Novel Chemical Strategies for Gas Sensing and Separations

DISSERTATION

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Abstract

Detection of trace gases are relevant for environmental, combustion and health-related applications. Resistive semiconducting metal oxide sensing platforms are extensively studied for gas detection. Two important aspects of gas sensing are enhancing sensitivity and selectivity. Mixtures of WO$_3$ and Cr$_2$O$_3$ in varying weight ratios as well as adjacent alignment of these two powders were both examined as possible designs for NO-selective sensor. Studies focused on resistance measurements toward NO and CO at 300°C were carried out. Using the sensor design with the adjacent alignment of n-type WO$_3$ and p-type Cr$_2$O$_3$ resulted in optimal performance. This sensor design exploits the different majority carriers in these two semiconducting oxides for selective NO gas sensing. The advantage of such a sensor system is that the device can be sensitive to NO at low ppb level (18 ppb detection limit) and discriminate against CO at concentrations a thousand-fold higher (20 ppm). The sensing mechanism was investigated by in situ diffuse reflectance infrared studies. Characterization of the adjacent p-n interface was done by scanning electron microscopy (SEM) and Raman imaging study. Practical application of this device is demonstrated by measuring NO in human breath samples.

A sensor platform with n-type In$_2$O$_3$ and p-type NiO placed side by side was developed for the detection of trace NH$_3$. Our focus was to develop an ammonia sensor with ppb sensitivity, with possible application in breath analysis. With low concentrations of NH$_3$ (< 100 ppb), the change in resistance with NiO was anomalous at 300 °C, the
resistance decreased and then gradually increased over tens of minutes before decreasing again to reach the baseline. In situ diffuse reflectance infrared spectroscopy exhibited a band at 1267 cm\(^{-1}\), which was assigned to O\(_2^-\) and the change in intensity of this band with time mirrored the transient change in resistance with 1 ppm NH\(_3\) at 300\(^\circ\)C, indicating that NH\(_3\) chemisorption was correlated with the O\(_2^-\) species. Taking advantage of the transient resistance decrease of NiO with NH\(_3\), and combining the In\(_2\)O\(_3\) and NiO allowed selectivity enhancement towards NH\(_3\) at concentrations as low as 100 ppb. Interference to CO, NO\(_x\) and humidity were studied by selecting a suitable combination of both oxides, the response to CO at <10 ppm could be negated. Similarly, with NO at <10 ppb, there was minimal sensor response. The sensor was used to analyze NH\(_3\) mixed into human breath at 10-1000 ppb concentrations. Water had to be completely removed from the breath via a moisture trap, since water interfered with the NH\(_3\) chemisorption chemistry. Potential applications of this sensor platform in breath analysis are discussed.

Chemical absorption by aqueous amine solution and membrane gas separation are the leading technologies for CO\(_2\) capture. A simple, fast, and robust method was developed for assessing the effect of SO\(_2\) on CO\(_2\) absorption with monoethanolamine (MEA) solution by Horizontal Attenuated Total Reflectance (HATR) monitoring. This method aims at monitoring the influence of SO\(_2\) on CO\(_2\) absorption process by MEA, and obtaining information on speciation, concentration and kinetics. First, the absorption bands observed during CO\(_2\) reaction with MEA was assigned to characteristic vibration modes. Then, CO\(_2\) absorption in the presence of SO\(_2\) was studied. The chemical speciation was evaluated by kinetic measurements and tentative solutions were examined for quantitative analysis. The
present study used concentrations of SO$_2$ that can be observed in a typical flue gas stream after the power plant desulfurization process. Speciation of the MEA/PZ blends was analyzed by the HATR spectrum and the influence of PZ on CO$_2$ uptake by MEA was examined. As an application of IR spectroscopy for practical samples, the SO$_2$ effect on an amine based polymer membrane was assessed. In the presence of SO$_2$, the individual amine carrier was studied by transmission FTIR and the membrane was studied by ATR FTIR.

A strategy for growing CHA zeolite membrane on polymer support and demonstrating its viability for CO$_2$/N$_2$ separation was reported. CHA zeolite nanocrystals were synthesized by interzeolite conversion of H-form zeolite Y nanocrystals. A rapid synthesis approach was applied to crystallization of CHA zeolites, with a 4~6-fold increase in the rate of crystal growth, as compared to conventional hydrothermal process. Chabazite-type zeolite membranes were synthesized via the secondary growth method using a template-free solution. The variables affecting the quality of the resulting chabazite zeolite membranes including starting materials and synthesis time were investigated to determine the optimum conditions for chabazite membrane synthesis.
This dissertation is dedicated to my family.
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Chapter 1: Introduction

Summary

Solid-state materials, such as semiconducting metal oxides and zeolites, offer great potential for their application in the selective detection and separation of particular gases.

In the first part, a brief introduction is provide into the working principle of solid-state electrochemical sensors, which represent the major class of commercial sensors for trace gas detection, and to highlight challenges of the actual developments in real-world applications.

In the second part, the emphasis is on the significant challenge of CO₂ capture and introduction of recent advances in materials and emerging concepts. Particular attention is directed towards the latest developments in CO₂/N₂ separations using polymers and zeolites membranes.

1.1 Gas detection

1.1.1 Trace gases

Trace gases consist of less than 1 vol% of the earth atmosphere (Table 1.1). Despite their relative scarcity, the most important trace gases are the greenhouse gases, such as CO₂, methane, NO, water vapor and ozone.

In addition to natural sources, several trace gases are produced anthropogenically, including emissions from automobiles, agriculture and electricity generating units.
Through emissions of greenhouse gases, mankind has enhanced the natural greenhouse effect which may now be leading to a warming of the earth climate. The detection and quantification of trace gases in ambient air are of considerable importance for a number of applications, such as environmental monitoring, combustion diagnostics, and atmospheric chemistry.

Nitrogen oxides (NOx) are an important family of air polluting trace gases, which are produced through combustion by chemical plants and automobiles. The huge amount of NOx release into the atmosphere are causing problems to the environment and human beings. Among them, nitrogen dioxide (NO₂) is the most hazardous gas with threshold limit value (TLV) of 3 ppm, according to the safety standards given by the American Conference of Governmental Industrial Hygienist. NO₂ reacts in the presence of air and ultraviolet light in sunlight to form ozone and nitric oxide (NO) [1]. The NO then reacts with free radicals in the atmosphere, which are also created by the UV acting on volatile organic compounds (VOC). The free radicals then recycle NO to NO₂. In this way, each molecule of NO can produce ozone multiple times. NOx in the atmosphere are captured by moisture to form acid rain. Acid rain, along with cloud and dry deposition, severely affects certain ecosystems [2]. Short-term exposure to NOx gases induce and aggravate adverse respiratory effects including airway inflammation and asthma [3], while long-term exposure leads to pulmonary edema and death [4]. The detection and the emission control of NOx are crucial means to reduce their noxious effects on environmental and human beings. All of these facts indicate an obvious need to reduce NOx emissions.
Ammonia (NH₃) is the dominant basic trace gas in the troposphere. There are three ammonia sources [5]. The first source is via a process called nitrification for atmospheric nitrogen to enter the ecosystem. The second source in the overall nitrogen cycle is ammonification, a series of metabolic activities that decompose organic nitrogen like manure from agriculture and wildlife or leaves. The third source of ammonia is combustion, both from chemical plants and motor vehicles. Ammonia is produced by the chemical industry for the production of fertilizers and for the use in refrigeration systems. Despite its usefulness, ammonia is both caustic and hazardous to humans especially when its concentration exceeds threshold limit value (TLV) of 25 ppm. Ammonia vapor has a sharp, irritating, pungent odor that acts as a warning of potentially dangerous exposure. Exposure to very high concentrations of gaseous ammonia can result in lung damage and death [6]. There are different constituencies that are interested in measuring ammonia: environmental, automotive, chemical industry and medical diagnostics. The concentration levels of interest for the different application areas are summarized in Table 1.2.

1.1.2 The existing techniques of trace gas detection

Given the breadth of applications, a very wide range of analytical instrumentation is used for trace gas analysis [8]. This instrumentation utilizes broad based techniques such as mass spectrometry and infrared spectroscopy, chromatography and specific sensors.
1.1.2.1 NOx detection

There are several existing commercially available instruments for the measurement of NOx in automobile industry.

Spectroscopy

Vibrational spectroscopy, particularly infrared spectroscopy, has been used for monitoring trace NOx in the environment. Infrared absorption occurs at discrete wavelengths/energies dependent on the molecular species involved, i.e. it can be viewed as a fingerprint for the molecules. The energy of principal absorption bands for some key species of interest in automotive emissions are:

\[
\begin{align*}
CO & \ (2143 \ \text{cm}^{-1}), \ \ CO_2 & \ (2349 \ \text{cm}^{-1}), \ \ NO & \ (1876 \ \text{cm}^{-1}), \ \ NO_2 & \ (1617 \ \text{cm}^{-1}), \ \text{water vapor} & \ (1595, \ 3750 \ \text{cm}^{-1}), \ \text{hydrocarbons} & \ (2950 \ \text{cm}^{-1}).
\end{align*}
\]

Variants of infra-red instruments that are most commonly used are non-dispersive infrared (NDIR) [9] and Fourier transform infrared (FTIR) measurements [10].

However, infrared spectroscopy can measure NO, but not NO\(_2\) because of interference from water vapor [11]. Information from suppliers gives typical operating ranges of 0 – 500 ppm and of course the ability to simultaneously measure CO, CO\(_2\) and hydrocarbons.

Chemiluminescence

A completely automatic chemiluminescent instrument has been developed for in situ measurements of NO [12]. Nitric oxide reacts with ozone, a chemical form of oxygen, to give nitrogen dioxide in a reaction that generates light:

\[
NO + O_3 \rightarrow NO_2 + O_2 + \text{light emission.}
\]
The intensity of the light emitted is proportional to the mass flow-rate of nitric oxide into the reaction chamber and can be measured with high sensitivity using a photomultiplier tube. This, therefore, represents the basis for a sensitive, quantitative analysis of gaseous NO.

The light generating reaction requires ozone. This is usually made by a silent electric discharge (at several tens of kV) through a stream of externally provided oxygen and is generated in the ozonizer, which is usually an integral part of the analyzer.

The chemiluminescence technique can directly measure NO, but not NO\(_2\) (need conversion to NO) [13]. Information from suppliers gives typical operating ranges of 0 – 500 ppm. It does consume a gas, either O\(_2\) or compressed air, as a feed gas to the ozonizer, although an internal pump to use ambient air can be used. Both the meter and the converter’s efficiency require periodic calibration. Chemiluminescence tends to be the measurement technique preferred by automotive test houses. It is one of the 2 techniques specified in approval regulations. It also has the reputation of not being portable.

Electrochemical cell

Just as nitric oxide reacts with ozone to give nitrogen dioxide, the basis of chemiluminescence detection of NO, so too it can be oxidized in an electrochemical cell. Instead of the reaction generating light (as for chemiluminescence), in this form the reaction generates a small electric current which can be detected [14, 15]. The magnitude of the current is proportional to the mass flow-rate of nitric oxide into the reaction chamber and can be measured with high sensitivity using relatively standard electronics. The electrochemical cell requires an electrolyte that could be a liquid or, ideally, a solid. Some
key advantages of this approach to measuring NO are that it is cheap, simple and robust. However, it is fair to say that this technology is not as mature as either chemiluminescence detection or NDIR and durability might be an issue.

1.1.2.2 NH₃ detection

When it comes to quantifying ammonia gas, being able to isolate them from complex gaseous mixtures is important. Since the 1950s, techniques such as chemical ionization, gas chromatography, laser spectroscopy, and chemical detection have emerged as the key methods. Their sensitivity, precision and accuracy have proven suitable for selectively detecting and identifying low molecular weight species in gaseous form. Furthermore, combining these methods with each other in various ways (e.g., with mass spectrometry) shows potential for strengthening their detection capabilities.

Chemical Ionization

Chemical ionization uses the charge of a molecule to control how it reacts with other molecules. Under various pressures, the molecular reaction rate can also be controlled [16]. By combining atmospheric pressure chemical ionization with mass spectrometry (APCI-MS), a spectral image displaying the mass-to-charge ratio can be obtained [17]. Two chemical ionization techniques that are capable of ammonia detection are proton transfer reaction – mass spectrometry (PTR-MS) and selected ion flow tube – mass spectrometry (SIFT-MS). PTR-MS has been used mostly for air analysis and environmental studies where atmospheric ammonia gas can be detected between 90 and 270 ppt [18]. With SIFT-MS, the initial concept was used to investigate the kinetic behavior of gas phase ion-neutral...
reactions. Since then, thousands of gas reactions ranging from environmental to clinical have been studied using the SIFT-MS technique. Analysis of breath VOCs (including ammonia) is achieved in about 10 ms with a sensitivity as low as 10 ppb [19].

Gas Chromatography

Another technique which has been widely used in quantifying trace gases is gas chromatography (GC). This has been combined with sampling methods such as solid phase micro extraction (SPME) to collect the sample prior to their addition to the chromatographic column [20]. As the sample flows through the column, the individual gas molecules separate by their affinity for either the carrier gas or the liquid coating on the column [21]. However, since GC is reliant on first collecting a sample, quantification is not performed in real-time. Furthermore, SPME provides greater sensitivity, but concentration accuracy decreases due to possible loss during the collection process [22]. Chromatographic columns can also be damaged by moisture such as that found in humid breath sample. Hence, an additional drying method must be used to remove any water vapor that is present or the accuracy of readings could be affected. In conjunction with gas chromatography, ion mobility spectrometry (GC-IMS) is capable of analyzing the concentrations of ammonia found in human breath as low as 14 ppt [23]. Furthermore, results can be obtained in 20 ms to a few minutes depending on the number of spectra being studied.

Laser Spectroscopy

The measure of the absorbance in the far-infrared spectral region is a viable technique to measure the concentration of ammonia. Laser spectroscopy utilizes the characteristic
absorption or emission of energy by matter (in this case gas) at specific wavelengths when excited by a laser energy source [24]. Use of laser spectroscopy has shown high selectivity, high sensitivity, and real time potential for clinical breath ammonia analysis [25]. Advances in tunable laser sources allowed an increase of performance. The tunable diode laser absorption spectroscopy (TDLAS) gas measurement is based on the Beer-Lambert relationship using an infrared laser to measure the transmitted intensity [26]. TDLAS is capable of detecting breath ammonia at concentrations as low as 1 ppm in approximately 10 seconds [27]. Recently, a detection limit of 4 ppb with an integration time of 5 s has been obtained with a quantum cascade laser diode coupled with an astigmatic Herriot cell with 150m of optical path [28].

1.1.3 Challenges of trace gas detection

The detection and quantification of trace gases is of great interest in a wide range of applications such as pollution monitoring, industrial process control, toxic-gas detection and human breath analysis for medical diagnostics. At the same time the determination of trace gas concentration constitutes a challenge for the analytical techniques employed in several respects.

First, the techniques must be sufficiently sensitive to detect the species under consideration at their ambient concentration levels. This can be a very demanding criterion, for instance, species present at mixing ratios ranging from as low as 1 ppb to several ppm can have a significant influence on the chemical processes. Thus, detection limits from ppb to the ppm-range are required, depending on the application.
Second, it is equally important for measurement techniques to be specific, which means, that the result of the measurement of a particular species must neither be positively nor negatively influenced by any other trace species simultaneously present in the probed volume of air. Given the large number of different molecules present at the ppb level, even in clean air, this is also not a trivial condition.

Further desirable properties of a measurement technique include: simplicity of design and use of the instruments based on it, capability of real time operation (as opposed to taking samples for later analysis), and the possibility of unattended operation. Also to be considered are weight, portability, and dependence of the measurement on ambient conditions.

Today, there are different spectroscopic methods which can potentially meet some of these requirements. However, instruments for measuring trace gases are often bulky, and there is a drive for obtaining miniaturized sensors. Solid state electrochemical sensors have been developed for monitoring trace gases. This technology is attractive since it is possible to obtain high sensitivity, selectivity, and fast response time. In addition, these devices have advantages of low power consumption, light weight, low maintenance cost, harsh environment tolerance and portability. There are numerous papers on resistive semiconducting metal oxide sensors for the detection of trace gases. Same as other instrumentation, the development of sensors must embrace the challenges of real-world applications.
1.1.4 Applications of trace gas detection

1.1.4.1 Automotive industry

In urban areas, the major source of NOx release is combustion of fossil fuels, and increased use of fossil fuels in energy production, transportation and industry demands rugged and reliable detection methods capable of real-time monitoring for public health, environmental, industrial and safety applications.

Generally, the combustion operating conditions involve temperatures up to 1000 °C, thus calling for detection of low concentrations, e.g. <100 ppm of NOx under harsh conditions. The concentration range of NO\textsubscript{2} detection in automobile cabin is 0.5–5 ppm [29]. Thus, NOx sensors need to have high gas response as well as sufficient selectivity for automotive applications.

Modern diesel engines operate at high air-to-fuel ratios that result in an excess of oxygen in the exhaust gas, resulting in large concentrations of NOx [30]. Toxic NOx concentrations are lowered significantly by selective catalytic reduction (SCR) of NOx with NH\textsubscript{3}, according to the equation [31]:

\[
4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}
\]

Therefore, NH\textsubscript{3} is injected into the exhaust system (Figure 1.1). It is unfavorable to inject too much NH\textsubscript{3} for this is emitted into the atmosphere where it adds to the total pollution, known as ammonia-slip [33]. The injected amount can be optimized by measuring the excess ammonia concentration in the exhaust system. The concentration level that is of interest for this application depends on the controllability of the setup. When the controllability of the ammonia injection is very accurate, the used sensor should be able
to measure very low ammonia concentrations in a few seconds. Because measurements are performed in exhaust pipes, the sensor should be able to withstand elevated temperatures.

1.1.4.2 Biomedical application

The potential of breath analysis has attracted increasing interest for clinical diagnostics as more and more compounds found in human breath have been linked to physiological conditions. Human breath is a highly complex substance with numerous variables that can interfere with one another. Each human breath contains over 1,000 trace volatile organic compounds (VOCs). Within the 0.9% (w/v) of breath which constitutes inert gases and VOCs, the individual gas concentrations can range between parts-per-million (ppm) and parts-per-billion (ppb) (Table 1.3).

Fractional exhaled nitric oxide (FENO) is associated to the presence of inflammatory conditions of the airways, like asthma, and bronchiectasis among others [3]. A concentration below 25 ppb is considered normal, and a concentration above 50 ppb reveals an airway inflammation [35]. FENO measurement is a noninvasive, standardized, and validated technique for assessing airway inflammation in patients with asthma [36] with or without nasal polyposis [37]. FENO is also correlated with other diseases of the respiratory tract and in particular with chronic obstructive pulmonary disease (COPD) [38].

Ammonia has attracted increasing interest for clinical diagnostics such as in hemodialysis monitoring [39], asthma assessment [25], diagnosis of hepatic encephalopathy [40], detection of Helicobacter pylori [41], and analysis of halitosis [42]. The normal physiological range for human breath ammonia is in the region of 50 to 2,000
ppb [43]. To be effective, analytical techniques for breath ammonia quantification must be capable of a limit of detection of some 50 ppb.

With regard to breath analysis, development of breath monitors that are capable of effectively measuring breath in the clinical setting is a critical next step. The ideal breath monitoring device is one that is sensitive to the specific gas and capable of detecting it at the physiologically relevant concentrations in the ppb range with good precision and accuracy, insensitivity to interference (particularly temperature and humidity effects), is ideally portable for point-of-care use, provides ease-of-use to the user, displays real-time measurements, and is of low cost.

1.1.5 Semiconducting metal oxides gas sensors

The main advantage of semiconducting metal oxides are easy fabrication with low production cost, which means that well engineered metal-oxide sensors can be mass produced at reasonable cost. Moreover, these oxides are compact and durable. As a result, they are amenable to being used for in situ monitoring and harsh conditions.

1.1.5.1 Working principle

The electrical conductivity of a semiconductor falls between that of a conductor and an insulator. The conduction of electrical current in a semiconductor occurs through the movement of free electrons and holes as charge carriers. The major charge carriers in Si-based semiconductors can be manipulated by doping impurity atoms into their crystal
lattice [44]. When a doped semiconductor contains mostly free holes it is called "p-type", and when it contains mostly free electrons it is known as "n-type".

In the case of metal oxide semiconductors, the conductivity is determined by doping aliovalent cations [45] or by oxygen nonstoichiometry [46]. Undoped oxygen deficient metal oxide shows n-type semiconductivity since the formation of oxygen vacancies accompanies the generation of electrons [47], while p-type semiconductivity is caused by the deficiency of metal ions in the material [48].

Adsorption on the semiconductor surface can induce band bending near the surface [49]. Figure 1.2 summarizes three kinds of space charge regions schematically using n-type semiconductor as an example, in which the majority carriers are electrons, that is, the density of free electron carriers \( n_e \) is higher than that of hole carriers \( n_h \). There is no space charge in the flat band region. For downward band bending, positive charges exist at the surface and electrons accumulate in the semiconductor near the surface, causing an increase of \( n_e \) and a decrease of \( n_h \). This space charge region in the semiconductor is called the accumulation layer due to the accumulation of electrons in the semiconductor. In the upward band bending condition, negative charges exist at the surface and positive charges accumulate near the surface, causing a decrease of \( n_e \) and an increase of \( n_h \). This space charge region is called the depletion layer. In upward band bending, the semiconductor can change to a p-type semiconductor near the surface if the electrons are depleted below the intrinsic level \( n_i \), i.e., \( n_e < n_i < n_h \). For this condition, the space charge region is called the inversion layer. For p-type semiconductors, in which the majority carriers are holes, the surface band-bending is inverted (Figure 1.3).
When the metal oxide is heated in air, atmospheric oxygen molecules adsorb onto the surfaces and ionize into species such as $O_2^-$, $O^-$, and $O_2^2-$ by taking electrons from the conduction band [51]. The adsorption phenomena is explained by the following reaction paths:

\[
\begin{align*}
O_2 \text{ (gas)} & \Leftrightarrow O_2 \text{ (adsorbed)} \\
O_2 \text{ (adsorbed)} + e^- & \Leftrightarrow O_2^- \\
O_2^- + e^- & \Leftrightarrow 2O^- \\
O^- + e^- & \Leftrightarrow O_2^2-
\end{align*}
\]

The oxygen ions $O_2^-$, $O^-$, and $O_2^2-$ are stable below 150$^\circ$C, between 150 and 400$^\circ$C, and above 400$^\circ$C, respectively [52].

The adsorption of oxygen leads to the formation of an electronic core-shell configuration (Figure 1.4) [53]. For the n-type semiconductor, there is a semiconducting core and a resistive shell. For the p-type semiconductor, there is an insulating core and a semiconducting shell.

Although both n- and p-type semiconductors establish electrical core-shell layers by adsorbing oxygen, they exhibit significantly different conduction behaviors. The resistance of n-type oxide is determined by the resistive shell to shell contacts formed between the particles, which can be explained by equivalent circuits of serial connections between semiconducting cores and resistive interparticle contacts (Figure 1.5). The electron transfer from the conduction band to the chemisorbed oxygen results in the decrease in the electron concentration near the surface and the formation of the electron depletion layer. Since the majority carriers of n-type oxide are electrons, an increase in the resistance is observed.
This situation can be described as an upward band bending (Figure 1.6), which means that the electrons need more energy to get to the surface (compared to a flat band situation) [52, 54]. The presence of the negative surface charge generates a surface potential barrier $eV_{\text{surf}}$ of 0.5 to 1.0 eV. The height ($eV_{\text{surf}}$) and depth ($\Lambda_{\text{air}}$) of the band bending depend on the surface charge, which is determined by the amount and type of adsorbed oxygen. At the same time, $\Lambda_{\text{air}}$ depends on the Debye length $L_D$, which is a characteristic of the semiconductor material for a particular donor concentration

$$L_D = \sqrt{\frac{\varepsilon_0\varepsilon k_B T}{e^2 n_d}}$$

where $k_B$ is Boltzmann’s constant, $\varepsilon$ the dielectric constant, $\varepsilon_0$ the permittivity of free space, $T$ the operating temperature, $e$ the electron charge, and $n_d$ the carrier concentration, which corresponds to the donor concentration assuming full ionization. As an example, $L_D$ for SnO$_2$ at 523 K is about 3 nm, with $\varepsilon$=13.5, $\varepsilon_0$=8.85×10$^{-12}$ Fm$^{-1}$, and $n_d$=3.6×10$^{24}$ m$^{-3}$ [55].

