdS) and acceptors (TiO₂ or platinum) are easily incorporated into zeolites by an ion-exchange approach [34,38,41,92-99].

For most applications, the use of zeolite particles is impractical due to the fact that newly formed redox species can react with each other, thus decreasing the efficiency of the electron transfer reaction. However, zeolite crystallites can be beneficial in the development of an artificial photosynthetic assembly, which is briefly described here. Although there are no reports of CdS and titania being successfully incorporated into the microporous structure of zeolites at the same time, Fox et al. first investigated the photoactivity of zeolite supported CdS in the presence of other co-catalysts [34]. Upon photoexcitation of the CdS within the zeolite, the hydrogen evolution was found to be dependent upon the availability of a catalyst on the surface of the CdS particles. Although hydrogen was detected in the absence of co-catalysts, evolution rates were found to increase from 8 to 25 times with the deposition of either platinum or zinc sulfide. This work was later extended by the use of titanosilicate zeolites known as ETS-10, which contain –Ti-O-Ti- quantum wires in their framework. Upon the incorporation of CdS into the framework, the results suggested that the encapsulation of CdS in ETS-zeolites was
effective for separating charge-carriers photogenerated in CdS and for improving both the activity and stability [100,101].

Nanocrystalline zeolites with high surface areas have also been used as hosts; however, as previously mentioned, zeolite particles can be impractical for use in a photosynthetic assembly [102]. In natural photosynthesis, the membrane plays a key role in keeping the oxidative and reductive part of the photochemical chains separated. Defect-free zeolite membranes have been prepared via secondary growth methods and charge transport across the membrane has been demonstrated [103]. Using ruthenium based photosensitizers on the membrane surface and viologens inside the membrane, electron propagation was verified by the formation of a propylviologen sulfonate radical on the other side of the membrane, according to the scheme shown in Figure 1.18 [104]. Despite the remarkable progress in the construction of molecular assemblies to enhance population of the charge-separated states, challenges still exist both to understand the mechanisms and to harvest the stored energy for useful chemical work.

1.9 Mixed Gas Separations

The manufacturing of fuel and chemicals has indeed been subject to large technological improvements during the past century. Headway has been made for instance in catalysis, heat integration, product purification and effluent clean-up. However, further improvements are still needed in processes and catalysts, as well as novel manufacturing technologies. Membrane reactors are one of such evolving technologies that have huge promise to deliver processes that are more compact, less capital intensive, offer improved conversion for equilibrium limited reactions, allow
controlled operation and have substantial savings in energy and resultant costs due to feed/product separation at elevated process temperatures [105]. Although the concept of membrane reactors has already been introduced in the 1950s, it was only with the advent of new inorganic materials and high-temperature membrane systems in the last 30 years that considerable growth in the research and development of membrane reactor technology has been achieved [106,107].

Inorganic membranes, which contain sub-nanometer pores, are useful for the separation of gas mixtures under severe conditions where organic membranes are not functional. Gavalas et al. reported the first successful preparation of an amorphous silica membrane, which had a high hydrogen permselectivity in pores of a Vycor glass tube [108]. Using a sol-gel technique, Raman and Brinker prepared a silica-based membrane capable of separating carbon dioxide from methane [109]. Zeolites, on the other hand, can be designed to separate CO₂, N₂, CH₄, and H₂, as well as hydrocarbon molecules. van Bekkum et al. prepared an MFI-type zeolite membrane on a porous stainless steel disk that showed a high permselectivity of n-butane to i-butane at room temperature [110]. Kusakabe et al. have reported numerous types of gas separations involving zeolite membranes of the faujasite type [111-118]. In zeolite-based membrane reactors, the membrane normally consists of a thin film of a mesoporous or microporous zeolite on a macroporous support, typically α-Al₂O₃, stainless steel or carbon. This thin film may simultaneously serve (i) as both a catalyst and a permselective membrane, (ii) as a permselective diffusion barrier or (iii) as an inert non-selective reactant distributor. Permselectivity depends on the size of the permeating molecules relative to the pore size of the membrane, the chemical nature of the permeating molecules and the membrane
material. Also, the adsorption properties of the membrane can greatly contribute to improved separations in a mixture of components with different adsorption characteristics. Under these circumstances, the stronger adsorbing compound will permeate preferentially [119].

1.10 Scope of this Work

The research described in this thesis is aimed at developing zeolite-based artificial photosynthetic assemblies and zeolite membranes with the goal of photolytic water splitting, gas sensing and gas separations. To improve the charge propagation across the zeolite membrane, we developed the technology for the eventual synthesis of oriented zeolite L membranes (Figure 1.19). Four different morphology types of zeolite L were synthesized and characterized by electron microscopy and X-ray diffraction. By carefully controlling the zeolite concentration and solution rheology, uniform zeolite L seed layers were deposited onto porous alumina supports using dip-coating. Micron and sub-micron thick membranes were prepared using optimized secondary growth conditions. The thickness and densification of the membranes were characterized by SEM and spectroscopic ellipsometry, while the crystal structure was determined using X-ray diffraction. Single gas permeation was utilized to verify the integrity of the membranes.

We also explored faujasite-type zeolite membranes for use as chemiresistive sensors in the detection of chemical warfare agents, as well as in mixed gas separations. We found that zeolite Y membranes could be prepared ranging from a few hundred nanometers to several microns thick, depending on the composition of the zeolite seed layer. For the zeolite membranes applied as sensors, we found that dense, defect free
membranes could be synthesized in a single day using nanocrystalline zeolite Y, with growth times as short as two hours. In order to study the integrity of the membranes, electron microscopy was used to monitor the transformation of the zeolites into membranes. Using electrodes on the membrane surface, impedance spectroscopy was applied to monitor the changes in resistance within the membrane upon exposure to simulants of chemical warfare agents. This data was then used to show that the membranes could be utilized as sensors for the rapid detection of DMMP.

Previous zeolite Y membranes synthesized by the Dutta research group were prepared using a procedure which required up to seven days before dense membranes were obtained [89,103,104,120,121]. Following similar procedures, large surface area zeolite Y membranes were produced using sub-micron seed crystals. Single and mixed gas permeation experiments were used to characterize the interconnectivity of the membranes, as well as measure the separation ability of the zeolite Y membranes. This study provided us with a wealth of information about how zeolite Y membranes are formed and the optimal conditions for generating defect free membranes that are capable of separating mixed gases. The successful synthesis of large surface area, defect free zeolite Y membranes also presents new possibilities in artificial photosynthetic assemblies and charge propagation.

Use of zeolite membranes allows for spatial separation of the hole and electron chemistry, thereby minimizing energy wasting recombination processes. Even without a membrane, the framework of type Y zeolite crystallites can be used to organize a hybridized photocatalyst system for the photoconversion of water into hydrogen. In order to prevent the energy wasting electron/hole recombination in zeolite bound CdS, we
developed a systematic method for the incorporation of three different catalytic materials into the microporous structure of zeolite Y. CdS, TiO₂, and Pt were all synthesized within the framework of zeolite Y using novel techniques in order to maximize the amount of nanoparticle contact between the materials. Using the ion-exchange properties of zeolite Y, ionic species of cadmium, titanium and platinum were converted into their respective catalytic forms of CdS, TiO₂ and metallic Pt. Optical and spectroscopic studies, as well as electron microscopy, showed the successful incorporation of all three materials. Several different synthesis strategies were used to optimize the catalytic water splitting ability of the zeolite-based photocatalyst. Due to the ability of zeolite Y to organize these materials in close proximity, the charge transfer efficiency and hydrogen activity were greatly improved.
1.11 References


\[
\begin{align*}
\text{CdS} & \rightarrow e_{\text{CB}}^- + h_{\text{VB}}^+ \quad \text{(I)} \\
2e_{\text{CB}}^- + 2\text{H}_2\text{O} & \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{(II)} \\
\text{CdS} + 2h_{\text{VB}}^+ & \rightarrow \text{Cd}^{+2} + \text{S}_2^{2-} \quad \text{(III)} \\
2\text{S}^{2-} + 2h_{\text{VB}}^+ & \rightarrow \text{S}_2^{2-} \quad \text{(IV)} \\
\text{S}_2^{2-} + \text{SO}_3^{2-} & \rightarrow \text{S}_2\text{O}_3^{2-} + \text{S}^{2-} \quad \text{(V)}
\end{align*}
\]

**Scheme 1.1:** Reaction scheme of the sulfide/sulfite sacrificial electron donor system.
Figure 1.1: Total world energy demand.
Figure 1.2: Breakdown of world’s 2004 power usage by fuel type.
Figure 1.3: Possible total amounts of carbon-free energy resources.
Figure 1.4: Solar energy as it is dispersed on the planet and radiated back to space.
Figure 1.5: Schematic of energy conversion strategies.
Figure 1.6: Schematic of operation of the dye-sensitized electrochemical photovoltaic cell.
Figure 1.7: “Z scheme” of photoelectron transfer in natural photosynthesis.
Figure 1.8: Schematic of natural photosynthetic architecture.
Figure 1.9: Schematic of molecular assembly for artificial photosynthesis.
Figure 1.10: Energy level diagram of CdS.
Figure 1.11: Energy level diagram for CdS/TiO₂ coupled system.
Figure 1.12: Free energy-coordinate curves illustrating the three cases for electron transfer: (A) in the normal region with $-\Delta G^0 < \lambda$, (B) at the barrierless point, where $-\Delta G^0 = \lambda$ and $k_{ET} = v_{ET}$, and (C) in the inverted region, where $-\Delta G^0 > \lambda$. 
Figure 1.13: Dependence of $\Delta G^\circ$ on CdSe nanoparticle size for electron transfer.
Figure 1.14: The framework structure of zeolites.
Figure 1.15: Secondary building units and framework structure of zeolite L.
Figure 1.16: TEM/SEM images depicting the different morphology types of zeolite L.
Figure 1.17: Secondary building units and framework structure of zeolite Y.
Figure 1.18: Charge transport through a zeolite Y membrane.
Figure 1.19: Zeolite L membrane based artificial photosynthetic system.
CHAPTER 2
SYNTHESIS OF ZEOLITE L MEMBRANES WITH SUB-MICRON TO MICRON THICKNESSES

2.1 Introduction

Zeolites have been extensively studied for industrial applications, including catalysis, ion exchange, gas separation, nuclear waste disposal, chemical sensing and light-harvesting devices [1-5]. The preparation of supported zeolite films/membranes with controlled microstructure is attractive for a number of applications, particularly for separations and catalytic applications. In supported zeolite membranes, the support provides the required mechanical strength without imposing additional mass transfer resistance. Generally, the intercrystalline porosity [6,7], crystal size [8], crystal orientation relative to the membrane layer [9,10] and thickness and uniformity of the zeolite membranes [11] determine their performance. The framework of the Linde Type L zeolite (LTL) provides ideal geometrical properties for the arrangement and stabilization of incorporated supramolecular systems due to its one-dimensional pore structure [12,13]. To the best of our knowledge, only one report of zeolite L films/membranes has been described, in which Tsapatsis et al. prepared a nanocrystalline zeolite L/boehmite cast that was later grown into a thin, randomly oriented self-supported
film [14,15]. These fragile nanocrystalline casts were converted into much larger zeolite L crystals following secondary growth.

The emphasis on the development of novel architectures for integrating photochemical molecular assemblies into practical devices for conversion of solar to chemical energy has rapidly increased due to the increasing demands of energy consumption. Dutta et al. have demonstrated that ruthenium-based photosensitizers can be attached to the pores of zeolite Y membranes for light harvesting reactions [16]. Since the zeolites provide the proper spatial arrangement for long-lived charge separation, it was shown that a sturdy zeolite membrane provided access to the photochemically generated redox species for reactions such as the conversion of water to H₂ [17].

Motivated by these demands, this chapter is focused on the development of zeolite L membranes with controlled thickness for the eventual preparation of oriented zeolite L membranes. Factors such as seed layer deposition, secondary growth conditions, time and temperature on the growth of sub-micron to micron sized membranes were examined.
2.2 Experimental Section

2.2.1 Materials

Aluminum hydroxide (Al(OH)₃, 80.5%) was purchased from Alfa Aesar. Sodium hydroxide from Mallinckrodt (NaOH, 98.8%) and potassium hydroxide from GFS Chemicals (KOH, 85%) were used. Ludox LS-30 (SiO₂, 30%) and Ludox HS-40 (SiO₂, 40%) were obtained from Aldrich (Milwaukee, WI, USA). All chemicals were used without further purification. AKP15 and AKP30 α-alumina powders were obtained from Sumitomo (Japan). The H₂O used in this study was purified by a Millipore ultrapure water system.

2.2.2 Synthesis

The influence of chemical composition on the morphology of zeolite L (LTL) seed crystals is described in the literature [15,18-22]. All zeolite precursor solutions described below were mixed in polypropylene bottles to prevent contamination.

*Disk-shaped Linde Type L Zeolites.* Disk-shaped Linde Type L zeolites were prepared from an opaque gel with the following composition:

\[ 5.4K₂O:5.7Na₂O:1Al₂O₃:30SiO₂:500H₂O \]

This precursor gel was prepared by thoroughly mixing 48.4 g of water, 1.55 g of Al(OH)₃, 5.7 g of KOH and 3.69 g of NaOH. After stirring for 15 minutes, this alkaline potassium/sodium aluminate solution becomes clear. Once dissolved, this solution was added to a vigorously stirred solution containing 36.05 g of Ludox HS-40 colloidal silica. Upon mixing the two solutions, a very thick, opaque gel is formed, which was then stirred for 15 minutes. The viscous gel was placed into a
125 mL Teflon-lined Parr general purpose digestion vessel and heated using static
conditions at 170°C for 70 hours prior to quenching in cold water.

_Nanocrystalline Linde Type L Zeolites_. Nanocrystalline Linde Type L zeolites
were synthesized from a clear solution with the following composition:
10K₂O:1Al₂O₃:20SiO₂:400H₂O. For the synthesis of nanocrystalline zeolite L, a
potassium aluminate solution was made by dissolving 0.276 g of Al(OH)₃ in an alkaline
solution prepared by dissolving 1.89 g of KOH in 5.95 g of water. This aluminate
solution was vigorously stirred for 15 minutes prior to adding to a separately stirred
solution containing 5.72 g of Ludox LS-30 colloidal silica solution, which was sonicated
for 20 minutes prior to mixing. Upon mixing, the clear solution was vigorously stirred for
15 minutes before being placed into a 25 mL Teflon-lined Parr general purpose digestion
vessel. Nanocrystalline zeolite L were produced by rotating (16 rpm) the vessel at 170°C
for 6 hours prior to quenching in cold water.

For both disk-shaped and nanocrystalline zeolite L, the zeolites were removed
from their mother liquors and centrifuged/washed with water until the pH of the
supernatant was neutral. To prevent agglomeration, the zeolite seed crystals were stored
as aqueous stock suspensions (0.054 g/mL for disk, 0.08 g/mL for nano) for the
preparation of zeolite L seed layers by dip-coating technique. In the case of using dried
zeolite powders, the neutralized slurry was dried at 60°C overnight, followed by grinding
into a fine powder using a mortar and pestle.

_α-Al₂O₃ Macro-porous Supports_. Detailed information about the macro-porous
supports, upon which the zeolite membranes were prepared, has been described
elsewhere [23]. Briefly, the macro-porous supports were prepared with commercially
available AKP15 or AKP30 high-purity alumina powder. Single batches of dispersion for colloidal filtration were prepared from 50 mL of aqueous Aluminon solution (the triammonium salt of aurin tricarboxylic acid) mixed with 50 g of α-Al₂O₃ powder. Optimum dispersion of the as-delivered powder was achieved by ultra-sonic treatment for 10 minutes at a power of 80 watts. Disk-shaped α-Al₂O₃ compacts were made by vacuum filtration on a 220 nm pore polysulfone membrane. The α-Al₂O₃ compacts were sintered at 1050°C in air for 10 hours with a heating and cooling rate was 2ºC/min. This procedure leads to a surface pore size of 40-60 nm, a porosity of 33 %, a surface roughness of ~20 nm and a He permeance of $2.8\times10^{-6}$ kmol m⁻² s⁻¹ kPa⁻¹. A surface view of a 42 mm diameter, defect free, optically smooth support is provided in Figure 2.1, which illustrates the large workable surface for seed layer deposition/membrane formation.

Zeolite L Seed Layers. Zeolite L seed layers were deposited on the alumina supports by dip-coating with a MEMDIP coating unit (Pervatech BV, The Netherlands) (Figure 2.2), using the zeolite dispersions described below. Throughout this entire study, seed layers were deposited from a single dip-coating cycle. The starting solution for the dip-coating process was prepared by mixing disk-shaped or nanocrystalline zeolite L particles into an aqueous solution of polyethyleneimine (PEI), having an average molecule weight of 1800 Daltons. Using a 0.5-1 wt% solution of PEI in water, a 0.95-2.03 mg/mL dispersion of disk-shaped LTL (0.08-2.0 mg/mL for nanocrystallites) was prepared in an ultrasonic bath for one hour. Throughout the sonication, the temperature of the dispersion was maintained below 20°C. During dip-coating, the substrate was withdrawn at a speed of 0.01 m/s from a watch-glass filled with 15 mL of the zeolite suspension. The zeolite L seed layers were dried overnight at approximately 40°C and
then fired in air at a temperature of 500°C (0.5°C/min heat/cool rate) to remove the organic polymers.

*Zeolite L Membranes.* The supported zeolite seed layers were crystallized into membranes using hydrothermal secondary growth. The secondary growth solution used was adapted from a previous report of secondary growth on unsupported zeolite L films [14,15]. A clear solution was prepared with a molar composition of 10K$_2$O:1Al$_2$O$_3$:20SiO$_2$:2000H$_2$O, in which 84.78 g of water, 0.456 g of Al(OH)$_3$, and 3.11 g of KOH were thoroughly mixed. After stirring for 15 minutes, this solution was added to a vigorously stirred solution containing 9.43 g of Ludox LS-30 colloidal silica. Upon mixing the two solutions, a clear solution is formed, which was then stirred for 15 minutes. Suspended in a 125 mL Teflon-lined Parr digestion vessel, the membranes were grown by placing the supported zeolite seed layers vertically in the secondary growth solution (filled to 80% of total vessel volume). The vessel was heated using static conditions at 170°C for 70 hours prior to quenching in cold water. To optimize the secondary growth time and temperature, the synthesis temperatures were varied from 110 to 175°C with times of 20-90 hours. At least three membranes were prepared at each growth time and temperature to support the experimental findings.

### 2.2.3 Characterization Techniques

Phase composition of zeolite materials and membranes was determined with a Rigaku Geigerflex X-ray diffractometer using nickel-filtered CuKα (λ=1.5405 Å) radiation. The zeolite membrane surface morphology was investigated by scanning
electron microscopy (JEOL JSM-5500, JEOL, Tokyo, Japan) on carbon or gold coated specimens. In addition, membrane densification and thicknesses were investigated by SEM of fracture cross-sections of the supported membrane structure.

The thickness of the nanocrystalline zeolite L seed layers was verified non-destructively with a vertically-oriented variable angle spectroscopic ellipsometer (V-VASE, J.A. Woollam Co. Inc., Lincoln, NE). As homogeneous, dense packed, nanocrystalline zeolite L is optically transparent, the dispersion in refractive index, $n$, can be described as a Cauchy type material with the following equation:

$$n^2 = c_1 + \frac{c_2}{\lambda^2} + c_3\lambda^2$$  \hspace{1cm} (2.1)

Here $\lambda$ is the wavelength of the light and $c_1$, $c_2$, and $c_3$ are fitting parameters. The optical constants of the porous $\alpha$-alumina supports were determined prior to analyzing the zeolite layer in order to accurately characterize the ellipsometric response from the thin zeolite films. VASE analysis of the bare supports exhibit absorption in the visible region of the spectrum due to light scattering form the surface and/or near bulk. This absorption is represented by a generalized oscillator model consisting of a single Tauc-Lorentz type oscillator. The index is then matched using a pole in the ultraviolet and an offset to the Kramers-Kronig transformation of the absorption [24].

Single gas permeation experiments were employed to investigate the optimum hydrothermal conditions in which dense, defect free zeolite L membranes could be achieved. These measurements were carried out in the non-stationary dead-end mode [25]. The supported membranes were mounted in aluminum gas permeation cells and evacuated under vacuum at 80°C overnight prior to applying a permeate gas. As shown in
Figure 2.3, a constant pressure (2 bar) of test gas is supplied at the feed side. Gas passes through the compact into a pre-evacuated reservoir with volume $V_{\text{cell}}$. The feed and permeate pressure, respectively $p_f^0$ and $p_p$, are measured with a pressure transducer (model PX303-200G10V Omega Engineering, Inc., USA). Assuming the ideal gas law to be valid, the gas permeance, $f$, is determined for isothermal conditions by non-linear regression using eq. 2.2:

$$\ln\left(\frac{p_f^0}{p_f^0-p_p}\right) = f\left(\frac{A}{X}\right) \left(\frac{RT}{V_{\text{cell}}}\right)t$$  \hspace{1cm} (2.2)

where $A$ is the apparent membrane surface, $X$ the support thickness, $R$ the gas constant, $T$ the absolute temperature, and $t$ the relative time. This setup is capable of measuring gas permeance values as low as $10^{-13}\ \text{kmol m}^{-2}\ \text{s}^{-1}\ \text{kPa}^{-1}$.

### 2.3 Results and Discussion

#### 2.3.1 Micron-thick Zeolite L Membranes

Zeolite L with disk-like morphology was synthesized using a static hydrothermal technique. The scanning electron micrograph in Figure 2.4 suggests that crystals ranging primarily from 0.5-2 µm in diameter and comparable thicknesses are being formed. As shown in the top pattern of Figure 2.5, X-ray diffraction was used to characterize the crystallinity of the zeolite and when compared to the standard pattern of zeolite L (lower), it was confirmed that no impurity phases were present.

Zeolite membranes are most commonly obtained by hydrothermal secondary growth of an existing seed layer on a support [26-33]. The zeolite seed layer is critical in
determining the quality of membrane produced; therefore, the morphology of the seed crystallites and their extent of agglomeration determine the quality of the membrane. Several techniques for seed layer deposition are currently available, which include: rubbing [26-28,34], spin coating [35,36], electrostatic adsorption [29,31,32,37-39], electrophoretic deposition [40-42], and dip coating [26,30,32]. Due to the existence of relatively high capillary forces in the alumina supports being used, dip-coating has been found appropriate for producing uniform seed layers with optimum adhesion. This method is also preferred for practical applications since it does not require time-consuming and costly surface pre-treatment of support and/or particles [26,32].

In order to prevent agglomeration of the zeolites, various polymers such as polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), and polyethyleneimine (PEI) were added to the zeolite suspensions. Polymers ranging from 1-5 wt% were used. It was found that PVA and PVP did not improve the surface coverage when compared to dip-coatings performed without polymer addition. However, as shown in Figure 2.4, 1 wt% PEI was shown to provide good surface coverage of the alumina support. Figure 2.4 also illustrates that the particle size distribution is advantageous for generating continuous films in that the smaller crystals can fill in the large inter-zeolite gaps. Little improvement was observed when the concentration of polymer was increased to 5 wt%.