As shown in Figure 1.7, the work function $\Phi$-defined as the energy which is necessary to remove an electron from the Fermi level ($E_F$) to the vacuum level ($E_{\text{vacuum}}$) of the material-can be expressed by:

$$\Phi = qV_s + \chi + (E_C - E_F)_{\text{bulk}}$$

where $qV_s$ is the surface band bending, $\chi$ represents the electron affinity and $(E_C - E_F)_{\text{bulk}}$ defines the difference between the conduction level in the bulk and the Fermi level.

In the normal operation temperature range of metal oxide gas sensors ($\leq 400$ °C) the main effects of gas interaction are restricted to the surface, leaving the material’s bulk
unaffected; therefore \((E_C - E_F)_{\text{bulk}}\) does not change. Only the surface band bending \(qV_s\) has an impact on the overall sensing layer resistance to an extent that is different for the two types of semiconducting oxides.

When the n-type oxide is exposed to a reducing gas, e.g., CO, the adsorbed oxygen ions react with the reducing gas and release electrons into the electron depletion layer, which decreases the resistance proportional to the concentration of the reducing gas. Those redox reactions free electrons, which can be released to the conduction band and decrease the upward band bending by \(q\Delta V\). This in turn makes it easier for the electrons to pass the Schottky barrier between the grains.

The conduction in p-type oxide can be explained by a parallel paths across the resistive core and along the semiconducting shell (Figure 1.8). The adsorbed oxygen ions extract electrons from the surface and a hole accumulation layer is formed, which determines an upward band bending \(qV_s\) (Figure 1.9) and accordingly, the surface space charge layer becomes more conductive in comparison to the bulk. Upon exposure to a reducing gas, the surface negative charge is decreased as a result of the oxidation reaction between the reducing gas and the oxygen ions. The electrons injected into the material through the oxidation reaction decreases the concentration of holes in the shell layer, which in turn decrease the upward band bending by \(q\Delta V\) and increases the resistance of the accumulation layer.
1.1.5.2 Strategies of optimizing selectivity

A range of reducing gases can similarly react with oxygen anions on the surface of oxide semiconductors, which often hinders distinguishing among various gases. The design of oxide semiconductor gas sensors to selectively detect specific gas remains challenging.

Conducted research have shown that gas sensing effect in metal oxides is very complicated phenomenon, which depends on all metal oxide parameters (Figure 1.10) [57]. Analysis carried out has shown that the influence of these parameters on gas sensing characteristics takes place through the change of parameters such as effective area of grain contacts, adsorption/desorption processes, number of surface sites, concentration of charge carriers, coordination number of metal atoms on the surface, gas penetrability of sensing matrix, etc.

At present, material engineering of metal oxide films is one of the most effective methods used for optimization of solid state gas sensors [58]. The considerable improvement of operating parameters such as selectivity can be achieved due to optimization of chemical, structural, bulk and surface properties of applied metal oxides. There are a great number of technological methods which could be used for optimization of sensor parameters (Figure 1.11) [59].

Among them, many strategies including promoting specific gas-sensing reactions by loading catalyst [60], varying temperatures [61], controlling the size and number of nanopores and mesopores [62], tuning the acidity or basicity [63, 64], and using catalytic filtering layers [65] have been suggested to enhance the gas selectivity of n-type oxide semiconductor gas sensors.
It is noteworthy that most p-type oxide semiconductors such as NiO, CuO, Co₃O₄, Cr₂O₃, and Mn₃O₄ are oxides of transition metals, which exhibit various oxidation states because of the electrons in the d shell of the metal atom. These materials generally show distinctive catalytic activities because p-type oxide semiconductors show an affinity with oxygen and multivalent characteristics [66]. This means that p-type oxide semiconductors are promising platforms for developing high-performance gas sensors that exhibit new functions [53]. Applying p-type oxides as dopants that exhibit catalytic activity can enhance not only the gas response by electronically sensitizing the sensors, but also the gas selectivity by chemically sensitizing them.

When p-type and n-type materials are placed in contact with each other, p-n junctions are created at the interface or boundary of the two materials. To date, there has been research on the design of high-selectivity gas sensors fabricated using longitudinal oxide p–n junctions [67], nanocomposites sandwiched between p- and n-type oxide semiconductor nanoparticles [68], and 1-dimensional n-type oxide semiconductors decorated with p-type oxide semiconductor nanoclusters [69].

1.1.6 Research summary

The research on mixtures of p- and n-type materials above clearly demonstrate that it is possible to use the p–n cancelation with the interfering gas to generate a selective sensor. Placing the powders adjacent to each other and including different lengths of the powders in making resistance measurements parallels the concept of making powders of different ratios, but the experimental design is considerably simplified, since we are dealing with
only one sample, but obtaining multiple sensor measurements. With this device design, the response to the analyte gas can be continuously varied by choosing to include different fractions of the metal oxide. For a particular choice, a sensor can be designed that is selective to the analyte gas and discriminates against the interfering gas that is present at significantly higher concentrations.

In Chapter 2, mixtures of WO$_3$ and Cr$_2$O$_3$ in varying weight ratios as well as adjacent alignment of these two powders were both examined as possible designs for NO-selective sensor. Studies focused on resistance measurements toward NO and CO at 300 °C were carried out. Using the sensor design with the adjacent alignment of n-type WO$_3$ and p-type Cr$_2$O$_3$ resulted in optimal performance. This sensor design exploits the different majority carriers in these two semiconducting oxides for selective NO gas sensing. The advantage of such a sensor system is that the device can be sensitive to NO at low ppb level (18 ppb detection limit) and discriminate against CO at concentrations a thousand-fold higher (20 ppm). Practical application of this device is demonstrated by measuring NO in human breath samples.

In Chapter 3, a combined n-type In$_2$O$_3$ and p-type NiO placed side by side with a shared interface as the sensing design was developed. The substrate on which these metal oxides are placed allows for measuring the resistance change upon exposure of gas across In$_2$O$_3$, NiO or a combination of both oxides. Our focus was to sense ammonia in the presence of CO as a model interferent gas, the latter at 10 -100 times higher concentration. With CO, resistance changes on In$_2$O$_3$ and NiO showed opposite trends, and by selecting a suitable combination of both oxides, the response to CO at 10 ppm could be negated.
Taking advantage of the transient resistance decrease of NiO with NH₃, and a pulse of analyte gas on for two minutes, a satisfactory resistance profile was obtained. Combining the In₂O₃ and NiO allowed an additive effect with selectivity enhancement towards NH₃ at concentrations as low as 100 ppb, with minimal interference from co-present CO at 10 ppm concentration. This selectivity and sensitivity was used to analyze NH₃ spiked into human breath at 10-1000 ppb concentrations.

1.2 Gas separation

The control of anthropogenic carbon dioxide emissions is one of the most challenging environmental issues all over the world, because of the implications to atmospheric carbon dioxide levels and climate change. Burning of fossil-fuels is responsible for the majority of these carbon dioxide emissions, and therefore there is significant interest in developing technologies for CO₂ capture.

Nowadays, there are three technological pathways for CO₂ capture [70]: post-combustion capture, pre-combustion capture, and oxy-combustion (Figure 1.12). Briefly, CO₂ is separated either from other gases produced by combustion in post-combustion capture or from the fuel before combustion in pre-combustion capture. Oxy-combustion takes place in a pressurized CO₂-rich recirculating stream in which nitrogen is completely excluded from the combustion process through a preliminary air separation step. Among them, post-combustion capture (PCC) applies mainly to coal power plants with air for combustion and generates a flue gas with a CO₂ concentration of less than 15% at atmospheric pressure (1 atm). Since the CO₂ partial pressure is less than 0.15 atm, the
thermodynamic driving force for the removal of CO$_2$ from flue gas is low, which leads to a technical challenge for the development of cost-effective capture process. Although current post-combustion techniques can be retrofitted to existing plants, the energy penalty for a coal power plant using traditional MEA absorption has been estimated as 25 to 40% [71].

The main challenge for gas separation is that the differences between the physical properties of the flue gas constituents are relatively small, such as the kinetic diameter of each gas. Therefore, alternate strategies focus on the differences between the chemical reactivity of the gas molecules. A further challenge is the inverse relationship between the adsorption and diffusion selectivity for meso- and microporous materials. There is a need to explore new materials in which one can tune the chemistry at a molecular level.

1.2.1 Membranes for CO$_2$ capture

Currently, CO$_2$ capture with amine absorption is the leading candidate technology because it is a proven technology used successfully to treat industrial gas streams for decades. For example, postcombustion “wet-scrubbing” CO$_2$ capture technologies have been employed industrially for over 50 years and are based predominantly on the primary alkanolamine MEA [72]. However, a number of studies have shown that amine absorption, when applied to flue gas CO$_2$ capture, is costly and energy intensive [73]. For example, regenerating the solvent requires high temperature in the stripper reboiler. One report predicted that an amine system used to capture 90% of the CO$_2$ in flue gas will require about 30% of the power produced by the plant and result in a CO$_2$ capture cost of $40–
100/ton CO₂ [74]. This translates to an increase in the cost of electricity (COE) of 50–90% if amines are used to remove 90% of the CO₂ from flue gas. These values are well above the DOE goal to achieve 90% CO₂ capture at an increase in the cost of electricity of less than 20% for post-combustion [70]. The associated cost and environmental impact means that there is need for other more efficient separation processes to be applied to carbon dioxide capture.

Another strategy for gas separation is the use of membranes. In 1980, Permea launched its hydrogen-separating Prism membrane [75]. This was the first large industrial application of gas separation membranes. Since then, membrane-based gas separation has grown into a $150 million/year business, and substantial growth in the near future is likely [76].

Gas separation membranes are now applied to a wide range of industrial processes. In particular, many of the early patents were awarded for the sweetening of natural gas by the removal of carbon dioxide [77, 78] and this is the foundation on which current carbon dioxide capture research is based. Membrane processes have been previously suggested for CO₂ capture from flue gas [79]. Membrane separation technologies are projected to attain a high efficiency for CO₂ capture owing to their selective extraction of CO₂ from mixed gas streams, their low energy requirements and the flexibility in their possible configurations in industrial plants relative to conventional amine absorber/desorber columns [80].
1.2.1.1 General principles of membranes for gas separation

Membranes act as filters to separate one or more gases from a feed mixture and generate a specific gas rich permeate, as shown in Figure 1.13. Two characteristics dictate membrane performance, permeability; that is the flux of a specific gas through the membrane, and selectivity; the membrane’s preference to pass one gas species and not another.

Permeance and permeability are usually used as a measure of the gas transport rate. The permeance (Q) is the pressure and area normalized parameter quantifying the productivity of an asymmetric membrane or thin film composite. The permeability (P) is typically used with dense films where the thickness (δ) is well defined and is the permeance normalized by the thickness P = Q × δ. Units for the permeance are mol m⁻² s⁻¹ Pa⁻¹ or, more conveniently Gas Permeation Units (GPUs), where 1 GPU = 10⁻⁶ cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹. Units for permeability are mol m m⁻² s⁻¹ Pa⁻¹ or Barrer, where 1 Barrer = 10⁻¹⁰ cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹. Hence a polymer with a permeability of 1 Barrer will have a permeance of 1 GPU if the thickness is 1 micron. When mixed gases are used, the partial pressure difference of a gas is used. The permeability of a polymer for gases is dependent on the membrane properties (e.g., physical and chemical structures), the nature of the permeant species (e.g., size, shape, and polarity), and the interaction between the membrane and permeant species. The selectivity of the membrane to specific gas or liquid molecules is subject to the ability of the molecules to permeate through the membrane. The permselectivity (or ideal separation factor, determined from the permeation of individual pure gases), α, is simply the ratio of two gases, A and B, being separated: \( \alpha_{A/B} = \frac{P_A}{P_B} \)
There are different mechanisms for membrane separation [81], Knudsen diffusion, molecular sieving, and solution-diffusion separation, which are schematically represented in Figure 1.14. Molecular sieving and solution-diffusion are the main mechanisms for nearly all gas separating membranes. Knudsen separation is based on gas molecules passing through membrane pores small enough to prevent bulk diffusion. Separation is based on the difference in the mean path of the gas molecules due to collisions with the pore walls. Molecular sieving relies on size exclusion to separate gas mixtures. Pores within the membrane are of a carefully controlled size relative to the kinetic (sieving) diameter of the gas molecule. This allows diffusion of smaller gases at a much faster rate than larger gas molecules. Polymeric membranes are generally non-porous, and therefore gas permeation through them is described by the solution-diffusion mechanism. This is based on the solubility of specific gases within the membrane and their diffusion through the dense membrane matrix. Hence, separation is not just diffusion dependent but also reliant on the physiochemical interaction between the various gas species and the polymer, which determines the amount of gas that can accumulate in the membrane polymeric matrix.

The cost of membrane separation post-combustion is associated with creating the pressure difference across the membrane to drive separation, usually achieved through feed gas compression. For most membranes, there is a trade-off between selectivity and permeability. A highly permeable membrane tends to have low selectivity, and vice versa. Robeson [83] has suggested that this trade-off may be represented as an upper bound to membrane performance. This upper bound can clearly be seen in Figure 1.15, for a range of membranes involved in CO₂/N₂ separations. Overcoming this upper bound is the focus
of many recently awarded patents in polymeric membranes, because achieving both high carbon dioxide permeability and selectivity is desirable.

Improving permeability and selectivity are not the only membrane properties that are important. For membrane materials to be viable, they need to be thermally and chemically robust, resistant to plasticization and aging affects to ensure continual performance over long time periods, and be cost effective to manufacture as standard membrane modules. The constituent materials of membranes are typically classified as: inorganic (ceramic, metal oxide, metallic, molecular sieves, metal–organic frameworks) or organic (cellulose acetate, polymers, hollow fibers). In this chapter, we focus on polymeric membranes and zeolite membranes.

1.2.1.2 Polymeric membranes

Despite the large number of polymeric materials investigated and developed for gas separation applications, the number of polymers used in commercial system is still limited [85]. The main rubbery and glassy polymers employed for polymeric membranes are listed in Table 1.4.

Within a polymer membrane, pores and channels have a wide range of sizes and topologies. Polymer free-volume, the fraction of the volume not occupied by the electronic clouds of the polymer, plays an important role in the transport properties of low molecular weight species and gases. An amorphous polymer kept above its glass transition temperature \( T_g \) is in a rubbery state. It presents a relatively large amount of free-volume, owing to transient voids between the highly mobile polymer chains. When the temperature
is lowered below its $T_g$, the polymer behaves as a rigid glass: the fractional free-volume decreases, resulting in insufficient space for large-scale co-operative movements of the polymer backbone.

Typically, rubbery polymers present high permeabilities and their selectivity is mainly influenced by differences in the condensability of the gas species. Among them, poly(organosiloxanes) were studied in detail because of the vast utility of polydimethylsiloxane (PDMS), which has high permeability coefficients, owing to its large free-volume, and high selectivities for condensable gases. Silicone rubber is extremely permeable and has adequate vapor/inert gas selectivities for most applications; composite membranes of silicone rubber are used in almost all of the installed vapor separation systems [87].

Glassy polymers possess high gas selectivity and good mechanical properties. Usually in glassy polymers the more permeable species are those with low molecular diameter and selectivity is due to differences in molecular dimension. The glassy state is characterized by a relatively small fraction of free-volume. A larger amount of free-volume (up to 20%) can be “frozen-in” by cooling or by a rapid removal of a solvent in some polymers with stiff molecular structures. These voids are not interconnected, and a low accessible surface area can be measured by gas adsorption. Medium to high free-volume glassy polymers (e.g., polyimides, polyphenyleneoxides, etc.) are used to produce membranes since the voids aid the transport of gas or liquid through the material.

Improving the performance of the CO$_2$-selective polymeric membrane is achieved by two approaches; increasing the solubility of carbon dioxide in the membrane through
changes in polymeric composition, and increasing the diffusion of carbon dioxide by altering the polymer packing within the membrane. Diffusion is generally enhanced by increasing the volume of free space within the membrane and this can sometimes be achieved through the addition of bulk substituent groups.

Facilitated transport membrane is a variant of polymeric membranes that rely on a chemical reaction occurring between the gas of interest and a component of the membrane (carrier). The reacted species is readily carried across the membrane, whereas diffusion of non-reactive gases is inhibited (Figure 1.16). The active carrier is generally basic in nature, given that carbon dioxide is acidic. The driving force for gas transport remains the partial pressure difference across the membrane; however the facilitator carrier increases both the permeability and selectivity of the membrane through the increased loading. The facilitator carrier can be either fixed-sited within the polymeric matrix or mobile. Fixed carriers for CO₂ separation are generally polyamines, examples are polyallylamine, polyethylenimine and polyvinylamine. Mobile carriers are basic compounds, and are often a combination of hydroxide salts, organic ammonium salts, aminoacids, carbonates, alkanolamines and polydentate ligands, such as EDTA [88].

Polymeric membrane-based separation processes provide several advantages over other conventional separation techniques. First, the membrane process is a viable energy-saving alternative for CO₂ separation, since it does not require a phase change of the gases. Second, the necessary process equipment is relatively simple with only a few moving parts such as compressors or vacuum pumps, compact, relatively easy to operate and control, and amenable to scale-up. It is envisioned that polymeric membranes can be effectively
used to separate CO$_2$ from the gases of power generation point sources, if the polymeric membranes have high CO$_2$ permeance (>1000 GPU) and moderately good CO$_2$/N$_2$ selectivity (>30). At CO$_2$/N$_2$ selectivities above 30, increases in membrane CO$_2$ permeance are more important than further increases in selectivity [90]. Consideration must also be given to the ability to fabricate membranes with a thin gas separating layer: either the skin layer of an asymmetric membrane or the coating of a thin-film composite (TFC). A polymer separating layer with a 100 nm effective thickness and a permeability coefficient of 100 Barrer will have a permeance of 1000 GPU, while a 1000 Barrer polymer with a layer thickness of 4 microns will have a permeance of only 250 GPU.

Membrane Technology Research Inc. (MTR Inc., Menlo Park, USA) developed the Polaris membrane, which is a TFC membrane in flat sheet format and packaged in spiral wound modules. A CO$_2$ permeance of 1000 GPU and a CO$_2$/N$_2$ selectivity of 50 are reported [90], with variations of this achieving 2000 and 4000 GPU with a concomitant selectivity decrease to 25 at the highest permeance. Research efforts are directed towards designing readily processable polymers that have desirable combinations of permeability and selectivity, with long-term stability, in order to have immediate significant impact on scale-up and commercialization.

1.2.1.3 Zeolite membranes

Inorganic membranes represent an alternative gas separation technology. In particular, inorganic membranes such as those fabricated from zeolitic materials are especially fascinating because of their high thermal, mechanical, and chemical stability. Zeolites are
aluminosilicates possessing microporous crystalline structure. Several unique properties of zeolites contribute to their industrial success, such as high adsorption capacity, catalytic sites within the framework, crystallographic structure, and excellent ion exchange capability.

In the last four decades, zeolite membranes were extensively studied, considering preparation techniques and separation features because of their higher thermal and chemical resistance compared with those of polymer membranes. Zeolite membranes in principle might separate continuous mixtures on the basis of differences in the molecular size and shape [91], but also on the basis of different adsorption properties [92]. The separation ability of a microporous membrane can be described by the interplay of the mixture adsorption equilibrium and the mixture diffusion in a way similar to the solubility-diffusion model.

Different methods for the controlled preparation of supported zeolite membranes have been established [93], as shown in Figure 1.17. Basically, they can be distinguished into one-step methods and in secondary growth (seeding techniques) methods. The former, also called “direct in situ crystallization”, makes a thin zeolite top layer crystallized hydrothermally in one step on the top of the support or inside the pores of the support (pore plugging). The latter, decoupling zeolite nucleation from crystal growth, allows optimizing the conditions of each step independently, reducing or suppressing any secondary nucleation [94]. Seeding, the first step, consists in the deposition of the crystal seeds on the surface of a support, followed by a crystal growth by means of a hydrothermal treatment. The advantage of the membranes made by secondary growth is the high flux and the
possibility to orient the seed crystals [95]; the drawback is the ease of formation of defects or non-zeolitic pores, which form intercrystalline pathways, larger than the zeolite pores and therefore not selective. In an interesting one-step method (pore-plugging synthesis) zeolite crystals are grown within the pores of a macroporous support, yielding very robust, defect-free MFI membranes [96], whose permeance however is not very high.

Y-type zeolite membranes were demonstrated as potential candidates for CO$_2$/N$_2$ separation. Literature reports of zeolite Y on alumina supports are compared in Table 1.5. Though all these studies were done in the same temperature range, the experimental parameters (e.g. flow rate, sweep gas, pressure) are not the same for all these experiments.

A major issue of concern for membrane technology professionals and researchers is the scale up from laboratory to industrial practice [93]. Even though many papers and patents claim the industrial application of zeolite membranes, only a few examples really deal with the large scale production and application of this kind of membranes. In 2000 the first industrial scale separation plant using zeolite NaA tubular membranes was developed by Mitsui Engineering and Shipbuilding Co. Ltd. in Japan for the dehydration of organic solvents by pervaporation [109]. Several decades after the first zeolitic membrane was reported, it is fair to admit that synthesis reproducibility is still the main drawback [110]. The irreproducibility can be related to the thickness of the membrane, the presence of different concentrations of intercrystalline defects [111], and also the distribution of the zeolite material in the support, since the resistance of the latter influences transport [112]. As zeolites cannot be prepared as self-supported membranes in a practical way, porous supports commonly of alumina or stainless steel are used as supports to grow the zeolite
membranes. The only industrial application of zeolite membranes uses tubular symmetric supports [109], while planar supports have been used for concept demonstration and easy testing [113].

The rough estimate of the costs of a zeolite membrane is $1100/m^2 [114] and the cost of a zeolite membrane module is estimated to be about $2500/m^2 of installed membrane area [91]. Even though some high performance zeolitic membranes have been synthesized in a very efficient way, the cost of such membranes is still very high when compared to some economic estimations that require a price close to the polymer membrane module cost of $50–500/m^2 used for processing natural gas. In such a membrane, most of the costs are attributed to the module and only 10–20% to the membrane itself. Since the membrane costs are further dominated by the support costs and not by the zeolite layer, an interesting alternative is the replacement of the expensive supports by cheaper alternatives.

1.2.1.4 Composite membranes

Commercial polymer materials have the benefits of being inexpensive to process, highly reproducible (easy to control the thickness and easy to prepare defectiveness dense membranes), and physically robust [115], therefore, solving the difficulties and addressing the opportunities pointed out above for pure zeolite membranes. Nevertheless, polymeric membranes, both at lab and commercial scale, still do not meet the requirements for the current advanced membrane technology due to their lower separation performance (moderate selectivities), when compared with the ones based only on crystalline materials with well-defined pore systems like zeolites [116]. In Robeson’s plot (Figure 1.15), there
is an “upper bound trade-off” line which conventional polymer membrane materials cannot overcome. This bound marks, to a certain extent, the polymer material performance for a specific gas mixture and emphasizes the need for choosing innovative materials or combining them within the polymer matrix with the purpose of overcoming the Robeson’s upper-bound, achieving a synergetic separation performance. In addition, since the overall cost of membranes is determined in large part by the support cost, it is desirable to develop inexpensive polymeric supports. This would overcome the current limitations of ceramic membranes, including their high failure rate and cost of manufacture.

Mixed matrix membranes (MMM) combining polymers with zeolites have long been studied extensively aiming at low-cost, high performance membranes [117]. Generally, MMMs are composed of nanostructured porous fillers embedded in a polymer matrix (Figure 1.18). This novel membrane approach adds better transport properties and higher thermal and chemical stability to the polymer phase, solving the inherent brittleness problems found in the pure inorganic membranes. However, the inherent incompatibility between zeolites and polymers still remains a limitation, while performance of these membranes has remained low to modest at best.

There are several zeolite/polymer composite membranes reported recently. A novel concept of multilayer polymer/zeolite Y composite membrane structure was developed and investigated for CO₂ capture from flue gas [119]. Zeolite Y nanoparticles with an average particle size of 40 nm were successfully deposited onto flexible polymer supports with uniform coverage by the vacuum-assisted dip deposition approach. The membrane of the multilayer composite structure showed a CO₂ permeance of 745 GPU and a CO₂/N₂
selectivity of 25.4 under flue gas operating conditions at 57 °C and ~1 atm. Synthesis of zeolite membranes on flat polymeric supports was also reported recently [120]. Faujasite membranes were synthesized on PES supports supported on a polyester backing. A continuous FAU membrane with a thickness of 500–700 nm was fabricated using just 1 hour of hydrothermal growth on seeded PES supports. The synthesis was further improved so that a 300 nm thick FAU membrane could be obtained on flat PES supports [97]. After elimination of intercrystalline defects by using a PDMS coating, CO$_2$/N$_2$ selectivities of ~72 could be obtained.