The zeolite concentration of the dipping solution determined the seed layer thickness. As demonstrated by the SEM cross-sections in Figures 2.6a and 2.6b, the zeolite seed layer thickness was tuned by changing the solid load of the dipping solution. The ~3.8 µm seed layer in Figure 2.6a was prepared from a 1.35 mg/mL zeolite concentration, while a concentration of 2.03 mg/mL provides a ~5.1 µm zeolite layer.
shown in Figure 2.6b. When the zeolite concentration is lowered to 0.95 mg/mL, the thickness is reduced to ~2.76 µm (discussed later). SEM was used to examine the zeolite coverage of the alumina supports for these three dipping suspensions, with Figure 2.4 being an example of a completely covered support using the 2.03 mg/mL dipping solution. These well-stabilized zeolite suspensions have also proven useful, in that uniform seed layers as large as 1133 mm² in area are readily deposited on the support. This dip-coating procedure can be generalized for seeding larger supports, as well as the preparation of uniform seed layers using many zeolite types.

Tsapatsis et al. reported a growth solution comprised of 10K₂O:1Al₂O₃:20SiO₂:2000H₂O for secondary growth of nanocrystalline zeolite L seed crystals [15]. Using this growth solution, our supported zeolite films were subjected to various growth temperatures to maximize membrane densification and to minimize the formation of other phases. As demonstrated by SEM in Figure 2.7a, secondary growth for 6 hours at 175°C led to the formation of phillipsite [43], which becomes more evident at 24 hours because the large phillipsite impurities covered the membrane surface (confirmed by XRD). At 150°C, phillipsite also began to develop after 6 hours of secondary growth. Even at 130°C, the phillipsite impurity appeared between 6-10 hours of growth. Figure 2.7b is a SEM of a zeolite L seeded layer that has undergone secondary growth for 72 hours at 110°C. As compared to Figure 2.7a, the micrograph in Figure 2.7b suggests a single phase, thus providing support that 110°C is the optimum temperature for zeolite growth. Decreasing the temperature below 100°C provided limited secondary growth, in which no densification of the zeolite seed layer was observed.
Using a set of five separately seeded zeolite films, the growth time was optimized by varying the time from 20 to 80 hours. Each of these seed layers was prepared by using a 1.35 mg/mL zeolite suspension. Figure 2.8(a-d) shows SEM images of these individually cross-sectioned zeolite membranes following the specified growth time at 110°C. At 20 hours growth (Figure 2.8a), individual zeolite crystals are still observed, despite the progression towards membrane densification. Zeolite intergrowth begins to occur, yet the intercrystalline pores between neighboring zeolites are still present. After 40 hours growth (Figure 2.8b), the individual zeolite crystals are difficult to recognize because of the increase in intergrowth. Membrane densification has increased from 20 hours; however, the intercrystalline pores are not completely closed. According to the SEM micrographs, growth times greater than 60 hours (Figure 2.8c) produce zeolite L membranes that appear to be dense. As observed in Figure 2.8d for 72 hours growth time, zeolite intergrowth has made it almost impossible to resolve individual crystals and the intercrystalline pores that were previously observed are no longer visible. Growth times up to 90 hours were utilized for these experiments; however, no major changes in the cross-sections were observed for times greater than 66 hours. Despite the long growth time, no impurities were noted.

Upon closer examination of the cross-sections in Figure 2.8, the average thickness of the zeolite membranes is 3.75±0.24 µm thick. Even after 72 hours of growth, the thickness of the membrane does not change from that observed at 20 hours growth. A second example of controlled thickness is provided in Figure 2.9, in which seed layers were deposited onto separate supports from a 0.95 mg/mL zeolite suspension. The SEM cross-sections show that the thickness remains the same with increasing growth time.
Due to the reproducibility in preparing seed layers on multiple supports, a membrane thickness of 2.76±0.05 µm was obtained for the samples prepared from a 0.95 mg/mL zeolite suspension. Based on the experimental data, lowering the temperature to 110ºC reduces the vertical growth of the zeolite membranes so that densification only occurs inside the seed layer, thus maintaining the same thickness as deposited during seeding.

To further support the fact that secondary growth is limited to the xy-plane, the surface of every membrane from Figure 2.8 was imaged following membrane densification. Figure 2.10 illustrates that secondary growth is simply filling in the inter-zeolite pores. The surface view in Figure 2.10a was collected prior to secondary growth, in which the boundaries of the zeolites are clearly defined because of the large inter-zeolite pores between them. However, after 72 hours of growth in Figure 2.10b, the inter-zeolite pores have begun to close, making it more difficult to resolve the individual crystals.

The X-ray diffraction patterns in Figure 2.11 were collected on a set of 3.75 µm zeolite membranes formed by secondary growth. Along with a pattern from a seeded support prior to secondary growth, patterns are also shown for membranes after 20 and 60 hours of secondary growth. Figure 2.12 compares the diffraction pattern of the randomly oriented zeolite L powder used for seeding to a membrane grown after 60 hours. For the randomly oriented powder, the peak intensity at 5.5º 2θ (100) is approximately 3 times larger than the peak at 11.7º 2θ (001). In the case of the membranes, the peak intensity ratio between these two peaks gets smaller, especially with longer growth time. Based on the diffraction pattern in Figure 2.12, the intensities of the (100) and (001) peaks are roughly the same height after 60 hours of secondary growth.
This supports the fact that there is some preferred orientation of the zeolites in the membrane along the (001) plane. There are also several peaks between 13-25° 2θ that have much lower intensities when compared to the randomly oriented powder. Collectively, these patterns provide evidence of the preferential orientation of the zeolite L crystals within the membrane following seed layer deposition and secondary growth.

Non-stationary single gas permeation was solely used to determine the integrity and densification of the 3.75 µm zeolite L membranes as a function of time. In Figure 2.13, the permeate pressure of the reservoir ($p_p$) is plotted as a function of time for zeolite L membranes that were achieved at different secondary growth times. At initial time, $t^0$, the reservoir was evacuated ($p^0 \sim 10$ kPa), and over time, He gradually fills the reservoir. The pressure closely follows the trend of eq. 2.2, from which it can be concluded that the permeance does not have pressure dependence (see Figure 2.13). Due to the design of the gas permeation cells and the operation temperature, the non-stationary gas permeation setup used has a detection limit of $10^{-12} \ldots 10^{-14}$ kmol m$^{-2}$ s$^{-1}$ kPa$^{-1}$ due to desorption and parasitic leaks. This was confirmed by using a, dense aluminum plate with negligible He permeance.

Figure 2.14 shows the overall $j_{He}$ values for supported zeolite L membranes prepared using a 1.35 mg/mL solution and grown at different times. Increased growth time leads to a decrease in He permeance. For comparison, the helium permeance of a denser α-alumina support immersed into the growth solution for 72 hours resulted in a permeance of $1.6 \times 10^{-7}$ kmol m$^{-2}$ s$^{-1}$ kPa$^{-1}$. Despite inherently lower permeances of $2 \times 10^{-7}$ kmol m$^{-2}$ s$^{-1}$ kPa$^{-1}$ for these bare supports when compared to the supports detailed in the paper, it was concluded that the permeance of the support was not affected by the
secondary growth treatment. As the membrane growth time approached 60 hours, a limiting permeance \(10^{-9} \text{ kmol m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1}\) was measured.

Single gas permeation supports the results from electron microscopy that membrane densification improves with increased secondary growth times due to the fact that helium becomes unable to penetrate through the zeolite membrane. Based on the \(0.26 \text{ nm}\) kinetic diameter of He, the gas should easily penetrate the 0.71 nm pores of zeolite L; however, due to the orientation of the crystals, it is unlikely that a single one-dimensional pore from zeolite L spans its entire width. This implies that the absence of connected macro- and micro-defects in the supported membranes is confirmed by non-stationary single gas permeation.

### 2.3.2 Sub-micron Thick Zeolite L Membranes

As described above, the disk-like LTL crystallites of 0.5-2 µm are suitable for the preparation of membranes greater than one micron. In order to reduce the membrane thickness into the sub-micron regime, nanocrystalline zeolite L particles were utilized for making the initial seed layer. Nanocrystalline zeolite L was synthesized using a dynamic hydrothermal technique that produces crystals with a size of about 15 nm wide and 40 nm long, as revealed in the transmission electron micrograph in Figure 2.15. The X-ray diffraction pattern in Figure 2.16 confirmed that the particles were crystalline and smaller based on peak broadening when compared to the spectrum of micron-sized zeolite L.

Just as in the case with the micron-sized zeolite L, membranes on alumina supports were prepared from the dip-coating of well-dispersed solutions of
nanocrystalline zeolite L. Again, the zeolite seed layer is critical in determining the quality of the membrane after secondary growth. Due to the high surface energy of the nanoparticles, they tend to agglomerate into larger clusters (80-120 nm); therefore, the dipping solution was optimized using polymers to prevent agglomeration. A range of PEI and PVP (0.5-2 wt%) was used to disperse the particles, but PVP was found to promote particle agglomeration into 300-400 nm clusters. 0.5 wt% PEI was found to provide minimal particle agglomeration and good surface coverage of the alumina support was observed by SEM.

The zeolite concentration in the dipping solution determined the thickness of the deposited seed layer. Ellipsometry data shown in Figure 2.17 indicates that the thickness of the zeolite L seed layer can be tuned from 150-2000 nm by changing the zeolite concentration from 0.08-2.0 mg/mL. This plot indicates the linearity in the seed layer deposition with respect to zeolite concentration. Several examples of the as prepared nanocrystalline zeolite L seed layers are provided in the side and top view SEM images shown in Figure 2.18. These images provide confirmation of the seed layer thicknesses determined by spectroscopic ellipsometry. A non-continuous film generated from a 0.08 mg/mL solid load is shown in Figure 2.18(a-b). Figure 2.18(c-d) shows a continuous, 330-350 nm thick film, which was deposited using a 0.4 mg/mL zeolite concentration. The 1.2 µm thick seed layer in Figure 2.18(e-f) was generated from a 2.0 mg/mL dipping solution. As concluded from SEM, the seed layer is not continuous below 0.4 mg/mL. Seed layers prepared using a zeolite concentration of 0.4 mg/mL or higher gave an optically colored layer on the alumina support surface, as demonstrated in the before and after images of Figure 2.19.
Utilizing the same secondary growth solution and procedure previously described for the micron-sized membranes, the nanocrystalline zeolite L seed layers prepared using 0.4-2 mg/mL dipping solutions were subjected to hydrothermal secondary growth. Figure 2.20 provides SEM images of a nanocrystalline zeolite L membrane (1.0 mg/mL) following 48 hours growth time at 110°C. As observed in Figure 2.20, the zeolite intergrowth after 48 hours has fused neighboring particles to create what appears to be a dense zeolite L membrane.

Figure 2.20 provides an example of a nanocrystalline zeolite L membrane that was prepared using a 1.0 mg/mL solid load, which provides a seed layer thickness of approximately 650 nm. Upon close examination of the cross-section, the membrane has grown to approximately 1050 nm. Unlike the thickness of the micron-sized membranes remaining unchanged, the experimental data suggests that the nanocrystalline membranes almost double in thickness during secondary growth. After examining all nanocrystalline membranes by SEM, our findings indicate that one requires a dipping solution that deposits a zeolite layer greater than 350 nm and the final membrane thickness needs to be greater than 700 nm in order to create a uniform nanocrystalline zeolite L membrane.

Non-stationary single gas permeation was used to characterize the nanocrystalline zeolite L membrane (1.0 mg/mL solution) shown in Figure 2.20. Using helium as the permeate gas, the membrane was found to have a limiting permeance from 1-5×10⁻⁹ kmol m⁻² s⁻¹ kPa⁻¹ when cycled from 30-180°C at 50°C intervals. X-ray diffraction of the thin membrane provides very weak peaks, yet enough to suggest that preferred orientation of the crystals is not occurring (pattern not shown). Due to the random orientation of the zeolites within the membrane, low permeance values were expected. A membrane
prepared using a 0.2 mg/mL solid load was found to have a much higher permeance of 2-4x10^{-7} \text{ kmol m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1} and is due to insufficient surface coverage, thus an incomplete zeolite membrane. This data is consistent with the SEM images of the seed layers, in that complete surface coverage can obtained using zeolite concentrations of 0.4 mg/mL or higher. These helium permeances are consistent with the values obtained for the micron-sized membranes grown at 60 hours or more, thus supporting the fact these supported membranes are absent of connected macro- and micro-defects.

2.4 Conclusions

Zeolite L of disk-like and nanocrystalline morphology has been successfully dip-coated onto macro-porous alumina supports and grown into homogeneous, dense membranes, ranging from 0.7-5.1 \text{ µm} thick, using a hydrothermal secondary growth process. Through the use of stabilized zeolite suspensions, uniform zeolite seed layers of a desired thickness were prepared. Optimal secondary growth conditions were determined in order to minimize the growth of impurities, while at the same time, densifying the zeolite films laterally without changing their initial thicknesses. For the disk-shaped zeolites, secondary growth times above 60 hours yielded dense membranes, as demonstrated with SEM cross-sections. Membrane densification was also confirmed with single gas permeation experiments; however, the low permeation of helium suggests the lack of particle alignment or connectivity within the membrane. With nanocrystalline zeolite L as seed layers, membranes were formed above 48 hours of growth time, which was also confirmed using the same techniques. The strategies for the preparation of zeolite membranes discussed in the present study could be successfully applied for a wide
range of other zeolite types by tuning the experimental conditions to produce dense, controlled thickness, defect free membranes.
2.5 References


Figure 2.1: (a) Top view of 42 mm, optically smooth $\alpha$-alumina support (b) SEM showing the microporous structure of a sintered alumina support.
Figure 2.2: Drawing of the MEMDIP dip-coating instrument used for preparing zeolite L seed layers on alumina supports. Supports are attached to the motorized arm and slipped through the dipping suspension at a controlled speed.
Figure 2.3: Diagram of the non-stationary single-gas permeation setup.
Figure 2.4: SEM image of the disk-like zeolite L crystals following dip-coating with a 2.03 mg/mL zeolite suspension (1 wt% PEI) onto the α-alumina supports prior to secondary growth.
Figure 2.5: X-ray diffraction pattern of disk-like zeolite L (top) compared to the published pattern (bottom) for the elongated, cylindrical type of zeolite L.
Figure 2.6: SEM cross-sections of seed layers prepared from different zeolite concentrations using 1 wt% PEI. (a) ~3.8 µm layer from 1.35 mg/mL suspension, (b) ~5.1 µm layer from 2.03 mg/mL suspension. (White bar shows demarcation between zeolite seed layer and support)
Figure 2.7: SEM images of the surface of zeolite seeded layers after secondary growth at the specified times and temperatures (Presence of phillipsite indicated by arrows). (a) 6 hrs at 175°C, (b) 72 hrs at 110°C.
Figure 2.8: SEM cross-sections (a-d) of zeolite L membranes formed at various secondary growth times at 110°C. Seed layers prepared using 1.35 mg/mL suspension. (a) 20 hrs, (b) 40 hrs, (c) 66 hrs, (d) 72 hrs. Dense membranes are observed at times from 60 hours of secondary growth. (White bar shows demarcation between zeolite membrane and support)
**Figure 2.9**: SEM cross-sections of seed layers prepared from a 0.95 mg/mL zeolite solution and later grown into zeolite L membranes. (a) 20 hrs, (b) 40 hrs, (c) 60 hrs. Minimal vertical growth was observed. (White bar shows demarcation between zeolite membrane and support)
Figure 2.10: SEM surface views of zeolite L seed layers at various secondary growth times at 110°C. (a) 0 hrs, (b) 72 hrs.
Figure 2.11: Stacked X-ray diffraction spectra showing secondary growth of the zeolite L membranes at 110°C with increasing growth time. Diffraction peaks from α-alumina are denoted with an (*).
Figure 2.12: X-ray diffraction pattern comparison of a randomly oriented zeolite L powder to a membrane grown for 60 hours (baseline corrected).
Figure 2.13: Permeate pressure vs. time obtained for zeolite L membranes prepared at various secondary growth times. (a) 20hrs, (b) 40 hrs, (c) 80hrs.
Figure 2.14: Helium permeance of supported zeolite L membranes as a function of secondary growth time.
Figure 2.15: Transmission electron micrograph of nanocrystalline zeolite L.
Figure 2.16: Normalized X-ray diffraction pattern of nanocrystalline zeolite L compared to micron sized zeolite L (baseline corrected).
Figure 2.17: Plot showing the linearity of the nanocrystalline zeolite L seed layer thickness versus the zeolite concentration of the dipping solution, as determined by spectroscopic ellipsometry.
Figure 2.18: SEM top-view and cross-sections of nanocrystalline zeolite L seed layers using 0.5 wt% PEI at various concentrations. (a-b) 0.08 mg/mL (c-d) 0.4 mg/mL (e-f) 2.0 mg/mL. (White bar shows demarcation between zeolite seed layer and support)
**Figure 2.19**: Alumina support before and after dip-coating using nanocrystalline zeolite L seed crystals. Optically colored layer formed with concentrations greater than 0.4 mg/mL.
Figure 2.20: SEM top-view and cross-section of a dense, nanocrystalline zeolite L membrane after 48 hours of secondary growth. Seed layer was deposited using a 1.0 mg/mL suspension. (White bar shows demarcation between zeolite membrane and support)
CHAPTER 3

FABRICATION OF ZEOLITE Y MEMBRANES FOR APPLICATIONS IN SENSING AND SEPARATIONS

3.1 Introduction

The preparation of supported zeolite films/membranes with controlled microstructures can have an impact on a number of applications. These include catalysis, ion-exchange, nuclear waste disposal, light harvesting devices, chemical sensing and gas separations [1-5]. In the first half of this chapter, the fabrication and optimization of ultra-thin zeolite Y membranes was studied for the eventual use in selective and sensitive detection of organophosphates. Through the use of nanocrystalline zeolite Y crystallites, ultra-thin seed layers were converted into defect-free membranes with tunable thicknesses. By attaching electrodes to the membrane surface, impedance spectroscopy was used to show the sensitivity and sensor response of the membrane in the presence of DMMP.

Considerable efforts have been directed towards developing novel detection strategies for chemical warfare agents (CWAs) [6-9]. Commercially available detection includes detection paper, gas detection tubes, flame photometric detector, ion-mobility spectrometers, surface acoustic wave arrays and gas chromatography-mass spectrometry devices. Because of the inability of these commercially available devices to meet all
CWA detection requirements, new sensing principles and devices are being explored, including enzymatic, chemical and supramolecular sensors [8,9].

Chemiresistive type sensors were devised, which operate based on changes in resistance of the sensing element in the presence of CWAs [10]. Metal oxides were also investigated for detection of CWAs at elevated temperatures [11-13]. Thin-film metallophthalocyanines (MPC) semiconductor based sensors have also been explored for the detection of DMMP (dimethyl methylphosphonate), a typical simulant for other more toxic chemical warfare agents [14]. Some of the benefits of these sensor types include: simple working principle, good sensitivity, easy miniaturization and low cost. However, they have their issues such as the interference from background gases such as hydrocarbons, CO and NOx, as well as difficulties in recovering after removing DMMP due to the so-called ‘poisoning effect’ [11,12].

Recently, ammonia sensors have been developed by Moos et al. that utilize the change in ionic conductivity within the zeolite in the presence of ammonia [15]. In fact, the effect of the different polar and non-polar organic vapors on the ionic conductivity of zeolites has been thoroughly investigated in literature. However, few reports are available to study the effects of CWAs and their simulants such as DMMP on the ionic conductivity of zeolites. Little or no work has been carried out in which the ionic conductivity of the zeolite is utilized as sensor signals for the detection of CWAs and vapors of their simulants.

Separation of gases using ceramic membranes is a dynamic and growing field, in which efforts have been made in developing membranes for use in harsh conditions or high temperatures. Separation of a gas mixture can be achieved based on differences in
their molecular weight, size or shape, or on the differences in the affinity of the gas molecules to the membrane surface [16]. The two types of inorganic ceramic membranes suitable for separations are dense and porous, especially microporous membranes.

According to the IUPAC definition, microporous membranes are referred to as those with a pore diameter smaller than 2 nm [17]. Microporous ceramic membranes are usually comprised of zeolites, which have polycrystalline structures consisting of many crystallites packed together, and in the ideal case, without any grain boundaries [18].

Gas permeation through porous inorganic membranes is often explained by one or a combination of: (1) Knudsen diffusion, (2) surface diffusion or flow, and (3) molecular sieving. The Knudsen mode of gas transport is considered to be the predominant mechanism when the mean free path ($\lambda$), defined in eq. 3.1, of the gas is much greater than the pore size ($r_p$) of the membrane ($(r_p/\lambda) < 0.05$) [19].

$$\lambda = \frac{RT}{\sqrt{2\pi d^2 N \bar{p}}} \quad (3.1)$$

In eq. 3.1, $R$ is the gas constant, $T$ is temperature in Kelvin, $d$, the collision diameter of gas molecules in meters, $N$, the Avogadro number, and $\bar{p}$ is the average pressure across the membrane in Pa. In such situations, the collisions of the molecules with the pore wall are more frequent than the collisions among the molecules themselves. This mechanism is often predominant in macroporous and mesoporous membranes (>2 nm pores), as well as can be used to explain the behavior of zeolite membranes with pinholes and defects [17,20-22]. As shown in Figure 3.1a, the majority of the molecules incident from the gas phase rebound and do not enter the pores [23]. The probability of small molecules
entering the pore is higher than that of larger molecules. Assuming that a membrane has
Knudsen-like behavior, the single gas permeance \( f^{Kn} \) can be estimated using eq. 3.2:

\[
f^{Kn} = \frac{\phi_p \Omega_p}{3 \tau_p X} \sqrt{\frac{8}{\pi R T M}}
\]

where \( \phi_p \) is the relative porosity, \( \Omega_p \) is the pore diameter, \( \tau_p \) is the tortuosity, \( X \) is the
membrane thickness and \( M \) is the molar mass of the gas of interest [24].

The second mode of gas transport common in zeolite membranes is referred to as
surface diffusion or flow, in which the permeating species exhibits a strong affinity for
the membrane surface and adsorbs along the pore walls at sufficiently low temperatures
and/or high pressures. When the adsorbed molecules are mobile, they preferentially enter
the zeolite pore where surface flow can take place, as shown in Figure 3.1b [23]. Also,
surface flow often occurs in parallel with other transport mechanisms such as Knudsen or
activated diffusion [17]. Activated diffusion can be considered a type of surface diffusion
in the limit where the pore size becomes comparable to the molecular size. This
mechanism can be applied to gas mixtures in which one gas interacts strongly with the
pore walls, while the other is less adsorptive [25]. Even though the zeolite pore diameters
are typically larger than common gas species, the adsorbed species can restrict the pore
diameter, thus promoting activated diffusion of the second gas species. This is perceived
as an ‘activated’ process because of the positive activation energy for permeation [22].

Gas separation using inorganic zeolite membranes can also be explained by
molecular sieving when the size of the zeolite pore is roughly the same as the size of the
molecules to be separated. In this mechanism, the membrane is capable of distinguishing molecules based on their sizes, but the permeation rate via a molecular sieving mechanism is typically low, as shown in Figure 3.1c [26].