The composite approach offers a clear opportunity for improving the already commercial polymer membranes regarding the processability in terms of costs, reproducibility, the facility to prepare nondefective membranes and the membrane performance, resulting in an overall superior gas separation selectivity.

1.2.2 Research summary

The 30% aqueous MEA solution has been utilized in an industrial scale to capture CO$_2$ for many years. Although there are numerous investigations on the performance of MEA solutions as CO$_2$ absorbents, the characterization of the structural changes during CO$_2$ absorption at a molecular level is vital to understand the chemical mechanism. In addition, SO$_2$ in the flue gas is one of the main factors causing loss of free amine, which leads to increased cost of CO$_2$ capture. Therefore, it is necessary to assess the effect of SO$_2$ on the kinetics of CO$_2$ absorption by aqueous amines. In Chapter 4, a technique based on HATR-FTIR has been developed for facile monitoring aqueous MEA solution and
qualitative analysis of the speciation during CO₂ absorption. The effect of SO₂ on CO₂ absorption is not significant at low temperature and short exposure time. SO₂ induced-pH change can interfere in the equilibriums of amine, as evidenced by the cyclic experiments that show the regeneration of MEA becomes worse as a result of accumulated effect of SO₂. The speciation of MEA/PZ blends demonstrate the CO₂ absorption characteristics of PZ, giving insights of the structure – activity relationship of the reaction between PZ and CO₂. Example of a practical application of using IR spectroscopy is demonstrated by explaining the SO₂ effect on amine membrane performance. Since developing new solvent systems for CO₂ capture includes the finding of an ideal compromise between the energy requirements and reaction rates, such attempts will be strongly supported by the fundamental spectroscopic investigation.

As discussed before, a major technical hurdle is the long time it takes to synthesize zeolites, which is incompatible with polymer membrane manufacturing methods. A second issue is that inter-particle defects appear during the zeolite growth process, no matter what the support, which leads to low performance reproducibility. These two issues have been addressed in Chapter 5 by providing strategies to accelerate zeolite crystallization and fabricate continuous zeolite membrane. To the best of our knowledge, growing CHA membrane on polymer support and demonstrating its viability for CO₂/N₂ separation has not yet been reported. CHA-type nanocrystals are synthesized by interzeolite conversion of H-form zeolite Y nanocrystals. The rapid synthesis approach is applied to crystallization of CHA zeolites, with a 4–6-fold increase in the rate of crystal growth, as compared to conventional hydrothermal process. Chabazite-type zeolite membranes are synthesized via
the secondary growth method using a template-free solution. The variables affecting the quality of the resulting chabazite zeolite membranes including starting materials and synthesis time are investigated to determine the optimum conditions for chabazite membrane synthesis.
References


[88] W.W. Ho, Membrane formed from a polyamine or its blend; at least one group 1a, 2a, 3a, or amine salt of an aminoacid of given formula; and a crosslinking agent; membrane permselective for carbon dioxide, Google Patents2000.


### Atmospheric Gases

<table>
<thead>
<tr>
<th>Atmospheric Gases</th>
<th>Average vol% in atmosphere</th>
</tr>
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<tbody>
<tr>
<td>Ar</td>
<td>0.934</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0314</td>
</tr>
<tr>
<td>He</td>
<td>0.000524</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.000179</td>
</tr>
<tr>
<td>H₂</td>
<td>0.000055</td>
</tr>
<tr>
<td>NOₓ</td>
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</tr>
<tr>
<td>O₃</td>
<td>0.000007</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.00000019</td>
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Table 1.1. Selected Trace Gases in Atmosphere
<table>
<thead>
<tr>
<th>Application</th>
<th>Detection limit</th>
<th>Required response time</th>
<th>Temperature range</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Environmental Monitoring ambient conditions</td>
<td>0.1 ppb to &gt;200 ppm</td>
<td>Minutes</td>
<td>0-40</td>
<td>Reduce environmental pollution</td>
</tr>
<tr>
<td>Measure in stables</td>
<td>1 to &gt;25 ppm</td>
<td>~1 min</td>
<td>10-40</td>
<td>Protect livestock animals and farmers</td>
</tr>
<tr>
<td>Automotive</td>
<td>NH₃ from vehicles</td>
<td>4 to &gt;2000 g/min</td>
<td>Seconds</td>
<td>Up to 300</td>
</tr>
<tr>
<td>Passenger cabinet air control</td>
<td>50 ppm</td>
<td>~1 s</td>
<td>0-40</td>
<td>Automotive air quality sensor mainly aim on NOx and CO levels</td>
</tr>
<tr>
<td>Detect ammonia slip</td>
<td>1-100 ppm</td>
<td>Seconds</td>
<td>Up to 600</td>
<td>Control urea injection in SCR NOx reduction</td>
</tr>
<tr>
<td>Chemical Leakage alarm</td>
<td>20-&gt;1000 ppm</td>
<td>Minutes</td>
<td>Up to 500</td>
<td>Concentrations can be very high at NH₃ plants and can even be explosive</td>
</tr>
<tr>
<td>Medical Breath analysis</td>
<td>50-2000 ppb</td>
<td>~1 min</td>
<td>20-40</td>
<td>Diagnosis of peptic ulcer cause by bacteria, small gas volumes</td>
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Table 1.2. Requirements for Ammonia Analysis Equipment in Different Application Areas [7]
<table>
<thead>
<tr>
<th>Breath gas</th>
<th>Concentration range (ppb)</th>
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<tbody>
<tr>
<td>Acetaldehyde</td>
<td>6-33</td>
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<tr>
<td>Acetone</td>
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<tr>
<td>Ammonia</td>
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<tr>
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<tr>
<td>Ethanol</td>
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<tr>
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<tr>
<td>Isoprene</td>
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<tr>
<td>Nitric oxide</td>
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<td>Propanol</td>
<td>0-135</td>
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Table 1.3. Concentration of Gases in Human Breath [34]
<table>
<thead>
<tr>
<th>rubbery polymers</th>
<th>glassy polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(dimethylsiloxane)</td>
<td>cellulose acetate</td>
</tr>
<tr>
<td>ethylene oxide/propylene oxide – amide copolymers</td>
<td>polyperfluorodioxoles</td>
</tr>
<tr>
<td></td>
<td>polycarbonates</td>
</tr>
<tr>
<td></td>
<td>polyimides</td>
</tr>
<tr>
<td></td>
<td>poly(phenylene oxide)</td>
</tr>
<tr>
<td></td>
<td>polysulfone</td>
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Table 1.4. Most Important Glassy and Rubbery Polymers Used in Industrial Membranes [86]
<table>
<thead>
<tr>
<th>Ref</th>
<th>Membrane support</th>
<th>Membrane thickness/μm</th>
<th>Synthesis condition</th>
<th>Temperature/℃</th>
<th>CO₂ permeance/GPU</th>
<th>CO₂ selectivity</th>
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<tr>
<td>[98]</td>
<td>α-alumina tube</td>
<td>10</td>
<td>90°C, 24h</td>
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<td>289</td>
<td>50</td>
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<tr>
<td>[99]</td>
<td>α-alumina tube</td>
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<td>90°C, 24h</td>
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<td>836</td>
<td>45</td>
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<td>[100]</td>
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<td>[101]</td>
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<td>32</td>
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<td>3</td>
<td>90°C, 24h</td>
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<td>[103]</td>
<td>α-alumina disk</td>
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<td>90°C, 12h</td>
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<td>20</td>
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<td>[104]</td>
<td>α-alumina tube</td>
<td>10</td>
<td>85°C, 24h</td>
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<td>1039</td>
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<tr>
<td>[105]</td>
<td>α-alumina tube</td>
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<td>90°C, 24h</td>
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<td>2567</td>
<td>19</td>
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<tr>
<td>[106]</td>
<td>from SS plate</td>
<td>60</td>
<td>80°C, 30h</td>
<td>25</td>
<td>1612</td>
<td>20</td>
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<td>[107]</td>
<td>α-alumina disk</td>
<td>50</td>
<td>100°C, days</td>
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<td>448</td>
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<td>[108]</td>
<td>α-alumina disk</td>
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<td>12</td>
<td>&gt;550</td>
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<td>100°C, 7d</td>
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<td>290</td>
<td>503</td>
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<tr>
<td>[97]</td>
<td>PES membrane</td>
<td>0.3</td>
<td>100°C, 1h</td>
<td>25</td>
<td>789</td>
<td>72</td>
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Table 1.5. Comparison of Published Zeolite Y Membranes for CO₂/N₂ Separations [97]
Figure 1.1. Major equipment in SCR design [32].
Figure 1.2. Schematic diagrams showing the energy levels and free charge carrier densities on (logarithmic scale) from the n-type semiconductor surface to the bulk. The blue dotted lines indicate the corresponding space charge region of thickness, D. $n_e$ = free electron density; $n_h$ = free hole density; $n_i$ = intrinsic carrier density [49]
Figure 1.3. Band diagram showing inversion, depletion, and accumulation layers as well as flat bands at surfaces of p-type semiconductor [50].
Figure 1.4. Formation of electronic core–shell structures in (a) n-type and (b) p-type oxide semiconductors [53].
Figure 1.5. Gas-sensing mechanism and equivalent circuit of n-type oxide semiconductors [53].
Figure 1.6. Simplified model illustrating band bending in a wide band gap semiconductor after chemisorption of charged species (here the ionosorption of oxygen) on surface sites. 

$E_C$, $E_V$, and $E_F$ denote the energy of the conduction band, valence band, and the Fermi level, respectively, while $\Lambda_{\text{air}}$ denotes the thickness of the space-charge layer, and $eV_{\text{surface}}$ the potential barrier. The conducting electrons are represented by $e^-$ and $+$ represents the donor sites [52, 54].
Figure 1.7. Change of the work function and the band bending of a n-type semiconductor due to the reaction with reducing gases, shown for the example of CO sensing [56].
Figure 1.8. Simplified gas sensing mechanism and equivalent circuit of p-type oxide semiconductors [53].
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Chapter 2: Nitric Oxide Sensors Using Combination of p- and n-type Semiconducting Oxides and Its Application for Detecting NO in Human Breath

2.1 Introduction

There is extensive research in developing selective and sensitive gas sensors for applications spanning an incredible range of technologies, from environmental, energy optimization, food, health and security. Just as the applications are varied, so are the types of gas sensing technologies that are being developed, with major advances being made in optical and electrochemical devices [1-3]. There have been some remarkable successes, the ubiquitous electrochemical oxygen sensor for combustion control as well as fire detection sensors. The challenges in this field continue to be developing selectivity and sensitivity with respect to specific gases present in harsh environments, and reducing the foot print of the sensing device and measurement system.

A good example of a sensing need at present is control of NO emissions for transportation systems running on diesel fuel. In the after treatment system for reducing NO emissions, NO sensors are required with discrimination against other combustion gases, and capable of operation under very harsh environments [4-6]. NO sensors are also required for breath analysis for diagnosis of respiratory diseases [7]. The most common measurement technique in breath monitoring is the chemiluminescence analyzer, however this apparatus is bulky, and requires a supply of ozone [8]. There is considerable interest in
developing minaturizable electrochemical sensors that have high sensitivity (ppb level) to NO and yet can discriminate against hundreds of other molecules in breath [9, 10].

The concept of using p and n-type semiconducting oxide as well as their mixtures to improve sensor performance is reported in the literature [11-18]. For the mixtures of p and n-type materials, there are primarily two strategies, mixing p- and n-type powders or creating a p–n diode-type junction.

We have investigated powder mixtures of n-type anatase and p-type rutile and found that for particular ratios of these mixtures, the resistance change is minimal toward CO and CH₄ [12]. Based on a polychromatic percolation model, it was proposed that at these particular powder mixture ratios, the two parallel conduction pathways based on n–n and p–p paths cancel each other. Other studies have noted similar effects, for mixtures of ZnO (n-type) and Al-doped CuO (p-type), increasing the amount of CuO, the sensor exhibited lower response to CO [13]. In another study, Pt loading on mixtures of n-type ZnO and p-type CuO, led to an overall p-type response toward CO [14]. CO selectivity was also noted for CuO/ZnO heterocontacts [15]. Other strategies have been to put p-type Co₃O₄ nanoparticles on n-ZnO nanowires [16], as well as nanocomposites [17] and p-type CuO on n-type SnO₂ nanorods exhibited high sensitivity to H₂S [18].

There are several studies in the literature focused on gas sensing which report the formation p–n junctions that exhibit I–V characteristics indicative of rectification. These include n-ZnO/p-CuO [19], Pt/SnO₂/n-Si/P+ – Si/Al [20], p-ZnO/n-ZnO [21], ZnO (p-type)/n-Si heterojunctions [22], and n-SnO₂/p-Co₂O₃ (or Cr₂O₃) [23].
This study focuses on n-type WO$_3$ and p-type Cr$_2$O$_3$ and these semiconducting oxides were chosen for the following reasons. Previous studies have demonstrated that both WO$_3$ and Cr$_2$O$_3$ exhibit an increase in resistance upon exposure to NO [24-26], whereas in the presence of CO, there is an increase in resistance for Cr$_2$O$_3$ and a decrease in resistance with WO$_3$ [27, 28]. We report below a new sensor design that exploits the different majority carriers (holes/electrons) in these two oxides to build sensitivity and selectivity to NO at ppb levels, while discriminating against CO at concentrations a thousand-fold higher (ppm) and spread over a considerable range (0–20 ppm). Practical application of this sensor system for detecting NO in human breath is demonstrated.

2.2 Experimental

2.2.1 Materials

Chromium (III) oxide (99%) powder, tungsten (VI) oxide (99.8%) powder, alpha-terpineol (96%) and gold wires (0.127 mm dia, 99.99%) were purchased from Alfa Aesar (Ward Hill, MA, USA). The sensor substrate (17.5 mm × 4.5 mm) was obtained from Form-Factor INC (USA). It is made of polymer (maximum heating temperature at 350°C) with gold microspring arrays. All test gases including N$_2$, O$_2$ and NO were obtained from Praxair (Danbury, USA).

2.2.2 Sensor fabrication

Two types of devices were examined, a mixture of powders and powders adjacent to each other. For powder mixtures, alumina substrates of 15 mm × 10 mm with
interdigitated gold lines of 0.25 mm spacing were used (obtained from Case Western Reserve University Electronics Design Center). Gold lead wires (Alfa Aesar) were connected with gold paste from Heraeus. The devices were heated at 600 °C for 2 h in order to remove organic binders from the gold paste. The powders of Cr₂O₃ (Aesar), and WO₃ (Alfa Aesar) were suspended in α-terpineol and sonicated for 10 min. The suspensions were drop casted onto the interdigitated gold electrodes and dried at 300 °C for 10 h.

For the adjacent placement of powders, a polymer based sensor substrate was used. WO₃ or Cr₂O₃ powder was ground thoroughly and then mixed with alpha-terpineol to form a paste, which was then painted on either side of the substrate surface and calcined in a tube furnace (Lindberg/Blue) at 300 °C for 12 h. Before testing, all samples were exposed to flowing 20% O₂/N₂ at 300 °C overnight.

2.2.3 Characterization

X-ray diffraction (XRD) analysis was carried out on a Rigaku Geigerflex X-Ray powder diffractometer using Cu-Kα radiation. The Raman measurements were performed on a Renishaw – Smiths Detection Combined Raman – IR Microprobe with laser at 632.8 nm. The SEM images of the WO₃, Cr₂O₃ and their interface of the electrode film were recorded using JEOL JSM-5500 scanning electron microscope. The current–voltage measurements were performed on a CHI760D electrochemical workstation (CH Instruments, Inc., USA) under a scan rate of 0.1 V/s from −6.0 to 6.0 V. IR experiments were performed on Perkin Elmer 400.
2.2.4 Gas sensing measurements

The gas sensing experiments were performed within a quartz tube placed inside a tube furnace (Lindberg/Blue) at 300 °C, with a PC-controlled gas delivery system with calibrated mass flow controllers (Sierra Instruments INC.). The test gas mixtures containing different concentrations of NO at constant oxygen content of 20 vol% were prepared by diluting NO with O₂ and N₂. The total flow rate was maintained at 200 cm³/min. The resistance of the sensor was recorded by an Agilent 34972A LXI data acquisition/switch unit or a HP34970A at a scan rate of 0.1 Hz. The accurate concentration of NO in the ppb range was independently performed by using pre-calibrated Sievers 280i nitric oxide analyzer (GE Electronics, Boulder, CO, USA).

2.2.5 Human breath sensing measurements

Exhaled breath samples were collected from volunteers, as previously described [10]. Typically, for healthy volunteers, the amount of NO is less than 10 ppb. Thus, to establish the capability of the sensor system it was necessary to get higher concentrations of NO into the bag. This was done by introducing small amounts of bottled NO into the bag containing the human breath, and the exact level of NO in the bag was measured using the Sievers 280i Nitric Oxide Analyzer (GE Electronics, Boulder, CO). The concentration ranges examined were between 67 and 290 ppb NO. The Mylar bags were reused and thoroughly cleaned before each use with flowing nitrogen (99.998% purity) gas. Instead of mass flow controllers, a pump (Hargraves Technology Corporation, Mooresville, NC) was used to maintain a constant flow rate of 200 cm³/min. In the experimental setup, the breath sample
and the ambient air were bubbled through water at room temperature. The inlet of the quartz tube was connected with a three way valve which allows either breath sample or ambient air.

2.3 Results

2.3.1 Properties of metal oxides

Figure 2.1 shows the XRD of a mixture of WO$_3$/Cr$_2$O$_3$ at room temperature and after heating at 500 °C. All the peaks observed after thermal treatment can be assigned to WO$_3$ and Cr$_2$O$_3$, indicating that there is no chemical reaction between these oxides up to temperatures of ~500 °C. Figure 2.2 shows the SEM of the heated powders, showing that the particles sizes are <200 nm in both cases.

2.3.2 Infrared studies

The protocol for in situ diffuse reflectance infrared studies involved heating the metal oxide in air to 500 °C, and cooling to room temperature and obtaining an IR spectrum. Then the oxide was heated to 300 °C, exposed to NO, cooled to room temperature in presence of NO, and the spectrum recorded. This was followed by reheating the sample to 500 °C in air and cooling to room temperature and rerecording the spectrum. Figure 2.3a shows the data for WO$_3$; the only reproducible change (2–3 independent measurements) that we observed upon exposure to NO was in the 1050–1150 cm$^{-1}$ region. A band appears at 1095 cm$^{-1}$ upon NO exposure and disappears with heating in air. Assignment of this peak to NO$^-$ was made by comparison with literature [29, 30]. In the case of MgO and CeO$_2$, a strong band
has been reported at 1160 and 1171 cm\(^{-1}\), respectively and assigned to NO\(^{-}\) species. These are also weaker bands at \(~1250\) and \(~850\) cm\(^{-1}\) that is also reported, but we did not observe these bands. Along with NO\(^{-}\) on MgO, CeO2, bands due to NO\(_2\) \(^{-}\) and N\(_2\)O\(_2\) \(^{2-}\) were also reported.

The experiment was repeated with Cr\(_2\)O\(_3\) with 1000 ppm NO, but no spectroscopic changes were observed. So, the experiment was repeated with 50% NO/N\(_2\), and a band at 2080 cm\(^{-1}\) was reproducibly observed, this band disappeared on heating, and this data is shown in Figure 2.3b. The band at 2080 cm\(^{-1}\) is being assigned to NO\(^{+}\), based on reports in the literature [31-34]. There is a report of NO adsorption on reduced chromia, and prominent bands at 1735 and 1865 cm\(^{-1}\) were reported, and assigned to a N\(_2\)O\(_2\) dimer. With chromia on alumina, a band at 2260 cm\(^{-1}\) was assigned to NO\(^{+}\) [32]. Adsorption of NO on zeolites led to a broad band at 2160 cm\(^{-1}\) (with a shoulder at 2215 cm\(^{-1}\)), and assigned to NO\(^{+}\).

2.3.3 Sensing characteristics

2.3.3.1 Mixture of powders

Mixtures of WO\(_3\) and Cr\(_2\)O\(_3\) in weight ratios varying from 1:1 to 11:1 were prepared and the resistance changes with NO (2, 5, 10 ppm) and CO (10, 20, 30 ppm) in a background of 20% oxygen (rest N\(_2\)) was examined at 300 °C. The data for three of these mixtures with weight ratios of WO\(_3\) and Cr\(_2\)O\(_3\) of 1:1, 3:1 and 11:1 are shown in Figs. 4 and 5. For NO, with all the powder mixtures, the resistance exhibits an increase (Figure 2.4). For CO, however the resistance exhibited an increase with 3:1 WO\(_3\):Cr\(_2\)O\(_3\) ratio.
(Figure 2.5a), a diminished signal (almost no change in resistance at \( \sim 20 \text{ ppm CO} \)) for the 9:1 ratio (Figure 2.5b) and a decrease in resistance (clearly for 20 and 30 ppm CO) for the 11:1 ratio (Figure 2.5c).

2.3.3.2 Adjacent alignment of powders

An alternative arrangement of the two powders was also examined. Figure 2.6a shows the substrate, a plastic device (left of Figure) on which \( \text{WO}_3 \) and \( \text{Cr}_2\text{O}_3 \) were deposited and in contact at a common interface (right of Figure). The substrate was designed in such a fashion that resistances across different lengths of \( \text{WO}_3 \) and \( \text{Cr}_2\text{O}_3 \) could be measured (via the Au wires shown in the Figure).

2.3.3.3 Characterization of the interface

Figure 2.6b shows the SEM of the interface, exhibiting intermixing of the two particles at the interface. A more detailed view of the intermixing is evident from Raman imaging studies. As shown in Figure 2.7, the Raman spectra of \( \text{Cr}_2\text{O}_3 \) and \( \text{WO}_3 \) are quite distinct, with prominent bands for \( \text{WO}_3 \) at 273, 717 and 806 cm\(^{-1} \) and relatively weak bands for \( \text{Cr}_2\text{O}_3 \) at 349, 551 and 609 cm\(^{-1} \). In the Raman imaging study, spectra were collected along \( \sim 2 \text{ mm} \) of the interface (proceeding from the \( \text{WO}_3 \) side to the \( \text{Cr}_2\text{O}_3 \) side) and the intensities in the regions 537–568 cm\(^{-1} \) (indicative of \( \text{Cr}_2\text{O}_3 \)) and 774–841 cm\(^{-1} \) (indicative of \( \text{WO}_3 \)) were computed. Figure 2.7c shows a plot of the integrated intensities, the \( \text{WO}_3 \) signal is maximum at \( 0 \text{ m} \) and begins to decrease at \( \sim 500 \text{ m} \) and reaches zero counts at \( \sim 1500 \text{ m} \) and there is a symmetry in the increase in the \( \text{Cr}_2\text{O}_3 \) peaks. These imaging
studies indicate that the particles are intermingled over length scales of about a millimeter. The I–V curve measured across the Cr$_2$O$_3$–WO$_3$ interface is shown in Figure 2.8. The curves are linear, exhibiting an Ohm’s law relationship, with no evidence of any rectification, and the slope of the linear curve being 2 M Ohm.

2.3.3.4 Sensing behavior

Figure 2.9 shows the resistance changes gases for mixtures of 63 ppb and 113 ppb NO with varying quantities of CO (0, 3, 10, 20 ppm) and CO alone (3, 10, 20, 50 and 100 ppm). These experiments were done at 300 °C, because the polymer substrate decomposed at 350 °C. Temperatures below 300 °C degraded the sensor response. The duration of the time the analyte gases were flowing over the sensor was 10 min, chosen so as to achieve the steady state signal (discussed later in Figure 2.11a). Figure 2.9a shows a schematic of the sensor. In case of channel 1(CH1) resistance across WO$_3$ is measured, and for CO alone, there is a decrease in resistance, as shown in Figure 2.9b. For NO alone (63, 113 ppb), there was an increase in resistance for CH1. With mixtures of NO and CO, the resistance change in the presence of NO becomes increasingly smaller, indicating that there is a significant interference being caused by CO.

Resistance measurements made across Channel 2 (CH2), which is primarily due to Cr$_2$O$_3$ (Figure 2.9a) are shown in Figure 2.9c. For CO alone, there is an increase in resistance. For NO alone, there is a slight increase in resistance. For the mixture of gases, the resistance seems dominated by CO, thus suggesting strong interference toward NO signal.
The resistance changes across the Cr\textsubscript{2}O\textsubscript{3}–WO\textsubscript{3} boundary with different lengths of each metal oxide included was examined. Figure 2.10 shows the data for a particular distance between the two oxides and is referred to as Channel 3 (CH3, defined in Figure 2.10a). Figure 2.10b shows that with this optimum contributions from the two oxides, the interference of CO toward NO is largely eliminated. For CO alone, it is observed that the signal from 3 to 20 ppm CO is also negated, with slight resistance increases for 50 and 100 ppm. Comparing the mixtures of NO and CO, it is clear that the interference from <20 ppm CO to NO is minimized. Figure 2.10c shows the calibration curves to NO at concentrations <400 ppb, the signal being defined as R/R\text{Ro} where R and R\text{Ro} are resistances in the presence of NO (with 20\% O\textsubscript{2}, N\textsubscript{2}) and R\text{Ro} due to the background gas (20\% O\textsubscript{2}, N\textsubscript{2}).

Figure 2.11a shows the data with 58 ppb NO (CH3) with the transient time for each gas exposure extended to 60 min, the sensor transients are better shaped, and it is clear that steady state is being reached in about 10 min. With this sensor, we also investigated a wider range of concentrations, and the calibration between 18 ppb (detection limit) and 10 ppm is shown in Figure 2.11b. At concentrations above 1 ppm, the sensor response is no longer linear. Figure 2.11c compares the sensor response of 10 ppm NO and NO\textsubscript{2}, and shows that NO\textsubscript{2} gives a response about 6 times higher than NO. To verify that the sensing data presented in Figs. 9 and 10 is due to NO, the concentration of NO was measured prior to the inlet of the test chamber and after the gas exits the test chamber with a chemiluminescence analyzer. For 170 ± 4 ppb NO (in 20\% O\textsubscript{2}/N\textsubscript{2}) entering the test chamber maintained at 300 °C, the concentration at the exit of the chamber was 169 ± 5 ppb. Thus, there is no conversion of NO into NO\textsubscript{2} in the test chamber.
2.3.3.5 Detection of NO in human breath

Human breath samples were collected in Mylar bags and spiked with different concentrations of NO (67, 103, 205, 290 ppb), and concentration independently measured by a chemiluminescence analyzer. These gas mixtures were then passed over the p–n sensor and the resistance changes corresponding to CH3 were measured. For the background, air bubbled through water was used. Figure 2.12 shows the traces for the different concentrations, with several repeat measurements. The response/recovery time for the signal was of the order of 60 min. Figure 2.13 shows the calibration curve obtained for these measurements.

2.4 Discussion

2.4.1 Response of individual metal oxides

WO3 is one of the most extensively studied n-type semiconducting metal oxides for gas sensing [28]. The resistance decrease with CO (Figure 2.9b) is explained by the following reaction $O_{ad^-}\cdot WO_3 + CO(ad) \rightarrow CO_2 + WO_3 (e)$. With NO, an increase in resistance of the WO3 film is observed, as has been reported previously [25]. Based on the IR data shown in Figure 2.3, we propose that NO$^-$ is being formed on the WO3 surface, and the increase in resistance is attributed to abstraction of electrons from the conduction band of the semiconductor.

Cr2O3 is a p-type semiconductor [35]. In the case of CO, the film of Cr2O3 shows an increase of resistance, and has been reported previously [27]. CO will react with
chemisorbed oxygen forming CO₂ and release electrons that can trap the majority hole carriers and result in increase in resistance. More interesting is the observation with NO, which also exhibits an increase of resistance of the Cr₂O₃ film. This observation with NO has also been reported, though no explanations have been forthcoming [24]. The infrared data (Figure 2.3b) suggests that NO is acting as an electron donor forming NO⁺ and possibly reducing Cr⁴⁺ to Cr³⁺. Such electron transfer will result in neutralizing holes in the conduction band, and increase in the resistance. Breakdown voltages of Cr₂O₃ in the presence of NO, NO₂ have been reported and used as a basis for sensing these gases, and the formation of NO⁺ on Cr₂O₃ has also been proposed [36].

2.4.2 Response of mixture of powders of WO₃/Cr₂O₃

The XRD of the mixture of the powders of Cr₂O₃ and WO₃ heated to 500 °C indicate that there is no chemical reaction between these oxides. From the resistance changes to NO and CO of the mixture (Figs. 4 and 5), several trends are evident. In the case of NO, for all mixtures ratios, there is an increase in resistance. However for CO, there is a trend of resistance increase at higher relative concentrations of Cr₂O₃ (3:1 WO₃:Cr₂O₃) and resistance decrease at higher concentrations of WO₃ (11:1 WO₃:Cr₂O₃) with the 9:1 WO₃:Cr₂O₃ mixture exhibiting minimal resistance change (e.g., 20 ppm CO almost remains at baseline resistance). We need to point out two relevant observations. First, it is difficult to reproduce the exact ratio of powders at which the cancelation takes place, though the trends indicated above are always observed. Second, the cancelation in signal appears for only a certain concentration of CO e.g., with the 9:1 ratios, 10 ppm and 30 ppm
CO provide resistance increases and decreases, respectively, while there is an almost null response to 20 ppm CO.

The irreproducibility with mixing the powders arises from the size and density differences of the particles and different settling dynamics once the ink is deposited on the interdigitated alumina substrate. Also, the exact layer from which the sensing occurs is debated, with the likelihood that it is the layer closest to the electrodes, and so the settling of the particles becomes critical in determining response.

However, the trend of resistance changes (from increasing to decreasing) with CO for mixtures of p- and n-type semiconducting oxides (TiO$_2$) has been reported in the literature [12]. Several explanations have been suggested, including percolation paths for p and n type that interfere with each other resulting in cancelation. With p-type Co$_3$O$_4$ on n-type ZnO, as the thickness of the p-type layer increased, sensitivity toward both oxidizing and reducing gases decreased. This was attributed to lack of porosity, but could be also due to the electrical cancelation effect from the p- and n-type material [17]. Our observation that with the Cr$_2$O$_3$/WO$_3$ mixture, the presence of NO always leads to an increase in resistance is consistent with the results from individual powders exposed to NO (Figure 2.9).

### 2.4.3 Adjacent placement of powders

The results with mixtures of powders above clearly demonstrate that it is possible to use the p–n cancelation with the oxidizing gas (CO) to generate a selective sensor to NO. However, the issues with reproducibility in the powder preparation and deposition and the fact that cancelation at a particular powder mixture only occurs for a particular
concentration of CO makes this impractical. Placing the powders adjacent to each other and including different lengths of the powders in making resistance measurements parallels the concept of making powders of different ratios, but the experimental design is considerably simplified, since we are dealing with only one sample, but obtaining multiple sensor measurements.

There are several studies in the literature that have explored adjacent p–n materials, but the focus has been on creating rectifying devices [19–23]. As seen from the I–V measurements, we do not observe any rectification. This is consistent with literature, where it has been observed that rectification is only observed if two sintered metal oxides are joined to each other. In a study of ZnO/CuO contact ceramics prepared by presenting the two pellets against each other, it was noted that ZnO pellet sintered at 900 °C produced a linear I–V characteristic, whereas ZnO pellet sintered at 1100 °C exhibited characteristics of a p–n diode. (CuO sintered in both cases at 880 and 895 °C). Clearly, the nature of the interface determined I–V curve. It was concluded that that in the more poorly sintered sample, leakage current was dominant [37]. The Raman imaging studies show that the interface is about ∼1000 _m where the WO$_3$ and Cr$_2$O$_3$ are intermixed, and reminiscent of a poorly sintered sample.

With this device design, the response to CO and NO can be continuously varied by choosing to include different fractions of the metal oxide, as shown in Figs. 9 and 10. For a particular choice (CH3), a sensor can be designed that is selective to NO (ppb) and discriminates against CO that is present at significantly higher concentrations (ppm). The calibration curves obtained with NO demonstrate that sensitivities in the tens of ppb is
readily attained. Another advantage of the design is that there is a broad range of CO concentrations over which cancelation takes place (0–20 ppm) as compared to the powder mixtures.

For a practical demonstration of this device, spiked NO in human breath samples was measured. There are hundreds of other molecules in breath, and the humidity is almost 100%. So, the background used was humidified air. The data shown in Figure 2.12 indicates that the sensor is responding to NO in human breath, though the response and recovery times are slow. Also, the magnitude of the signal is lower than that measured in dry air (Figure 2.10c).

2.5 Conclusion

In conclusion, we demonstrate that a novel arrangement of p- and n-type metal oxides can lead to selective gas sensing. However, the choice of NO as the sensing gas was critical, because it has structural and electrical features that allow it to both accept and donate electrons, and therefore the signal on both the n- and p-type material provide an additive effect. If this device is used for sensing CO, it would always lead to reduced signals. Though, it is likely that for different reducing gases (CO vs. C₂H₅OH), the cancelation of signals will occur with different contributions from the two oxides (experimentally manifested in canceled resistance observed at different lengths for different reducing gases), providing an opportunity for selectivity, but with reduced sensitivities.
References


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Figure 2.1. XRD patterns of (a) mixture of WO$_3$ and Cr$_2$O$_3$ powder (1:1 wt%), and (b) same mixture as in Figure 2.1a after heating at 500 °C for 3 h. WO$_3$ peaks are indicated with asterisks, Cr$_2$O$_3$ peaks are indicated with triangles.
Figure 2.2. SEM micrographs for (a) Cr$_2$O$_3$ and (b) WO$_3$ films after heating at 300 °C for 10h.
Figure 2.3. IR spectra of (a) WO$_3$ powder (all spectra acquired at room temperature) (1) after heating to 500 °C in air for one hour (2) sample (1) heated again up to 500 °C, cooled to 300 °C and then treated with flowing 1000 ppm NO and cooled room temperature, (3) sample (2) heated to 500 °C in air and cooled to room temperature. (b) Cr$_2$O$_3$ powder (all spectra acquired at 300 °C) (1) sample heated in air to 500 °C and then cooled to 300 °C (2) sample (1) exposed to 50% NO at 300 °C and spectrum recorded, (3) sample (2) heated to 500 °C and then cooled to 300 °C in air and spectrum recorded.
Figure 2.4. Change in resistance of mixtures of WO$_3$:Cr$_2$O$_3$ at 300 °C with (a) 3:1, (b) 9:1 and (c) 11:1 w/w ratios upon exposure to 2, 5 and 10 ppm NO in 20% O$_2$. 
Figure 2.5. Change in resistance of mixtures of WO$_3$:Cr$_2$O$_3$ at 300 °C with (a) 3:1, (b) 9:1 and (c) 11:1 w/w ratios upon exposure to 10, 20 and 30 ppm CO in 20% O$_2$ at 300 °C.
Figure 2.6. (a) Photograph of bare sensor substrate with four gold wires (left) and sensor with adjacent Cr$_2$O$_3$ and WO$_3$ films (right). (b) SEM micrograph of interface of Cr$_2$O$_3$ and WO$_3$ films on the sensor substrate after heating at 300 °C for 10 h.
Figure 2.7. Raman spectra of (a) WO$_3$ powder, (b) Cr$_2$O$_3$ powder (excitation wavelength 632 nm), and (c) integrated Raman intensities from a map of interface of WO$_3$ and Cr$_2$O$_3$: straight line with circle markers: WO$_3$ signal between 774 and 841 cm$^{-1}$; dashed line with square markers: Cr$_2$O$_3$ signal between 537 and 568 cm$^{-1}$. Both lines are smoothed with a 6-order polynomial curve.
Figure 2.8. I–V characteristics across interface of Cr$_2$O$_3$ and WO$_3$ films in 20% O$_2$ balanced with N$_2$ at 300 °C. (Scan rate (V/s) = 0.1).
Figure 2.9. (a) Schematic diagram of the sensor. (b) Typical resistance response curves of CH1 (defined in Figure 2.9a) at 300 °C for mixtures of 63 ppb and 113 ppb NO with varying concentrations of CO and CO alone (200 ccm flow rate). (c) Typical resistance response curves of CH2 at 300 °C for mixtures of 63 ppb and 113 ppb NO with varying concentrations of CO and CO alone (200 ccm flow rate). Analyte gas is on for 10 min.
Figure 2.10. (a) Schematic diagram of the sensor. (b) Typical resistance response curves of CH3 (defined in Figure 2.10a) at 300 °C for mixtures of 63 ppb and 113 ppb NO with varying concentrations of CO and CO alone (200 ccm flow rate). (c) Calibration curve based on relative resistance ($R/R_0$) changes of CH3 (data from Figure 2.10b) upon exposure to varying concentrations of NO in 20% O$_2$ (balance N$_2$). Analyte gas is on for 10 min.
Figure 2.11. (a) Sensor response to 58 ppb NO with gas on for 60 min to get a better idea of the sensor behavior (b) calibration curve with a wider range of concentrations (18 ppb–10 ppm) (c) Comparison of the sensor response to 10 ppm NO and NO₂, plotted on the same resistance scale. All experiments done at 300 °C in 20% O₂ (balance N₂) using CH₃.
Figure 2.12. Sensor response with breath sample containing (a) 67 ppb NO, (b) 103 ppb NO, (c) 205 ppb NO and (d) 290 ppb NO. Sensor at 300 °C and 300 cm³/min flow rate.
Figure 2.13. Calibration curve for relative resistance ($R/R_0$) changes of CH3 upon exposure to varying concentrations of NO in breath sample.
Chapter 3: Selective Detection of Part per Billion Concentrations of Ammonia Using a p-n Semiconducting Oxide Heterostructure

3.1 Introduction

Methods for measurement of ammonia (NH₃) are relevant to environmental, combustion and health related industries [1]. Ammonia in atmosphere arises primarily from anthropogenic sources, including agriculture (nitrogen fixation, ammonification) and emissions from chemical industry involved in development of refrigeration and fertilizers. Ammonia is a lachrymatory gas, and breathing ammonia at high concentrations (~1000 ppm) can induce laryngospasms, and cause bronchiectasis [2, 3], and thus need for environmental ammonia monitors. The transportation industry is interested in measuring ammonia from exhaust emissions, air quality control in passenger compartment and in a new generation of lean-burn combustion engines, where the exhaust gas after-treatment includes reaction of nitrogen oxides with ammonia. Ammonia is also produced in the human body and the health industry is interested in monitoring ammonia in exhaled human breath for disease diagnosis. In particular, breath ammonia measurement has the potential to probe several diseases including malfunctioning of liver and kidney [4], H. pylori infection [5] and halitosis [6]. The concentration ranges over which ammonia detection is relevant for these applications range from 0.1 ppm (health) to hundreds of ppm (environmental).
Different measurement principles have been applied for the detection of ammonia, including optical spectroscopy, electrochemistry and wet-chemistry methods. A particularly challenging application is the detection of ammonia in human breath. [7]. Tunable diode laser absorption spectroscopy has been used to detect ammonia in breath, with detection limit of 1 ppm [8]. A quantum cascade laser diode was able to measure ammonia as low as 4 ppb [9]. Other strategies include use of quartz crystal microbalance [10] and liquid-film conductive sensor [11]. Sensors based on conducting polymer junctions can detect ppb ammonia in human breath [12-15], and a p-n heterojunction polyaniline-TiO$_2$ sensor is reported to have ppt sensitivity [16]. Mass spectrometry also can measure ammonia down to ppb levels [17]. Instruments for measuring ammonia are often bulky [18], and there is a drive for obtaining miniaturized sensors.

Solid state electrochemical sensors have been developed for monitoring ammonia. This technology is attractive since high sensitivity, selectivity, and fast response time are possible. In addition, these devices have advantages of low power consumption, lightweight, low maintenance cost, harsh environment tolerance and portability. There are numerous papers on resistive semiconducting metal oxide sensors for ammonia. The working principle of these devices is associated with the adsorption of gas molecules on the oxide’s surface inducing charge transfer, which result in changes in resistance of the oxide. Semiconducting metal oxides such as n-type WO$_3$ [19-21], SnO$_2$ [22, 23], In$_2$O$_3$ [24, 25], ZnO [26, 27], TiO$_2$ [28], MoO$_3$ [29] as well as p-type Cr$_2$O$_3$ [30], NiO [31], CuO [32], have been studied as sensing materials to detect NH$_3$. To promote sensitivity and selectivity, noble metals like Pt [33], Pd [34], Au [35] and Ag [36] have been introduced to metal
oxides. Of these, MoO$_3$-based sensors have been developed for measuring ammonia in human breath [29, 37].

However, developing an electrochemical sensor platform that can measure low concentrations of ammonia in the environment, in optimizing combustion processes and in human breath is still a challenge. There is the need for ppb sensitivity, discrimination against other gases present at much higher concentrations, and in the case of combustion, the ability to tolerate harsh environments, and be insensitive to other exhaust gases.

Mixtures of p- and n- semiconducting oxides can improve sensor performance. Examples include anatase/rutile for CO detection, ZnO/NiO for NH$_3$ detection, In$_2$O$_3$/NiO for ethanol detection, and CuO/SnO$_2$ for H2S detection [38-41]. These designs are mixtures of p- and n- powders, or the p-type material grown on n-type powders and vice versa. In addition, isotype heterojunctions, prepared by mixing powders, such as WO$_3$ and ZnO have also shown selective gas sensing [42].

We recently reported a different way of combining p- and n-type semiconducting oxides, and demonstrated sensing of nitric oxide gas in ppb levels [43]. In this paper, we explore a similar design for sensing ammonia. The sensor device comprises adjacent alignment of p-type NiO and n-type In$_2$O$_3$ deposited on a gold microspring array. We demonstrate detection of ammonia at ppb levels, while discriminating against nitric oxide at ppb levels, and carbon monoxide at significantly higher ppm concentrations using this semiconductor hetero-junction structure. A potential application of detection of ammonia in human breath samples is also demonstrated, suggesting the application of this sensor platform in a future breath monitoring device.
3.2 Experimental

3.2.1 Chemicals and materials

Indium (II) oxide (99.99%, metals basis, ~325 mesh powder), nickel (II) oxide (99.998%, metals basis), alpha-terpineol (96%), gold wires (0.127 mm dia, 99.99%) were purchased from Alfa Aesar (Ward Hill, USA). The plastic substrates with gold microspring arrays were obtained from FormFactor, Inc. (USA). The interdigitated electrodes were obtained from Case Western Reserve University. All test gases including nitrogen, oxygen, ammonia and carbon monoxide were supplied by Praxair (Danbury, USA).

3.2.2 Sensor fabrication

The procedures of sensor fabrication is shown in Figures 3.3 and 3.4. The plastic substrate was washed by ethanol and distilled water. Gold wires were connected with the gold microsprings on the substrate. The commercial powders were ground thoroughly before use. 1 g of NiO powder was dispersed in 0.4 mL terpineol and blended into a thick slurry. 80 mg of the obtained NiO slurry was evenly painted onto the left side of the substrate. Then 1 g of In$_2$O$_3$ powder was mixed with 0.4 mL terpineol and 20 mg of the slurry was painted onto the right side of the substrate with a common interface. According to the area divided by vertical lines of four gold microsprings, the as-fabricated area ratio of the two semiconductors turned out to be 14:4 on the surface of the substrate (17.5 mm $\times$ 4.5 mm). The substrate was designed in such a fashion that it has several leads at different distances, so that resistance across different lengths of the oxides could be
measured. The sensor was calcined in air at 320°C for 2 hours and kept in a tube furnace at 300 °C with flowing 20% O₂ in N₂ overnight before testing. The polymer substrate decomposed at 350°C, so alumina substrates of 10 × 10 mm with interdigitated gold lines of 0.25 mm spacing were used for high temperature measurements. After calcination at 320 °C in air for 2 h, the semiconductor layer was typically about 200 μm thick (discussed later).

3.2.3 Characterization

The phase and crystallinity of the metal oxides were analyzed by a Bruker D8 Advance X-ray diffractometer. The surface morphology of the sensor was investigated by a Quanta 200 scanning electron microscope. The chemical state of the metal oxides was examined by a Kratos X-ray photoelectron spectrometer with a mono Al source. The current-voltage measurement was performed on a CHI760D electrochemical workstation. The gas-solid interactions were studied by a PerkinElmer Spectrum 400 FTIR spectrometer coupled with a diffuse reflectance accessory. The Raman mapping of the interface was performed on a Renishaw - Smiths Raman Microprobe.

3.2.4 Gas sensing measurements

All gas sensing experiments were performed within a quartz tube placed inside a tube furnace (Lindberg/Blue) at 300°C, with a PC-controlled gas delivery system with calibrated mass flow controllers (Sierra Instruments INC.). The test gas mixtures containing different concentrations of NH₃ at constant oxygen content of 20 vol% were prepared by diluting
NH$_3$ with O$_2$ and N$_2$. The total flow rate was maintained at 200 cm$^3$/min. The resistance of the sensor was recorded by an Agilent 34972A LXI data acquisition/switch unit or a HP34970A at a scan rate of 0.1 Hz.

3.2.5 Human breath sensing measurements

A system that simulates human breath with trace ammonia gas was developed. The system comprises a Mylar bag containing exhaled human breath samples and an ammonia gas cylinder. The trace ammonia gas at physiologically relevant concentrations was determined by controlling the flow rates of breath samples from the Mylar bags and ammonia supply, respectively. The total flow rate was maintained at 200 cm$^3$/min. Three setups were designed. A first setup used a 37°C water vapor bath to keep a constant humidity in the mixture of NH$_3$ and breath sample. The second setup used a dry ice/acetonitrile bath maintained at -20 to -25°C to completely remove humidity in the mixture of breath + NH$_3$ and also an ice bath to reduce humidity. In both these setups, the breath sample was used as the background and NH$_3$ was spiked into the sample at increasing concentrations. In the third setup, air was used as the background, and the breath sample was measured, and then increasing amounts of NH$_3$ was added in, all gases passing through a moisture trap at -20 to -25°C.
3.3 Results

3.3.1 Characterization

The two semiconducting oxides of interest in this study are NiO and In$_2$O$_3$, were obtained from commercial sources. Detailed characterization is presented in Figures 3.1 and 2 for NiO and In$_2$O$_3$ annealed at 320°C, respectively.

NiO: The X-ray diffraction (XRD) pattern (Figure 3.1a) is typical of the cubic structure of NiO (JCPDS No. 04-0835). Scanning electron microscopy (Figure 3.1b) suggest particle diameters around 200-300 nm. X-ray photoelectron spectroscopy (XPS) of the O 1s region (Figure 3.1c) suggest the presence of lattice oxygen (O$^{2-}$, binding energy 529.4 eV), hydroxyl groups (binding energy 531 eV), and strongly chemisorbed oxygen (533 eV) [44, 45]. In the nickel 2p$_{3/2}$ region, peak at 853.7 is assigned to NiO$_6$ bulk cluster and peak at 855.8 eV to oxygen screened surface NiO$_5$ and nonlocal second neighbor screening of NiO$_6$ and NiO$_5$ [46, 47]. The satellite region was fit to two peaks at 861.0 eV and 864.5 eV.

In$_2$O$_3$: XRD pattern of In$_2$O$_3$ shown in Figure 3.2a is indicative of cubic crystalline structure (JCPDS No. 06-0416). Size of the particles from the SEM micrograph (Figure 3.2b) is <100 nm. XPS (Figure 3.2c) indicates two peaks at 444.7 and 452.2 eV assigned to In 3d$_{5/2}$ and 3d$_{3/2}$ states, typical of In$^{3+}$ [48]. The O 1s spectra is asymmetric with two peaks at 530.2 and 532.0 eV, with the former assigned to the oxygen lattice state, and the broad envelop at 532.0 eV to oxygen ions in oxygen deficient- regions (vacancies) [48].
3.3.2 Sensor characteristics

Design: Figure 3.3 shows a schematic of the steps involved in the sensor design, and Figure 3.4 shows characteristics of the sensor. The two oxides are placed adjacent to each other on a plastic substrate and share a common interface. Substrate design makes it possible to measure resistances across varying lengths of the metal oxides (CH1 is defined as In$_2$O$_3$, CH2 as NiO and CH3 as a combination of both oxides, the choice of this combination is readily varied on the same sample). Figure 3.4b shows a photograph of the sensor, with and without the oxide coating. The gold wires are used for the resistance measurements. Figure 3.4c shows a side view of the sensor, indicating that the oxide films are ~200 µm thick. These devices are heated at 320°C in air for 2 hours, prior to making measurements at 300°C. Figure 3.4d is the current-voltage (I-V) plot at 300°C and displays a linear relationship, indicating there is no rectification, as expected for a diffuse mixing of the powders [49].