CO₂ separation is one of the most studied applications for faujasite-type zeolite membranes because of its industrial significance, such as CO₂ capture for carbon sequestration, natural gas purification, and separation of product streams from water gas shift reactions for hydrogen production [23,27-29]. The literature results of CO₂ separation have been qualitatively consistent in showing that zeolite Y membranes are CO₂-selective over N₂ [30]. The molecular transport of these two gases in zeolite Y micropores has been described by both the activated diffusion and surface diffusion mechanisms [23]. Surface transport is due to the hopping movement of CO₂ between adsorption sites and activated transport is due to the movement of N₂ within the confined space created by the adsorbed species. Although good selectivity between CO₂ and N₂ have been obtained, further improvement of the CO₂/N₂ separation properties of zeolite Y membranes that are capable of separations at high temperatures and pressures is essential, as the second half of this chapter is focused on this goal. Two different hydrothermal secondary growth procedures were examined for the synthesis of defect-free zeolite Y membranes. The permeation/separation properties between CO₂ and N₂ were compared to show that gas permeation of membranes prepared using sub-micron sized seed crystals is highly dependent upon the secondary growth process.
3.2 Experimental Section

3.2.1 Materials

Aluminum hydroxide (Al(OH)$_3$, 80.5%) was purchased from Alfa Aesar. Sodium hydroxide from Mallinckrodt (NaOH, 98.8%) and tetramethylammonium hydroxide (TMAOH, 25%) from SACHEM were used. Ludox SM-30 (SiO$_2$, 30%), Ludox HS-30 (SiO$_2$, 30%), tetramethylammonium bromide (TMABr, 98%), aluminum isopropoxide (Al[OCH(CH$_3$)$_2$]$_3$, 97%), dimethyl methylphosphonate (DMMP) and Dowex proton-exchange resin were obtained from Aldrich (Milwaukee, WI, USA). All chemicals were used without further purification. The H$_2$O used in this study was purified by a Millipore ultrapure water system.

3.2.2 Synthesis

The influence of chemical composition on the particle size of zeolite Y seed crystals is described in the literature [31-37]. All zeolite precursor solutions described below were mixed in polypropylene bottles to prevent contamination.
Sub-Micron Zeolite Y. Faujasite zeolite Y ranging from 80-200 nm in size were prepared from a clear solution with the following composition:

\[0.037\text{Na}_2\text{O}:1.0\text{Al}_2\text{O}_3:3.13(\text{TMA})_2\text{O}:4.29\text{SiO}_2:497\text{H}_2\text{O}\] [38,39]. This precursor gel was prepared by thoroughly mixing 152 g H\text{2}O, 4.58 g Al(OH)\text{3} and 53.6 g TMAOH and stirred for 2 hours. Meanwhile, 25 g Ludox SM-30 was adjusted to pH 8.1 using Dowex proton-exchange resin. Upon removal of the resin from the silicate solution, 20 g was added to the vigorously stirred tetramethylammonium aluminate solution. 30 mg of NaOH was added to the solution, followed by stirring for 3 hours. The clear solution was placed into a 250 mL Nalgene bottle and heated using static conditions at 98ºC for 4 days.

Nanocrystalline Zeolite Y. Nanocrystalline zeolite Y (nano-Y) ranging from 25-50 nm in size were prepared from a clear solution with the following composition:

\[0.048\text{Na}_2\text{O}:1.0\text{Al}_2\text{O}_3:4.36\text{SiO}_2:2.39(\text{TMA})_2\text{O}(2\text{OH}^-):1.19(\text{TMA})_2\text{O}(2\text{Br}^-):249.00\text{H}_2\text{O}\] [31]. A typical batch weight composition was prepared by first dissolving 12.5 g aluminum isopropoxide in 76.5 g H\text{2}O and 52.3 g TMAOH. This solution was vigorously stirred at 70ºC until the solution became clear. After the addition of 11.3 g TMABr and 26.2 g colloidal silica (Ludox HS-30), the bottle was tightly sealed. The zeolite pre-cursor solution was aged for 3 days at room temperature with vigorous stirring, followed by heating with stirring in a 100ºC oil bath for 4 days. Due to the small particle size, the nanocrystalline zeolites remain suspended in solution; therefore, no precipitate is observed. The suspension begins to look translucent after the third day of heating.

The newly formed crystallites from both syntheses were removed from their mother liquors and centrifuged/washed with water until the pH of the supernatant was
neutral. Without drying, a stable colloidal suspension of nanocrystalline zeolite Y seed crystals was stored as an aqueous stock suspension (0.08 g/mL) for the preparation of zeolite Y seed layers by dip-coating. For those experiments using the sub-micron zeolite Y, the zeolites were dried at 60ºC overnight, followed by calcination at 550ºC in flowing air for 24 hours to remove the templating agent from the micropores of the zeolite.

\textit{α-Al}_2\textit{O}_3 Macro-porous Supports.} Detailed information about the macro-porous supports, upon which the zeolite membranes were prepared, has been described in Chapter 2 [40].

\textit{Zeolite Y Seed Layers.} Zeolite Y seed layers were deposited on the alumina supports using the same dip-coating apparatus detailed in Chapter 2. Throughout this entire study, seed layers were deposited from a single dip-coating cycle. The dipping suspension for nano-Y was prepared by mixing specific volumes of the stock solution into an aqueous solution of polyethyleneimine (PEI, 1800 Daltons) containing ammonia. Using a 1.5 wt% solution of PEI in water (0.05 M NH$_3$), a 1.2-20 mg/mL dispersion of nano-Y was prepared in an ultrasonic bath for 15 minutes. Due to the formation of well-dispersed nanoparticles in solution, excessive sonication was not necessary.

As for the sub-micron zeolite Y, the dip-coating solution was prepared using no dispersants and only one concentration of zeolite. 100 mg of the dried powder was dispersed into 20 mL of water and sonicated for 2 hours to reduce the number of large agglomerates in solution. The zeolite suspension (5 mg/mL) was then filtered using a 20 micron nylon mesh to remove any remaining particulates that might prevent the formation of a continuous seed layer. During dip-coating, the substrate was withdrawn at a speed of 0.01 m/s from a watch-glass filled with 16 mL of the zeolite suspension. The
zeolite Y seed layers were dried overnight in a vacuum oven at room temperature and then fired in air at a temperature of 550°C (0.2°C/min heat/cool rate) to remove the organic polymers and templating agent from the seed layer.

**Zeolite Y Membranes.** Two different secondary growth solutions were used to convert the supported zeolite seed layers into membranes using hydrothermal secondary growth, which were adapted from previous reports of zeolite Y membranes [23,28,29,38,39,41-45]. Both nanocrystalline and sub-micron zeolite Y seed layers were grown using an opaque gel with a molar composition of 17Na$_2$O:1Al$_2$O$_3$:12.80SiO$_2$:975H$_2$O, in which 85.24 g water, 2.208 g Al(OH)$_3$, and 7.29 g NaOH were thoroughly mixed (Synthesis #1). After stirring for 15 minutes, this solution was added to a vigorously stirred solution containing 13.85 g Ludox SM-30 colloidal silica. Upon mixing, a moderately viscous gel is formed, which is then aged while stirring for 4 hours. Suspended in a 125 mL Teflon-lined Parr digestion vessel, the membranes were grown by placing the supported zeolite seed layers vertically in the secondary growth solution (filled to 80% of total vessel volume). The vessel was heated using static conditions at 90°C for various times prior to quenching in cold water. Due to the absence of a templating agent, no further heat treatment was needed for membranes synthesized using this particular growth solution.

The zeolite pre-cursor solution used for the synthesis of sub-micron zeolite Y was also used for the conversion of sub-micron zeolite films into membranes (Synthesis #2). In a 250 mL Nalgene polypropylene bottle, the seeded supports were placed face up at a 45° angle using pieces of inert Teflon and then tightly sealed. Secondary growth was carried out for 7 days at 100°C, prior to rinsing and drying the supported membrane.
Despite the presence of tetramethylammonium ions within the membrane, calcination was not used to remove the templating agent in order to prevent cracking of the membrane. Future experiments will include the removal of the templating agents.

3.2.3 Characterization Techniques

Phase composition of zeolite materials and membranes was determined with either a Rigaku Geigerflex or a Bruker D8 X-ray diffractometer using nickel-filtered CuKα (λ=1.5405 Å) radiation. The zeolite membrane surface morphology was investigated by scanning electron microscopy (SEM) (JEOL JSM-5500, JEOL, Tokyo, Japan and Sirion FEG, FEI Company, US) on carbon or gold coated specimens. In addition, seed layer and membrane thicknesses were investigated by SEM of fracture cross-sections of the supported membrane structure. The thickness of the nanocrystalline zeolite Y seed layers was also verified non-destructively with a vertically oriented variable angle spectroscopic ellipsometer, as described in Chapter 2.

Scanning transmission electron microscopy (STEM) (Tecnai F20, Philips, Holland) was used to determine the particle size and morphology of nanocrystalline zeolite Y. High resolution cross sections of the ultra-thin nano-Y membrane were prepared using a Helios NanoLab 600 focused ion-beam (FIB) (FEI Company, US) and imaged using transmission electron microscopy (TEM) (CM200, Philips, Holland). Raman spectroscopy was performed using a Renishaw - Smiths Detection Combined Raman - IR Microprobe equipped with the 514.5 nm laser line of an argon ion laser.
The nano-Y zeolite membrane based sensor was prepared by first fracturing a full supported membrane (4 mg/mL, ~1 µm thick) into smaller pieces, which resembled a section of pie. Two thin strips of gold paste were painted in parallel directly on the surface of the membrane to serve as electrodes, as shown in Figure 3.2. A gold wire was bonded to each of the electrodes, which will act as leads to be connected to both terminals of the impedance spectrometer. The fabricated membrane sensor was then calcined at 700ºC for 2 hours in order to completely bond the electrodes to the zeolite membrane. Using the sensor setup detailed in Figure 3.3, the membrane-based sensor was placed in a both-ends sealed quartz tube, where the entire setup was positioned within a programmable high temperature furnace and heated to 320ºC. DMMP gas vapors were introduced by bubbling air through the liquid DMMP that was constantly kept at ~0.5ºC. Impedance spectroscopy (Gamry Instr. EIS300) was employed to generate the cycling excitation voltage with a magnitude of 100 mV. A frequency range from 1Hz to 105Hz was conducted during each experimental scan.

A typical impedance spectrum for a solid state electrochemical cell with one ionic conducting electrolyte in between two metal electrodes closely resembles a depressed semi-circle. The depressed portion of the semi-circle at higher frequencies is typically considered as the contribution from the bulk material and the straight ‘tail’ line at lower frequencies is due to the polarization behavior of the interface between the metal electrode and electrolyte [46]. Thus, the depressed semi-circle can be simulated by an equivalent electric circuit: a resistor (R) in parallel with a capacitive component (CPE: constant phase element) representing a bulk resistance (R) and a geometrical capacitance
(CPE) of the electrochemical cell. The peak frequency ($\omega_p$) of the semicircle satisfies eq. 3.3:

$$\omega_p \cdot R \cdot CPE = 1$$  \hspace{1cm} (3.3)

The impedance of the bulk materials for the semicircle part can be expressed as eq. 3.4:

$$Z = Z' + Z'' = R/(1 + Z_{CPE}) = R/(1 + (j \omega \tau) n)$$  \hspace{1cm} (3.4)

where $Z'$ is the real component and $Z''$ is the imagery portion of the impedance. $Z_{CPE}$ represents the impedance contributed from the capacitor component, $\omega$ is angular frequency, the constant relaxation time $\tau = RC$ and $n$ is the fractional index representing the degree of suppression of the semicircle above the real axis. The CPE will become more capacitive when $n$ approaches 1, whereas more resistive when it approaches zero.

Single gas permeation experiments were employed to investigate the permeation properties of the sub-micron membranes only. These measurements were carried out in the non-stationary dead-end mode, as detailed in Chapter 2. The supported membranes were mounted in aluminum gas permeation cells and evacuated under vacuum at 150$^\circ$C overnight prior to applying a permeate gas in order to remove bulk water from the zeolite pores. All measurements were carried out at a constant pressure of 2 bar, using He at either 30, 80 or 130$^\circ$C.

Mixed gas separation experiments were used to determine the separation factors between CO$_2$ and N$_2$ on sub-micron zeolite Y membranes. These measurements were carried out using the setup shown in Figure 3.4. The supported membranes were mounted
in aluminum gas permeation cells and heated at 150°C overnight in the presence of a 50/50 mixture of CO₂:N₂ feed gas in order to accelerate the removal of water from the membrane. To start the experiment, the oven temperature was adjusted from 130 to 30°C after drying. As shown in Figure 3.4, a constant pressure (2-4 bar) of feed gas is supplied at the feed side, by which the composition is controlled using adjustable mass flow controllers. The overall feed pressure is controlled by a tunable pressure controller that is coupled to a pressure transducer. CO₂/N₂ passes through the supported membrane into the permeate side of the cell, which is then swept away by a constant feed of He sweep gas. The permeate gas composition is then sampled using an externally controlled gas chromatograph (GC). In order to verify the composition of the feed gas and to determine the separation factor for the mixed gases under investigation, a valve is used to toggle between the permeate and feed side of the membrane (not shown in Figure 3.4). The separation properties of the zeolite membranes are determined based on the separation factor \( S \) between CO₂ and N₂, which is determined by eq. 3.5 based on our experimental setup.

\[
S = \frac{\left(\frac{\text{CO}_2}{\text{N}_2}\right)_{\text{sweep}}}{\left(\frac{\text{CO}_2}{\text{N}_2}\right)_{\text{feed}}}
\]

(3.5)
3.3 Results

3.3.1 Nanocrystalline Zeolite Y Seeded Membranes

3.3.1.1 Synthesis

Nanocrystalline zeolite Y, having an octahedral morphology, was synthesized using a tetramethylammonium ion (TMA) template-based hydrothermal technique from a pre-cursor solution with the following composition:

\[ 0.048\text{Na}_2\text{O} : 1.0\text{Al}_2\text{O}_3 : 4.36\text{SiO}_2 : 2.39\text{(TMA)}_2\text{O(2OH}^-\text{)} : 1.19\text{(TMA)}_2\text{O(2Br}^-\text{)} : 249.00\text{H}_2\text{O}. \]

The transmission electron micrograph in Figure 3.5 suggests that 25-50 nm crystals were formed. As shown in the top pattern of Figure 3.6, X-ray diffraction was used to further characterize the nanoparticles and when compared to the standard pattern (lower), it was confirmed that the product was crystalline zeolite Y and no impurity phases were present.

As described in Chapter 2, zeolite membranes are most commonly obtained by hydrothermal secondary growth of an existing seed layer on an alumina support. Due to the existence of a capillary action in the alumina supports, dip-coating was used for producing uniform seed layers of nano-Y with optimum adhesion. Just as shown with zeolite L, the zeolite seed layer is critical in determining the quality of membrane produced, which is governed by the morphology of the seed crystals and their extent of agglomeration. Due to the high surface energy of the nano-Y, they tend to agglomerate. Therefore, to optimize the dipping solution, 1.5 wt% polyethyleneimine (PEI) as a dispersant was found to provide minimal particle agglomeration.

The SEM cross-sections in Figure 3.7 demonstrate how the nano-Y concentration of the dipping solution can be used to tune the thickness of the seed layer. The \(~100\) nm
thin film of nano-Y in Figure 3.7a was prepared from a 1.2 mg/mL zeolite concentration, while a concentration of 3.2 mg/mL provides a ~350 nm zeolite layer shown in Figure 3.7b. When the zeolite concentration is raised to 8 mg/mL, the thickness increases to ~1.1 µm, as revealed in Figure 3.7c. SEM was also used to examine the nano-Y coverage of the alumina support, with Figure 3.8 being an example of a top-view image of a completely covered support using a 3.2 mg/mL dipping solution.

Upon forming uniform seed layers of nano-Y on the alumina support, the surface of the supports become optically colored depending on the zeolite concentration. The formation of these optically colored layers is demonstrated in Figures 3.9-3.12. Figure 3.9 shows before (a) and after (b) images of a support seeded using a 1.6 mg/mL zeolite concentration. As the seed layer thickness increases (8 mg/mL), the support surface takes on more red and green tones, whereas the thinner seed layer appears to be more reddish-purple (Figure 3.10). Figure 3.11a-b illustrates the effect of calcination on the seed layer after seeding using a 4 mg/mL dipping solution, where (a) represents the seed layer prior to calcination and (b) shows the changes in the surface color of the support following calcination of the same exact seed layer. In order to demonstrate the reproducibility of the dip-coating procedure in the formation of nano-Y seed layers, Figure 3.12 shows several fired supports that were seeded using same dipping suspension. In Figure 3.12, three seeded and calcined supports show very similar color patterns with a reddish-purple appearance. However, due to the angle at which the photograph was taken, the lower support appears to be yellow and green near the upper edge, but when viewing the seeded supports perpendicular to their surface, they all have the same appearance.
Non-destructive spectroscopic ellipsometry was utilized to further characterize the two seeded supports shown in Figure 3.11, which demonstrates the effect of removing the polymer via calcination from the nano-Y seed layer. Ellipsometric data (not shown) from the pre-heated sample indicates the thickness of the seed layer to be approximately 570 nm, while the thickness of the calcined sample was reduced to roughly 500 nm in thickness.

Kusakabe et al. previously reported a membrane growth solution comprised of 17Na2O:1Al2O3:12.80SiO2:975H2O for secondary growth of micron-size zeolite Y seed crystals for times up to 24 hours [23,28,29,41-45]. Using this growth solution, our supported nano-Y seed layers were subjected to various growth times ranging from 2 to 24 hours at 90ºC (Synthesis #1). Based on the extent of membrane densification observed in SEM cross-sections, membranes grown at shorter growth times (~2 hrs) very closely resembled that for longer growth times (e.g. 4 hrs). Due to the fact that extended growth times were not necessary for the synthesis of dense membranes, all membranes prepared in this study were subjected to secondary growth for only 2 hours. Figure 3.13 provides examples of six separately seeded zeolite films grown for 2 hours using the following zeolite concentration: (a) 1.6 mg/mL, (b) 2.4 mg/mL, (c) 3.2 mg/mL, (d) 4 mg/mL, (e) 8 mg/mL and (f) 20 mg/mL. The thickness of each zeolite Y membrane is denoted in Figure 3.13, while the data is summarized by the linear plot in Figure 3.14.

As observed in Figure 3.13, dense zeolite Y membranes as thin as 400 nm were prepared; however, we also investigated the fabrication of thinner membranes. Using a dip-coating suspension containing 1.2 mg/mL nano-Y, the membrane shown Figure 3.15 was prepared after 2 hours of secondary growth. Focused ion-beam was utilized to obtain
a 150-200 nm thin slice of the supported zeolite membrane, which is shown in Figure 3.15a. TEM provided the means to collect high resolution micrographs of the extremely thin zeolite Y membrane, which has a thickness ranging between 225-300 nm (Figure 3.15(a-d)). During membrane synthesis, it was determined that the rate of calcination to remove the polymer from the seed layer was very critical in the formation of continuous membranes. The SEM top and side-views in Figure 3.16 show the effects of a fast calcination versus a slow removal of the polymer from the membrane. The severely cracked membrane in Figure 3.16(a-b) was calcined using a heating and cooling rate of 0.5°C/min, while the uniform, dense membrane in Figure 3.16(c-d) was fired using a heating and cooling rate of 0.2°C/min, with an extended burn at 350°C. This particular slow calcination process was determined to provide the optimal heating rate for the removal of TMA while maintaining the integrity of the membrane.

The X-ray diffraction patterns in Figure 3.17 were collected on two zeolite membranes of different thicknesses. Along with a pattern from a zeolite Y standard powder (a), patterns are also shown for membranes prepared using (b) 20 mg/mL and (c) 8 mg/mL nano-Y concentration. The $\alpha$-Al$_2$O$_3$ diffraction peak at 25.5\(^\circ\) 2\(\theta\) has been labeled with an “*”. X-ray diffraction on membranes prepared using zeolite concentrations less than 4 mg/mL provided no diffraction peaks; therefore, minimal information was obtained regarding their crystallinity. Due to the sensitivity of Raman spectroscopy, the ultra-thin zeolite Y membranes were further characterized to verify the presence of a crystalline microstructure.

Although zeolites exhibit moderately weak Raman bands, the strongest Raman band around 510 cm\(^{-1}\) provides some insight into the crystallinity of the zeolite. The
Raman spectra in Figure 3.18 were collected on membranes of three different thicknesses, as well as a blank alumina support (a). Spectra b-d were obtained on membranes prepared using a concentration of (b) 2.4 mg/mL, (c) 4 mg/mL and (d) 8 mg/mL, respectively. The red lines in Figure 3.18 indicate the center of the main zeolite Raman band for the three increasing thicknesses. This data is summarized in Table 3.1, which suggests that the Raman band is shifting with membrane thickness. In order to determine the cause of the Raman spectral shift upon increasing membrane thickness, 5 different zeolite Y powder samples of varying particle sizes were also examined using Raman spectroscopy. The Raman spectra of these five zeolite Y powders are collectively shown in Figure 3.19. Again, the red line indicates the centroid of the main Raman band for each zeolite Y particle size and this data is summarized in Table 3.2. From the table, it is shown that the largest zeolite particles give rise to a 15 cm\(^{-1}\) red-shift in the location of the main zeolite band with respect to the smallest zeolite particles.

### 3.3.1.2 Sensing

Calcined nanocrystalline zeolite Y membranes were tested by Dr. Xiaogan Li for their sensing ability in the presence of a common simulant for more dangerous chemical warfare agents (CWA). Upon exposure of the membrane to 56 ppm dimethyl methylphosphonate (DMMP), impedance spectroscopy was utilized to monitor the change in impedance of the membrane due to the interaction with DMMP. A significant reduction of the depressed semicircle was observed, as shown in Figure 3.20, as the membrane was exposed for a prolonged period of time. The change in the impedance of the membrane was then utilized as the sensor signal. Figure 3.21 demonstrates the
sensor’s response to DMMP with increasing time by plotting the data from Figure 3.20 at a fixed frequency of 3162 Hz. For a more practical application, the total impedance of the sensor at one fixed frequency was measured as a function of time. The dynamic response of the sensor at 320°C to ~56 ppm DMMP at 300 Hz as a function of time is illustrated in Figure 3.22. The sensor showed decreased impedance when exposed to DMMP and upon removing DMMP from the gas stream, the sensor signal partially recovered.

3.3.2 Sub-micron Zeolite Y Seeded Membranes

3.3.2.1 Synthesis

Sub-micron zeolite Y was also synthesized using a hydrothermal technique in the presence of the tetramethylammonium ion (TMA), where the composition of the precursor solution was the following: 0.037Na₂O:1.0Al₂O₃:3.13(TMA)₂O:4.29SiO₂:497H₂O. Dynamic laser scattering by Dr. Haoyu Zhang suggests that the crystal size ranges from 100-250 nm. The X-ray diffraction pattern in Figure 3.23a confirms that the product was crystalline when compared to the zeolite Y standard pattern. Unlike the nano-Y, the synthesis procedure for the sub-micron zeolite Y yields a small impurity phase of zeolite A (<5%), which is denoted by the asterisk in Figure 3.23a.