Microstructure: Figure 3.5a shows the top-view SEM of the NiO/In$_2$O$_3$ interface. The NiO side of the sensor is characterized by Raman bands at 500, 740, 900 and 1090 cm$^{-1}$ (Figure 3.5b), with the strongest bands at 500 and 1090 cm$^{-1}$, assigned to first and second order longitudinal optical modes, respectively [50]. On the In$_2$O$_3$ side, bands observed at 307, 366, 494 and 627 cm$^{-1}$ (Figure 3.5c) is consistent with previous literature [51]. Raman spectra were recorded along a 180 µm length across the interface and the intensities of Raman bands of NiO (500 cm$^{-1}$) and In$_2$O$_3$ (307 cm$^{-1}$) are plotted in Figure 3.5d. There is intermixing of the two oxides over a ~30 µm distance at the interface.
3.3.3 Electrical characteristics

Figure 3.6a is the resistance change of NiO after exposure to 1 ppm NH₃ at 300°C. With the gas pulse on, there is a decrease in resistance, followed by a slow increase. After the gas pulse is turned off after 10 minutes, the resistance continues to increase for 10 min (crosses the baseline), followed by a slow decrease to the baseline over the next 25 min. Figure 3.6b shows that if the NH₃ gas pulse is only on for 2 min at 300°C, only a resistance decrease is observed, with both the response and recovery to the baseline occurring relatively rapidly (minutes). We use the 2 min exposure for all sensing experiments described later. At a temperature of 500°C, the 1 ppm NH₃ registers a resistance increase (Figure 3.6c). Figure 3.6d shows an increase in resistance for 10 ppm NH₃ at 300°C.

3.3.4 Infrared spectroscopy

Infrared spectroscopy of the NiO surface was examined upon NH₃ exposure at 300°C. Figure 3.7a focuses on the 1220-1320 cm⁻¹ spectral region, where we did observe changes with 1-10 ppm NH₃. With higher concentration of NH₃ (100 ppm), we did observe a band at 3220 cm⁻¹ in the presence of oxygen (shown in Figure 3.8). With N₂ passing over the NiO sample, there is no band in the 1200-1300 cm⁻¹ region (Figure 3.7a), but with 20% oxygen in the background gas, a band at 1267 cm⁻¹ appears. With 1 ppm NH₃, there is an initial increase in this band (10 min) followed by a gradual decrease (30 min), which is reversed upon the removal of NH₃ with 20% O₂. Figure 3.7b shows spectral changes with 10 ppm NH₃, with the intensity of the 1267 cm⁻¹ band decreasing with time. Figure 3.7c is a plot of the integrated intensity of the 1267 cm⁻¹ band versus time with 1 and 10 ppm
NH$_3$. The increase in the intensity of the 1267 cm$^{-1}$ is obvious with 1 ppm NH$_3$, though with the 10 ppm, the intensity increase is not as clear, though the decrease in intensity of this band with time is more marked. We discuss later the similar trends in resistance changes (Figure 3.6a) and the intensity of the 1267 cm$^{-1}$ peak (Figure 3.7a).

3.3.5 Sensing characteristics

Carbon monoxide: All sensing experiments were done with 2 min pulses of the analyte gas. Figure 3.9 shows the behavior of the integrated NiO – In$_2$O$_3$ sensor (Figure 3.4 a,b) towards pulses of CO (10, 3, 1 ppm). Resistance across three channels are shown, comprising In$_2$O$_3$ (CH1), NiO (CH2) and the In$_2$O$_3$-NiO combination (CH3). With CO, the In$_2$O$_3$ shows a decrease in resistance (n-type behavior), and with NiO, an increase in resistance (p-type behavior). With the appropriate inclusion of both oxides, the change in resistance in the presence of CO is severely reduced.

Nitric Oxide: Figure 3.10 shows the data with 5 and 10 ppb NO. Similar to the CO response, the NiO and the In$_2$O$_3$ show opposite responses (Figure 3.10ab), but because NO is an electron acceptor, the direction of the resistance change is reversed, as compared to CO. Nevertheless, when the two metal oxides are combined (CH3), the response to NO is minimized (Figure 3.10c).

Ammonia: With NH$_3$ (1ppm, 0.5 ppm, 0.1 ppm) on for a 2 min pulse, as shown in Figure 3.11, both In$_2$O$_3$ and NiO show a decrease in resistance, and when both oxides are included, the signal even at 100 ppb remains significant.
Mixture of gases: These experiments were then repeated with both NH$_3$ and CO in the gas stream with the 2 min pulses of gas. Figure 3.12 shows the results. With In$_2$O$_3$, NH$_3$ (0.1, 0.5, 1 ppm) gives rise to a decrease in resistance (CH1). If CO (1, 3, 10 ppm) is included with the NH$_3$, the NH$_3$ signal is overwhelmed (CH2). Similar situation exists for NiO, except that a resistance increase is observed if CO is included in the gas pulse. However, the signal from the combination NiO - In$_2$O$_3$ channel (CH3) only exhibits a signal for NH$_3$, and the effect of CO, even at a concentration 100 - fold higher than NH$_3$ is nullified.

3.3.6 NH$_3$ in human breath

Three sets of experiments were carried out with human breath samples, and are schematically represented in Figure 3.13.

Using breath as background: Breath samples were collected in Mylar bags, as previously described [52]. These samples were independently mixed via mass flow controllers with 10, 50, 100, 500, 1000 ppb of NH$_3$ and these samples were analyzed using the combined NiO - In$_2$O$_3$ sensor (CH3). In these experiments, the background signal was that of the breath alone, followed by introducing NH$_3$ in the gas mixture. The first experiment involved equilibrating the breath with water vapor at 37°C with a measured relative humidity of 93% [15] (Figure 3.13a), followed by the sensing measurement. The second experiment involved passing the breath through an ice bath resulting in a humidity of 30% (using apparatus in Figure 3.13b). The third experiment involved passing the breath through a moisture trap at -20 to 25°C, with a resulting humidity of 0% (Figure 3.13b) The
resulting sensing data using CH3 is shown in Figure 3.14 (Figure 3.15-17 shows the data for all channels). With both the humid samples (Figure 3.14a,b), the signal to NH3 was poor. The presence of water influenced the sensing signal of NH3 on both NiO and In2O3, particularly the former (Figure 3.15), with the NiO exhibiting a resistance increase with NH3, the opposite of the observation with dry gas (Figure 3.11). With the breath sample mixed with NH3 (bpt – 33.7°C) passing through the -20°C trap, the expected signal to the spiked NH3 was realized (Figure 3.14c). The calibration curve with the breath sample is shown in Figure 3.14d, and indicates saturation with increasing concentrations.

Using air as background: In another set of experiments, air was used as the background (Figure 3.13c), and a breath sample was measured using CH3 (all samples passing through the dry ice trap at -20 to -25°C). Figure 3.18a shows that the breath alone provides a signal, though we cannot ascertain what species are causing this signal. However, there was an increase in signal if the breath is mixed with NH3, as shown in Figure 3.18a. Such a standard addition experiment clearly indicates that the sensor is detecting NH3. The background breath signal was normalized to \( R_0/R \) of 1, and the increased signal (measured as \( R_0/R \)) due to the spiked NH3 is shown in Figure 3.18b.

### 3.4 Discussion

In order to demonstrate the practical application of the sensor described in this paper, we chose to work with human breath sample. Detection of NH3 in human breath at ~ ppb levels can be helpful for diagnosis of various diseases. Typical levels for CO and NO in human breath are at ppm and ppb levels, respectively [43]. The outcome of this study is a
sensor that can detect NH₃ at low concentrations (< 1000 ppb) with selectivity against CO at ppm and NO at ppb levels.

The sensor design used in this study is similar to our recent report on NO sensors [43]. The concept is to use a mixture of p- and n-type semiconducting oxide, but physically separated with a common interface (Figure 3.3, 3.4). The separated p and n-oxides allows for altering the contribution of each oxide to the resistance more readily than physical mixture of powders.

The two oxides examined here are n-type In₂O₃ and p-type NiO. The conduction model for both n-type and p-type metal oxide gas sensors has been reviewed [53-55]. In both n- and p-type oxides, oxygen ionosorption plays a key role in the sensing paradigm. In the case of n-type, such chemisorption leads to a decrease of majority carrier electrons at the surface of grains, whereas in p-type oxides, the oxygen ionosorption leads to a surface accumulation of holes. In n-type oxides, conduction is through the bulk of the oxide, whereas in p-type, conduction is along the surface. Under certain conditions, resistance changes from n- to p-type and vice versa has been observed. This effect is observed on Fe₂O₃, MoO₃, In₂O₃, SnO₂, TeO₂ and TiO₂, and several explanations have been proposed, including formation of a surface inversion layer driven via surface adsorption, different types of surface reactions, influence of polymorphs and morphology, as well as the effect of ionic dopants/impurities [29, 56-61].

The resistance changes of NiO and In₂O₃ to CO and NO were as expected (Figure 3.9ab, 3.10ab). NiO is behaving as a p-type semiconductor, with hole conduction as the main contribution. CO reacts with chemisorbed oxygen on the oxide surface releasing
electrons, which raise the resistance of p-type NiO and lowers the resistance of n-type In$_2$O$_3$. With the appropriate contributions from both oxides, the resistance change to CO can be nullified (Figure 3.9c). Similar observation are made with NO (Figure 3.10c).

Under conditions in which NH$_3$ can react with chemisorbed oxygen, it usually behaves as a reducing gas, with proposed reactions such as [62]

\[
2\text{NH}_3 + 3\text{O}^- \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 3e^- \quad (1)
\]
\[
2\text{NH}_3 + 5\text{O}^- \rightarrow 2\text{NO} + 3\text{H}_2\text{O} + 5e^- \quad (2)
\]

These reactions are more favorable at higher temperature. The resistance changes upon interaction of NH$_3$ with metal oxides can be anomalous. For n-type oxides, such as In$_2$O$_3$ and WO$_3$, at lower temperatures (< 300°C), there is a resistance decrease. However at higher temperatures, initial resistance decrease is followed by a resistance increase [62-65]. For n-type semiconductors, NO, the product of NH$_3$ oxidation upon chemisorption will lead to an increase in resistance. This competition between NH$_3$ oxidation and NO chemisorption is used to explain the anomalous sensing behavior. For avoiding the anomalous sensing behavior due to NOx, low temperature operation or the use of catalysts have been suggested [66]. Other explanations for anomalous behavior, as in hexagonal-WO$_3$ have been ascribed to the formation of an inversion layer [67].

Our data on In$_2$O$_3$ at 300°C indicates that NH$_3$ is behaving as a reducing gas (Figure 3.11a), with a decrease in resistance, as has been observed by others [24, 68]. The resistance changes with NH$_3$ on p-type NiO is more complicated. The resistance increase observed 500 °C with 1 ppm NH$_3$ (Figure 3.6c) and 10 ppm NH$_3$ at 300°C (Figure 3.6d) is explained by reactions (1) and (2), where the electrons created upon NH$_3$ oxidation combine with the
majority carrier holes, and lead to an increase in resistance, consistent with previous studies on NiO with 20 -50 ppm NH₃ [31]. The behavior with 1 ppm NH₃ at 300°C is not as expected and needs a different interpretation. As shown in Figure 3.6a, there is an initial decrease in resistance over the first few minutes, followed by a gradual increase. Differences in direction of resistance changes as a function of analyte concentrations has been noted. On p-type TeO₂ at low temperatures (80°C), a resistance decrease with ethanol (< 300 ppm), an anomalous behavior, whereas with higher concentrations of ethanol, the resistance increased, as expected for an reducing gas on a p-type material has been reported [59]. For p-type CuO nanowires, with NO₂ an oxidizing gas, at concentration < 5 ppm, the resistance increased (anomalous behavior), whereas with 30 -100 ppm NO₂, the resistance decreased, as expected for an oxidizing gas and p-type material [69]. No clear mechanistic information for such behavior is available in the literature.

The in-situ IR spectra shown in Figure 3.7 provide some clues. Formation of a band at 1267 cm⁻¹ on NiO is observed as gas is switched from N₂ to 20% O₂ at 300°C (Figure 3.7ac). This band disappears if the O₂ is replaced with N₂, so we assign this band to chemisorbed oxygen species. Upon introduction of 1 ppm NH₃, there is an increase in intensity of this band, followed by a decrease. The change in intensity of the 1267 cm⁻¹ band in Figure 3.7c in the presence of 1 ppm NH₃ mirrors the change in conductivity upon 1 ppm NH₃ exposure to NiO, as shown in Figure 3.6a (the timings do not exactly overlap since the IR was done on a powdered sample).

Several previous studies have noted a band in the 1200-1300 cm⁻¹ region upon oxygen chemisorption on metal oxides [70]. On Fe₂O₃, bands between 1250 -1350 cm⁻¹ have been
assigned to perturbed $O_2^-$ species, and in particular, the band at 1270 cm$^{-1}$ is prominent and stable up to 300°C [71]. There are few infrared studies of oxygen adsorption on NiO, bands at 1070 and 1140 cm$^{-1}$ were observed at 77K and assigned to $O_2^-$ [70]. On Fe$_2$O$_3$, bands in the 900 -1100 cm$^{-1}$ were assigned to $O_2^{2-}$ species [72]. Formation of $O^-$ on NiO has been proposed, though no distinct infrared bands were identified [72]. Peroxo species ($O_2^{2-}$) have been proposed upon oxygen adsorption on NiO [73]. On CuCl and CuBr, a band around 1270 cm$^{-1}$ has been assigned to $O_2$ coordinated with Cu$^+$, and intensity of this infrared band also decreased upon exposure to NH$_3$ [74]. Based on these studies, we assign the band at 1267 cm$^{-1}$ (Figure 3.7 a,b) on NiO to $O_2^-$.  

The reactivity of NH$_3$ on metal oxide surfaces is enhanced in the presence of oxygen. On Mg (0001) surface, NH$_3$ was reactive with the surface only in the presence of oxygen [75]. Chemisorbed oxygen on Ni (110) and Ni (100) is reactive with NH$_3$ with H abstraction and formation of NHx species [76]. Surface spectroscopic studies have shown the high reactivity of NH$_3$ with adsorbed oxygen on Ni (111) [77].

It has been proposed that the $O_2^-$ is in equilibrium with $O^-$ [75]

$$O_2^- \rightleftharpoons O^- + O$$  \hspace{1cm} (3)

NH$_3$ chemisorption at lower temperatures is proposed to lead to NH$_2$ and OH$^-$ via reaction with the O$^-$ [75]

$$M^{x+} \ldots NH_3 + O^- \rightarrow M^{x+} \ldots NH_2 + OH^-$$  \hspace{1cm} (4)

Ammonia adsorption on alumina surface (acid/base sites) was proposed to lead to NH$_2$ and OH formation for about 10% of all the NH$_3$ molecules that are absorbed [78]. Bands due to NH$_2$ were reported at 3386 and 3355 cm$^{-1}$ [76]. Dissociative chemisorption of NH$_3$
to NH$_2$ and OH driven by oxygen functionality is noted on epoxide groups in reduced graphene oxide, with vibrational bands assigned as 3208, 3270 cm$^{-1}$ (NH$_2$) and 3400 cm$^{-1}$ (OH) [79]. With the 1 ppm NH$_3$ on NiO, we did not observe any bands due to NH$_2$, but with 100 ppm NH$_3$ on NiO at 300°C, and subsequent cooling to room temperature, a band appears at 3220 cm$^{-1}$ in the presence of O$_2$, but not in the presence of only N$_2$ (these spectra are shown in Figure 3.8). We assign the 3220 cm$^{-1}$ band to N-H stretching.

Based on these observations, we explain the anomalous behavior of 1 ppm NH$_3$ observed in Figure 3.6a. We hypothesize that reactions (3) and (4) will take place on the NiO surface (we have IR evidence for the O$_2^-$ species), and with (4) occurring, it will lead to more O$_2$ chemisorption as O$_2^-$, as O$^-$ is used up in reaction (4). IR indicates transient increase of the O$_2^-$ band upon exposure to NH$_3$ (Figure 3.7a). With increased O$_2$ chemisorption as O$_2^-$, it will lead to a decrease in resistance. The increase in resistance observed later occurs due to subsequent reactions (1) and (2) due to oxidation of NH$_3$. At higher temperatures, or with higher concentrations of NH$_3$, the transient decrease in resistance is not observed (Figure 3.6c, d) as reactions (1) and (2) are promoted.

We have exploited the transient decrease in resistance upon exposure of low levels of NH$_3$ on NiO for amplifying the sensor signal. This was done by exposing the NiO to only 2 min of NH$_3$ thus giving time for the chemisorption effects to occur (reactions 3 and 4, Figure 3.6b), but not the chemical reactions (reactions 1 and 2). The resistance of NiO decreases and then recovers quite rapidly, as compared to the 10 min exposure, where the products of the chemical reaction form and need to be desorbed, before the sensor baseline is reached, and at 300°C, takes 40 minutes. With the 2 min NH$_3$ exposure, both NiO and
In$_2$O$_3$ show a decrease in resistance, so the sensing data that combines both oxides (CH3) lead to an additive effect, amplifying the response from NH$_3$ (Figure 3.11) while with CO and NO, the opposite response lead to a cancellation of signal (Figure 3.9,3.10). This strategy allows us to sense the presence of NH$_3$ in the concentration range of NH$_3$ in the concentration range <1000 ppb, in the presence of CO as seen in Figure 3.12.

Since the need for detecting NH$_3$ in human breath is of the order of hundreds of ppb, we used breath samples as a possible application of this sensor. The high humidity in breath posed a significant interference (Figure 3.14a, b), and only upon removal of water from the breath by a cold trap (-20°C), the signal due to NH$_3$ could be retrieved (Figure 3.14c). Since NH$_3$ and H$_2$O can both act as Lewis bases, it is not surprising that humidity poses an interference to NH$_3$. Interference to humidity not only is present for NH$_3$ [80], but to other gases such as CO [81], and for both n- and p-type materials. Chemisorption of water can follow the same as reaction (4), leading to formation of hydroxyl groups [53], with M$^{x+}$-OH bond formation. The observation that in the presence of water, there is an increase in resistance of NiO to NH$_3$ (Figure 3.15) indicates that the water adsorption disrupts the oxygen chemisorption as O$_2^-$, possibly by adsorbing at these sites. Thus, the p-n oxide arrangement can minimize interferences from other gases, such as CO, but because of the pronounced water interaction with the oxides, in general, humidity will be a strong interference to NH$_3$.

By removing the humidity, the sensor can detect NH$_3$ that is mixed into the breath. We have done the breath+NH$_3$ experiments in two ways. The breath is used as the background sample, and any increase in NH$_3$ in breath can be measured (Figure 3.14cd).
Or, the breath can be measured using air as the background sample, the breath alone gives a signal and then any increase in NH₃ can be measured from the increased signal (Figure 3.18ab). The possible biomedical application we see of this sensor is measuring an increase of NH₃ in breath. For H. Pylori infection diagnosis, the current standard of measurement involves feeding the patient a sample of 13 or 14C-labeled urea. The urease in the stomach (due to the bacteria) decomposes the urea to ¹³CO₂ or ¹⁴CO₂ and NH₃. The radioactive ¹⁴CO₂ in breath is then measured [82]. With ¹³CO₂, a mass spectrometer is necessary to carry out the measurement [82]. Because the sensor we have developed can measure NH₃ at ppb levels, the strategy would be to feed the patient regular urea and measure the released NH₃. There would still be the need of the humidity trap to remove water. The trap can remove other organic volatiles in breath, but is not an issue in the application we are proposing for this sensor. Gases such as CO and NO (along with the NH₃) will still come through the trap, and the p-n strategy as outlined in this paper minimizes the influence of these interferents, while enhancing the signal for NH₃.

3.5 Conclusions

This study demonstrates the concept of using p-type of NiO and n-type In₂O₃ placed side-by-side on a substrate with common interface as a sensor platform. The adjacent placement of the oxides allows for ease of variation of the amount of oxide to be included for making the resistance measurements in the presence of analyte gas. With this strategy, the change in resistance with 3-10 ppm CO was almost nil, since In₂O₃ and NiO give opposite responses to CO. Ammonia is also a reducing gas, but at low concentrations of
NH$_3$ (< 1 ppm) at 300°C, the response with In$_2$O$_3$ was as expected (resistance decrease), but with NiO, the resistance change was anomalous. For the first 8 min of a 10 min exposure to NH$_3$, there was a resistance decrease followed by a gradual resistance increase over the next 20 min, followed by a 10 min decrease to baseline resistance. With the help of in-situ infrared spectroscopy, this behavior was correlated with NH$_3$ chemisorption and involvement of O$_2^-$ species. Advantage was taken of the transient decrease with NH$_3$ on NiO to design a sensor that shows a resistance decrease for both NiO and In$_2$O$_3$ by controlling the gas pulses to a duration of 2 min. With this strategy, combining the two oxides enhanced the signal of NH$_3$, allowing ready detection at 100 ppb concentration. These sensors were used to detect NH$_3$ that was mixed with human breath. As long as the humidity is completely removed from the breath sample, 10-1000 ppb of added ammonia could be detected. Water interference arises from competing reactions with O$_2^-$ and the transient decrease in resistance with NH$_3$ on NiO is no longer observed, thus removing the amplification. A potential application of such a sensor would be in H.Pylori diagnosis.
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Figures & Tables

Figure 3.1. (a) XRD patterns of NiO powder annealed at 320 °C; (b) SEM image of NiO film on the sensor; (c) XPS spectra of the Ni 2p and O 1s region for NiO powder annealed at 320°C.
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Chapter 4: Infrared Spectroscopic Study of Carbon Dioxide Absorption in Aqueous Amine Solutions

4.1 Introduction

Flue gas from the combustion of fossil fuel contributes the most significant source of CO₂ emission. It is well known that CO₂ plays a dominant role in the global warming and thus CO₂ capture technologies are of growing demand to address this environmental concern. One of the most effective and mature technologies for CO₂ capture from flue gas is chemical absorption using aqueous amine solutions, with monoethanolamine (MEA) being the one most widely studied [1].

The 30% aqueous MEA solution has been utilized in an industrial scale to capture CO₂ for many years (Figure 4.1) [2]. Briefly, the gas to be treated is delivered through the pipe 12, and passes up through the absorber. The carbon dioxide, sulfur dioxide, or hydrogen sulfide, is removed by the action of the absorbent, and the stripped gas passes out the pipe 13. The absorbent with the absorbed gas is removed through the pipe 14, heated by the heater 18 and interchanger 22, and delivered near the top of the regenerator. Within the latter apparatus the liquid trickles down through to the bottom and gives up the absorbed gas which later escapes through the pipe 19. A further portion of the absorbed gas is removed by the heating coil 18, and the regenerated absorbent is cooled in the heat interchanger 22 and cooler 23 and returned for reuse in the absorber.
The reaction of CO$_2$ with amines has been extensively studied. There are three published empirical reaction mechanisms that adequately model the measured gas absorption data. The most prominent mechanism involves the formation of a zwitterionic form of the carbamate followed by a slow proton exchange reaction with a base [3].

$$\text{CO}_2 + \text{RNH}_2 \rightleftharpoons \text{RNH}_2^+\text{CO}_2^-$$

$$\text{RNH}_2^+\text{CO}_2^- + \text{B} \rightleftharpoons \text{RNHCO}_2^- + \text{BH}^+$$

The proton exchange reaction as represented in the second step is diffusion controlled and essentially instantaneous, and thus the kinetics of this process cannot be observed.

Another suggested mechanism includes a termolecular reaction between CO$_2$, the amine, and a base [4].

$$\text{B} + \text{RNH}_2 + \text{CO}_2 \rightleftharpoons \text{RNHCO}_2^- + \text{BH}^+$$

They can be used to empirically describe observations; however, on a molecular basis they are always combinations of sequential lower order reactions.

The third mechanism is based on the direct reaction of the amine with dissolved CO$_2$, followed by the deprotonation of the carbamic acid in a normal protonation equilibrium [5].

$$\text{CO}_2 + \text{RNH}_2 \rightleftharpoons \text{RNHCO}_2\text{H}$$

$$\text{RNHCO}_2\text{H} \rightleftharpoons \text{RNHCO}_2^- + \text{H}^+$$

However, it is not sufficient to explain the kinetics of formation of carbamate, and the reactions of the amines with carbonic acid and bicarbonate have to be included in the reaction mechanism.
Whilst postcombustion methods are advantageous in that the technology is commercially mature and can be easily retrofitted into existing power plants, they suffer a number of drawbacks. These include the considerable energy requirements for solvent regeneration and the necessary use of inhibitors to control corrosion. The sensitivity of the solvents to chemical degradation from other by-products in the flue gas streams, such as SO₂ and NOₓ, also lead to reduced efficiencies and increased costs for electricity production.