Just as in the case with nano-Y, membranes on alumina supports were prepared from the dip-coating of well-dispersed solutions of sub-micron zeolite Y. Unlike nano-Y, sub-micron zeolite Y was dried and calcined at 550°C to remove the TMA ions, which could then be re-dispersed to form aqueous suspensions. Stable colloidal suspensions of sub-micron zeolite Y were prepared in the absence of any dispersants in order to prevent
from introducing cracks within the membrane structure during calcination. Extended periods of sonication were used to ensure minimal particle agglomeration. SEM was used to examine the surface coverage of the alumina supports, with Figure 3.24a being an example of a completely covered support using a 5 mg/mL dipping solution. In this surface view, the impurity phase of zeolite A can be seen dispersed throughout the seed layer, which has a cubic morphology. An SEM cross-section of the same seed layer in Figure 3.24a is shown in Figure 3.24b, which confirms that a well established seed layer is present (1.4 µm thick).

Upon forming continuous seed layers of sub-micron Y on the alumina support, the surface of the supports become very dull and are not optically colored, thus indicating a roughened surface and thicker seed layer. Because of the surface roughness of the sub-micron seed layers, ellipsometry could not be used to further characterize the seeded supports. Utilizing the procedures previously described, the sub-micron zeolite Y seed layers were subjected to hydrothermal secondary growth for either two consecutive 8 hour experiments at 90°C with Synthesis #1 (17Na₂O:1Al₂O₃:12.80SiO₂:975H₂O) or 7 days at 100°C for Synthesis #2 (0.037Na₂O:1.0Al₂O₃:3.13(TMA)₂O:4.29SiO₂:497H₂O). Based on the extent of membrane densification observed in SEM, sub-micron zeolite Y membranes require longer growth times, especially to ensure that all micro-cracks and pinholes were completely filled in.

When using Synthesis #1, the membrane prepared in this study was subjected to 2 consecutive secondary growths, consisting of 8 hours each. A second, fresh growth solution was used due to the fact that most of the nutrients in the pre-cursor solution have been exhausted after 8 hours of heating, which is evident by the incomplete membrane
densification and the significant precipitation of crystalline zeolite Y from the growth solution. Figure 3.25 provides more insight into the incomplete membrane formation after 8 hours of secondary growth. The SEM top-view in Figure 3.25a shows a partially grown membrane after 8 hours and it is clear that the inter-particle growth is not complete during this allotted time. Void spaces in between neighboring particles are clearly visible in the micrograph, thus suggesting that more time is needed for the formation of a dense membrane. After growing the membrane a second time in a fresh solution, these inter-particle spaces are no longer visible, as demonstrated in Figure 3.25b. Therefore, it was concluded that the membranes visually appear to be dense after 16 hours of total growth time and a third growth experiment was not necessary.

Figure 3.25c provides a representative SEM cross-section image of a sub-micron zeolite Y membrane following two consecutive secondary growth experiments, in which the thickness is approximately 1.8-2 microns. Due to the fact that the sub-micron zeolite Y powders were calcined prior to use and no dispersants were used in the preparation of the seed layers, calcination of the dense membrane was not necessary. Therefore, cracking of the membrane was prevented or minimized. The membrane produced from Synthesis #2 was subjected to a single 7 day growth; however, representative SEM images were not collected on this membrane type due to ongoing gas separation experiments. Given the long secondary growth time and the thickness of the seed layer, the thickness of the membrane #2 is estimated to be 4-7 microns. Dr. Verweij’s research group is further exploring the gas separation properties of this membrane; therefore, the exact thickness cannot be determined until testing is completed.
The X-ray diffraction pattern shown in Figure 3.23b was collected on a membrane after two 8 hour growths using Synthesis #1. Along with a pattern from the sub-micron zeolite Y seed crystals (a), derived patterns are also shown for zeolite Y and alumina. The diffraction peaks from the alumina support are very strong in comparison to the others, those of which correlate very strongly to those of the seed crystals. For the powder pattern in Figure 3.23a, the peak intensity of the 100% peak for zeolite A (denoted by *) is approximately 5.8% of the peak intensity for that of zeolite Y (6.1° 2θ). Following 16 hours of secondary growth, the zeolite A peak increases in intensity to 13.3% of the main zeolite Y peak. On the other hand, the change in peak intensity for the zeolite A peak in membrane #2 is much more significant (Figure 3.23c). The zeolite A peak intensity increases to 26.4% of the most intense zeolite Y diffraction peak. Also, the four diffraction peaks from the alumina substrate are less intense when compared to the peaks of the highly crystalline membrane.

### 3.3.2.2 Gas Separation

The single gas permeance and gas separation properties reported here are from long-term experiments on a single membrane of both membrane types. Non-stationary single gas permeation was used to determine the permeance of He through the sub-micron zeolite Y membranes, which provides some indication about the connectivity of the intra-zeolite spaces. It was determined experimentally that without drying the membrane, no gas passes through the membrane, thus giving a limiting permeance of $10^{-12}$ kmol m$^{-2}$ s$^{-1}$ kPa$^{-1}$. Permeance values this low are consistent with that measured using a
dense aluminum plate rather than a porous support, which indicates the limitations of the instrument. Therefore, the cell-mounted membranes were heated overnight to 150ºC (10ºC/hr) and then at 130, 80 and 30ºC. The temperature dependent single gas permeance of He through each membrane type has been compiled in Table 3.3. From the table, membrane #2 was 10-15 times more permeable compared to the membrane prepared by Synthesis #1. In the case of a damaged or defective membrane, the He permeance was found to be much higher (10^-6-10^-7 kmol m^-2 s^-1 kPa^-1), which very closely resembles the single gas permeance of the alumina support alone.

Utilizing a 50/50 mixture of CO\textsubscript{2}/N\textsubscript{2}, gas separations were used to further characterize the properties of the sub-micron zeolite Y membranes. Just as described for the single gas experiments, the membrane was heated to 150ºC (10ºC/hr) prior to testing. Temperature (30-130ºC) and pressure dependent experiments (1.4-4 bar) were carried out on the membranes and the data is summarized in Table 3.4. Figures 3.26 and 3.27 illustrate the temperature dependent separation properties of membranes #1 and #2 respectively, while Figures 3.28 and 3.29 demonstrate the pressure dependent separation properties of the two membrane types. Both membrane types show that the feed pressure greatly influences the separation factor between CO\textsubscript{2} and N\textsubscript{2}. Separation factors greater than 550 were obtained for the membrane #1 at a feed pressure of 2 bar regardless of the operating temperature. A separation factor of 550 approaches the detection limit of the chromatographic setup; therefore, a 100% or infinite CO\textsubscript{2} separation is assigned an upper limit of 550. At all experimental temperatures, membrane #2 showed similar results in that the best separations were achieved at the lowest pressure of 1.4 bar. With respect to temperature, membrane #1 gave the best results when operated at temperatures below
70°C, while membrane #2 showed the highest separation at 80°C. This data reveals how both membrane types can be applied over a broad temperature range and feed pressures.

3.4 Discussion

3.4.1 Nanocrystalline Zeolite Y Seeded Membranes

Highly crystalline nano-zeolite Y was successfully applied for the formation of uniform, ultra-thin supported seed layers, which were then converted into membranes by hydrothermal secondary growth. Stable, transparent colloidal suspensions of nano-Y were obtained by preparing dip-coating solutions from an aqueous stock of nano-Y, which was never dried. This precaution to keep the seed crystals wet was necessary since it was discovered that uniform seed layers could not be generated when attempting to re-suspend a dried or calcined nano-Y powder. This is due to the high surface energy of the nanocrystalline zeolite Y and its tendency to bind to neighboring particles in the presence of heat or high electrolyte concentrations, thus forming inseparable agglomerates. Even with extensive sonication, the zeolites could never be re-dispersed into a transparent solution.

The formation of optically colored, ultra-thin nano-Y seed layers can be attributed to nanoparticle size, as well as the fact that they were well dispersed. Having zeolites less than 50 nm in diameter leads to the formation of densely packed seed layers, which has been demonstrated in Figure 3.7. The octahedral morphology of the zeolite Y nanocrystals allows for much tighter packing, thus minimizing the amount of void space between neighboring crystals. In fact, the dense particle packing of the seed layer
provides strength to the seed layer, thus preventing the layer from being removed. When larger zeolite Y particles are used, one can easily wipe the seed layer off the support with the swipe of a finger. However, the nano-Y seed layers remain intact even after rubbing a finger across the support surface.

The myriad of colors in the optically colored seed layers is due to the localized scattering of light, which is highly dependent upon the thickness of the seed layer, as well as the surface roughness. Following the preparation of seed layers with varying thickness, one could estimate the thickness of the seed layer based on the color of the surface of the alumina support. Thinner membranes tended to give off shades of purple or violet, whereas the thicker seed layers contained more tones of green, yellow and red. As suggested by ellipsometry, there is a decrease in the seed layer thickness by 70 nm upon calcination of the seed layers. Figure 3.11 also provides evidence that the thickness is decreasing based on the fact that the optically colored support changes colors upon removing the polymer from the membrane. During the deposition of the nano-Y seed layer, the PEI creates a physical barrier for neighboring particles to contact one another, but upon removal of the polymer, the seed layer collapses leading to a more densely packed film of zeolites.

For the conversion of nano-Y seed layers into dense membranes, growth times ranging from 2 to 24 hours at 90ºC were utilized. It was quickly determined using SEM analysis that the density of the membranes appeared the same regardless of growth times greater than 2 hours. Most existing technology for preparing zeolite Y membranes requires growth times from 5 to 24 hours, depending on the composition of the growth solution. Previous work on zeolite Y membranes by members of the Dutta research lab
have shown that growth times up to 7 days are required for the fabrication of good quality membranes. By using nanocrystalline zeolite Y as the seed crystals for a membrane, this time has now been greatly reduced, primarily for two reasons. The first being the quality of the seed layer and the dense particle packing achieved by the small crystallite size. The second factor that reduces the growth time is that the nano-Y act as good seed crystals, upon which secondary growth can immediately begin to take place above a certain temperature. The combination of these two has led a considerable reduction time in the synthesis of ultra-thin zeolite Y membranes.

The data shown in Figure 3.14 indicate that the thickness of the membranes after 2 hours of growth is linear with the zeolite concentration of the dipping suspension. Therefore, depending on the seeding solution concentration, one should be able to estimate the thickness of the membrane without having to physically destroy the membrane.

In order to further characterize the microstructure of the ultra-thin nano-Y membranes, FIB was employed to prepare a thin slice of the membrane that is transparent under an electron beam for imaging. The high-resolution TEM images in Figure 3.15 provide evidence that the synthesis procedure being used results in dense membranes. In Figures 3.15(a-c), the dark layer on top of the zeolite membrane is a layer of platinum that was deposited in order to protect the membrane during the ion-milling process. Upon closer examination of the alumina support in Figure 3.15d, the inter-particle spaces between neighboring grains appear as bright white areas in the image. The high-resolution images of the nano-Y membrane do not contain any of these bright white void spaces, which would indicate the presence of defects or holes in the membrane. Also, the
grain boundaries between zeolite particles cannot be distinguished, which suggests that the membrane is dense. Within the membrane microstructure, there are areas that appear to be brighter in comparison to the bulk of the membrane. We hypothesize that these areas arise due to the instability of zeolites under a strong electron beam. It is well known that the electron beam of a TEM can easily damage or destroy the crystalline structure of zeolites; therefore, given the thickness of the membrane and the nano-Y particle size, it is not unlikely that these so called “holes” were beam induced [47-50].

With respect to the optimal calcination procedure for the preparation of defect free membranes, slow calcinations (0.2°C/min) were shown to minimize the cracking within the thin films. Even at relatively low polymer concentrations, a fast calcination can lead to localized heat pockets within the seed layer, thus leading to a more violent removal of the organics. A slow, controlled calcination slows the removal of the polymer, which in turn allows for less expansion within the seed layer to alleviate stress on the film. Due to severely cracked seed layers, the final membrane products will also contain cracks, as demonstrated in Figure 3.16.
Electron microscopy provides insight to the structural integrity and properties of the membranes; however, these techniques suggest nothing about the composition of the membranes. X-ray diffraction indicates that membranes prepared using the as described secondary growth procedure have the same crystal structure as the starting material, which is zeolite Y. There is a thickness dependence when collecting a diffraction pattern because below a concentration of 4 mg/mL (1.5 µm), no diffraction peaks were observed. It could be assumed that membranes prepared with dipping solutions of 4 mg/mL would have the crystalline structure of zeolite Y. However, XRD could not confirm this; therefore, Raman spectroscopy was used to gain further insight into the crystallinity of the ultra-thin membranes.

Based on the data shown in Table 3.1, the main Raman band arising from the zeolite membrane shifts to lower energies upon increasing the thickness of the membrane. One might question the crystalline structure of these membranes due to the fact that the primary Raman band of other zeolites with similar structures appears in this region as well. However, it is demonstrated in Figure 3.19 and Table 3.2 that the location of the main Raman band for zeolite Y is dependent upon the zeolite particle size. Upon increasing particle size, the Raman band shifts to lower energies, which resembles the shift observed for the zeolite membranes as well. Therefore, it can be concluded that the ultra-thin membranes are of the zeolite Y crystal structure, but as the membrane thickness increases, the vibrations in the membrane more closely resemble those of larger crystal sizes.

Ultra-thin, calcined nanocrystalline zeolite Y membranes were applied in the fabrication of ion conductive sensors for the detection of chemical warfare agents.
Chemical vapors of DMMP were exposed to pieces of nano-Y membranes containing electrodes, which measure the changes in ionic conductivity within the membrane upon exposure. The change in the impedance of the membrane in flowing air at 320ºC is shown by the data in Figure 3.20. When the membrane-based sensor was exposed to 56 ppm DMMP, a significant reduction in the depressed semi-circle was observed. This indicates that the bulk impedance decreased in the presence of DMMP relative to the membrane sensor in air alone. Upon increasing the exposure time from 20 to 50 minutes, there is a smaller change in impedance, which is likely due to the saturation of the membrane with DMMP.

When analyzing the changes in impedance at a fixed frequency (Figure 3.21), one can correlate the sensitivity of the sensor with time to show that the response time of the sensor is quite rapid within the first 5-10 minutes of exposure. In order to apply the sensor to a practical sensor application, the total impedance of the sensor at a fixed frequency was measured as a function of time in the presence and absence of DMMP. The trace in Figure 3.22 suggests that the membrane-based sensor can be utilized for detecting DMMP, but despite the rapid response time, the sensor signal could not be fully recovered after removing DMMP from the air stream within the testing period at the working temperature.

Although the exact mechanism for the interaction of DMMP with the zeolite is under current investigation, a possible mechanism (Figure 3.30) has been proposed for the interaction of DMMP with metal oxides (zeolites) at elevated temperatures, which leads to their eventual use as sensor materials [51,52]. This mechanism implies that DMMP vapor molecularly adsorbs onto the surface of metal oxides and loosely bonds
with the framework cations (Na⁺). This “bridging” process would stretch the Na⁺ ion further from the Na⁺-AlO₄⁻ bond, thus leading to the higher mobility of Na⁺ and a lower impedance, as observed in this work. Loosely bound DMMP would then be easily desorbed in a stream of air, which should lead to the full recovery of the sensor signal.

However, the sensor trace in Figure 3.22 shows that that the sensor signal does not recover upon removal of DMMP from the system. Given the nature of and level of densification in the nano-Y membranes, we believe that the sensor signal does not recover because DMMP is simply getting trapped inside the micropores of the zeolite membrane. The geometric restrictions imposed by the membrane prevent DMMP from coming out of the pores in all but one direction, which is the membrane surface. The process of removing DMMP will require a much longer time and possibly higher temperatures in order for the signal to return to its normal state in air. Although the nano-Y membrane-based sensor has a long recovery time, it has been shown that it can still be applied for the rapid detection of phosphonate-based chemical warfare agents, such as DMMP.

### 3.4.2 Sub-micron Zeolite Y Seeded Membranes

Sub-micron zeolite Y was utilized for the formation of supported seed layers, which were then converted into membranes by hydrothermal secondary growth. Due to their larger particle size, non-transparent colloidal suspensions of these zeolites were prepared by the re-dispersion of previously dried and calcined crystallites. Unlike the nano-Y, the sub-micron zeolites do not significantly agglomerate after heating, thus making them much easier to disperse using sonication. Although several attempts have
been made, the small component of zeolite A in the zeolite powder has only been minimized but not completely removed (Figure 3.24). Despite the small content, the zeolite A particle size is similar to that of zeolite Y; therefore, the seed layer should not be greatly affected.

Without the use of any polymeric dispersants, uniform sub-micron zeolite Y seed layers were formed. Varying the concentration of zeolite in the dipping suspension and tuning the membrane thickness was not of interest for this type of zeolite Y membrane. Therefore, a higher concentration of zeolite was chosen to ensure that the seed layer was continuous and thick enough to grow into a well formed membrane. The SEM images in Figure 3.24 confirms the presence of a relatively thick (1.4 µm), continuous sub-micron zeolite Y seed layer. As demonstrated by Figure 3.25, the conversion of these seed layers into membranes using Synthesis #1 required two separate growth experiments to ensure complete densification of the membrane. Due to ongoing gas separation experiments, no Synthesis #2 membranes were analyzed by SEM, but previous reports concluded that 7 days of secondary growth was optimal for this particular synthesis [38,39]. Depending on the desired membrane thickness, it is possible that shorter secondary growth times could be used to produce quality membranes.

With respect to the X-ray diffraction patterns of the sub-micron zeolite Y membranes, both synthesis procedures produce a crystalline membrane. However, the effect that the two growth solutions have on the content of zeolite A in the final product is different. The slow growth process in Synthesis #2 leads to a membrane that has a higher content of zeolite A, thus suggesting that this growth solution promotes growth of both zeolite Y and A. It is known that this synthesis procedure produces a small amount
of zeolite A as an impurity, which could precipitate out of solution onto the membrane surface. The combination of precipitation and the growth of existing zeolite A within the seed layer produces membranes that contain approximately 5 times the amount found in the seed crystals. The more rapid membrane growth in Synthesis #1 leads to a membrane with only 2.5 times the zeolite A content when compared to the powder. This can be explained by the fact that there are no impurity phases produced from the secondary growth solution of Synthesis #1.

Although SEM suggests that the sub-micron zeolite Y membranes are dense, further confirmation of these results was needed. By applying a feed pressure of 2 bar, non-stationary single gas permeation experiments confirmed that the membranes were indeed dense to helium at room temperature. After applying a feed gas for 24 hours or more, He did not permeate through the membrane, thus giving permeances of $10^{-12}$ kmol m$^{-2}$ s$^{-1}$ kPa$^{-1}$. However, upon heating the supported membranes to 150ºC and cooling, He began to permeate through the zeolite membrane, thus increasing the permeance values by 100-10000 times depending on the membrane synthesis method. These results indicate that by heating the membrane, water is driven out of the zeolite pores, which then opens up the micropores for gas transport. Similar results have been reported in the literature for zeolite membranes in general; however, only bulk water is being removed from the pores of zeolite Y at these temperatures. For both membrane types, temperature did not have a dramatic effect on the permeation of helium. Due to the fact that gas permeates through the membranes, it can be concluded that there is some connectivity between neighboring particles; otherwise, gases would not move across the membrane because all of the passages would be blocked. Based on the Knudsen model of gas transport through porous
membranes, the single gas permeance for helium was estimated to be from $2.5 \times 10^{-6}$ to $7 \times 10^{-7}$ kmol m$^{-2}$ s$^{-1}$ kPa$^{-1}$ for a 2 and 7 µm thick membrane, respectively. A tortuosity factor ($\tau_p$) of 4 was chosen because of the large number of possible paths for a gas to permeate through the membrane. Previous experiments have determined the porosity or the void space of zeolite Y to be approximately 16%; therefore, this value was used for $\varphi_p$ [23]. Given that membrane #1 has permeances on the order of 1000 times less than the predicted Knudsen value, it can be concluded that the predominant method of gas transport in the membrane is not Knudsen. This further indicates that there are no pinholes or micro-defects in the membranes; otherwise, the Knudsen diffusion would dominate. The same applies for membrane #2 because there are no similarities in the experimental data when the Knudsen diffusion model is applied.

Upon comparing the permeation of He through the two membrane types, there is an obvious difference between them, especially due to the fact that they are both crystalline zeolite Y membranes. Both membrane types were prepared using the same seed crystals and dip-coating procedures, but yet one is 10-15 times more permeable than the other. A hypothesis has been proposed to explain this difference, which is based on the particular secondary growth solutions/procedures used to convert the supported seed layers in membranes. Synthesis #1 can be considered a rapid growth solution because after 4-6 hours of heating at 90ºC, large crystalline zeolite Y particles begin to precipitate out of solution. After 10 hours, the supernatant from the initial pre-cursor solution is completely clear, thus indicating that there are minimal nutrients left for further membrane growth. Nanocrystalline and sub-micron zeolites have high surface areas and when placed into this rapid growth solution, they immediately begin to build onto the
existing seeds. In order to have good interconnectivity between particles, the secondary growth must proceed in a manner that allows neighboring zeolite pores to be constructed together. However, the synthesis occurs so quickly that the secondary growth continues in an uncontrollable fashion, which leads to zeolite particle fusion rather than particle growth. Rather than the supercages connecting together, neighboring zeolites simply fuse together and restrict the connectivity between them. Even during rapid membrane growth, there is still a possibility that a small portion of the pores can align and be connected throughout the membrane. According to this hypothesis, nano-Y seeded membranes prepared using Synthesis #1 would share similar gas separation properties with the sub-micron seeded membranes because of their rapid growth and the lack of connectivity between neighboring particles. For this reason, nano-Y seeded membranes were not tested for their gas separation properties.

In comparison, Synthesis #2 is considered to provide a slower templated growth because 3-4 days of heating at 100°C is required for sub-micron zeolite Y particles begin to form in solution. Unlike the rapid growth of Synthesis #1, this process promotes good interconnectivity between particles by allowing neighboring zeolite pores to be constructed together. Although some pore blockage is likely between particles, a more controlled growth leads to less restricted pathways, hence higher gas permeance. The experimental single gas permeances for the two membrane types provide supporting evidence of this hypothesis. The 10-15 times increase in He permeance for membrane #2 indicates that the interconnectivity between the pores of neighboring particles is much higher than that for membrane #1. From this, it can be concluded that Synthesis #2 is
better suited for the fabrication of zeolite Y membranes using sub-micron seed crystals, especially for more practical applications where faster gas transport is required.

Sub-micron zeolite Y membranes were utilized as mixed gas separation membranes because of their stability and rugged design. 50/50 mixtures of CO₂ and N₂ were applied to the membrane and the composition of the gas permeating through the membrane was measured using gas chromatography. Although the chromatograms are not shown, the peak intensity for both CO₂ and N₂ were approximately 10-15 times higher for membrane #2 when compared to membrane #1 at the same temperature. This is reflected in the single gas permeances, where helium is more permeable for membrane #2. The overall performance of membrane #1 was found to be better with respect to the separation, especially at 70°C or below where factors greater than 60 were obtained at all feed pressures. However, from a practical standpoint, membrane #2 was more realistic because of a compromise between improved flux and good separation factors. For both membrane types, the general trend was found to be a decrease in separation with an increase in feed pressures. This trend is based on the breakdown of the transport mechanism that governs the CO₂/N₂ separation at lower pressures, as proposed by Kusakabe et al. [23,28,29,53]. When utilizing lower pressures, carbon dioxide molecules adsorb onto the outside of the membrane, where they migrate into the micropores by surface diffusion. Nitrogen molecules, which are not adsorptive, primarily penetrate into the zeolite pores by an activated mechanism from the outside gas phase. Adsorption of CO₂ near the mouth of the micropores can cause narrowing which blocks N₂ molecules from entering the pores. Higher feed pressures shift the concentration of CO₂ and N₂ within the zeolite membrane because of an increase in the number of molecular
collisions. These collisions force more N₂ into the pores, thus causing them to permeate through the membrane at a lower CO₂/N₂ separation factors.

With respect to temperature, CO₂ has been shown to condense within the micropores of zeolite Y and interact very strongly at lower temperatures [23,29]. When CO₂ molecules are strongly adsorbed on the pore wall, the CO₂ permeation rate will be low even if CO₂ is concentrated in the pore. This strong interaction between CO₂ and the zeolite can be used to explain the extremely high separations in membrane #1 at temperatures below 70°C. A combination of condensation and slow hopping of CO₂ in the pores limits the amount of N₂ that permeates through the membrane, hence separation factors ranging from 60-550. The condensation of CO₂ becomes less of a factor at higher temperatures, which makes it difficult to apply this mechanism to membrane #2. This slow growth membrane has optimal separation between CO₂ and N₂ at 80°C, which is not typically observed for zeolite Y membranes. The optimal temperature for achieving the highest CO₂/N₂ separations has been consistently reported as 30°C [23,28-30,53,54]. Due to the fact that only one membrane was tested and this membrane was not calcined prior to use, more experiments are needed to develop a better understanding of the separation mechanism at higher temperatures.

In order to demonstrate the feasibility of these zeolite Y membranes relative to existing zeolite Y membrane technology, their ability to separate CO₂ and N₂ is compared to published values. When comparing the single gas permeances of membrane #1 and membrane #2 to those previously reported permeances, a direct comparison cannot be made due to the fact that helium was used as a model gas rather than CO₂ and N₂. Unlike CO₂, which interacts with the walls of the zeolite, He and N₂ have not been reported to
interact with the zeolite; therefore, the permeance of these two gases can be compared based on similarities in their gas transport properties within zeolite Y. Nitrogen permeances ranging from $1-5 \times 10^{-8}$ kmol m$^{-2}$ s$^{-1}$ kPa$^{-1}$ at experimental temperatures of 30-130°C have been reported, which is 10-100 times more permeable than He for membrane #1 [23,28-30,53,54]. With He permeances from $1-1.25 \times 10^{-8}$ kmol m$^{-2}$ s$^{-1}$ kPa$^{-1}$, these findings show that membrane #2 agrees well with those permeances reported for N$_2$.

A separation factor of 100 is one of the highest reported for CO$_2$/N$_2$ separation, which was obtained between 25-35°C at a feed pressure of 1 bar [23,53]. Even though membrane #1 is superior to this value at room temperature, it is more realistic to compare membrane #2 because of its higher permeance. Membrane #2 gave a separation factor of 70 at 1.4 bar feed pressure and based on the observed trend, this value would have increased when lowering the pressure to 1 bar. However, due to instrumental limitations, lowering the pressure was not possible. Reported CO$_2$/N$_2$ separation factors range from 2-20 at temperatures above 30°C, but the interesting feature about this membrane is its ability to separate at higher temperatures, even at higher than average feed pressures (>100 at 80°C and >50 at 130°C). Therefore, membranes prepared using Synthesis #2 have potential applications in situations where CO$_2$/N$_2$ separations are required at elevated temperatures and pressures.

3.5 Conclusions

Nanocrystalline and sub-micron zeolite Y have been successfully dip-coated onto macro-porous alumina supports and grown into homogeneous, dense membranes, ranging from 0.2-7 µm thick, using a hydrothermal secondary growth process. Through the use of
stabilized nanocrystalline zeolite Y suspensions, uniform zeolite seed layers of a desired thickness were prepared. Secondary growth conditions were optimized to produce dense membranes in only 2 hours. These membranes were shown to have applications in the development of zeolite based sensors for the detection of chemical warfare agents. They were shown to have a quick response in the presence of DMMP; however, their recovery was quite slow upon removal of DMMP. For the sub-micron zeolites, two different secondary growth solutions were utilized in order to determine the optimal growth conditions for the fabrication of gas separation membranes. Although a rapid growth procedure was found to produce highly selective membranes, their permeances were extremely low for realistic applications. A slower, more controlled procedure was utilized in which highly crystalline zeolite Y membranes were produced. The effectiveness of this growth procedure was demonstrated by improved single gas permeances and the ability of the membrane to selectively separate CO\textsubscript{2} from N\textsubscript{2} over a wide range of temperatures and pressures.
3.6 References


<table>
<thead>
<tr>
<th>Raman Spectrum</th>
<th>Zeolite Concentration</th>
<th>Membrane Thickness</th>
<th>Position of Main Raman Band</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>N/A</td>
<td>Bare Al₂O₃</td>
<td>N/A</td>
</tr>
<tr>
<td>(b)</td>
<td>2.4 mg/mL</td>
<td>~0.6 µm</td>
<td>518 cm⁻¹</td>
</tr>
<tr>
<td>(c)</td>
<td>4 mg/mL</td>
<td>~1 µm</td>
<td>518 cm⁻¹</td>
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<tr>
<td>(d)</td>
<td>8 mg/mL</td>
<td>~1.8 µm</td>
<td>508 cm⁻¹</td>
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</table>

*Table 3.1:* Dependence of main Raman band location on membrane thickness.
<table>
<thead>
<tr>
<th>Respective Raman Spectrum and Zeolite Y Particle Size</th>
<th>Position of Main Raman Band</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 25-50 nm</td>
<td>518 cm⁻¹</td>
</tr>
<tr>
<td>(b) 80-200 nm</td>
<td>518 cm⁻¹</td>
</tr>
<tr>
<td>(c) 450-600 nm</td>
<td>510 cm⁻¹</td>
</tr>
<tr>
<td>(d) 600-800 nm</td>
<td>504 cm⁻¹</td>
</tr>
<tr>
<td>(e) 850-1100 nm</td>
<td>503 cm⁻¹</td>
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**Table 3.2**: Dependence of main Raman band on zeolite Y particle size.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Synthesis #1 Membranes (kmol m^{-2} s^{-1} kPa^{-1})</th>
<th>Synthesis #2 Membranes (kmol m^{-2} s^{-1} kPa^{-1})</th>
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<tbody>
<tr>
<td>30</td>
<td>1.1x10^{-9}</td>
<td>1.0x10^{-8}</td>
</tr>
<tr>
<td>80</td>
<td>9.0x10^{-10}</td>
<td>1.3x10^{-8}</td>
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<tr>
<td>130</td>
<td>1.1x10^{-9}</td>
<td>1.1x10^{-8}</td>
</tr>
</tbody>
</table>

Table 3.3: Single gas permeances of helium through membrane #1 and #2 at various temperatures.
### Synthesis #1 Membranes

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Feed Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 bar</td>
</tr>
<tr>
<td>30</td>
<td>&gt;550</td>
</tr>
<tr>
<td>50</td>
<td>&gt;550</td>
</tr>
<tr>
<td>70</td>
<td>&gt;550</td>
</tr>
<tr>
<td>90</td>
<td>&gt;550</td>
</tr>
<tr>
<td>110</td>
<td>&gt;550</td>
</tr>
<tr>
<td>130</td>
<td>&gt;550</td>
</tr>
</tbody>
</table>

### Synthesis #2 Membranes

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Feed Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.4 bar</td>
</tr>
<tr>
<td>30</td>
<td>70.2</td>
</tr>
<tr>
<td>80</td>
<td>250.0</td>
</tr>
<tr>
<td>130</td>
<td>53.1</td>
</tr>
</tbody>
</table>

**Table 3.4**: CO₂/N₂ separation factors for membranes #1 and #2 at various temperatures and feed pressures.
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Figure 3.12: Image demonstrating the reproducibility in seed layer formation using a 4 mg/mL zeolite concentration (All 3 supports calcined).
Figure 3.13: SEM cross-sections (a-f) of nano-Y membranes formed after 2 hours of secondary growth using increasing zeolite concentrations (a) 1.6 mg/mL (b) 2.4 mg/mL, (c) 3.2 mg/mL, (d) 4 mg/mL, (e) 8 mg/mL, (f) 20 mg/mL. (White bar shows demarcation between zeolite membrane and support)
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Figure 3.15: TEM cross-sections of nano-Y membrane prepared using a 1.2 mg/mL zeolite concentration. Thin membrane cross-sections were produced using FIB.
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Figure 3.30: Proposed mechanism for the molecular adsorption and desorption of DMMP on metal oxides.
CHAPTER 4

ZEOLITE Y BASED ARTIFICIAL PHOTOSYNTHETIC ASSEMBLIES

4.1 Introduction

Recent emphasis has been placed on the development of photocatalysts that extend the amount of usable solar light into the visible region for the generation of hydrogen from water. A large number of photocatalysts such as ZnO, TiO₂, CdS and ZrO₂ have been reported to have activities for splitting water [1-9]. Typically used as particle dispersions, most photocatalysts perform only under ultraviolet light because of their wide-bandgaps, which limits their practical use for H₂ production from water. Cadmium sulfide (CdS) has been shown to be a potential candidate as a photosensitizer for water splitting because of its visible region bandgap (2.42 eV). Absorption of light by these particles creates mobile electrons, e⁻, and holes, h⁺, that migrate to the surface and undergo redox processes with adsorbed chemical species [10]. Due to the short lifetimes of these photogenerated carriers, only very fast reactions with surface bound species lead to the formation of reduced or oxidized species in solution.

CdS with various morphologies, sizes and crystal structures have been extensively studied in an effort to improve the photochemical formation of H₂ by water reduction [10-21]. Depending on the particular method chosen for CdS synthesis, two different crystalline phases can be obtained; hexagonal and cubic. Few reports claim that the cubic
phase was found to be more catalytically active, but the more stable, hexagonal phase of CdS is most often noted as the more active crystalline phase for water splitting [11,15,16]. However, even in early experiments, it was determined that the use of CdS alone as a photocatalyst has its limitations. Besides low H₂ yields, it is well known that CdS photocorrodes when irradiated in water due to inefficient charge separation (electron/electron hole pair recombination) [22-24].

The production of hydrogen from water using CdS in the presence of certain electron donors/scavengers have shown to slow the rate of photocorrosion [14,16-18,25-28]. The most common electrolyte solution for CdS based water splitting is a mixture of sulfide/sulfite. Sulfides, S²⁻, are used as electron hole scavengers, which slow the back electron transfer from the conduction band to the valence band in CdS. Sulfite is utilized to eliminate the newly formed sulfur species that can affect the catalytic reaction by absorbing useful light. Despite the observed improvements in stability with electron donors (ED), Kusakabe et al. have shown that bare CdS loses its catalytic activity even in the presence of a fresh ED solution [29,30]. From this, they concluded that photocorrosion leads to the dissolution of Cd²⁺ ions from the surface of CdS by the oxidation of the sulfide with photogenerated valence band holes. Although the presence of S²⁻ in the ED solution slows the photocorrosion, scavenging these valence band holes cannot fully protect CdS from decomposition.

In an attempt to improve the photoactivity and photostability of CdS, it has been coupled with other materials such as ZnO, ZnS, TiO₂, Pt and MoS₂, which promotes a better charge separation between the electron and electron hole [11,12,19,31-37]. Several different strategies have been used in developing these composite photocatalysts.
including physical mixing, layering, incorporation into solid matrices and colloidal synthesis. The solid matrix of aluminosilicate zeolites is of particular interest because of their well-defined, three-dimensional microporous structure. The nanometer sized cages of zeolite Y have been utilized for the incorporation of size-constrained CdS and TiO₂ [38-52]. These materials in zeolite Y have been studied separately for their catalytic properties, but no reports exist of the two being coupled together in zeolite Y.

Not only can the zeolite increase the surface area of CdS as a photocatalyst, but it has also been proposed that the zeolite framework helps to stabilize CdS and slows the photocorrosion [15,39]. It has been hypothesized that the zeolite can slow the dissolution of Cd²⁺ from the surface of zeolite-bound CdS because the CdS is now surrounded by the framework of the zeolite. The zeolite creates a barrier for the Cd²⁺ ions to escape, thus the ions are added back to CdS nanoparticles in the presence of sulfide ions [29,30]. Therefore, the zeolite structure helps to slow down photocorrosion and stabilizes the nanoparticles during photocatalysis. With respect to the incorporation of titania into zeolite Y, an ion-exchange procedure has been developed using titanyl salts that can oxidize to form TiO₂ in the zeolite. However, a clear understanding of the growth mechanism of zeolite-bound TiO₂ has not been well-established. Zeolite Y encapsulated titania has been shown to have good catalytic properties for the decomposition of organic dyes and molecules, but because of its high-energy bandgap, the usefulness of the material for water splitting is limited [40-43,53,54].

The interesting feature about zeolite Y is that neighboring supercages are connected through 0.74 nm windows, which allows incorporated species to come into intimate contact with one another. In order to improve the photocatalytic properties of
zeolite-bound CdS and TiO₂, a novel method for the synthesis of binary and ternary photocatalyst systems organized using the micro-structure of zeolite Y has been developed and thoroughly characterized. Well-defined nanoparticles of CdS, TiO₂, and Pt were all assembled using zeolite Y as the scaffold. Taking advantage of the titania incorporation process and the ion-exchange properties of the zeolite, co-localization of these materials within the zeolite was found to provide effective contacts between these materials. This configuration of composite photocatalysts demonstrates the capabilities of zeolite Y to organize supramolecular species that yield high rates of hydrogen production under light from water containing sulfide and sulfite as sacrificial reagents.

4.2 Experimental Section

4.2.1 Materials

Commercially available zeolite Y was purchased from Union Carbide (LZY-52, Si/Al = 2.6). Sodium hydroxide (NaOH, 98.8%) and sodium sulfite (Na₂SO₃, 98%) from Mallinckrodt were used. Ammonium titanyl oxalate (ATO), tetraammineplatinum chloride (Pt(NH₃)₄Cl₂), chloroplatinic acid (H₂PtCl₆), hydrazine hydrate (N₂H₄·XH₂O, 98%) and sodium sulfide (Na₂S, 98%) were obtained from Aldrich (Milwaukee, WI, USA). Cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O, 99%) was from GFS Chemicals and hydrogen sulfide (H₂S, 99%) gas was purchased from AGA Specialty Gases. High purity methanol (MeOH, 99.99%) from Alfa Aesar was also used. The H₂O used in this study was purified by a Millipore ultrapure water system. No further treatment or purification was necessary for all chemicals.
4.2.2 Synthesis

Prior to the synthesis of any catalytic materials, zeolite Y (~600 nm) was first calcined at 600°C overnight (1°C/min), followed by cooling to 100°C, where water filled air was passed over the zeolite until room temperature was reached. Following calcination, the zeolite was ion-exchanged using 0.1 M NaCl for 2 hours. The sodium zeolite Y (Na-Y) was washed and filtered until no Cl\(^-\) was detected in the supernatant and dried at 70°C. The naming scheme employed throughout the next three sections has been extensively described in detail in Table 4.1.

**TiO\(_2\) Zeolite Y.** The inclusion of titanium dioxide nanoclusters into the framework of zeolite Y was carried out following a common procedure, which is further described here [41-44]. Using calcined Na-Y, titanium dioxide was synthesized inside zeolite Y using 1 to 3 pre-cursor incorporation steps. In a typical synthesis, 3 grams of Na-Y was added to 30 mL of 0.2 M ammonium titanyl oxalate (ATO) solution and stirred for 2 hours. The titanyl-exchanged zeolite Y was then washed and centrifuged immediately until oxalate was no longer found in the wash. The zeolite was then air-dried at room temperature before the oxidation to form TiO\(_2\) at 550°C (2°C/min) for 5 hours in the presence of flowing air. The first ATO exchanged/calcined sample will be referred to TiO\(_2\)-Ya. For a second titanyl exchange, TiO\(_2\)-Ya was placed back into a 0.2 M ATO solution (100mg/1mL) and stirred 2 more hours. Following the clean-up and air drying, the sample was once again oxidized at 550°C for 5 hours, thus generating TiO\(_2\)-Yb. In the case of a third titanyl treatment, the ion-exchange process was repeated once again, followed by a thorough washing, drying and oxidation at 550°C (TiO\(_2\)-Yc).
Cds Zeolite Y. The inclusion of cadmium sulfide nanoparticles into zeolite Y was carried out following a well-established procedure, which is summarized here [38,39,46,47,49,51,52]. Using calcined Na-Y, Cds was synthesized inside zeolite Y using two different methods. In a typical synthesis, 3 grams of Na-Y was added to 50 mL of 0.2 M cadmium nitrate solution and stirred at room temperature overnight. The zeolite was centrifuged and placed back into a fresh solution of cadmium nitrate and stirred for 8 more hours. The excess cadmium was removed by washing and centrifugation. The cadmium exchanged zeolite Y (Cd-Y) was dried at 70°C before being converted into Cds.

Synthesis of Cds was done using H2S gas in an inert atmosphere and Na2S in an aqueous environment. 500 mg of Cd-Y was placed into a quartz vacuum tube and activated at 550°C for 1 hour while under a vacuum (10^-5 Torr). Upon cooling, the cadmium-containing zeolite was exposed to 1 atm of H2S and allowed to react for 1 hour. The H2S was then removed from the system and the zeolite treated a second time with H2S using the same procedure to ensure a complete reaction. A vacuum was pulled on the system for two hours after the reaction to remove all un-reacted gas. The cadmium sulfide containing zeolite Y (Cds-Y(g)) was then exposed to the atmosphere for several days allowing water to fill the supercages of zeolite Y. When using Na2S as the sulfur source for the synthesis of zeolite bound Cds, 500 mg of Cd-Y was added to a stirred solution containing an excess of sodium sulfide. Upon addition, the solution immediately turns a bright orange-yellow color. This Cds zeolite Y (Cds-Y(s)) was stirred for 2 hours prior to removing the un-reacted sulfide using several centrifugation and washing steps. The Cds-Y(s) was then dried under vacuum without any heat to prevent any changes in the Cds.
**Binary Catalyst Systems.** For the fabrication of zeolite-bound binary systems containing either CdS/TiO₂ or Pt/TiO₂, similar procedures as described above were followed. When combining CdS and TiO₂ into the same zeolite system, two different approaches were used. The first approach involved consecutive ion-exchanges of ATO (1 to 3 exchanges), followed by oxidation at high temperatures. Regardless the number of titanyl exchanges, 600 mg of the zeolite sample was then ion-exchanged for 2 hours in a 0.2 M cadmium nitrate solution. A second cadmium exchange was also used to ensure maximum loading with the TiO₂ zeolite Y samples. Upon removal of the excess cadmium and drying, the zeolites were treated with H₂S as previously described. Samples generated using this protocol will be referred to as CdS/TiO₂-Y(1a-c), thus corresponding to the number of ATO exchanges. The second approach for this binary system was to alternate the synthesis of TiO₂ and CdS, rather than consecutive synthesis of each. The first ATO exchange and oxidation was followed by a cadmium exchange and exposure to a sulfide source. This process of alternating the materials was carried out up to three complete cycles and will be referred to as CdS/TiO₂-Y(2b-c), thus corresponding to the number of ATO exchanges.

In order to compare the zeolite-bound and non-zeolite-bound binary system of CdS/TiO₂, the two materials were isolated from the zeolite matrix. 500 mg of CdS/TiO₂-Y(1b) was placed into 20 mL of 20% hydrofluoric acid (HF) in a Teflon-vessel and allowed to stir for 1 hour. The solution was then centrifuged to collect the orange-yellow precipitate, followed by several washes to neutralize the acid and remove the fluoride ions. The extracted CdS/TiO₂(np) was kept as a wet paste rather than drying into a powder.
Just as described for the CdS/TiO$_2$ binary system, Pt/TiO$_2$ zeolite photocatalysts were also prepared by varying the synthesis approach. The first approach involved the consecutive incorporation of titania, followed by the formation of platinum nanoclusters within the zeolite. Using a similar procedure detailed by Dutta et al., 200 mg of the both TiO$_2$-Ya and TiO$_2$-Yb were ion-exchanged in 5 mL of a 2 mM solution of Pt(NH$_3$)$_4$Cl$_2$ for 24 hours at room temperature [55]. This concentration of Pt(NH$_3$)$_4$Cl$_2$ corresponds to 1 wt% platinum with respect to the mass of zeolite in the exchange solution. After washing and centrifugation, the platinum exchanged TiO$_2$-Y was dried overnight at 70ºC. Platinum reduction was achieved at 450ºC for 6 hours (1ºC/min) in 5% H$_2$ balanced with N$_2$, followed by cooling in the same reaction environment (Pt/TiO$_2$-Y(1a-b)).

The second approach for this binary system was to vary the order of synthesis for TiO$_2$ and Pt, rather than consecutive synthesis of titania followed by platinum. Using 200 mg of Pt/TiO$_2$-Y(1a), a second ATO exchange and oxidation were carried out the singly exchanged Pt/TiO$_2$-Y sample. In order to keep the Pt loading the same after the first exchange, no further tetraammineplatinum chloride exchanges were performed (Pt/TiO$_2$-Y(2b)).

*Ternary Catalyst Systems.* For the fabrication of a zeolite-bound ternary system containing Pt, CdS and TiO$_2$, similar procedures as described above were followed. In a series of experiments, platinum was deposited in or onto CdS/TiO$_2$-Y(1b) using four different methods. The first 3 methods utilize H$_2$PtCl$_6$ as the platinum precursor, which has to be wet-impregnated within the zeolite because of the anionic nature of the complex. In a typical wet-impregnation, 1 mL of a 10.2 mM solution (1 wt% Pt) was added to 10 mL of water containing 200 mg of CdS/TiO$_2$-Y(1b). The pH of the solution was adjusted
between 3-4 using dilute HCl and allowed to stir for 1 hour. The solvent was removed using a rotovaporizer, thus forcing the platinum precursor to deposit onto the zeolite.

Platinum reduction for the wet-impregnated zeolite was first reduced using high temperatures in a reducing environment. As previously described, the zeolite was heated to 450ºC for 6 hours in a steady flow of reducing gas (Pt(1)/CdS/TiO₂-Y(1b)). The second reduction method was a light induced photoreduction in the presence of a sacrificial electron donor. 200mg of the wet-impregnated zeolite was placed into 5 mL of 20% ethanol in water. After degassing the sample using argon, the zeolite suspension was irradiated using ultraviolet/visible light (2 W/cm²) from a Thermo 500W arc lamp. The solution was irradiated for one hour prior to washing and drying the zeolite (Pt(2)/CdS/TiO₂-Y(1b)). The third reduction process using the H₂PtCl₆ impregnated zeolite was by a chemical reduction. This was carried out by first preparing a reducing solution at 50ºC, which contains 200 µL of hydrazine hydrate in 5 mL of water. The pH of this solution was adjusted to 10.8-11 using dilute ammonia. The zeolite was directly added to the vigorously stirred reducing solution, where it was mixed for one hour. Several washing steps were needed to remove the un-reacted hydrazine, followed by drying at room temperature (Pt(3)/CdS/TiO₂-Y(1b)).