Although there are numerous investigations on the performance of MEA solutions as CO₂ absorbents, the characterization of the structural changes during CO₂ absorption at a molecular level is vital to understand the chemical mechanism. Speciation studies in aqueous MEA solution at different CO₂ loadings have been conducted via nuclear magnetic resonance (NMR) spectroscopy [6-9]. However, in situ measurements are not easily performed and acquisition times for quantitative NMR experiments are unsuited for kinetic experiments. Raman spectroscopy has been investigated for the quantitative determination of the species distribution in alkanolamine-H₂O-CO₂ systems [10], which is considered as a highly efficient tool for the improvement of both thermodynamic and kinetic models. In-situ FTIR has been proved to be a reliable technique to monitor the evolution of this process [11]. The speciation of CO₂–H₂O–alkanolamine system has been determined and the species concentrations are calculated by fitting of a thermodynamic model to multivariate spectroscopic measurements using nonlinear regression, leading to the determination of the amine protonation and carbamate equilibrium constants. Analysis of the position, shape and intensity of peaks in infrared spectrum reveals details about the molecular structure,
allowing identification and quantification of the sample. Qualitative identification by ATR-FTIR of amine, carbamate, and bicarbonate species during the absorption of CO\textsubscript{2} in aqueous solutions of monoethanolamine (MEA), 2-amino-2-methyl-1- propanol (AMP), methyldiethanolamine (MDEA) [12], and some heterocyclic amines have been recently reported [13, 14]. The molecular structure of relevant amines are shown in Figure 4.2.

In the flue gas stream, the SO\textsubscript{2} concentration is in the range of 6-300 ppm after wet desulfurization [15]. The adverse effect of SO\textsubscript{2} has been consistently reported in the literature [16-24], indicating that the influence of SO\textsubscript{2} results in amine degradation, with the formation of heat stable salts such as sulfites and sulfates. SO\textsubscript{2} is reported to react with MEA and form isothiocynatoethane and tetrahydrothiophene, which cannot be reclaimed [17]. It is one of the main factors causing loss of free amine, which leads to an increase in cost of CO\textsubscript{2} capture. However, NMR studies demonstrated that in aqueous solutions, SO\textsubscript{2} does not react with amines at low temperature [25, 26]. Therefore, it is necessary to assess the effect of SO\textsubscript{2} on the kinetics of CO\textsubscript{2} absorption by aqueous amines.

Many researchers have been interested in piperazine (PZ)-based blends with other amines. Their results indicated that PZ is an effective promoter for CO\textsubscript{2} absorption in monoethanolamine (MEA), methyldiethanolamine (MDEA), and potassium carbonate (K\textsubscript{2}CO\textsubscript{3}) solutions from both thermodynamic and kinetic perspectives [27-29]. Since PZ is a cyclic secondary diamine (Figure 4.2), its efficiency is attributed to its cyclic diamine structure that may favor rapid formation of carbamates with CO\textsubscript{2}. Also, the molecule can theoretically absorb 2 mol of CO\textsubscript{2} for every 1 mol of amine [29]. In the CO\textsubscript{2}-MDEA-PZ system [30], CO\textsubscript{2} could be transferred via PZ bound CO\textsubscript{2} (denoted by R’’(NHCOO)\textsubscript{2} ) to
MDEA (denoted by R₃N) by the reaction $\text{R}''(\text{NHCOO})_2 + 2 \text{R}_3\text{N} \rightleftharpoons \text{R}''(\text{NH})_2 + 2 \text{R}_3\text{NCOO}^-$ and the overall rate of absorption is enhanced.

Chemical reactions associated with the absorption of CO₂ into aqueous blends of piperazine (PZ) with aqueous amines were studied by 13C-NMR spectroscopy [31]. ATR-FTIR spectroscopic investigation of the CO₂ absorption characteristics of PZ has been reported to probe the structure–activity relationship of the reaction between heterocyclic diamines and CO₂ [13]. It was also reported that the rate constant of PZ with CO₂ is an order of magnitude higher than that of conventional MEA [32]. Among the PZ-based solutions, MEA/PZ blends have been proven to be efficient for capturing CO₂. The absorption rate of CO₂ at 40 and 60 ℃ in aqueous MEA with 0.6-1.2 mol/L PZ is 1.5-2.5 times greater than that in MEA alone [28]. The removal efficiency of CO₂ from gases containing 10% CO₂ by MEA/PZ solution was found to be superior to that of AMP/PZ, MDEA/PZ, and MEA. Hence, the aqueous solution of blended MEA and PZ has been demonstrated to be a promising solvent for CO₂ capture from coal-fired power plant flue gas due to its capture performance and energy efficiency. Although there is some research data available on kinetics and solubility of MEA/PZ blends, no research has been done to investigate the speciation of MEA/PZ blends by FTIR.

Attenuated Total Reflectance (ATR) is a widely used FTIR sampling tool. ATR generally allows qualitative or quantitative analysis of samples with little or no sample preparation, which greatly speeds sample analysis. With ATR sampling the IR beam is directed into a crystal of relatively higher refractive index. The IR beam reflects from the internal surface of the crystal and creates an evanescent wave, which projects orthogonally...
into the sample in intimate contact with the ATR crystal. Some of the energy of the evanescent wave is absorbed by the sample and the reflected radiation (with reduced intensity) is returned to the detector. This ATR phenomenon is shown graphically in the following representation of single reflection ATR (Figure 4.3).

In this study, we present a simple, fast, and robust method for assessing the effect of SO$_2$ on CO$_2$ absorption with MEA by Horizontal Attenuated Total Reflectance (HATR) monitoring. HATR measures a thin layer of the sample with a constant and reproducible effective pathlength, making this technique perfectly suited for quantification of liquid samples. This method aims at monitoring the influence of SO$_2$ on CO$_2$ absorption process by MEA, and obtaining information on speciation, concentration and kinetics. First, the absorption bands observed during CO$_2$ reaction with MEA was assigned to characteristic vibration modes. Then, CO$_2$ absorption in the presence of SO$_2$ was studied. The chemical speciation was evaluated by kinetic measurements and tentative solutions were examined for quantitative analysis. The present study used concentrations of SO$_2$ that can be observed in a typical flue gas stream after the power plant desulfurization process. Speciation of the MEA/PZ blends was analyzed by the HATR spectrum and the influence of PZ on CO$_2$ uptake by MEA was examined. As an application of IR spectroscopy for practical samples, the SO$_2$ effect on an amine based polymer membrane was assessed. In the presence of SO$_2$, the individual amine carrier was studied by transmission FTIR and the membrane was studied by ATR FTIR.
4.2 Experimental

A schematic of the absorption reactor apparatus used to analyze aqueous CO₂/MEA reactivity is shown in Figure 4.4. Research grade O₂, N₂, CO₂ and SO₂ were all supplied from Praxair (Columbus, USA). A gas stream with various compositions were bubbled through an aqueous solution of MEA (ACS reagent, ≥99.0%, SigmaAldrich) in a three-neck flask maintained at 40°C by a temperature-controlled water bath. The flow rate was maintained at 100 sccm. O₂ reacts with MEA to form heat-stable salts (HSS) identified to consist of acetates, formates, and oxalates, which can be reclaimed [33]. The effect of O₂ is not considered in this work as our objective focuses on the effect of SO₂. A composition of 6% O₂ is fixed in the gas stream. The gas outlet at another neck of the reactor was connected to a condenser for preventing solvent loss. Solution volumes of 50 mL were used for all experiments. Pure N₂ was used to purge the reactor before the absorption experiments. A 0.5 mL sample of the aqueous solution was withdrawn from the reactor at appropriate intervals and was analyzed by a PerkinElmer Spectrum 400 coupled with a 20-reflection PIKE HATR accessory. Each spectrum was recorded as the average of 256 scans over the spectral range of 4000-800 cm⁻¹ with a resolution of 8 cm⁻¹. The HATR is an in-compartment design for samples which fit into the FTIR sample compartment (Figure 4.5). The HATR crystal plate used in present study is in trough plate configuration (Figure 4.6). The trough plate is designed for easy sampling, with a large, recessed germanium (Ge) crystal to accommodate the liquid sample. Typically, only a thin layer of the sample needs to be applied onto the crystal surface.
The obtained ATR spectra are similar to those collected by transmission measurements. However, subtle differences exist because ATR sampling depth since depth of penetration depends on the wavelength of light, which makes IR absorption bands at long wavelength have higher absorbances than those of shorter wavelength. Performing the ATR correction is a recommended procedure for qualitative analysis. Therefore, all spectra were processed by the ATR correction feature of the FTIR software package. This will scale the intensities by a factor that is inversely proportional to wavelength and its result will more closely resemble the transmission spectrum. For each characteristic peak, the relative peak height was obtained by drawing a baseline tangent to both shoulders of the band of interest and then measuring from the maximum height of the curve to the baseline. The relative peak area was integrated from the area between the curve and the linear baseline.

The pH value of the solution during gas absorption was monitored by an Accumet AB15 pH meter (Fisher Scientific).

4.3 Results and Discussion

4.3.1 Reactivity of MEA with CO₂

The interaction of MEA with CO₂ has been extensively studied, which incorporates three groups of reactive species (↔ arrows for instantaneous protonation equilibria and ⇌ for kinetically observable reactions and equilibria) [34]:

Group 1: the CO₂/carbonate family

\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \]
\[
\begin{align*}
\text{CO}_2 + \text{OH}^- & \rightleftharpoons \text{HCO}_3^- \\
\text{CO}_3^{2-} + \text{H}^+ & \rightleftharpoons \text{HCO}_3^- \\
\text{HCO}_3^- + \text{H}^+ & \rightleftharpoons \text{H}_2\text{CO}_3
\end{align*}
\]

Group 2: amine in protonated/deprotonated forms
\[
\text{RNH}_2 + \text{H}^+ \leftrightarrow \text{RNH}_3^+
\]

Group 3: carbamate in protonated/deprotonated forms
\[
\begin{align*}
\text{RNH}_2 + \text{CO}_2 & \rightleftharpoons \text{RNHCOOH} \\
\text{RNH}_2 + \text{H}_2\text{CO}_3 & \rightleftharpoons \text{RNHCOOH} + \text{H}_2\text{O} \\
\text{RNH}_2 + \text{HCO}_3^- & \rightleftharpoons \text{RNHCOO}^- + \text{H}_2\text{O} \\
\text{RNHCOO}^- + \text{H}^+ & \leftrightarrow \text{RNHCOOH}
\end{align*}
\]

Spectra of aqueous MEA at different CO\(_2\) exposure times are given in Figure 4.7 with peak assignments (Table 4.1) [11]. MEA prior to CO\(_2\) showed vibration modes at 955 cm\(^{-1}\) (C-N-H out-of-plane wagging and C-NH\(_2\) twisting) and 1362 cm\(^{-1}\) (NH\(_2\) twisting). In the presence of CO\(_2\), the 1568 cm\(^{-1}\) and 1486 cm\(^{-1}\) peaks were assigned to COO\(^-\) asymmetric and symmetric stretching respectively, and N-COO\(^-\) stretching vibration at 1322 cm\(^{-1}\) to the carbamate species. Several peaks shift due to the protonation of the amine group, in particular, C-N and C-OH stretching shifts from 1076 to 1066 cm\(^{-1}\) and 1024 to 1013 cm\(^{-1}\), respectively. At low CO\(_2\) loading, carbonate is the most abundant species, with a typical absorption peak at 1386 cm\(^{-1}\) corresponding to the doubly degenerate stretching mode.
The relative peak intensity at selected wavenumbers are plotted against CO$_2$ exposure time (Figure 4.8) and allow evaluation of the reactivity of 30 wt% MEA with CO$_2$. The selected bands are characteristic of free MEA (MEA, 1362 cm$^{-1}$), carbonate (CO$_3^{2-}$, 1386 cm$^{-1}$), protonated MEA (MEAH$^+$, 1066 cm$^{-1}$) and MEA carbamate (NCOO$^-$, 1322 cm$^{-1}$). The protonation of MEA results in shift of the C-N stretching band from 1076 cm$^{-1}$ to 1066 cm$^{-1}$, the relative peak intensity at 1066 cm$^{-1}$ was acquired by peak fitting (Figure 4.9).

During 9 h of CO$_2$ absorption, the amount of MEA keeps dropping while there is protonated MEA produced, which indicates that the pH decrease due to CO$_2$ dissolution plays an important role in the protonation equilibrium of MEA (Group 1: CO$_2$ + H$_2$O $\rightleftharpoons$ 2H$^+$ + CO$_3^{2-}$) and the absorption ability of MEA will be affected by factors that affect pH (Group 2: RNH$_2$ + H$^+$ $\leftrightarrow$ RNH$_3^+$). There is an increase in the relative peak intensity of carbamate and carbonate. It has been reported that the contributions of the CO$_2$ reactions with OH$^-$ and H$_2$O to the overall rate are negligible [35, 36], most CO$_2$ will take the amine path to form the carbamate (Group 3: RNH$_2$ + CO$_2$ $\rightleftharpoons$ RNHCOOH).

Based on the reaction 2RNH$_2$ + CO$_2$ $\rightleftharpoons$ RNHCO$_2^-$ + RNH$_3^+$, the 2:1 reaction stoichiometry restricts CO$_2$ absorption capacity of primary amines to a theoretical upper limit of 0.5 mol CO$_2$/mol amine. The carbamate species may undergo hydrolysis to produce bicarbonate and regenerate a free amine by the reaction RNHCOO$^-$ + H$_2$O $\rightleftharpoons$ RNH$_2$ + HCO$_3^-$, however, given the chemical stability of the carbamate derivative of primary and amine, it does not occur at an industrially relevant rate [37]. At high CO$_2$ loadings (>0.5 mol CO$_2$/mol amine), there is a significant pH decrease due to CO$_2$ dissolution. It is reported that the hydrolysis of carbamate proceeds via an acid-catalyzed pathway at low
pH [3]. The concentration of free amine has dropped down to zero. The amine is now either protonated or has reacted to carbamate. Therefore, further CO$_2$ absorption promotes carbamate reversion to bicarbonate and free amine. The concentration of the protonated amine continues to rise by $\text{RNH}_2 + \text{H}^+ \leftrightarrow \text{RNH}_3^+$, but this can only occur at the expense of the carbamates. Since we do not observe a decrease in the carbamate, this indicates that the saturation limit has not been reached in 9 h with 30 wt% MEA.

4.3.2 Effect of lower MEA concentration

The initial MEA concentration was evaluated for its contribution to the CO$_2$ absorption. Based on the result obtained from 30 wt% MEA (4.9 M) in 100 sccm CO$_2$, the speciation diagram shows that complete reaction did not occur during the experimental time (9 h). The absorption behavior of 15 wt% MEA (2.5 M) was studied in the presence of CO$_2$ with the same flow rate. Figure 4.10 shows the evolution of infrared spectra of 2.5 M MEA exposed to 15% CO$_2$/6% O$_2$ at 40°C for 5 h. Similar to 30 wt% MEA, the characteristic peaks of MEA, carbamate, carbonate and protonated MEA were observed. Then the relative peak height of the above peaks were plotted against time (Figure 4.11). A more complete path for the CO$_2$/amine reaction was observed with the diluted MEA.

During the first 3 h, the IR absorption of each species changes almost linearly. The amount of free MEA has dropped down to almost zero after 2 h, while the amount of protonated MEA keeps increasing. After reaching its maximum at 3 h, the concentration of carbamate starts to decrease by $\text{RNHCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{RNH}_2 + \text{HCO}_3^-$, and the free amine contributes to the growth of protonated MEA by $\text{RNH}_2 + \text{H}^+ \leftrightarrow \text{RNH}_3^+$. Carbonate shows
the same trend with its maximum at 3 h and a drop of peak intensity at 1386 cm$^{-1}$ after 3h. It is noteworthy that at 1382 cm$^{-1}$ a small shoulder is visible after 3h, which represents the C-O stretching of bicarbonate [38]. The results indicate the CO$_2$ absorption capacity of 2.5 M MEA reaches its upper limit at 3h and bicarbonate starts to form by the reaction CO$_3^{2-}$ + H$^+$ $\leftrightarrow$ HCO$_3^-$ after 3h. By comparing the results of the two initial concentrations of MEA, it shows that the reaction of MEA and CO$_2$ is complete with the lower MEA concentration within the time frame examined.

4.3.3 Reactivity of MEA with SO$_2$

The chemical reactions between SO$_2$ and MEA is based on SO$_2$ reactions with water [39] and aqueous alkali solution [40]:

SO$_2$ + H$_2$O $\rightarrow$ 2H$^+$ + SO$_3^{2-}$

H$_2$SO$_3$ + 2RNH$_2$ $\rightarrow$ (RNH$_3$)$_2$SO$_3$

The overall reaction of MEA-SO$_2$-H$_2$O system is

SO$_2$ + 2RNH$_2$ + H$_2$O $\rightarrow$ 2RNH$_3^+$ + SO$_3^{2-}$

Infrared spectra of 30 wt % aqueous MEA was recorded in the presence of 151 ppm SO$_2$/6% O$_2$ (Figure 4.12). Sulfite ion, SO$_3^{2-}$, shows two absorption bands at 1010 and 961 cm$^{-1}$, which are attributed to the asymmetric and symmetric S-O stretching [41]. Meyer et al. [42] list vibrational modes $\nu$1 and $\nu$3 for aqueous SO$_3^{2-}$ at 933 and 966 cm$^{-1}$ respectively. Sulfate (SO$_4^{2-}$) gives absorption band at 1105 and 1140-1190 cm$^{-1}$ [41]. There were neither sulfite/sulfate nor protonated MEA peaks observed after 27h with 30 wt% MEA. The sulfite peak at 936 cm$^{-1}$ was observed in the 2.5 M MEA solution after five days in the
presence of 151 ppm SO$_2$/6% O$_2$, along with a redshift of the peak at 1076 cm$^{-1}$ with an increasing intensity indicates the formation of protonated MEA (Figure 4.13).

It is reported in the literature that amine capacity for CO$_2$ capture is reduced by SO$_2$ as a result of irreversible reaction of amine with sulfur species. It should be noted that the experimental time of most such studies [21, 23, 24] is much longer than that of this work and low concentrations of sulfur species are detected by ion chromatography. Sulfite, sulfate, and thiosulfate generated in 4.4 mol/kg MEA loaded with 0.057 mol SO$_2$/mol of MEA were quantified using ion chromatography [21], showing a concentration of 95, 35, 10 mmol/kg after 1 week at 120 °C, respectively. According to the ion chromatography, a run in a CO$_2$ capture pilot plant using 30 wt% MEA with a feed gas of 12 vol% CO$_2$, 18 vol% O$_2$ and 200 ppm SO$_2$, the concentration of sulfite and sulfate were 8650 and 33,837 mg/L after 430h at 46°C, respectively [23]. For an operation of 0.1 mol/L MEA in 12.5 vol% CO$_2$ and 294 ppm SO$_2$, the sulfite and sulfate started to show up after 3 days and reached 3 mmol/L and 30 mmol/L after 15 days, respectively [24].

SO$_2$ in gas or liquid form reacts with neat amines to form thionylamines (R-N=S=O) [43] with absorption bands at 1300-1230 cm$^{-1}$ (asymmetric NSO stretch) and 1180-1110 cm$^{-1}$ (symmetric NSO stretch) [44, 45], however, little detail is available about what happens in aqueous solution. It has been investigated if SO$_2$ undergoes the equivalent reactions to Group 3 (section 4.3.1) under CO$_2$ capture relevant conditions. Qualitative 1H-NMR spectroscopic studies [25, 26] of interactions of MEA with sulfur species did not show any sign of interactions between MEA and SO$_2$. To investigate this, MEA was equilibrated with sulfite solutions at different pH, adjusted by addition of different amounts
of hydrochloric acid. No sign of formation of sulfurous acid amide was observed when held at 40°C for a period of two weeks. At high temperatures of 100°C with the reaction going on for more than one year, and recording their 1H-NMR spectra regularly, no interaction was noted. As a consequence of the 1H-NMR study, it was found that no direct reaction occurs between SO₂ and MEA at either absorber or desorber conditions. The relevant reactions are presented in the equations (1) to (5).

\[
\begin{align*}
\text{SO}_2 (\text{aq}) + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{SO}_3 \\
\text{SO}_2 (\text{aq}) + \text{OH}^- & \leftrightarrow \text{HSO}_3^- \\
\text{SO}_3^{2-} + \text{H}^+ & \leftrightarrow \text{HSO}_3^- \\
\text{HSO}_3^- + \text{H}^+ & \leftrightarrow \text{H}_2\text{SO}_3 \\
\text{SO}_2 (\text{aq}) & \leftrightarrow \text{SO}_2(\text{g})
\end{align*}
\]

SO₂ reacts with H₂O (1) and OH⁻ (2) respectively. The protonation reactions can be considered instantaneous on timescales relevant for this work, and are defined by equilibrium constants. Reaction (5) is the solubility of gaseous SO₂ dissolved in water defined according to Henry’s law, and this is also defined as an equilibrium. There is also a slight shift of CH₂ peaks of MEA with time to higher ppm. The shift is the evidence of the protonation of the nitrogen atom. This can be as a result of oxidation of S (IV), sulfite, to S (VI), sulfate, in the presence of dissolved oxygen. Sulfuric acid is a stronger acid than sulfurous acid and oxidation will reduce the pH causing protonation of MEA.

Based on the literature and our results, we conclude that in aqueous solutions and under our experimental conditions, there is no direct chemical reaction between SO₂ and MEA. The existing known aqueous chemistry of SO₂ reflects the chemistry of absorption
into aqueous amine solutions and affects the protonation equilibria of amine by pH effect. It took a long time to detect the formation of sulfite and protonated MEA due to the low concentration of SO$_2$ and the detection limit of FTIR. In addition, the first-order rate constants of the reactions for SO$_2$ and CO$_2$ with water are $3.4 \times 10^6$ and 0.14 s$^{-1}$, respectively, and the Henry’s law solubilities are 1.2 and 0.034 mol/L atm, respectively [46]. Based on the larger reaction rate constants with water and greater solubility for SO$_2$, it would be expected that SO$_2$ absorption is favored over CO$_2$ and a competition between the two gases should exist during absorption in MEA. Further discussion is presented in the following sections.

4.3.4 pH effect

Considering that there is no observable direct chemical interaction between SO$_2$ and MEA, the remaining effect of accumulation of SO$_2$ into the MEA solution is the acid behavior from the aqueous chemistry of SO$_2$.

As discussed in section 4.3.3, SO$_2$ can react with water to form sulfurous acid, which will dissociate releasing two protons and the sulfite ion, SO$_3^{2-}$. The sulfite ions will not play an important role (rather than formation of heat stable salts) but the released protons by lowering the pH will interfere in the equilibriums of the amine, hydroxide, and CO$_2$ in the formation of carbamate and carbonate species.

$$\text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HSO}_3^{-} \text{ (bisulfite)}$$
$$\text{HSO}_3^{-} \leftrightarrow \text{H}^+ + \text{SO}_3^{2-} \text{ (sulfite)}$$
$$\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \leftrightarrow 2\text{H}^+ + \text{SO}_4^{2-} \text{ (sulfate)}$$
MEA and its carbamate are involved in pH-dependent protonation equilibria at the primary amine for MEA and the carboxylate group of the carbamate [34]. As a consequence, the equilibrium shifts of the two species are pH-dependent. The released protons by lowering the pH can interfere in the following equilibriums:

\[
R{-}NH_2 + H^+ \leftrightarrow RNH_3^+
\]

\[
R{-}NHCOO^- \text{ (carbamate)} + H^+ \leftrightarrow R{-}NHCOOH \text{ (carbamic acid)}
\]

\[
CO_3^{2-} + H^+ \leftrightarrow HCO_3^-
\]

There are several effects of lowering of the pH. The immediate kinetic effects include:
(a) protonation of MEA, reducing the concentration of free MEA that reacts with CO\(_2\), thus reducing the kinetics of carbamate formation; (b) lowering the hydroxide concentration, thus reducing the kinetics of carbonate formation. If these reactions were to occur, there should be a reduction of the absorption capacity of the amine solution with increasing accumulation of SO\(_2\).