The fourth protocol for the deposition of Pt in the ternary system is through the use of the same Pt(NH₃)₄Cl₂ ion-exchange process previously detailed for the binary system. Rather than ion-exchanging the zeolite for 24 hours, the zeolite in the ternary system was exchanged for only one hour prior to removing the solvent using a rotovaporizer. Reduction was carried out at high temperature in a reducing environment (Pt(4)/CdS/TiO₂-Y(1b)).
4.2.3 Characterization Techniques

The absorption spectra of the zeolite-containing photocatalysts were characterized using a Shimadzu diffuse reflectance integrating sphere. All spectra were converted using the Kubelka-Munk transformation with zeolite Y as the reference. Crystal structure and phase composition of zeolite-bound photocatalysts were determined with either a Rigaku Geigerflex or a Bruker D8 X-ray diffractometer using nickel-filtered CuKα (λ=1.5405 Å) radiation. Raman spectroscopy was performed using a Renishaw - Smiths Detection Combined Raman - IR Microprobe equipped with the 514.5 nm laser line of an argon ion laser. Diffuse reflectance infrared spectra (DRIFTS) were collected using a Perkin-Elmer infrared spectrometer equipped with a Pike Technologies diffuse reflectance heat chamber. High resolution electron microscopy (EM) was used to determine the particle size and crystalline structures of the zeolite bound photocatalysts. Transmission and scanning transmission EM were performed on either a Tecnai F20 (Philips, Holland) or Titan 3 Probe-Corrected Monochromated electron microscope (FEI Company, US) operated 260-300 kV. Both TEM instruments were equipped with energy-dispersive analysis of X-rays (EDAX) for in-situ elemental analysis. Elemental analysis of zeolite bound catalysts was performed by Galbraith Laboratories (Knoxville, Tennessee).

Photocatalytic production of H₂ was carried out in a 50 mL cylindrical Pyrex reactor for all photocatalysts. For all zeolite samples containing CdS, 50 mg of the photocatalyst was dispersed in 30 mL of water containing Na₂S (0.1 M), Na₂SO₃ (0.5 M) and NaOH (1.0 M), which serve as sacrificial reagents in the reaction. The same electrolyte solution was also used for the CdS/TiO₂ binary system extracted from the zeolite using HF. All of the precipitate collected from the extraction was utilized for
hydrogen evolution experiments, which was later dried into a powder for further analysis. Photolysis experiments on the Pt/TiO₂ binary systems were performed in 30 mL of 33 vol% methanol in water, which has also been shown to serve as an electron donor [3,56,57].

All solutions were sonicated for 5-10 minutes to ensure that the zeolites were well-dispersed. Prior to photolysis, the solution was purged with argon for 30 minutes to remove any air from the reaction vessel. In all experiments, irradiation of the photocatalysts was carried out using a 200W Hg(Xe) lamp with an optical cut-off filter (Oriel 66228, 320<λ>570), as well as a water filter to prevent infrared radiation from heating the sample. The radiation energy from the Hg(Xe) lamp to the reaction cell was determined to be 250 mW/cm² after passing through a collimating lens, which focuses the light exiting the water filter. The reaction was performed while stirring using a magnetic stirring rod. The amount of evolved H₂ was analyzed by manually injecting 50 µL of the headspace into a gas chromatograph equipped with a molecular sieve 5A column. All experimental data and reaction rates were based on irradiation times ranging from 4 to 8 hours.
4.3 Results

The characterization and experimental results described below are presented in the order by which the photocatalyst systems were developed. Characterization of the single zeolite-based catalyst systems of TiO$_2$ and CdS are detailed first, followed by the binary systems of CdS/TiO$_2$ and Pt/TiO$_2$. The ternary system of Pt/CdS/TiO$_2$ is then explained prior to the experimental hydrogen evolution data for a total of 16 different photocatalyst systems.

4.3.1 TiO$_2$ Zeolite Y

Titanium dioxide was incorporated into the microstructure of zeolite Y using a titanium precursor that contains the titanyl cation. The set of Raman spectra in Figure 4.1 were collected after each ammonium titanyl oxalate (ATO) ion-exchange and calcination at 550ºC in flowing air. After the first exchange/calcination, Figure 4.1c demonstrates that the only subtle change in TiO$_2$-Ya was the broadening of the 503 cm$^{-1}$ band when compared to zeolite Y in Figure 4.1a. Figure 4.1d shows the Raman spectrum for TiO$_2$-Yb after the second exchange/calcination, in which several changes were observed in the spectrum. Three new bands appear at Raman shifts of 142, 395, and 639 cm$^{-1}$, all of which agree with those of anatase TiO$_2$ (Figure 4.1b). Upon the third ion-exchange and calcination, major changes occur in the Raman spectrum, as indicated in Figure 4.1e. All zeolite bands present in Figure 4.1d, except the primary band, are no longer observed for TiO$_2$-Yc. The intensity of the main zeolite band around 503 cm$^{-1}$ has been greatly reduced; however, it still appears in the spectrum as a shoulder to the 514 cm$^{-1}$ band of
anatase TiO$_2$. The Raman bands corresponding to anatase TiO$_2$ in Figure 4.1e have become more intense and more clearly defined when compared to that of TiO$_2$-Yb.

A diffuse reflectance infrared study of the initial titanyl-exchanged zeolite Y as a function of temperature was carried out. Figure 4.2 shows the diffuse reflectance infrared spectra (Kubelka-Munk transformed) of ATO exchanged (0.2 M, 2 hours) zeolite Y at increasing calcination temperatures. At room temperature (bottom most spectrum), the characteristic 908 cm$^{-1}$ titanyl band is present (indicated by arrow). Despite the changes in the background upon heating the sample in-situ to 550ºC in flowing air, the titanyl band begins to disappear. At 550ºC (top-most spectrum), the 908 cm$^{-1}$ band almost disappears from the spectra.

Figure 4.3 shows the diffuse reflectance (DR) absorption spectrum of TiO$_2$-Y(a-c), as well as that for bulk anatase TiO$_2$. The bandgap of the titania in TiO$_2$-Y(a-c) was calculated from a Tauc plot, which is a linear correlation between $[F(R)h\nu]^2$ and $h\nu$ [58]. The intercept in the energy ($h\nu$) axis in the straight linear $[F(R)h\nu]^2$ versus $h\nu$ is the bandgap for the particular material of interest. TiO$_2$-Ya contains species that do not show a clear bandgap with respect to bulk anatase, which has a bandgap of 3.0 eV. However, upon further treatment of the zeolite, a bandgap for TiO$_2$-Yb is observed at 3.5 eV, as well as an overall increase in the absorption intensity. The DR spectrum for TiO$_2$-Ye red-shifts even further (3.43 eV) and has a significant intensity increase compared to the TiO$_2$-Ya and TiO$_2$-Yb.

X-ray diffraction in Figure 4.4 shows the crystalline diffraction pattern of zeolite Y before any ATO exchanges, as well as the diffraction pattern for TiO$_2$-Y(a-c). When comparing the diffraction peak intensities of the ATO exchanged/calcined zeolites to
untreated zeolite Y, they become less intense and less distinct upon increasing the number of titania treatments. There were no new TiO$_2$ diffraction peaks observed for any of the ATO treated samples, only the loss of zeolite peaks. HR-TEM of TiO$_2$-Yb in Figure 4.5 confirms the presence of nanometer sized crystalline material near the edges of the zeolite, which are highlighted by bold white circles. The zeolite bound particles appear to be on the order of 3 to 10 nm and they contain well-defined lattice fringes with a d-spacing of 0.352 nm.

### 4.3.2 CdS Zeolite Y

Zeolite bound CdS was synthesized using two different sulfide sources and the results suggest that the two products are not identical. Figure 4.6 shows the DR absorption spectrum of CdS-Y prepared using both H$_2$S and Na$_2$S. The bandgap for both CdS-Y samples was estimated using a Tauc plot to be 2.31 (CdS-Y(g)) and 2.33 eV (CdS-Y(s)). The diameter of the CdS nanoparticles was estimated by using eq. 4.1, which was developed by Brus [59]:

$$E = E_g + \frac{h^2}{8r^2} \left[ \frac{1}{m_e} + \frac{1}{m_h} \right] - 1.8e^2/4\pi\varepsilon\varepsilon_0 r$$

(4.1)

where $E$ is the bandgap of the nanoparticle, $E_g$ is the bandgap of the bulk solid, $h$ is Planck’s constant, $r$ is the radius of the nanoparticle, $m_e$ is the effective mass of an electron in the solid, $m_h$ is the effective mass of a hole in the solid, $\varepsilon$ is the dielectric constant of the solid, and $\varepsilon_0$ is the permittivity of a vacuum. Using the Brus equation, the
CdS in both CdS-Y samples was estimated to be greater than 10 nm, which is the estimated size for bulk CdS with a bandgap of 2.42 eV.

Both CdS-Y samples were a bright orange-yellow color when collecting DR data; however, CdS-Y(g) has a very different absorption spectrum immediately following the synthesis. Figure 4.7 illustrates the changes that take place in the H2S treated zeolite over time upon exposure to the atmosphere. After 18-24 hours of exposure to the atmosphere, the DR spectrum very closely resembles that shown in Figure 4.6 for the same sample. The absorption edge of CdS-Y red-shifts by 130 nm (0.94 eV) when exposed to moisture in the atmosphere, as compared to the same sample in pristine dry conditions immediately following the synthesis.

The presence of the CdS in both CdS-Y(g) and CdS-Y(s) was confirmed by the existence of the characteristic 300 and 600 cm⁻¹ phonon bands shown in Figure 4.8(b-c), respectively. A third vibrational band is also present in both Raman spectra, which corresponds to the most intense band of zeolite Y (Figure 4.8a). The only difference between the two is the location of this primary zeolite Y Raman band, which is located at 526 and 497 cm⁻¹ for CdS-Y(g) and CdS-Y(s), respectively. X-ray diffraction was used to further examine the CdS-Y samples in order to determine if they are in fact similar in structure, as suggested by Raman spectroscopy. Figure 4.9 shows XRD patterns of (a) zeolite Y, (b) CdS-Y(g) and (c) CdS-Y(s), as well as the derived patterns for the two crystalline phases of CdS. Regardless of the sulfide source used for the synthesis of CdS-Y, the aluminosilicate matrix appears crystalline in both cases. Two new broad humps between 24-30° and 42-46° 2θ were present in the diffraction patterns of CdS-Y(g) and (s). There is good agreement in the location of these peaks with respect to the derived
patterns for CdS shown at the bottom of Figure 4.9, thus suggesting the presence of either hexagonal or cubic CdS within or on the surface of zeolite Y. Although the derived CdS diffraction patterns share few similarities, the resolution of these broad diffraction peaks makes it difficult to determine the exact crystalline structure of the CdS in both zeolite-bound samples, except that nano-sized particles were formed.

Figure 4.10 shows high-resolution TEM images collected from (a) CdS-Y(g) and (b) CdS-Y(s). The inset in Figure 4.10a illustrates that well defined lattice fringes from CdS nanoparticles decorate the surface of the zeolite. Not only does CdS appear to lie on the surface of the zeolite, but Figure 4.10a also suggests that crystalline CdS remains trapped inside the zeolite Y (denoted by white circles). CdS particle sizes were estimated from TEM to be 3-10 nm. Figure 4.10b also indicates that crystalline CdS nanoparticles (5-10 nm) are formed on the surface of the zeolites using Na₂S as the sulfide source (denoted by white circles). Although they are more difficult to distinguish, lattice fringes are also highlighted below the surface of the zeolite in Figure 4.10b.

The synthesis of crystalline CdS within zeolite Y has been demonstrated using the two different methods as previously described; however, the data was inconclusive with respect to the exact crystal structure of CdS for each method. Therefore, CdS from both CdS-Y(g) and CdS-Y(s) was extracted and isolated from the zeolite by dissolving away the framework of zeolite Y. The orange-yellow precipitate from each extraction was collected and dried for analysis using XRD and Raman. Figure 4.11a shows that CdS removed from CdS-Y(g) has seven diffraction peaks at 25.03º, 26.59º, 28.26º, 36.85º, 43.87º, 48º, and 52.01º. These peaks correlate very strongly to the derived diffraction pattern for the hexagonal crystal structure. The CdS isolated from CdS-Y(s) in Figure
4.11b has peaks at the diffraction angles of 25.03°, 26.58°, 30.8°, 43.9°, 52.03°, and 54.58° 2θ, as well as two small shoulders around 28° and 51° 2θ. The location of these diffraction peaks match up well with the cubic phase, but the sample also contains three shoulder peaks that correspond to the hexagonal phase. With the zeolite framework removed, Raman spectroscopy of the two isolated CdS samples shows in Figure 4.12 that there is a slight difference in the location of the CdS phonon bands (from 296 to 301 cm⁻¹ and from 597 to 603 cm⁻¹ for CdS extracted from CdS-Y(g) and CdS-Y(s), respectively). The Raman spectrum for CdS collected from CdS-Y(g) has a 5-8 cm⁻¹ Raman shift to higher energies, which suggests structural differences in the crystalline lattice.

4.3.3 Binary Systems

4.3.3.1 CdS/TiO₂ Zeolite Y

Based on the results thus far, it has been demonstrated that either TiO₂ or CdS can be incorporated into zeolite Y. Using similar synthesis procedures, both semiconductors were synthesized together within zeolite Y to form a binary catalyst system. All of the characterization described in this section is based on the binary system of CdS/TiO₂-Y(1a-c), in which the synthesis procedures are detailed in Table 4.1. Since it was only used for comparison purposes with respect to its catalytic activity, CdS/TiO₂-Y(2a-c) is discussed later. Figure 4.13 indicates that upon forming CdS on TiO₂-Y(a-c) using H₂S, a significant red-shift is observed in the DR absorption spectra of CdS/TiO₂-Y(1a-c) when compared to TiO₂-Y(a-c) containing no CdS. For CdS/TiO₂-Y(1a), the absorption edge shifts to greater than 500 nm, which closely resembles the DR absorption spectra for
CdS-Y(g). The shift in the absorption onset for CdS/TiO$_2$-Y(b-c) is not quite as dramatic (495 nm). With respect to absorption intensity, the absorption band corresponding to CdS is the highest in CdS/TiO$_2$-Y(1a), while the intensities for (1b) and (1c) are more similar.

The set of Raman spectra in Figure 4.14 confirms the presence of CdS and TiO$_2$ in a binary zeolite system. When TiO$_2$-Yb (a) is combined with CdS (b), the resulting Raman spectrum is shown in Figure 4.14c. A total of seven Raman bands are observed for CdS/TiO$_2$-Y(1b), including the two characteristic phonon bands of CdS (300 and 603 cm$^{-1}$), three bands for anatase TiO$_2$ (153, 404 and 647 cm$^{-1}$) and the primary Raman band of zeolite Y, which has split into two bands (464 and 506 cm$^{-1}$). XRD of CdS/TiO$_2$-Y(1b) in Figure 4.15d provides further evidence for the incorporation of CdS into a titania-containing zeolite system. When compared to the diffraction pattern of zeolite Y in Figure 4.15a, the zeolite in the binary system has retained some of its crystallinity. Although the diffraction pattern of TiO$_2$-Yb in (b) shows no peaks corresponding to TiO$_2$, other characterization techniques have confirmed its existence. The diffraction pattern in Figure 4.15d has been magnified to emphasize the presence of two broad diffraction peaks between 24-30° and 42-46° 2θ, both of which correspond well with the diffraction pattern of CdS-Y(g) in Figure 4.15c.

Characterization of CdS/TiO$_2$-Y(1b) using X-ray diffraction and optical spectroscopy suggests the existence of the two materials within the same zeolite sample. This binary system was further analyzed using high resolution TEM in order to determine their spatial arrangement with the zeolite framework. Although the exact identity of the crystalline material in Figure 4.16a cannot be determined from the image, there appears to be two distinct crystalline materials, which is based solely on the fact that they have
different morphologies and crystal lattice spacings. The boundaries of the two nanoparticles emerge as being in very intimate contact with one another. Similar observations can also be made in Figure 4.16b, in which visually different crystalline materials are overlapping or contacting each other.

4.3.3.2 Pt/TiO$_2$ Zeolite Y

Based on the same principles of generating a zeolite-bound binary catalyst system comprised of CdS and TiO$_2$, a second binary system consisting of metallic platinum and TiO$_2$ was synthesized (Pt/TiO$_2$-Y(a-b)). Due to the fact that metallic Pt nanoparticles have very weak optical properties, morphological characterization techniques can be performed to confirm its presence in the system. Following the deposition and reduction of Pt within TiO$_2$-Yb, the zeolite went from a bright white color to a brownish-grey color, which is an indication that Pt was being deposited onto the zeolite. The DR absorption spectrum of the Pt deposited sample was collected; however, due to the dark color of the sample, most of the details in the spectrum have been lost. The strong absorption band from titania in TiO$_2$-Yb had almost completely disappeared. Platinum is considered a Raman inactive material; therefore, no conclusive Raman data was gathered as well. X-ray diffraction of the binary zeolite system provided the only evidence that nanoparticles of Pt had been deposited on or within the zeolite. As shown in Figure 4.17b, a small broad peak shows up around 39° 2θ (indicated by arrow) in the diffraction pattern of Pt/TiO$_2$-Y(1b). When compared to the pattern of metallic Pt, the location of this broad peak agrees strongly with published data on Pt nanoparticles [60-62].
As demonstrated with CdS/TiO$_2$-Y(1b), high resolution electron microscopy provides a more in depth analysis of how Pt and TiO$_2$ are arranged with respect to each other and the zeolite framework. Due to its ability to provide good contrast between different materials, the inverted STEM image in Figure 4.18 illustrates the dispersion of 3-5 nm particles within or on the zeolite. EDAX was used to confirm that the well-dispersed nanoparticles were platinum. Based on this image, the Pt appears to be more centrally located in the zeolite rather than near the edges. The TEM image in Figure 4.19 was taken near the edge of a zeolite containing Pt and TiO$_2$; however, only well defined titania nanoparticles are observed. Figures 4.18 and 4.19 both suggest that TiO$_2$ and Pt are both present in the zeolite but further evidence is needed to indicate they are co-localized or intimately contacting each other.
Using the zeolite shown in Figure 4.18, EDAX was used for elemental analysis of 10 different areas of the zeolite. Some of the areas contained only the zeolite, while others contained the zeolite and Pt nanoparticles. A representative EDAX spectrum of an area containing no Pt nanoparticles is shown in Figure 4.20, and aside from the elements within the zeolite (Si, Al, Na, O) and TEM sample grid (Cu), the only other element detected was titanium. Figure 4.21 shows a representative EDAX spectrum from an area containing several Pt nanoparticles and the zeolite. Not only were the typical zeolite elements present, but also titanium and platinum. When an area containing Pt was analyzed by EDAX, titanium was always present in the spectrum; however, when areas containing only the zeolite were sampled, only titanium was detected and no platinum. Even though TEM did not provide evidence of Pt and TiO₂ nanoparticles being co-localized or contacting each other, this EDAX data provides confirmation that titania is not necessarily co-localized with Pt, but Pt was always co-localized with titania in the zeolite-based system.

4.3.4 Ternary Systems – Pt/CdS/TiO₂ Zeolite Y

Ternary catalyst systems consisting of Pt, CdS and TiO₂ assembled in the zeolite were prepared by depositing Pt nanoparticles onto CdS/TiO₂-Y(1b) using four different reduction techniques. H₂PtCl₆ was impregnated into CdS/TiO₂-Y(1b) for three of these samples, but each was reduced with a different technique. Pt(1)/CdS/TiO₂-Y(1b) was reduced at 450ºC for 6 hours in 5% H₂, Pt(2)/CdS/TiO₂-Y(1b) was reduced by photoreduction, while Pt(3)/CdS/TiO₂-Y(1b) was reduced by chemical reduction using hydrazine. The fourth ternary system was synthesized by ion-exchanging Pt(NH₃)₄Cl₂
into the zeolite, followed by reduction at 450°C for 6 hours in 5% H₂. Due to the weak optical properties of metallic Pt, the only necessary characterization for the zeolite-based ternary system was electron microscopy. Figure 4.22 shows a high-resolution TEM image of Pt(1)/CdS/TiO₂-Y(1b), which was chosen as a representative sample for the Pt/CdS/TiO₂ ternary system. In this image, the edge of the zeolite is decorated with crystalline nanoparticles ranging from 3-10 nm in size (indicated by white circles). However, it is difficult to differentiate between the three catalytic materials in the zeolite. In order to confirm the presence of Pt, CdS, and TiO₂ in the sample, elemental analysis was performed using EDAX. Along with an inverted STEM image detailing the particular area sampled, Figure 4.23 presents a representative EDAX spectrum for Pt(1)/CdS/TiO₂-Y(1b). The high contrast in the STEM image suggests the presence of extremely small nanoparticles dispersed throughout the zeolite. Elemental analysis within the area of interest shows that all of the components making up the ternary system are present (Cd, S, Ti, Pt).

**4.3.5 Photocatalytic Activity**

Table 4.2 summarizes the amount of H₂ evolved from water for 16 different zeolite-based photocatalyst systems using light from 350-550 nm as a function of reaction time. Due to an observed induction period of 0-3 hours in all photolysis experiments, the reaction rates were calculated from the line slopes once the steady state H₂ evolution was established, which was after 3 hours of sample irradiation. Figure 4.24 compares the catalytic reaction rate for CdS-Y generated using the two different sulfide sources. Since
the cadmium loading in both of these samples was the same, the plot shows that after 4 hours of irradiation, the rate for CdS-Y(s) increases to 1.4 µmol/hr when compared to 0.9 µmol/hr for CdS-Y(g).

As illustrated in Figure 4.25 and detailed in Table 4.2, the combination of CdS and TiO₂ in the same zeolite system increases the rate from 0.9 µmol/hr (CdS-Y(g)) to 8.22 µmol/hr, which is a 9 fold increase in the H₂ evolution rate. Although CdS/TiO₂-Y(1a) shows an improved rate of 3.41 µmol/hr, the highest water splitting rates were obtained with CdS/TiO₂-Y(1b and 1c). These two zeolite samples both had very similar H₂ evolution rates (8.03 and 8.22 µmol/hr for CdS/TiO₂-Y(1b) and CdS/TiO₂-Y(1c), respectively), despite CdS/TiO₂-Y(1c) having at least twice the content of TiO₂. The data in Figure 4.26 shows the hydrogen evolution from CdS/TiO₂-Y(2a-c). These systems were synthesized by alternating the incorporation of titania and CdS in the zeolite, rather than consecutive TiO₂ treatments followed by CdS formation. The H₂ evolution rates for systems (1a) and (2a) are identical because they are both the same sample; however, the reactions rates for CdS/TiO₂-Y(2b-c) were about 10-15% less than CdS/TiO₂-Y(1b-c). A decrease from 8.03 µmol/hr with CdS/TiO₂-Y(1b) to 7.2 µmol/hr with CdS/TiO₂-Y(2b) was observed. CdS/TiO₂-Y(2c) dropped to 7.83 µmol/hr from 8.22 µmol/hr with CdS/TiO₂-Y(1c). Unlike CdS/TiO₂-Y(1b-c), which had very similar reaction rates, CdS/TiO₂-Y(1c) increased by 0.6 µmol/hr over CdS/TiO₂-Y(1b) when TiO₂ and CdS were incorporated into the zeolite for a third time.

A binary catalyst system of Pt and TiO₂ incorporated into zeolite Y was also analyzed for its ability to split water into H₂. The steady state hydrogen evolution rates are summarized in Table 4.2, whereas the time-dependent H₂ evolution plot is shown in
Figure 4.27. The photocatalytic properties of TiO$_2$-Yb were verified, only to find a $\text{H}_2$ evolution rate of less than 50 nmol/hr. Nonetheless, a $\text{H}_2$ evolution rate of 3.21 µmol/hr was observed when Pt and TiO$_2$ were coupled together in Pt/TiO$_2$-Y(1b), which is an improvement by 107 times. The same rate increase was not observed for Pt/TiO$_2$-Y(2b), in which Pt was reduced into the zeolite after the first titanyl exchange/calcination rather than after the second exchange/calcination, as in Pt/TiO$_2$-Y(1b). Under the same experimental conditions, Pt/TiO$_2$-Y(2b) was found to generate $\text{H}_2$ from water 30 times slower than Pt/TiO$_2$-Y(1b), with a rate of 0.11 µmol/hr.

Pt, CdS and TiO$_2$ were all three incorporated into zeolite Y (Pt(1-4)/CdS/TiO$_2$-Y(1b)) via four different Pt reduction methods. The catalytic activity of each was found to be dependent upon the method of platinum deposition. By means of the CdS/TiO$_2$-Y(1b) binary system, the reduction of 1 wt% Pt at 450°C for both H$_2$PtCl$_6$ and Pt(NH$_3$)$_4$Cl$_2$ lead to very similar results (11.8 and 11.75 µmol/hr for Pt(1)/CdS/TiO$_2$-Y(1b) and Pt(4)/CdS/TiO$_2$-Y(1b), respectively), as indicated by the traces in Figure 4.28. The photoreduction method of Pt (Pt(2)/CdS/TiO$_2$-Y(1b)) yielded the lowest hydrogen evolution rate of 2.97 µmol/hr, while the chemical reduction method (Pt(3)CdS/TiO$_2$-Y(1b)) at 9.53 µmol/hr was approximately 2 µmol/hr lower than Pt(1&4)/CdS/TiO$_2$-Y(1b).

When comparing the rate of hydrogen evolution from the best ternary system (11.8 µmol/hr) to that of the binary system (8.03 µmol/hr), Figure 4.29 demonstrates that the addition of platinum into the zeolite promotes faster rates of $\text{H}_2$ evolution. The steady state $\text{H}_2$ evolution increases by a factor of 1.5 upon the addition of Pt to CdS/TiO$_2$-Y(1b). The plot in Figure 4.29 also reveals the change in the hydrogen evolution rate for the
various zeolite-based photocatalyst systems as each additional material is incorporated into the system. By combining TiO₂-Y, which has minimal water splitting activity in this system (0.03 µmol/hr), and CdS into the same zeolite system, rates as high as 8.2 µmol/hr were obtained. However, when the framework of zeolite Y is removed from the system (CdS/TiO₂(np)), this binary system of CdS and TiO₂ drops by 72% to a rate of 2.25 µmol/hr. The formation of a ternary system using the zeolite Y framework promotes a further increase in H₂ evolution to 11.8 µmol/hr, thus leading to a 13 fold increase when compared to CdS in the zeolite alone.

4.4 Discussion

4.4.1 Single Catalyst Systems

For the incorporation of TiO₂ into zeolite Y, several reports have shown that ion-exchange of the titanyl moiety into the zeolite using titanyl salts is possible. Although the exact mechanism of exchange has yet to be determined, it has been hypothesized that it enters into the zeolite as Ti=O²⁺, which ultimately converts into TiO₂ upon heating. After following the published protocols for ion-exchanging zeolite Y with ammonium titanyl oxalate, it was discovered that ion-exchange concentrations greater than 0.2 M causes severe zeolite framework destruction, especially with exchange times greater than 2 hours. Solutions of commercially available ATO (0.2 M) are acidic (pH~3) and zeolites tend to be susceptible to framework damage in highly acidic media. Therefore all TiO₂-Y samples were prepared by ion-exchange of 0.2 M ATO for only 2 hours, followed by extensive washing to reduce the extent of zeolite damage.
Because of its good sensitivity, Raman spectroscopy was used to confirm the formation of anatase TiO$_2$ within the microstructure of zeolite Y. However, the generation of any form of crystalline titania was not apparent after the first ion-exchange/oxidation process. The Raman spectrum of TiO$_2$-Ya suggests that only minor changes occurred in the zeolite framework and no bands corresponding to TiO$_2$ were observed. DRIFTS was utilized to further investigate whether titania was formed following the first ATO exchange and oxidation. Figure 4.2 shows the 908 cm$^{-1}$ titanyl band in the zeolite sample prior to heating, thus confirming that the titanyl exchange was successful. Upon heating the titanyl exchanged zeolite to 550ºC, this infrared band disappears, thus indicating that the titanyl species has been converted into some other species.

Given the oxidation conditions, the likely product from the decomposition of the titanyl moiety is some TiO$_x$ species within the zeolite. The experimental data provides evidence that this newly formed species is not crystalline TiO$_2$ because it cannot be detected using Raman or XRD; however, it could exist as a TiO$_x$-zeolite complex. Despite the lack of a well-defined bandgap, the diffuse reflectance absorption spectrum of TiO$_2$-Ya coincides with the infrared and Raman experiments, in that a titania-like species is formed during this first ion-exchange/calcination process.

The second ATO exchange/oxidation process led to the first indication of TiO$_2$ within the zeolite by the presence of Raman bands corresponding to anatase. Even though X-ray diffraction did not provide any evidence of crystalline TiO$_2$ in TiO$_2$-Yb, there was loss in the zeolite peak intensities when compared to TiO$_2$-Ya. The loss in peak intensity was not specific to certain diffraction planes but rather proportional for most of the
diffraction peaks, thus indicating an overall loss of crystallinity in the zeolite framework. It has been well established that the absorption edge of semiconductor nanoparticles, such as TiO$_2$ and CdS, can red or blue-shift according to changes in the core particle size [63-68]. The red-shift in the DR absorption spectrum for TiO$_2$-Yb can be explained by the increase in the zeolite-bound titania particle size. This increase in particle size also leads to the appearance of Raman bands corresponding to anatase TiO$_2$.

The mechanism that leads to the formation of larger titania nanoparticles within the zeolite upon further ATO treatments has been partially explained by Matsumoto et al. [42]. However, the mechanism can be further explained by Scheme 4.1, as well as the experimental data described above. During the first ATO exchange into Na$^+$-zeolite Y (Na-Y), two sodium ions are removed for each titanyl exchanged. Ammonium ions (NH$_4^+$) are also ion-exchanged in competition with the titanyl species due to its presence in the salt. Upon calcination of the zeolite at high temperatures, the titanyl species becomes oxidized into a TiO$_x$ species that remains inside the zeolite Y supercages. These once ion-exchanged species are no longer associated with the framework of the zeolite; therefore, regenerating the ion-exchange sites. As NH$_4^+$ decomposes at high temperatures, protons are left behind in these exchange sites to balance the charge left behind from the formation of titania. When a second ATO exchange is carried out, the same ion-exchange sites remain active, thus allowing the titanyl species to be positioned in close proximity to the titania-like species within the zeolite. Acting as seeds, the extremely small TiO$_x$ react with the nearby titanyl ions when the zeolite is heated to form larger, well-defined nanoparticles of anatase TiO$_2$. For the synthesis of even larger zeolite-bound TiO$_2$, the process can be repeated a third time due to the fact that the nearby ion-exchange sites
have been regenerated once again. Optical spectroscopy was used to show that this proposed scheme was demonstrated by the synthesis of TiO$_2$-Yc. As observed in the Raman spectrum in Figure 4.1e, further increases in band intensity for TiO$_2$-Yc suggests the formation of larger nanoparticles or a higher concentration of titania within the zeolite.

The 0.1 eV red-shift in the bandgap for TiO$_2$-Yc provides additional confirmation about the change in titania particle size, as well as the fact that the proposed mechanism in Scheme 4.1 holds true for at least three titanyl incorporations. TEM of TiO$_2$-Yb offered more insight into the microstructure of these zeolite-bound nanoparticles. The crystalline lattice fringes in Figure 4.5 correlate well with the (101) diffraction plane of anatase TiO$_2$. Based on the estimated particle sizes (3-10 nm) from the images, TiO$_2$ is most likely on or near the surface of the zeolite, but small internalized nanoparticles cannot be excluded. Titania nanoparticles as small as 3 nm have been shown to give rise to broad X-ray diffraction peaks and given the size of these zeolite-bound TiO$_2$, diffraction peaks corresponding to crystalline TiO$_2$ should be present in Figure 4.4 [69-72]. However, even after a third exchange, X-ray diffraction showed no titania diffraction peaks, which indicates that there is significant interference from the zeolite framework. As previously described, zeolites are sensitive to acidic conditions and can be destroyed with extended exposure times. Figure 4.4 demonstrates the effect of the acidic ATO exchange solution on the zeolite framework because there was significant destruction in TiO$_2$-Yc, based on the loss of peaks or decreases in peak intensities.

The incorporation of CdS into zeolite Y was first demonstrated by Herron et al. in 1987 with the use sodium sulfide as the S$^{2-}$ source [49]. Since then, numerous others have followed similar procedures, as well as substituting hydrogen sulfide as the S$^{2-}$ source.
Regardless of the sulfide source, both ultimately generate CdS in the presence of extra framework cadmium ions within zeolite Y. The synthesis of CdS using Na\textsubscript{2}S is most commonly carried out in aqueous solutions, which completely hydrates the inside and outside of zeolite Y. H\textsubscript{2}S on the other hand can be introduced into dehydrated zeolites, thus allowing for the synthesis of CdS-Y in the absence of moisture. The precipitation of CdS under hydrated conditions is instantaneous because of the low k\textsubscript{sp} (1x10\textsuperscript{-27}), in which an orange-yellow product is formed. However, the formation of CdS using H\textsubscript{2}S under dehydrated conditions is less obvious.

Yoon et al. have extensively studied the encapsulation of CdS nanoparticles within the zeolite Y structure using H\textsubscript{2}S [38,47,52]. They have shown that it is possible to form CdS nanoparticles on the size regime of 1.3 nm within the framework of zeolite Y. The first DR absorption spectrum collected on dehydrated CdS-Y(g) at time zero in Figure 4.7 demonstrates that the CdS nanoparticles strongly absorb in the ultraviolet region, hence no color change in the zeolite upon the initial exposure (remains bright white). However, when the activated zeolite is exposed to moisture in the atmosphere, it quickly absorbs water into its pores. Water, which has a strong affinity for the walls of zeolite Y, slowly forces CdS to re-organize itself within the supercages. Eventually, these mobile CdS nanoparticles will come into contact with other particles, which generate even larger CdS clusters, thus turning the zeolite a yellow-orange color. The time-dependent absorption spectrum of dehydrated CdS-Y(g) in Figure 4.7 explicitly illustrates this process as water slowly begins to fill the zeolite supercages. The zeolite-bound CdS undergoes dramatic changes in only a few hours.
Figure 4.6 shows that the DR absorption spectrum for hydrated CdS-Y(g) and CdS-Y(s) appear to be very similar and their estimated bandgaps to be approximately the same. Bulk CdS has a bandgap of 2.42 eV and corresponds to a particle size of 10 nm; however, the Brus equation is no longer valid for bandgaps greater than 2.42 eV. According to the Brus equation, the CdS particle size for both zeolite samples was calculated to be greater than 10 nm. HR-TEM of both CdS-Y samples indicates that crystalline CdS nanoparticles are 10 nm or less in size. Nevertheless, the calculated particle size of the zeolite bound CdS is larger than the supercage of zeolite Y (1.3 nm), which would force the CdS nanoparticles to the exterior of the zeolite. Once again, TEM confirms the existence of CdS nanoparticles having sizes of 3-10 nm and similar morphologies on the surface of zeolite Y for CdS-Y(g) and (s). Another possible explanation for the larger than expected CdS particle sizes could be that the growth of CdS causes internal destruction of the zeolite, thus allowing CdS nanoparticles in neighboring supercages to aggregate, yet remain inside the zeolite. However, it has been suggested that zeolite pore-bound CdS exhibits a quantum tunneling effect that arises from the electronic interconnection imposed by the internal pore structure of the zeolite [38,47,52]. This interconnection in turn forms CdS cluster arrays that have optical properties resembling those of bulk CdS, which could account for the difference between the estimated particle size and the expected size from the zeolite supercage.

Raman spectroscopy and X-ray diffraction indicate that both CdS-Y samples appear to be similar in their crystalline structure. Based on the Raman spectra of CdS-Y(g) and (s) in Figure 4.8, the only noticeable difference between the two is the location of the primary zeolite Y Raman band (526 and 497 cm\(^{-1}\) for CdS-Y(g) and CdS-Y(s),
respectively). These Raman shifts suggest structural differences in the zeolite framework due to the interaction with CdS. XRD of both samples indicate that the aluminosilicate matrix remains crystalline, although careful studies have shown that the zeolite framework does undergo destruction upon CdS incorporation [38]. The only other information extracted from these diffraction patterns is the existence of some form of crystalline CdS; either hexagonal or cubic. In the presence of the zeolite, phase identification becomes very difficult, until the aluminosilicate framework is removed and the bare CdS nanoparticles are characterized. From our results on the extracted products, it can be concluded that the crystalline phase of CdS generated within zeolite Y is dependent upon the sulfide source. XRD verifies that CdS prepared using H2S leads to the hexagonal phase, while Na2S predominantly precipitates the cubic phase. The presence of several small shoulders in the diffraction pattern in Figure 4.11b indicates that there is a small component of hexagonal phase CdS present. A slight change in the location of the CdS phonon bands in Raman for the two isolated samples connects well with the structural data from XRD, as well as the literature. This Raman band shifting for the two phases of CdS has been demonstrated by others where the cubic phase is typically blue-shifted relative to the hexagonal phase by 3-8 cm⁻¹ [73-76]. It has also been noted that small Raman shifts for CdS could be due to differences in particle size and phonon confinement.

### 4.4.2 Binary Catalyst Systems

After careful studies on the incorporation of each material into zeolite Y independently (CdS-Y, TiO2-Y), the zeolite was used as a host to incorporate and
organize binary systems of these photocatalytic materials. The incorporation of CdS into hydrated titania-containing zeolite Y leads to significant red-shifts (150-200 nm) in the DR absorption spectra for CdS/TiO$_2$-Y(1a-c). Figure 4.13 shows that an increase in the number of titanyl exchanges causes a smaller red-shift in the absorption edge for CdS. This 30-40 nm blue-shift can be attributed to a decrease in CdS particle size due to the presence of titania occupying more of the void space within the zeolite. Although it is difficult to be quantitative using diffuse reflectance, one can generally make assumptions regarding concentrations based on absorption intensities. The CdS absorption intensity between 350-500 nm has decreased by a factor of two or more when further ATO exchanges have been carried out on the zeolite. Therefore, the CdS loading in CdS/TiO$_2$-Y(1a) is approximately twice that found in CdS/TiO$_2$-Y(1b-c). The amount of volume being occupied by titania in the zeolite is quite small after one titanyl treatment and most of the cadmium exchange sites are still readily accessible. As the titania grows larger, the possibility of blocking active exchange sites increases, causing the CdS loading to decrease.

Since well-established protocols were used for fabrication of CdS/TiO$_2$-Y binary systems, little or no changes were expected in the Raman spectra and X-ray diffraction patterns. Since TiO$_2$-Yb was used in the synthesis of CdS/TiO$_2$-Y(1b), it can be concluded from Raman that crystalline titania is present in the zeolite, despite the absence in the XRD pattern in Figure 4.15b. Raman bands corresponding to both TiO$_2$ and CdS, as well as broad diffraction peaks matching those of CdS, show that both materials exist in the same zeolite sample. However, the data provides no insight into the spatial arrangement of CdS and TiO$_2$ on or within the zeolite. HR-TEM in 4.16a shows two very
distinct nanoparticles in intimate contact with each other. Since the only two materials in this binary zeolite sample are CdS and TiO$_2$, this image implies that the two semiconductor catalysts could be co-localized together. This co-localization has been shown to improve the photocatalytic water splitting properties of these two materials because of more efficient charge injection/separation [31,33,34,77-81]. Further evidence of co-localization is provided in Figure 4.16b, but particle boundaries are less-defined in this micrograph.

The second binary zeolite system consists of depositing platinum into titania-containing zeolite. X-ray diffraction confirms the successful deposition of Pt nanoparticles within TiO$_2$-Yb by the formation of a broad diffraction peak in Figure 4.17b. The maximum Pt loading in this sample is 1 wt % based on the concentration of platinum in the ion-exchange solution. The low Pt loading explains the weak diffraction intensity, while the broadening of the peak indicates the formation of nanometer sized Pt particles. Based on the STEM image in Figure 4.18, it can be concluded that 3-5 nm Pt particles have been included into zeolite Y. The Pt appears to be dispersed throughout the zeolite, but the majority of the nanoparticles are more centralized. Given the ion-exchange process of Pt(NH$_3$)$_4$Cl$_2$, it is not unlikely that platinum is deposited deep within the bulk of the zeolite. During the reduction process, Pt seeds can migrate to form larger nanoparticles. TEM also shows that crystalline titania is present near the outer edges of the zeolite, but Pt nanoparticles could not be easily distinguished. Electron microscopy confirms the dual existence of Pt and TiO$_2$ in the same zeolite, but it does not indicate that they are co-localized or contacting one another.
Scheme 4.2 illustrates the proposed mechanism by which these two species can interact or be placed within close proximity to each other within the zeolite. Elemental analysis using EDAX on Pt/TiO$_2$-Yb was used to show that it is possible for the two materials to be interacting with each other within the zeolite. Out of 10 areas analyzed, it was determined that those containing TiO$_2$ may or may not contain Pt. However, all areas containing Pt nanoparticles were always found to co-exist with titania. Therefore, elemental analysis shows that TiO$_2$ is well-dispersed throughout the zeolite, even towards the center of the zeolite. It also indicates that Pt is only detected in the presence of TiO$_2$. Based on these results, it may be suggested that Pt and TiO$_2$ are co-localized together with the possibility of having intimate contact between neighboring particles.

4.4.3 Ternary Catalyst Systems

Utilizing the binary system of CdS/TiO$_2$-Y(1b), platinum was deposited using four different techniques in order to determine the optimal method. The advantage of using chloroplatinic acid and the wet impregnation method is the ability to control the amount of Pt deposited onto the zeolite. Conversion of this platinum pre-cursor into metallic Pt by either heat reduction, chemical reduction or photoreduction all produced a zeolite sample that was a grey-brown color. Reduction of the Pt(NH$_3$)$_4$Cl$_2$ exchanged zeolite also leads to a product having a similar appearance. Using Pt(1)/CdS/TiO$_2$-Y(1b) as a representative sample, HR-TEM was used to emphasize the possible co-localization of these three materials within the same zeolite. Although the identity of the numerous crystalline nanoparticles in Figure 4.22 is unknown, this image once again suggests potential overlap/contact between the particles. Although only two general areas in
Pt(1)/CdS/TiO₂-Y(1b) were sampled using EDAX and the same results were obtained for both, the data suggests that these three catalytic materials could be co-localized on or within the zeolite microstructure. Co-localization of these materials also implies that the nanoparticles have the opportunity to come into close contact with one another.

### 4.4.4 Photocatalytic Water Splitting

The combinations of CdS/TiO₂ and Pt/TiO₂ have been used for several catalytic applications; however, the most common use for these materials is the light-induced photolysis of water, as demonstrated in Scheme 4.3. Looking more closely at the hydrogen evolution plots shown in Figures 4.24-4.29, they all contain an induction period for the production of H₂. Without an induction period, the evolution of H₂ should be linear, just as shown after 3 hours of irradiation in all zeolite-based catalyst systems. Several hypotheses have been used to explain this induction period, including the reduction of residual oxygen, since O₂ is reduced in preference to water in the given system [39,78]. Fox and Pettit have also reported the formation of cadmium metal, which has also been shown to act as a catalyst for hydrogen production [39]. Similar results were also obtained by Jang et al. in their CdS based photocatalysts prior to establishing the steady state. By investigating the oxidation state of cadmium in their catalyst using XPS, they attributed this induction period to surface oxidation of CdS [31,79].

Based on all of the photocatalyst systems used, it was concluded that the observed induction periods are principally due to the consumption of oxygen during the first three hours of photolysis. Nevertheless, changes in the oxidation state of cadmium are not being ruled out, as shown be Jang et al., but our data indicates this is not the primary
cause for the induction period. An induction period is noted in all 16 samples, even with Pt/TiO2-Y, in which no CdS is present to undergo changes in oxidation state. Since the same trend occurs in all 16 catalyst systems, it can be concluded that the induction period in H2 evolution is most likely due to the residual oxygen remaining in solution. Therefore, the steady state is reached once the rate of H2 production exceeds that of O2 consumption, which is between two and three hours in these experiments.

In order to understand the water splitting capabilities of the binary and ternary zeolite-based systems, the single component systems were first studied. Starting with zeolite-bound CdS, the H2 evolution reaction rates were determined. Under the same experimental conditions and cadmium loading, CdS-Y(s) was found to be a better water splitting catalyst compared CdS-Y(g), although the difference was not significant. Having determined the CdS crystalline structure for each of these samples, the cubic phase out performs the hexagonal phase when incorporated into zeolite Y based on the 0.5 μmol/hr improvement in the hydrogen evolution rate.

Several reports have indicated that the hexagonal phase is the more active phase for water splitting, where these studies were carried out on CdS nanoparticles dispersed in an electron donor solution. One possible explanation for the improvement in the H2 evolution rate is the mechanism by which CdS is formed for the two sulfide sources. Because the zeolite is fully hydrated when using Na2S, the CdS has a greater possibility of initially forming on the surface of the zeolite due to rapid precipitation. Also, the Na+ ions in the sulfide solution can remove Cd²⁺ ions from the zeolite, thus yielding a higher concentration of surface bound CdS. This could ultimately lead to CdS that has a more accessible surface upon which the reduction of H⁺ can occur.
Hybridization of CdS with TiO$_2$ has been proven to yield a better photocatalyst because of an improved electron charge separation due to the location of the energy levels responsible for the photochemical reactions, as illustrated in Scheme 4.3. Although CdS and TiO$_2$ alone are capable of water splitting, the reaction rates are quite slow relative to binary systems of the two. Upon successfully incorporating CdS and TiO$_2$ into the same zeolite system, the H$_2$ evolution reaction rate for CdS/TiO$_2$-Y(1a) was found to be roughly 3.5 times higher than CdS-Y(g). This indicates that the TiO$_x$ species in the zeolite is helping to facilitate the water splitting reaction, but in order for this to take place, the two materials must be in intimate contact with each other. Some of the photogenerated electrons are being separated from CdS onto TiO$_x$, thus helping to improve the reaction rate by slowing the electron/electron hole recombination in CdS. Otherwise, the catalytic reaction rate should resemble that of CdS-Y(g). It has been demonstrated that the efficiency of the charge injection from CdS to TiO$_2$ is dependent upon the size of the TiO$_2$ nanoparticles. Extremely small TiO$_2$ particles have conduction bands that exist above that of CdS; therefore, limiting the amount of injected electrons [77,80]. Although these findings could be used to explain the lower hydrogen evolution rates for CdS/TiO$_2$-Y(1a) when compared to CdS/TiO$_2$-Y(1b-c), the more likely explanation is based on the fact that a non-crystalline TiO$_x$ species exists within CdS/TiO$_2$-Y(1a) rather than crystalline TiO$_2$.