The pH value of the 30 wt% MEA solution has been monitored during the absorption reactions. As shown in Figure 4.14, there is a slight pH change from 11.9 to 11.8 induced by 151 ppm SO\(_2\). Despite the significant pH change caused by CO\(_2\) from 11.9 to 10.4, SO\(_2\) shows minor effect on the pH of the MEA solution with a further decrease to a value of 10.3. For 2.5 M MEA, Figure 4.15 displays the pH drops from 11.7 to 9.8 over 6 h with or without SO\(_2\). The pH effect of CO\(_2\) is dominant and overwhelms the effect of SO\(_2\). Therefore, the pH effect of 151 ppm SO\(_2\) is insignificant compared with 15% CO\(_2\).
4.3.5 Effect of SO$_2$ on CO$_2$ absorption

It is of interest to examine how low concentrations of SO$_2$ (151 ppm) affect CO$_2$ absorption by MEA. It has been reported that the rate of MEA loss was retarded with the inclusion of CO$_2$ in the MEA-SO$_2$-CO$_2$-O$_2$-H$_2$O system [20]. The experiments were conducted at 373 K for 5 mol/L MEA with a SO$_2$ concentration of 6 ppm, a O$_2$ concentration of 6%, and a CO$_2$ loading of 0.25 mol CO$_2$/mol MEA. The results obtained were compared with those obtained from 5 mol/L MEA at the corresponding SO$_2$ and O$_2$ concentrations and temperatures without CO$_2$. The concentration of MEA dropped from 5 mol/L to 4.5 mol/L after 200h with CO$_2$, and from 5 mol/L to 4 mol/L after 200h without CO$_2$. The authors concluded that if CO$_2$ displaces SO$_2$ from the solution, it means that SO$_2$ will be absent or of sufficiently low concentration to cause severe degradation, thereby making CO$_2$ an inhibiting agent.

In order to study the SO$_2$ effect on CO$_2$ absorption, 151 ppm SO$_2$ was mixed with 15% CO$_2$ and 6% O$_2$. The evolution of relative peak height as a function of time is shown in Figure 4.16 for 30 wt% MEA and Figure 4.18 for 2.5 M MEA. The peak height change was compared with the results without SO$_2$ (Figure 4.17 for 30 wt% MEA and Figure 4.19 for 2.5 M MEA). For both cases, the speciation with SO$_2$ remained similar as compared with the results without SO$_2$, indicating the influence of 151ppm SO$_2$ on CO$_2$ absorption by MEA is negligible. For the previous proposed pH effect, there is no retardation observed on the kinetics of carbamate and carbonate formation, thus confirming that low concentration of SO$_2$ has no effect on pH of the solution. All reaction products are from
the CO₂/MEA reaction, there is no heat stable salts such as sulfite or sulfate observed during the experimental period.

4.3.6 Cyclic experiment

Post combustion “wet-scrubbing” CO₂ capture technologies have been employed industrially for decades and are based predominantly on the industrially important primary alkanolamine MEA. The basic process (Figure 4.1), patented in 1930 [47], is one in which CO₂ is absorbed from a flue gas or combustion gas into an aqueous solution of amine with low volatility. The flue gas is delivered through the absorber, where the carbon dioxide, sulfur dioxide, or hydrogen sulfide, is removed. The absorbent with the absorbed gas is heated and delivered near the top of the regenerator. A further portion of the absorbed gas is removed by the heating coil, and the regenerated absorbent is cooled and returned for reuse in the absorber.

For industrial applications, the performance of solvent should be evaluated under a dynamic environment taking both absorption and desorption processes into account [48, 49]. Hence, the cyclic dynamic operation of absorption and desorption processes was carried out.

A 50 mL solution containing 2.5M MEA is degassed by pure N₂ and then loaded by bubbling 15% CO₂ and 6% O₂ at 40°C until saturated (the concentration of protonated MEA stops increasing). The temperature for desorption is maintained at 100°C. At the same time pure N₂ is bubbled through the saturated MEA until a steady state is reached (the concentration of protonated MEA stops decreasing). The peak height of carbamate and
carbonate is monitored by ATR to evaluate the rich and lean loading of MEA. The cyclic absorption-desorption process is carried out over three cycles. The initial absorption commences with fresh MEA and all subsequent cycles commence from the desorption equilibrium.

As can be seen in Figure 4.20, in the first cycle, the amount of carbonate increases in the first 2h and then starts to decrease, indicating the formation of bicarbonate. The amount of protonated MEA increases rapidly and reaches a plateau, indicating the solution is saturated and the first absorption process is complete. As the solvent temperature increases from 40 to 100 °C, the desorption process starts and lasts for 4 h. After the solution is cooled down to 40 °C, it is ready for processing the second cycle, and the further cycles follow the same procedure. The same cyclic procedures are carried out with 15% CO₂ and 6% O₂ in the presence of 151 ppm SO₂. Figure 4.21 displays the dynamic change of relative peak intensity over the absorption/desorption cycles.

The performance of aqueous MEA solution is evaluated using selected criteria. The regeneration efficiency is of particular interest to industrial applications as it is related to the energy consumption. Figure 4.22 summarizes the regeneration efficiency calculated according to the relative peak intensity at 1362 cm⁻¹ of free MEA after 3 cycles. In the presence of 15% CO₂/6% O₂, the amount of MEA regenerated after 3 cycles is 39% of initial MEA. In the presence of 151 ppm SO₂/15% CO₂/6% O₂, there is 40% MEA regenerated. Therefore the presence of 151 ppm SO₂ does not affect the MEA regeneration.
4.3.7 Quantitative analysis

Infrared monitoring can provide quantitative information using Beer–Lambert law (the absorbance changes linearly with species concentration). Determining speciation relies on calibration of pure components at different concentrations. With CO$_2$–H$_2$O–amine systems, these calibrations are based on a single peak evaluation (e.g., the amplitude of the absorbance peak at a certain wavenumber that is due to one species only).

However, the protonation of MEA results in shift of the C-N stretching band from 1076 cm$^{-1}$ to 1066 cm$^{-1}$ (Figure 4.9), and there is no MEA carbamate standard solution available. Therefore, the quantification of protonated MEA and MEA carbamate cannot be determined directly from Beer’s Law. Three methods were applied to address these issues. The first one is to use the characteristic peak of N-COO$^-$ stretching at 1375 cm$^{-1}$ in methyl carbamate as a standard to calibrate the concentration of MEA carbamate with the N-COO$^-$ peak at 1322 cm$^{-1}$. The second one is to calculate the concentration of protonated MEA by the known protonation equilibria of MEA. The third one is to calculate the value of the absorption coefficient ($\varepsilon$) for MEA carbamate assuming that the MEA/CO$_2$ reaction at low CO$_2$ loading leads to a 1:1 mixture of protonated MEA and carbamate.

Method one:

A series of standard solutions were prepared with pure MEA, methyl carbamate and sodium carbonate solutions. The absorbance of the characteristic peak of the standard solution was measured and used to prepare a calibration curve. For this experiment, the absorbance at 1362 cm$^{-1}$, 1375 cm$^{-1}$ and 1386 cm$^{-1}$ was used for MEA, methyl carbamate
and sodium carbonate, respectively. The points on the calibration curve should yield a straight line (Beer’s Law). The slope of that line provides a relationship between absorbance and concentration: \( A = \varepsilon C \), where \( \varepsilon \) is the proportionality constant. The corresponding species in MEA solution during CO\(_2\) absorption were then analyzed. The absorbance of each species was used with the slope from the calibration curve to calculate its concentration. The Beer’s Law graphs for three standard solutions are plotted in Figure 4.23, all of which show a linear relationship between absorbance and concentration.

It was assumed that the molar absorptivity for C-N stretching bands was the same for MEA carbamate at 1322 cm\(^{-1}\) as for methyl carbamate at 1375 cm\(^{-1}\). The concentration of protonated MEA ([RNH\(_3^+\)]\(_t\)) was determined based on a mass balance of nitrogen by subtraction of MEA carbamate ([RNHCOO\(^-\)]\(_t\)) and unprotonated MEA ([RNH\(_2\)]\(_t\)) from initial MEA concentration ([RNH\(_2\)]\(_0\)):

\[
[RNH_3^+]_t = [RNH_2]_0 - [RNH_2]_t - [RNHCOO^-]_t
\]

The absorbance of each species was converted to the corresponding concentration and plotted as a function of time for reaction of 15% CO\(_2\)/6%O\(_2\) with 30 wt% aqueous amine at 57 °C (Figure 4.24). Clearly, the concentration of carbamate predicted is too low. The problem of this method is using the 1375 cm\(^{-1}\) peak of methyl carbamate as a standard for the 1322 cm\(^{-1}\) peak of MEA carbamate. The following molecular formula shows the difference between methyl carbamate and MEA carbamate:

Methyl carbamate: \( \text{H}_2\text{NCOOCH}_3 \)

MEA carbamate: \( \text{HOCH}_2\text{CH}_2\text{NCOO}^- \)
Although both 1375 and 1322 cm\(^{-1}\) peak are assigned to N-COO\(^-\) stretching vibration, the peak shape and intensity are different. Therefore the absorption coefficient calculated from methyl carbamate cannot be used for MEA carbamate.

Method two:

The protonation of MEA results in the C-N stretching band shift from 1076 cm\(^{-1}\) to 1069 cm\(^{-1}\) (Figure 4.9). The quantification of protonated amine concentration cannot be determined directly from Beer’s Law. It is well known that the primary amine is involved in pH-dependent protonation equilibria: \(\text{Am} + \text{H}^+ \rightleftharpoons \text{AmH}^+\), where \(K\) is the equilibrium constant and \(K = \frac{[\text{AmH}^+]}{[\text{Am}][\text{H}^+]}\) with a value of \(\log K = 9.06\) [11].

The standard MEA solution was titrated with concentrated HCl and the concentration of MEA and protonated MEA at different pH has been calculated in Table 4.2 using the equilibrium constant.

By using the absorbance value of fitted MEAH\(^+\) peak at 1066 cm\(^{-1}\), the proportionality constant \(\varepsilon\) at each pH has been calculated, the average value of which are \(\varepsilon = 0.012\) for MEAH\(^+\). This value was used to calculate the concentration of MEAH\(^+\) produced in CO\(_2\) reaction. The concentration of MEA carbamate ([RNHCOO\(^-\)]) can be determined based on a mass balance of nitrogen by subtraction of protonated MEA ([RNH\(_3\)\(^+\)]) and unprotonated MEA ([RNH\(_2\)]) from initial MEA concentration ([RNH\(_2\)]\(_0\)):

\[
[\text{RNHCOO}^-]_t = [\text{RNH}_2]_0 - [\text{RNH}_2]_t - [\text{RNH}_3^+]_t
\]

The concentrations of different species have been plotted as a function of time (Figure 4.25). After 9 h of CO\(_2\) absorption, the concentration of MEA keeps dropping from 4.9 M to 0.7 M while there is a considerable amount of protonated MEA produced with a
concentration of 2.0 M. The concentration of carbonate presents in the solution is 0.06 M while the concentration of carbamate reaches 2.1 M. The evolution of carbamate shows a linear increase with a reaction rate of 0.0061 mol/L min in the first 300 min and slows down afterwards. The protonated MEA keeps growing with a steady rate of 0.0039 mol/L min. CO₂ absorption capacity or CO₂ loading, defined as moles of CO₂ absorbed per mole of amine in solution (mol CO₂/mol amine), can be calculated by the total amount of absorbed CO₂ in the form of carbonates and carbamates. When the experiment was completed at 9h, the CO₂ absorption capacity reached 0.44 mol CO₂/mol amine which approach to the theoretical upper limit of 0.5 mol CO₂/mol amine.

The problem of this method is that it could not be applied to 2.5 M MEA. The average value of ε = 0.015 was obtained for MEAH⁺, which is different from the ε = 0.012 in 30 wt% MEA. The as-calculated concentration change of carbamate in Figure 4.26 shows that it starts to decrease after 2h, which does not match the peak intensity change with the turning point at 3h in Figure 4.11.

Method three

According to the reaction path:

\[ 2RNH_2 + CO_2 \rightleftharpoons RNHCOO^- + RNH_3^+ \]

At low CO₂ loading (<0.5 mol CO₂/mol amine) when the carbamate-to-bicarbonate reversion is neglected because of the low reaction rate [37], the amount of protonated MEA and MEA carbamate should be the main reaction product with a 1:1 ratio and can be calculated from \[ [RNH_3^+]_t = [RNHCOO^-]_t = \frac{1}{2} ( [RNH_2]_0 - [RNH_2]_t ) \]. According to the peak intensity change in 30% MEA (Figure 4.8), the CO₂ absorption capacity does not
reach the theoretical upper limit of 0.5 mol CO₂/mol amine in 9 h. Therefore, the above relation is valid to quantify the species in 9 h and the concentration profile is plotted in Figure 4.27.

For 2.5 M MEA, the amount of protonated MEA and MEA carbamate should be the main reaction product with a 1:1 ratio before 3h and can be calculated from \([RNH₃^+]_t = [RNHCOO^-]_t = \frac{1}{2} ( [RNH₂]_0 - [RNH₂]_t )\). The average \(ε = 0.021\) of carbamate was obtained from the concentration and absorption before 3h and used to calculate the concentrations after 3h. And the concentrations of protonated MEA was calculated from \([RNH₃^+]_t = [RNH₂]_0 - [RNH₂]_t - [RNHCOO^-]_t\). As shown in Figure 4.28, the as-calculated concentrations profile matches well with the change of peak intensity in Figure 4.11, showing a turning point at 3h for carbamate concentration. The problem with this method is that the concentration of free MEA was 0.58 M at 1h, after which the FTIR reached its detection limit (~ 0.5M). The concentrations of free MEA were estimated to be 0.25 M at 2h and 0 M at 3h. This would affect the calculation of carbamate concentration from \([RNH₃^+]_t = [RNHCOO^-]_t = \frac{1}{2} ( [RNH₂]_0 - [RNH₂]_t )\).and further affect the calculation of average \(ε\). Although based on several assumptions, this method provides a reasonable representation for quantitative analysis.

4.3.8 Blended amines: MEA and piperazine (PZ)

The aqueous solution of blended MEA and PZ has been demonstrated to be a promising solvent for CO₂ capture. PZ has been shown to be an effective promoter in aqueous amine solutions due to its rapid formation of carbamates with CO₂.
The CO₂ absorption characteristics of an aqueous solution containing 5 wt% piperazine in the presence of 15% CO₂/6% O₂ was investigated by ATR-FTIR, and the spectrum is shown in Figure 4.29.

When CO₂ is added to aqueous PZ solutions, the main equilibria involved are [50]

\[
\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^-
\]
\[
\text{PZ} + \text{H}_3\text{O}^+ \leftrightarrow \text{PZH}^+ + \text{H}_2\text{O}
\]
\[
\text{CO}_2 + \text{PZ} + \text{H}_2\text{O} \rightleftharpoons \text{PZCOO}^- + \text{H}_3\text{O}^+
\]
\[
\text{CO}_2 + \text{PZCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{OOCPZCOO}^- + \text{H}_3\text{O}^+
\]

PZ is a diamine which can form both single and dicarbamate products. Given the chemical stability of carbamates formed from primary and secondary amines, hydrolysis does not occur at an industrially relevant rate. PZ forms a hydrolysis-resistant carbamate (PZCOO⁻), as well as a dicarbamate (OOCPZCOO⁻) [13].

The infrared peak assignments are summarized in Table 4.3 based on literature [13]. The carbamate (NCOO⁻) derivatives have been identified as giving rise to several strong bands, 1520 and 1426 cm⁻¹ are assigned to asymmetric and symmetric vibrations of the COO⁻ moiety respectively, and the N-C stretching vibration of the NCOO⁻ derivative in the 1300-1260 cm⁻¹ region (1289 and 1276 cm⁻¹). The protonated amine was found to generate a peak at 1473 cm⁻¹ and the bicarbonate species at 1342 cm⁻¹.

At low levels of absorbed CO₂ (<3h), the PZ/CO₂/H₂O system exhibits the COO⁻ (1432 cm⁻¹) and COO⁻ (1294 cm⁻¹) of the PZ-COO⁻ derivative. These peaks shift to 1426 and 1289 cm⁻¹, respectively, with increasing CO₂ absorption levels (>3h). It has been
reported that PZ can form the dicarbamate (‘OOC-PZ-COO’) at high CO₂ loadings [50].
The 1426 and 1289 cm⁻¹ bands are attributed to formation of ‘OOC-PZ-COO’.

As shown in Figure 4.30, when CO₂ is added to a fresh solution, the product is
piperazine carbamate. A near-linear relationship between relative peak height and time is
observed for the peak assigned to NH₂⁺ at 1473 cm⁻¹. At high levels of absorbed CO₂ (>3h)
the N-COO⁻ band at 1276 cm⁻¹ decreases correspondingly with a sharp increase in intensity
of the absorbance band at 1294 cm⁻¹ and a frequency shift to 1289 cm⁻¹, indicating the
reaction \( \text{CO}_2 + \text{PZCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{OOCPZCOO}^- + \text{H}_3\text{O}^+ \) took place. The rapid growth of
COO⁻ absorbance band at 1426 cm⁻¹ in the PZ system does not follow the trend observed
with the corresponding MEA system; that is, the depletion of carbamate bands with
concomitant increase in the bicarbonate band for high CO₂ loadings. The increase in
bicarbonate absorbance in the MEA system is attributable to hydrolysis of the initially
formed carbamate, which strongly suggests, consistent with the IR data presented herein,
that the PZ system forms a hydrolysis-resistant carbamate [13].

The infrared spectra of a blend of 5 wt% PZ and 2.5M MEA solution were measured
at 40°C in the presence of 15% CO₂/6% O₂ with a flow rate of 100 sccm. As shown in
Figure 4.31, the MEA carbamate peaks at 1568 cm⁻¹ and 1486 cm⁻¹ and PZ carbamate at
1426 and 1289 cm⁻¹ are observed. The carbonate peak at 1386 cm⁻¹ shifts to 1377 cm⁻¹ at
high CO₂ loadings, indicating the formation of bicarbonate.

The relative peak height at selected wavenumbers and the relative peak area at 955
cm⁻¹ are plotted against CO₂ exposure time (Figure 4.32) and allow further evaluation of
the reactivity of the blend with CO₂.
MEA was consumed rapidly and the 955 cm\(^{-1}\) peak completely disappeared after 3h. Correspondingly, the peak intensity of MEA carbamate at 1568 and 1486 cm\(^{-1}\) reached their maximum around 3h and started to drop after 3h, the peak intensity of carbonate at 1386 cm\(^{-1}\) reached its maximum around 3h, and peak intensity of protonated MEA at 1066 cm\(^{-1}\) keeps growing. A small shoulder at 1377 cm\(^{-1}\) is visible after 4h, which represents the C-O stretching of bicarbonate. The above trends indicate that the MEA carbamate decomposes to bicarbonate and amine by RNH\(_2\)COO\(^-\) + H\(_2\)O ⇌ RNH\(_2\) + HCO\(_3\)\(^-\) when CO\(_2\) absorption capacity reaches its theoretical upper limit around 3h. The pH of the solution keeps dropping due to the continuous flow of CO\(_2\) as discussed in 4.3.4, which also promotes the conversion of carbonate to bicarbonate.

Despite PZ being the minor constituent of the amine blend, the PZ COO\(^-\) band is prominent and shift from 1432 cm\(^{-1}\) to 1426 cm\(^{-1}\) after 3h, which indicates the change from single carbamate to dicarbamate. In addition, the PZ dicarbamate absorbance is seen to emerge at 1289 cm\(^{-1}\) after 3h when a high CO\(_2\) loading is reached, which is also generated by further reaction of PZ carbamate and CO\(_2\) through CO\(_2\) + PZCOO\(^-\) + H\(_2\)O ⇌ \(\cdot\)
OOC\(_2\)PZCOO\(^-\) + H\(_3\)O\(^+\).

In order to study the PZ effect on MEA, the relative peak intensity of free MEA, protonated MEA, MEA carbamate and carbonate is plotted over time with PZ and without PZ in Figure 4.33, respectively. The results demonstrate that the reaction rate of all reaction products and MEA consumption becomes slower when PZ is included. The amount of CO\(_2\) bubbled through the aqueous amine solution is fixed in a certain time period resulting in a constant dissolved concentration, and it would react with both MEA and PZ at the same
time as observed in the infrared spectrum in Figure 4.31. Thus the amount of CO$_2$ that could react with MEA is smaller when PZ is blended and this reduces the extent of CO$_2$/MEA reaction. There is no promotion effect on absorption rate by MEA that is caused by PZ. However, adding PZ enhances the CO$_2$ absorption capacity by increasing amine content in the MEA/PZ blend, as evidenced by an increase of the initial relative peak area of 955 cm$^{-1}$ band (C-N-H out-of-plane wagging) in Figure 4.33(c).

4.3.9 SO$_2$ effect on CO$_2$ capture functioning amine membrane

Other than the conventional chemical absorption using aqueous amine solution, there is also the possibility of using membranes to separate CO$_2$ from flue gas. Extensive studies have been done on the CO$_2$ facilitated transport membranes [51, 52]. In the facilitated transport membranes, there is a reversible reaction between CO$_2$ and a reactive carrier which usually contains an amino group. Fixed carriers (amine-containing polymers) and mobile carriers (amine-containing small molecules) are two major categories of carriers for CO$_2$ transport in facilitated transport membranes. In the facilitated transport membranes, CO$_2$ molecules react with amine carriers by the reaction CO$_2$ + R-NH$_2$ + H$_2$O $\rightleftharpoons$ R-NH$_3^+$ + HCO$_3^-$, and then the reaction products transport across the membrane, releasing the CO$_2$ molecules to the permeate side of the membrane. By this mechanism, the transport of CO$_2$ molecules through the membrane is greatly enhanced. On the other hand, the non-reactive N$_2$ molecules transport through the membrane only by the solution–diffusion mechanism. Therefore, CO$_2$ transport gets facilitated, and a high CO$_2$/N$_2$ selectivity can be achieved through the facilitated transport mechanism.
A novel CO$_2$-selective polymeric membrane that contained polymer Lupamine as a fixed carrier and potassium glycinate as a mobile carrier was prepared by Dr. Winston Ho’s group at the Department of Chemical Engineering.

Lupamine is a linear high molecular weight polyvinylamine:

\[
\text{CH}_2\text{CH-CH}_2\text{-CH-CH}_2\text{-CH-CH}_2\text{-CH-}\overbrace{\text{NH}_2\text{-NH}_2\text{-NH}_2\text{-NH}_2}\text{x}
\]

Potassium glycinate (GK) is an amino acid salt:

\[
\text{K}^+ \cdot \text{NH}_2\text{CH}_2\text{COO}^-
\]

The membrane showed good CO$_2$ permeability and CO$_2$/N$_2$ selectivity as shown in Figure 4.34. However, the membrane performance was degraded by introducing 5 ppm SO$_2$ (Figure 4.35). Both CO$_2$ permeance and CO$_2$/N$_2$ selectivity were reduced significantly in the presence of SO$_2$.

In order to understand interaction of SO$_2$ with amine membranes and correlate the membrane performance/degradation in the presence of SO$_2$, the strategy is to investigate the reactivity of the membrane with SO$_2$ and then the reactivity of each component by FTIR.

The infrared spectrum of the amine membrane before and after 5 ppm SO$_2$ treatment was recorded by ATR FTIR. As shown in Figure 4.36, a wide band between 1010 and 960 cm$^{-1}$ and a weak peak at 1520 cm$^{-1}$ appeared after SO$_2$ treatment, which can be assigned to the symmetric S-O stretching of sulfite (SO$_3^{2-}$) and NH$_3$ bending of protonated amine (NH$_3^+$).
The amine carrier of the membrane was studied separately by in-situ transmission FTIR. About 50 mg of amine carrier was placed on the KBr window and dried in flowing Ar at 102 °C for 30 min. The adsorption of SO\textsubscript{2} was carried out by switching the inlet flow from the inert gas stream (Ar) to the adsorbing gas stream (45ppm SO\textsubscript{2} in N\textsubscript{2}) when the gas cell was heated to 102 °C. The gas stream was bubbled through hot water corresponding to 100% humidity during absorption. In-situ FTIR spectra were then recorded at 102 °C.

In the presence of SO\textsubscript{2}, Lupamine alone shows a strong peak at 961 cm\textsuperscript{-1} assigned to S-O stretch of sulfite and a weak peak at 1510 cm\textsuperscript{-1} assigned to NH\textsubscript{3} bending of protonated amine (Figure 4.37). GK alone shows two absorption bands at 1010 and 961 cm\textsuperscript{-1} (Figure 4.38), which are attributed to the asymmetric and symmetric S-O stretching of sulfite. The protonated amine appears at 1505 cm\textsuperscript{-1} for GK.

Based on the infrared results, SO\textsubscript{2} reacts with water to form sulfite and release protons to get amine protonated through the reaction:

\[
\text{SO}_2 + 2\text{RNH}_2 + \text{H}_2\text{O} \rightarrow 2\text{RNH}_3^+ + \text{SO}_3^{2-}
\]

Sulfite salt, which is reported as a heat stable salt, accumulated on the membrane and degraded the membrane performance.