Upon further incorporation of titania into the zeolite (2-4X), the steady state hydrogen production increases by a factor of 9 over CdS-Y(g). Based on the DR absorption spectra in Figure 4.3, the absorption intensities indicate that the loading of titania in TiO$_2$-Yc is more than twice that found in TiO$_2$-Yb. Interestingly enough, the H$_2$
evolution rate for these two samples was approximately the same. Because hydrogen production is dependent upon the contact between CdS into TiO₂, these observations suggest that the number of junctions between these two materials does not improve upon incorporating CdS into TiO₂-Yc relative to TiO₂-Yb. In an attempt to improve the contact and charge injection for this zeolite-based binary system, a second strategy in the synthesis of CdS/TiO₂-Y was used. By alternating the synthesis of TiO₂ and CdS within the zeolite, it was believed that the nanoparticle contact between these two would improve. However, based on the hydrogen evolution data for CdS/TiO₂-Y(2b-c), it was determined that the optimal synthesis strategy for this binary system was CdS/TiO₂-Y(1b).
The mechanism proposed to explain the improvement in the H₂ evolution rate for CdS/TiO₂-Y(1b) is shown in Scheme 4.4. As previously described in Scheme 4.1, a titanyl ion-exchange and high temperature oxidation leads to regeneration of the once occupied exchange sites in the zeolite framework. When ion-exchanging Cd²⁺ into the zeolite, these divalent cations are positioned near well-established titania nanoparticles. In the presence of H₂S under dehydrated conditions, CdS nanoparticles are formed inside the zeolite supercages in very close proximity to TiO₂. The precipitation of CdS yields the release of protons from H₂S, which can act as an ion-exchange cation in the previously occupied exchange site. During hydration of the zeolite, the CdS migrates to form larger CdS nanoclusters, thus creating good contacts with TiO₂. For these reasons, it has been concluded that not only is the framework of the zeolite promoting co-localization of CdS and TiO₂, but also the regeneration of active ion-exchange sites during the oxidation of the titanyl species is vital in the process. With the loss or blockage of these sites, ion-exchange of other materials for the co-localization with TiO₂ would not possible.

Although TiO₂ is not considered to be the ideal photocatalyst because of its high energy bandgap, a zeolite-bound binary system of Pt and TiO₂ has been prepared to further support the proposed mechanism in Scheme 4.2. TiO₂-Yb was found to have minimal catalytic activity towards hydrogen evolution in a solution of methanol, which is due to the minimal light absorption of titania in the working wavelength range. When Pt was ion-exchanged into the zeolite and reduced using high temperatures, the evolution rate jumped from 0.03 to 3.21 µmol/hr, which is more than a factor of 100. Just as described for the combination of CdS and TiO₂, the contact between Pt and TiO₂ is
imperative in the water splitting reaction. This large rate increase implies that these two materials have good contact between them, otherwise, there would be very little H₂ produced. HR-TEM and EDAX data shown in Figures 4.18-4.21 can be used to further explain these observed improvements. The proposed mechanism in Scheme 4.2 for the binary system of Pt/TiO₂-Y(1b) is very similar that described for CdS/TiO₂-Y(1b). The ion-exchange sites for Pt²⁺ in the zeolite are positioned close to well-established titania nanoparticles. Following reduction, Pt nanoclusters are formed inside the zeolite supercages in very close proximity to TiO₂, thus creating good contacts with TiO₂.

In a similar experiment carried out by Matsumoto et al., they studied the hydrogen evolution from Pt/TiO₂-Y by using photoreduction to deposit Pt on their zeolite [42]. Based on their experimental data, minimal or no hydrogen was evolved after 24 hours of irradiation in ethanol for several Pt/TiO₂-Y systems. They attributed this lack of H₂ production to the existence of the zeolite-bound titania within a strong electrostatic field, thus preventing electron diffusion and the reaction of electrons with protons to form hydrogen. However, our 8 hour experimental data from a very similar system suggests otherwise because H₂ was being evolved from zeolite-bound TiO₂ and Pt. Therefore, it can be concluded that the photoreduction method of Pt does not generate good contacts between Pt and TiO₂. Photoreduction is more likely to reduce Pt nanoparticles onto the surface of the zeolite, whereas ion-exchange internalizes the platinum pre-cursor and ensures that Pt is being placed within close proximity to the zeolite-bound titania. Once again, these experimental findings provide further evidence of the mechanism proposed in Scheme 4.2. Since the ion-exchange sites within the zeolite were not exploited, no catalytic improvements were observed.
When the synthesis of TiO$_2$ and Pt was alternated for possibly increasing the H$_2$ evolution rate, it was determined that Pt/TiO$_2$-Y(2b) was 30 times slower than Pt/TiO$_2$-Y(1b). Both of these samples were ion-exchanged twice with ATO and once with Pt(NH$_3$)$_4$Cl$_2$; therefore, they should have behaved similarly. However, there was very little improvement in the H$_2$ evolution when compared to TiO$_2$-Yb alone. Given that Pt/TiO$_2$-Y(2b) closely resembles the reaction rate of TiO$_2$-Yb, it can be concluded that the growth of TiO$_2$ during the second ion-exchange/oxidation process was unsuccessful. Even after a second ATO treatment on Pt/TiO$_2$-Y(2a), the bandgap of the titania nanoclusters does not red-shift enough to facilitate an electron transfer to Pt because of poor light absorption. Scheme 4.5 summarizes this described mechanism and provides some insight into the reason why alternating the synthesis of Pt and TiO$_2$ is not ideal.

Previously detailed experiments indicate that ion-exchanging TiO$_2$-Ya with Pt$^{2+}$ will promote co-localization with small TiO$_x$ species in the zeolite. However, a second ATO exchange in the presence of Pt nanoparticles does not increase the amount of titania added to the system. This signifies that those ion-exchange sites once occupied by Pt$^{2+}$ are either blocked or damaged and titanyl cannot be placed nearby the existing TiO$_2$. In summary, alternating the exchange of these two materials is not ideal because the ion-exchange sites are not readily accessible upon the introduction of a new species into the zeolite. The mechanism used to explain the behavior of Pt/TiO$_2$-Y(2b) provides more supporting evidence that the regeneration of ion-exchange sites formed during the oxidation of titania is critical in developing zeolite-based photocatalyst systems. With the loss or blockage of these sites, ion-exchange of other materials for the co-localization with TiO$_2$ would not be possible. Based on these experimental findings, this mechanism
can be applied to other types of zeolite-bound photocatalyst systems that require well-established nanoparticles in good contact with each other. Co-localization can be improved by not only taking advantage of the spatial restrictions imposed by the zeolite framework, but also the chemical nature of the zeolite and its ion-exchange properties.

Due to the fact that ion-exchange sites can regenerated in CdS/TiO$_2$-Y(1b) following the H$_2$S reaction, a third photocatalytic material, such as Pt, can be incorporated into the system. The incorporation of Pt using ion-exchange/heat reduction of Pt(NH$_3$)$_4$Cl$_2$ was used to fabricate a ternary system, as well as three other Pt reduction methods. The four methods were compared to determine the optimal water splitting. Despite having the same 1 wt% Pt loading, the photoreduction method caused the ternary system to drop in H$_2$ production by a factor of 2.5 when compared to the best binary system. A loss in photocatalytic activity suggests that the component responsible for absorbing the light (CdS), was damaged during the reaction. The photoreduction process requires long exposure times to intense ultraviolet light, which could lead to severe photocorrosion of CdS, especially in the absence of a sulfide source.

Chemical reduction of Pt to generate the ternary system is the least harsh of all four methods; however, the H$_2$ evolution rate suggests that the contact between Pt and the existing materials was not optimized. While a small improvement was observed, it is possible that hydrazine was not able to access all of the internalized platinum pre-cursor; therefore, the additional charge separation onto Pt was incomplete. It was concluded that the heat reduction of Pt(1)/CdS/TiO$_2$-Y(1b) and Pt(4)/CdS/TiO$_2$-Y(1b) were the optimal zeolite-based ternary systems. They both had very similar catalytic properties, which is not unlikely given the similarities in the synthesis. The platinum pre-cursor, H$_2$PtCl$_6$,
carries a negative charge, thus making it less likely to enter into the negatively charged framework of the zeolite. However, the pH of the wet impregnation solution was adjusted between 3 and 4 in order to change the surface charge of the zeolite-bound titania. Under acidic conditions, titania takes on a positive charge, which will attract the negatively charged H$_2$PtCl$_6$. By changing the surface chemistry of TiO$_2$, the deposition of the platinum pre-cursor can then be considered an ion-exchange process. Upon reducing the samples, Pt nanoparticles form on or near the existing TiO$_2$, which can lead to better charge separation and improved catalytic activity.

The time dependent hydrogen evolution plot shown in Figure 4.29 summarizes the changes in the photocatalyst systems as additional materials are introduced into the zeolite. The data clearly shows that the combination of Pt, CdS and TiO$_2$ is superior to any of the other systems analyzed. Similar trends have been observed by others due to the fact that platinum has proven to be an ideal catalyst for this reaction because of its reduction potential relative to the splitting of water [31,32,34]. However, the most important observation regarding this work is the 75% loss in the catalytic activity for CdS/TiO$_2$-Y(np), in which the zeolite has been completely removed from the system. This significant loss does not even take into consideration the higher concentration of CdS as compared to the zeolite-based experiments. Given our approach to fabricate binary and ternary systems for photocatalysis, the absence of the zeolite host lessens the possibility of particle contact, especially when the materials are not chemically bound to each other. Once again, these results confirm that the contact between these materials is critical in achieving optimal charge separation, as well as the idea that the zeolite Y pore structure can act as a host to promote these materials to interact more strongly.
4.4.5 Comparison to Previous Studies

Aside from the previously proposed mechanisms and the regeneration of ion-exchange sites, this data provides substantial weight to the fact that the zeolite plays a key role in organizing these materials. As detailed in Table 4.3, we have shown that there is a 9 fold increase in the rate for the binary system of CdS/TiO2-Y(1b) when compared to CdS-Y(g) under the same experimental conditions. However, the amount of cadmium sulfide in these two systems is not the same and this difference must be accounted for in order to normalize the hydrogen evolution rates. Based on elemental analysis by Galbraith Laboratories, the Cd$^{2+}$ loading was determined to be 47.15 and 22.7 µmol Cd$^{2+}$ per gram of zeolite for CdS-Y(g) and CdS/TiO2-Y(1b), respectively. After normalization, the data in Table 4.3 indicates that the overall improvement in the H$_2$ evolution rate becomes greater than 18 when zeolite Y is utilized to organize these materials together.

In order to show that the zeolite serves as an ideal host for creating good junctions between CdS and TiO$_2$, it is fitting to compare the observed improvements in this work to previously reported systems containing the same materials. Hoffman et al. utilized colloidal dispersions of CdS and TiO$_2$ to demonstrate that a 3 fold increase in the normalized H$_2$ evolution rate could be obtained [32]. Further improvement was achieved by Kusakabe et al., in which CdS was incorporated into ETS-4, a titanosilicate zeolite [29,30]. They showed that this combination improved the hydrogen evolution rate by 6.25 when the Cd$^{2+}$ loading is normalized. In their system, the comparison to CdS is based on CdS nanoparticles prepared similarly to those included into ETS-4. In other attempts to improve the catalytic water splitting activity of CdS and TiO$_2$, Lee et al. generated nano-bulk composites of these materials. The coupling of these two
semiconductors through colloidal synthesis led to a 13.3 times increase (normalized to 
Cd\(^{2+}\) loading) in H\(_2\) evolution when compared to bulk CdS alone [31,79]. A third 
colloidal synthesis for the synthesis of CdS/TiO\(_2\) composites was carried out by Hirai et 
al., in which surface-capped CdS nanoparticles were immobilized onto TiO\(_2\) particles 
[78]. They reported a 13.8 fold increase in the photocatalytic water splitting rate upon 
coupling these two materials.

Each of these reports provides strong evidence that by coupling CdS and TiO\(_2\), 
improvements in the hydrogen evolution rate from water can be made. Their results also 
confirm that good particle junctions are necessary in order to promote the charge 
injection from CdS to TiO\(_2\). However, our data indicates that the 3-dimensional 
framework of zeolite Y can be utilized to further improve the contact between CdS and 
TiO\(_2\) nanoparticles. The zeolite-based binary system of CdS and TiO\(_2\) leads to an overall 
improvement that is almost 1.5 times those of similar systems when the amount of 
cadmium is normalized.

As previously described, the addition of Pt to the binary system of CdS and TiO\(_2\) 
creates an even better photocatalyst by increasing the H\(_2\) evolution rate to 11.8 µmol/hr. 
Upon normalization with respect to the cadmium loading, this yields a 1.5 times 
improvement over CdS/TiO\(_2\)-Y(1b) (Table 4.3). An improvement indicates that at least 
some platinum nanoparticles were formed in close proximity to TiO\(_2\); therefore, creating 
nanoparticle junctions (Scheme 4.6). Just as described for CdS and TiO\(_2\), these particle 
junctions promote further charge separation from CdS and faster rates of water splitting. 
Similar results were obtained by Lee et al., in which platinization of their CdS/TiO\(_2\) 
nanocomposites led to an overall rate increase of 1.5 when compared to the binary system.
The most notable improvement in hydrogen evolution upon adding Pt to a binary system of CdS and TiO$_2$ was observed by Hoffman et al., in which the rate increased by a factor of 21.

Although a rate improvement of 1.5 was observed for the ternary system of Pt(1)/CdS/TiO$_2$-Y(1b), the increase was not as significant as expected. The data shows that the incorporation of two catalytic materials into zeolite Y gives rise to notable improvements in nanoparticle junctions and H$_2$ evolution rates. However, the inclusion of a third material into the zeolite does not greatly improve the properties of the photocatalyst. Therefore, it can be concluded that zeolite Y is an ideal host for binary catalyst systems and only small improvements can be made in ternary systems.

4.5 Conclusions

Zeolite Y containing either cadmium sulfide or titanium dioxide nanoparticles showed no or very little photocatalytic activity for hydrogen production from water under UV/visible irradiation. Utilizing the microporous structure of zeolite Y, the photoactivity and stability of these two materials was improved by combining them into the same zeolite system, as well as with the addition of platinum. Several combinations of CdS, TiO$_2$ and Pt were used to demonstrate how the location and accessibility of ion-exchange sites within the zeolite framework are critical in the development of a multi-component photocatalyst system. Through the incorporation of Pt or CdS (or both) into the zeolite with TiO$_2$, improved charge separation from CdS was achieved with these hybridized catalysts, thus slowing the charge recombination and photocorrosion of CdS. The ternary
system of Pt(1)/CdS/TiO$_2$-Y(1b) was found to have the best photocatalytic activity when compared to the other 16 photocatalysts tested for H$_2$ production from water.

The results obtained in this study show that zeolite Y can serve as a potential host to photocatalytic materials for the eventual use in hydrogen production. The ion-exchange properties of zeolite Y allow for nanoparticles of different materials to be synthesized in close proximity to one another. At the same time, the pore structure of zeolite Y forces these nanoparticles to intimately contact one another for more efficient charge injections, thus increased hydrogen activity.
4.6 References


Table 4.1: Details the naming scheme for all zeolite-based photocatalysts and the synthesis procedure utilized for each.
<table>
<thead>
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<th>Catalyst</th>
<th>H$_2$ Evolution Rate (µmol hr$^{-1}$)</th>
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<td>CdS-Y(g)</td>
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<td>CdS-Y(s)</td>
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</tr>
<tr>
<td>Pt(3)/CdS/TiO$_2$-Y(1b)</td>
<td>9.53</td>
</tr>
<tr>
<td>Pt(4)/CdS/TiO$_2$-Y(1b)</td>
<td>11.75</td>
</tr>
<tr>
<td>TiO$_2$-Yb</td>
<td>0.03</td>
</tr>
<tr>
<td>Pt/TiO$_2$-Y(1b)</td>
<td>3.21</td>
</tr>
<tr>
<td>Pt/TiO$_2$-Y(2b)</td>
<td>0.11</td>
</tr>
</tbody>
</table>

**Table 4.2:** Summary of the steady state H$_2$ evolution rates for all zeolite-based photocatalysts.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CdS(A)</th>
<th>CdS/ TiO$_2$(B)</th>
<th>Increase (B)/(A)</th>
<th>Pt/CdS/ TiO$_2$(C)</th>
<th>Increase (C)/(B)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS Nanoparticles</td>
<td>0.139</td>
<td>1.85</td>
<td>13.31</td>
<td>2.8</td>
<td>1.52</td>
<td>[31,79]</td>
</tr>
<tr>
<td>CdS Nanoparticles</td>
<td>1.2x10$^{-2}$</td>
<td>7.5x10$^{-2}$</td>
<td>6.25</td>
<td>N/A</td>
<td>N/A</td>
<td>[29-30]</td>
</tr>
<tr>
<td>CdS Nanoparticles</td>
<td>1.96x10$^{-3}$</td>
<td>5.85x10$^{-3}$</td>
<td>2.98</td>
<td>0.123</td>
<td>20.9</td>
<td>[32]</td>
</tr>
<tr>
<td>CdS Nanoparticles</td>
<td>1.11x10$^{-2}$</td>
<td>0.153</td>
<td>13.78</td>
<td>N/A</td>
<td>N/A</td>
<td>[78]</td>
</tr>
<tr>
<td>CdS Zeolite Y</td>
<td>1.9x10$^{-2}$</td>
<td>0.352</td>
<td>18.53</td>
<td>0.518</td>
<td>1.47</td>
<td>Our Work</td>
</tr>
</tbody>
</table>

Table 4.3: Normalized hydrogen evolution rates for our binary and ternary photocatalyst systems compared to previously reported catalyst systems.
Scheme 4.1: Proposed mechanism for the synthesis of TiO$_2$-Y.
Scheme 4.2: Proposed mechanism for the synthesis of Pt/TiO$_2$-Y(1b).
Scheme 4.3: Depicts the processes involved in the photochemical splitting of water by CdS/TiO$_2$ and Pt/TiO$_2$.
Scheme 4.4: Proposed mechanism for the synthesis of CdS/TiO$_2$-Y(1b).
Scheme 4.5: Proposed mechanism for the synthesis of Pt/TiO$_2$-Y(2b).
Scheme 4.6: Depicts the processes involved in the photochemical splitting of water by Pt/CdS/TiO₂.
Figure 4.1: Raman spectra showing the formation of anatase titania in TiO₂-Y. (a) zeolite Y, (b) bulk anatase TiO₂, (c) 1ˢᵗ ATO exchange/calcination, (d) 2ⁿᵈ ATO exchange/calcination (e) 3ʳᵈ ATO exchange/calcination.
Figure 4.2: DRIFTS spectra showing the loss of the 908 cm$^{-1}$ titanyl band (indicated by arrow) upon heating to 550°C.
Figure 4.3: Diffuse reflectance absorption spectra of TiO$_2$-Y(a-c) compared to bulk anatase TiO$_2$. 
Figure 4.4: X-ray diffraction patterns of TiO$_2$-Y(a-c) compared to untreated zeolite Y.
Figure 4.5: HR-TEM image of TiO$_2$-Yb. Lattice spacings of 0.352 nm are indicated.
Figure 4.6: Diffuse reflectance absorption spectra comparison between CdS-Y(g) and CdS-Y(s).
Figure 4.7: Time dependent diffuse reflectance absorption spectra upon hydration of CdS-Y(g).
Figure 4.8: Raman spectra of CdS based photocatalysts. (a) zeolite Y, (b) CdS-Y(g), (c) CdS-Y(s).
Figure 4.9: X-ray diffraction patterns of CdS based photocatalysts. (a) zeolite Y, (b) CdS-Y(g), (c) CdS-Y(s). Derived patterns of CdS are shown below.
Figure 4.10: HR-TEM image of (a) CdS-Y(g) and (b) CdS-Y(s).
Figure 4.11: X-ray diffraction patterns of extracted CdS nanoparticles. (a) CdS from CdS-Y(g), (b) CdS from CdS-Y(s). Derived patterns of CdS are shown below.
**Figure 4.12:** Raman spectra comparison of isolated CdS nanoparticles.
Figure 4.13: Diffuse reflectance absorption spectra of CdS/TiO$_2$-Y(1a-c) binary systems.
Figure 4.14: Raman spectra of CdS/TiO₂ binary system. (a) TiO₂-Yb, (b) extracted CdS nanoparticles, (c) CdS/TiO₂-Y(1b).
Figure 4.15: X-ray diffraction patterns of CdS/TiO$_2$ binary system. (a) zeolite Y, (b) TiO$_2$-Yb, (c) CdS-Y(g), (d) CdS/TiO$_2$-Y(1b).
Figure 4.16: HR-TEM image of CdS/TiO$_2$-Y(1b) (both (a) and (b)).
Figure 4.17: X-ray diffraction patterns of Pt/TiO$_2$ binary system. (a) TiO$_2$-Yb, (b) Pt/TiO$_2$-Y(1b). Derived patterns of Pt and TiO$_2$ are shown below.
Figure 4.18: STEM image of Pt/TiO$_2$-Y(1b) (White arrows indicate Pt nanoparticles).
Figure 4.19: HR-TEM image of Pt/TiO$_2$-Y(1b).
Figure 4.20: EDAX spectrum of area containing no Pt nanoparticles in Pt/TiO$_2$-Y(1b) and the corresponding STEM image.
Figure 4.21: EDAX spectrum of area containing Pt nanoparticles in Pt/TiO$_2$-Y(1b) and the corresponding STEM image (White arrows indicate Pt nanoparticles).
Figure 4.22: HR-TEM image of Pt(1)/CdS/TiO$_2$-Y(1b).
Figure 4.23: EDAX spectrum of the designated area in Pt(1)/CdS/TiO₂-Y(1b) and the corresponding STEM image (White arrows indicate Pt nanoparticles).
Figure 4.24: Time dependent hydrogen evolution comparison of CdS-Y.
Figure 4.25: Time dependent hydrogen evolution of CdS/TiO$_2$-Y(1) binary systems.
Figure 4.26: Time dependent hydrogen evolution of CdS/TiO$_2$-Y(2) binary systems.
Figure 4.27: Time dependent hydrogen evolution of Pt/TiO$_2$-Y binary systems.
Figure 4.28: Time dependent hydrogen evolution of Pt/CdS/TiO$_2$-Y ternary systems.
Figure 4.29: Time dependent hydrogen evolution after the addition of each new material.
CHAPTER 1


CHAPTER 2


CHAPTER 3


CHAPTER 4