Heterogeneous reactions involve more than one phase (e.g., gas-liquid, gas-solid) and interaction between physical and chemical processes. The overall reaction rate is subject to the influence of parameters that affect both processes, such as interfacial surface area, mass transfer factors and patterns of phase contact [53]. For the reaction between aqueous amine solution (MEA) and SO\textsubscript{2}, it took several days to generate a weak peak at 936 cm\textsuperscript{-1} which is assigned to the vibrational mode \(\nu_1\) of aqueous sulfite [42], as discussed in section
4.3.3. However, solid-state amines (Lupamine, GK) that reacted with humidified SO\textsubscript{2} within hours and produced a strong peak at 961 cm\textsuperscript{-1}, which is assigned to the surface sulfite ion [41]. Therefore, the infrared peak of sulfite generated from the SO\textsubscript{2} absorption in amine depends on the amount of water in the system. The concentration of sulfite generated on the solid amine surface is much higher than that generated in the aqueous amine solution, which leads to stronger peak intensity according to Beer’s law.

4.4 Conclusions

In this chapter, a technique based on HATR FTIR has been developed for facile monitoring aqueous MEA solution and qualitative analysis of the speciation during CO\textsubscript{2} absorption. The effect of 151 ppm SO\textsubscript{2} on 15% CO\textsubscript{2} absorption is not significant at low temperature and short exposure time. SO\textsubscript{2} induced-pH change is not interfering in the equilibriums of amine, as evidenced by the cyclic experiments that show the regeneration of MEA is comparable to that with CO\textsubscript{2}. The speciation of MEA/PZ blends demonstrate the CO\textsubscript{2} absorption characteristics of PZ, giving insights of the structure–activity relationship of the reaction between PZ and CO\textsubscript{2}. Example of a practical application of using IR spectroscopy is demonstrated by explaining the SO\textsubscript{2} effect on the amine membrane performance. Since developing new solvent systems for CO\textsubscript{2} capture includes the finding of an ideal compromise between the energy requirements and reaction rates, such attempts will be strongly supported by the fundamental spectroscopic investigation. As such, there is a continuing need for understanding, and ultimately improving the performance by providing detailed predictions of the equilibria and the kinetics relevant to
post combustion capture of CO₂. Incorporating real time monitoring and mathematical modeling of the reaction mechanism will grant researchers easy intuitive and integrated access to information that is currently obscure. Therefore, FTIR can be considered either as a highly efficient tool for the improvement of both thermodynamic and kinetic models or a technique for monitoring gas absorption by amines.
References


### Figures & Tables

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<td>C-NH(_2) (MEA)</td>
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Table 4.1. Infrared Peak Assignments for CO\(_2\)-Loaded MEA Solution
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<th>[AmH(^+)] (mol/L)</th>
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Table 4.2. pH-dependent Amine Protonation Equilibria. ([Am]\text{TOTAL} = [Am] + [AmH\(^+\)] = 4.91 M)
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Table 4.3. Infrared Peak Assignments for CO\(_2\)-loaded PZ Solution
Figure 4.1. The amine scrubbing process invented by Bottoms in 1930 [1, 47].
Methyl diethanolamine (MDEA)

\[ \text{HO} \quad \text{N} \quad \text{OH} \]

Piperazine (PZ)

\[
\text{H} \\
\text{N} \\
\text{H} \\
\text{N} \\
\text{H}
\]

Monoethanolamine (MEA)

\[ \text{H}_2\text{N} \quad \text{OH} \]

2-Amino-2-methyl-1-propanol (AMP)

\[ \text{HO} \quad \text{C} \quad \text{NH}_2 \\
\text{CH}_3 \\
\text{H}_3\text{C} \]

Figure 4.2. Molecular structure of relevant amines.
Figure 4.3. Graphical representation of a single reflection ATR.
Figure 4.4. Schematic of CO₂ absorption apparatus.
Figure 4.5. In-compartment HATR accessory for liquid samples.
Figure 4.6. Schematic of the HATR trough plate.
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Figure 4.17. Comparison of relative peak intensities of 30 wt% MEA in 15% CO$_2$ / 6% O$_2$ at 57°C with or without 151 ppm SO$_2$ for (a) carbonate at 1386 cm$^{-1}$, (b) carbamate at 1322 cm$^{-1}$, (c) MEAH$^+$ at 1066 cm$^{-1}$, (d) MEA at 1362 cm$^{-1}$.
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Figure 4.21. Cyclic experiments for 2.5M MEA in the presence of 151 ppm SO₂ / 15% CO₂ / 6% O₂ at 40°C.
Figure 4.22. Regeneration efficiency for 2.5M MEA in the cyclic experiment with or without SO₂ at 40°C.
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Figure 4.36. Comparison of ATR infrared spectrum of an amine membrane before and after 5 ppm SO$_2$ treatment at 102°C.
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Chapter 5: Rapid Crystallization of Chabazite Zeolites and Synthesis of Chabazite/Polymer Composite Membrane for CO₂/N₂ Separation

5.1 Introduction

There is a substantial focus on reducing CO₂ emissions into the atmosphere, due to environmental effect of CO₂ on global warming. Postcombustion capture involves the separation of CO₂ from the flue gas coming from the combustion of fossil fuels. This technology involves CO₂ separation at a relatively low temperature, from a gaseous stream at atmospheric pressure and with low CO₂ concentration [1, 2].

Established technologies for CO₂ capture include solvent absorption, chemical and physical adsorption, and membranes processes. Amine absorption is today’s best available technology for postcombustion capture, based predominantly on primary alkanolamine [3]. As an environmentally friendly alternative to conventional amine-based absorption processes, membrane-based CO₂ separations have been studied with the overarching goal toward the realization of energy-efficient CO₂ separations on a large scale [4]. Along with polymer membranes, porous zeolite membranes are also promising to separate CO₂ from N₂ in post-combustion or CH₄ in natural gas upgrading [5]. The use of ionic liquid [6, 7], polymer [8, 9], and metal-organic frameworks [10, 11] has also been widely investigated to develop energy-efficient CO₂ capture processes.

In the last four decades, zeolite membranes have been extensively studied with new preparation techniques and separation features. Zeolites have higher thermal and chemical
resistance as compared to polymer membranes. Zeolite membranes, in principle, can separate gas mixtures on the basis of differences in the molecular size and shape \cite{12}, as well as on the basis of different adsorption properties \cite{13}.

Many types of zeolite membrane have been studied (e.g., MFI, LTA, MOR, FAU). The first commercial application is that of LTA zeolite membranes for solvent dehydration by pervaporation \cite{14}, in particular separating water from ethanol. There are no industrial applications reported for zeolite membranes in gas separation \cite{15}. The reasons for this limited application in industry is due to economic feasibility. The cost of a zeolite membrane module is estimated to be $5,000-$10,000/m$^2$. Development of higher flux membranes should reduce costs of membranes. In case of zeolites, the reproducibility of membrane fabrication has to be significantly improved.

So far, zeolite Y membranes with various Si/Al ratios have been synthesized and tested for the separation of CO$_2$ from gas streams \cite{16}. A promising rapid crystallization synthesis procedure of zeolite Y membranes with fewer defects have been developed with potential for scale-up \cite{17}. This procedure is sufficiently general and provides the opportunity to be extended to other framework structures.

Chabazite (CHA) is an important zeolite and has potential for the capture and removal of CO$_2$ from gas mixtures. The composite building-units of chabazite are the double 6-membered ring (D6R) and one large ellipsoidal cavity (7.3 Å × 12 Å) accessible by six 8-membered ring windows (free aperture ∼ 3.8 Å) (Figure 5.1). The pores of chabazite zeolite have dimensions of 0.38 × 0.38 nm.
If all molecules of the mixture have access to the internal surface of the porous adsorbents, then adsorption selectivity is based on differences in intermolecular interactions between these molecules and the surface. CO₂ is usually preferentially adsorbed over N₂ since it has stronger intermolecular interactions with polar surfaces. Two molecular parameters that are important for physisorption of CO₂ and N₂ are the quadrupole moment and polarizability. CO₂ has a higher quadrupole moment and polarizability (-1.4 x 10⁻³⁹ cm² and 29 x 10⁻²⁵ cm⁻³) compared with N₂ (-4.7 x 10⁻⁴⁰ cm² and 17.4 x 10⁻²⁵ cm⁻³) [10, 18].

An alternative separation mechanism relies on a steric mechanism (or molecular sieving). In this case, slightly larger molecules, such as N₂, can be excluded, whereas smaller molecules, such as CO₂, are transported through the zeolite, resulting in high selectivity even at high pressures. This separation mechanism requires that the material has a pore aperture diameter (d) between the molecular diameters of the components in a targeted gas mixture. For the exclusive uptake of CO₂ (kinetic diameter = 0.33 nm) from N₂ (kinetic diameter = 0.364 nm) as remaining components, a molecular sieve with pore aperture diameter of 0.33 < d < 0.364 nm is mandatory. Accordingly, the pore size of CHA zeolites (0.38 nm) is still slightly larger than the size of N₂.

A different separation mechanism occurring in some small-pore zeolites has been reported. In this “molecular trapdoor” mechanism [19], molecular size is not the dominant parameter. Rather, cations that are present in the pore apertures of these zeolites play a role in controlling the entry of molecule to the supercages. Molecules are admitted to the supercage of the zeolite based on their ability to coordinate with the cation blocking the
access, as well as moving the cation temporarily away from the pore aperture. Only “strong” molecules, such as CO$_2$, are able to pay the energy toll to move the “door-keeping” cations (such as K$^+$) temporarily and thus gain admittance to the zeolite supercage, whereas “weak” molecules, such as N$_2$, are excluded. Therefore, a high selectivity and acceptable capacity of CO$_2$ can be achieved by the “molecular trapdoor” effect. Zeolites, such as chabazites can separate gases in this manner.

It has been be reported that K$^+$–CHA has significantly lower BET area compared to the other cation-exchanged CHA [20]. The lower specific surface area could be due to pore blockage effects which resulted in limited uptake of N$_2$. Due to the large K$^+$ size (r = 0.133 nm), it was suggested that K$^+$ resides primary at the 8-ring window. Having this position in the CHA structure, K$^+$ can make N$_2$ inaccessible due to the steric hindrance.

The framework Si/Al atomic ratio of CHA-type zeolites can be finely tuned. Low-silica (chabazite) [21], high-silica (SSZ-13) [22] and all-silica (Si-CHA) [23] CHA zeolites that belongs to CHA type molecular architecture has attracted attention for separation applications. Hydrophobic CHA membranes, which are expected to alleviate the undesired effect of H$_2$O on CO$_2$ transport [24], are good candidates for CO$_2$ separations in the presence of H$_2$O.

It has been previously reported that among many kinds of naturally occurring and synthetic zeolites, chabazite (CHA) and 13X (FAU) are most suitable for CO$_2$ separation by pressure swing adsorption techniques [25]. In another study covering adsorption-based CO$_2$ capture [26], it was found that NaCHA and CaCHA held comparative advantages for high temperature CO$_2$ separation while NaX zeolites showed superior performance at
relatively low temperatures. Therefore, the CHA zeolite membrane is of interest to us for evaluation of its CO$_2$ separation behavior. The permeation selectivity of CO$_2$ over N$_2$ in CHA zeolite membranes is estimated to be as high as $\sim$20–30, indicating that CHA zeolites can serve as membrane materials for continuous CO$_2$ separations [27-29].

There is only limited literature involved in chabazite membrane preparation, and that too, only focusing on the application of pervaporation. Hasegawa et al. [30, 31] prepared chabazite membranes in a synthesis gel containing strontium cation, which worked as a pseudo-template for crystal growth of the CHA-type zeolite. The best membranes always contained a few merlinoite-type crystals. Li et al. [32] reported that chabazite membrane was synthesized in the presence of only potassium cation. The seeds for secondary growth of these membranes were all prepared by the conversion of Y-type crystal, in which all silica and alumina sources came from crystalline zeolite HY powder [30, 32-35]. It is the standard way for the preparation of chabazite crystals [36]. CHA seeds were prepared from template-free aluminosilicate gel with the addition of nano-sized zeolite T ($\sim$100 nm) [33]. Different substrates have been applied for the growth of CHA membranes, such as mullite [32], porous $\alpha$-Al$_2$O$_3$ [30, 34, 35], stainless steel [33]. These supports are expensive, mechanically rigid and difficult to fabricate in large-scale production. An alternative is using polymer supports, which if successful, can use all of the advances in polymer membrane fabrication to lower cost. However, a major technical hurdle is the long time it takes to synthesize zeolites, which is incompatible with polymer membrane manufacturing methods. A second issue is that inter-particle defects appear during the zeolite growth process, no matter what the support, which leads to low performance reproducibility [37].
These two issues have been addressed in this chapter by providing strategies to accelerate zeolite crystallization and fabricate continuous zeolite membrane. To the best of our knowledge, growing CHA membrane on polymer support and demonstrating its viability for CO₂/N₂ separation has not yet been reported. In present study, we report synthesis of chabazite nanoparticles and evaluate the rapid synthesis of chabazite, followed by chabazite/polymer composite membrane fabrication. Structural characteristics of this membrane were evaluated. Transport properties of these membranes for CO₂/N₂ separation were explored. The optimum conditions of growing CHA membrane were investigated.

5.2 Experimental

5.2.1 Synthesis of zeolite Y nanoparticles

40 nm zeolite Y was prepared with the molar composition 0.048 Na₂O; 1 Al₂O₃; 4.35 SiO₂; 249 H₂O; 2.40 (TMA)₂O(2OH); 1.2 (TMA)₂O(2Br) based on a reported procedure [38]. First, aqueous 30 wt% colloidal silica (Ludox SM-30, Sigma-Aldrich) was ion exchanged with acidic cation exchange resin (Dowex Marathon C hydrogen form) until pH=8, and then mixed with appropriate amounts of 25 wt% aqueous tetramethylammonium hydroxide solution (TMAOH, SACHEM) as solution A. Solution B containing distilled water, 25 wt% aqueous tetramethylammonium hydroxide solution, (TMAOH, SACHEM), and aluminum isopropoxide (97 wt%, Sigma-Aldrich), was stirred vigorously at 70 °C until the solution became clear. TMABr (98 wt%, Sigma-Aldrich) was then added to the solution B and stirred until completely dissolved. Solution A was then mixed with solution B, and the bottle was sealed tightly and aged for 3 days at room
temperature with vigorous stirring. The aged gel was heated with stirring in an oil bath at 100 °C for 4 days. The product was dialyzed in distilled water and washed by centrifugation until pH neutral; then decanting, and redispersion in distilled water with ultrasonication.

5.2.2 Synthesis of chabazite nanoparticles

The CHA seeds for secondary growth has been prepared by the inter-zeolitic conversion of zeolite Y. 40 nm zeolite Y was dispersed in 100 mL 0.1 mol/L acetic acid at room temperature with stirring overnight to acquire H-form zeolite Y. The ion-exchanged sample was washed by centrifugation five times in DI water. Potassium chabazite was synthesized following the reported procedure [39] with a modified composition. Typically, 1 g H-form nanocrystalline zeolite Y was added to 39.64 g DI water and 5.36 mL 45 wt% KOH solution. The molar composition of the prepared gel was 0.048 Na₂O; 8.4 K₂O; 1 Al₂O₃; 4.35 SiO₂; 593.6 H₂O. The mixture was aged 24h at room temperature and heated under reflux for 3 days. The product was centrifuged, washed by DI water, and ultrasonicated.

5.2.3 Rapid synthesis of CHA gel

The desired gel composition was SiO₂ : 0.19 Al₂O₃ : 0.39 K₂O : 0.06 SrO : 40 H₂O on a molar basis. In a typical synthesis, Ludox HS-30, potassium hydroxide pellets, strontium nitrate, aluminum isopropoxide, and distilled water were sequentially mixed with intense stirring and maintained at room temperature for 24h. The aged gel was transferred to a round bottom flask connected to a graduated pressure equalizing addition funnel topped
with a condenser (Figure 5.2). The initial gel was heated under reflux for 1h, with only the reflux part of the apparatus (temperature of reflux was 100-103 °C). Then over a period of 30 min, about 30 mL water was removed from the reaction system under reflux by condensation in the addition funnel (about half the volume of water in the flask), and the reflux continued. After 2h of this concentrated state, the collected water was then re-added back dropwise from the funnel to the concentrated gel over a period of 30 min, after which the gel was allowed to react under reflux without any further change.

As a complementary strategy to the conventional sol-gel method, CHA-type zeolite gel was also prepared by the inter-zeolitic conversion method. With a gel composition of 0.17 Na₂O : 2.0 K₂O : Al₂O₃ : 5.18 SiO₂ : 224 H₂O, a typical procedure involved addition of zeolite HY powder (CBV 400, Zeolyst) to distilled water and KOH solution. Adapting the original rapid synthesis method, the initial gel was heated under reflux for 1h after 24h aging at room temperature. Then over a period of 30 min, about half the volume of water was removed from the reaction system. After 2h of reaction in this concentrated state, the collected water was added back to the flask in 30 min and the reaction was continued in reflux.

Samples were removed at various times during the synthesis process. Once removed, samples were immediately cooled in an ice bath for 1h followed by 30 min of centrifugation at 2500 rpm. The pellets were lyophilized and stored under vacuum (50 mTorr) until analyzed.
5.2.4 Chabazite/polymer composite membrane synthesis

Nanocrystalline zeolite seed layer on PES support was prepared by vacuum dip-coating. The seeded support was placed in a sample holder and introduced into the reactor after dehydration. Then water was added back and the synthesis was continued under reflux. After washing by distilled water and drying at room temperature in air, the as-synthesized membrane was spin coated with 5 wt% polydimethylsiloxane (PDMS) monomer solution. PDMS monomer solution was prepared by adding PDMS monomer, crosslinker and catalyst in the ratio of 100:1:0.5 to heptane. For spin coating of PDMS onto a zeolite membrane, the membrane was first taped on the flat plate of the spin coater and PDMS monomer dispersion was added to cover the whole membrane. Spinning process consisted of 2000 rpm spin for 5 s and then 4000 rpm spin for 1 min. After spin coating, the membranes were kept at room temperature overnight for crosslinking of the PDMS.

5.2.5 Characterization

The phase and crystallinity of the zeolites were analyzed by a Bruker D8 Advance X-ray diffractometer. The surface morphology was investigated by a FEI Nova 400 NanoSEM scanning electron microscope. Transmission electron micrographs were collected using a FEI Tecnai G2 Biotwin TEM. The particle size was measured by Dynamic light scattering (DLS) on a Malvern Zetasizer.

A gas separation setup was constructed for CO$_2$/N$_2$ separation. The synthesized composite membrane was loaded into a stainless steel rectangular permeation cell inside a
temperature-controlled oven with an effective membrane area of 3.4 cm². Feed gas and
sweep gas compositions were controlled with a flow box and mass flow controllers from
SIERRA Instruments Inc. A countercurrent flow configuration with a dry feed gas flow
rate of 80 sccm and a dry sweep gas flow rate of 50 sccm was applied to offer the maximum
driving force across the membrane. The binary gas mixture containing 20% CO₂ and 80%
N₂ was used as the feed gas, while argon was used as the sweep gas. The testing
temperature was set to be 25 °C. The testing pressures were 20 psig for the feed side and
20 psig for the sweep side, respectively. The outlet gas compositions of both retentate and
permeate streams were analyzed by a SRI 310C gas chromatograph equipped with a Hysep
D column and TCD detector. From the GC analysis, CO₂ permeance and CO₂/N₂ selectivity
were calculated to characterize the membrane transport performance.

Permeance was calculated from the following equation:

\[ \text{Permeance} = \frac{\text{mole of gas transferred per unit time}}{(\text{membrane area})(\text{partial pressure difference})} \]

And selectivity of CO₂ to N₂ was defined by the ratio of permeances.

The common unit of permeance is the gas permeation unit (GPU), 1 GPU = 3.35 ×
10⁻¹⁰ mol/(m²·s·Pa).

5.3 Results and Discussion

The following sections discussed the synthetic strategy of CHA zeolite/polymer
composite membranes for CO₂/N₂ separation in detail:

- Synthesis of nanocrystalline CHA zeolite seeds for polymer support
- Rapid synthesis of CHA powders
• Synthesis of CHA membranes using nanocrystalline CHA zeolite seeds and the rapid method

• Transport properties of CHA membranes coated with PDMS

5.3.1 CHA synthetic strategy: interzeolite conversion

CHA-type aluminosilicate zeolite can be directly synthesized from an amorphous aluminosilicate gel by using N,N,N-trimethyl-1-adamantammonium hydroxide (TMAda⁺) as an organic structure directing agent (OSDA) [36]. However, from the viewpoint of the development of simple, economical and environmentally benign processes for zeolite synthesis, the method for the OSDA free synthesis of the zeolite has been highly desirable. Interzeolite conversion by the hydrothermal conversion of one zeolite into another has been investigated, attracting significant attention as an alternative strategy for zeolite synthesis [40]. By using FAU type zeolite as the starting material, in the presence of various OSDAs, different types of zeolites have been produced—BEA [41], RUT [42], LEV [43] and CHA [44]. The use of FAU-type zeolite as a starting material for the preparation of other zeolites result in a crystallization rate that is superior to that achieved in the conventional synthesis using amorphous aluminosilicate gel as the starting material. This enhanced crystallization rate arises because the decomposition/dissolution of the starting zeolite generates locally ordered aluminosilicate species (nanoparts) that assemble and evolve into another type of zeolite.

Since D6R is the common composite building unit for FAU and CHA framework, it is possible to synthesize CHA-type zeolite without the use of both OSDAs and seed crystals,
if the starting FAU-type zeolite is decomposed/dissolved into locally ordered aluminosilicate species (nanoparts) whose chemical structures are suitable for the crystallization of CHA-type zeolite. This process would just involve reassembly of the nanoparticles.

In the synthesis of most zeolites, an amorphous phase is converted into a given type of zeolite by the solution-mediated transformation process [45]. Because zeolites are metastable, a sequence from the amorphous phase through a less stable zeolite to the most stable zeolite is often observed. The transformation to the most stable zeolite is thermodynamically driven, final phase selection is controlled by the interplay of nucleation, growth and phase transformation kinetics. Theoretical calculations and calorimetric measurements have suggested that the stability of zeolites decreases as their porosity increases, that is, as the zeolite framework density decreases [46, 47]. The interzeolite conversion method is applied to the OSDA-free, seed-crystal-free synthesis of CHA-type zeolite with a framework density (FD) of 15.1 T/1000 Å³ from FAU-type zeolite with a FD of 13.3 T/1000 Å³. That is, CHA-type zeolite is transformed from less dense FAU-type zeolite. Taking into consideration that thermodynamic stability of zeolite decreases with decreasing framework density, transformation to thermodynamically stable CHA-type zeolite from thermodynamically less stable FAU-type zeolite is possible from the thermodynamic standpoint.
5.3.2 Synthesis of nanocrystalline CHA zeolite

Different methods for the controlled preparation of supported zeolite membranes have been established [48]. Basically, they can be distinguished into one-step method and secondary growth (seeding techniques) method. The latter, decoupling zeolite nucleation from crystal growth, allows optimizing the conditions of each step independently, reducing or suppressing any secondary nucleation [49]. Seeding, the first step, consists in the deposition of the crystal seeds on the surface of a support, followed by a crystal growth by means of a hydrothermal treatment. In the template-free synthesis of zeolites, seed crystals strongly affect the nucleation and crystallization processes. In order to be compatible with the mesoporous polymer support, it is vital to make appropriate nano-sized zeolite CHA seeds. As shown in Figure 5.14(a), the pore size of bare PES support is around 80-90 nm. The average size of CHA seeds must be smaller than 80 nm so that they can be loaded within the pores of the support.

There are limited reports of synthesis of nano-size CHA crystals. Pure CHA-type aluminosilicate zeolite with high crystallinity has been synthesized from an amorphous aluminosilicate gel with the addition of sodium-type Al-containing SSZ-13 ([Al]-SSZ-13) as seed crystals, and resulted in the formation of agglomerates of 70-150 nm roundish cubic crystals [50]. The CHA crystals prepared by interzeolite conversion of 100 nm zeolite T displayed a 2-4 μm walnut shape composite with hundreds of sub-micrometer crystals with good self-assembly [33]. These reported CHA seed crystals are formed by agglomeration of sub-micron crystals, which would be too large to be deposited into the pores of the polymer substrate, and cannot be used for the present application.
In present study, zeolite Y nanocrystals were used as a precursor for chabazite. The XRD pattern of crystals showed the presence of pure-phase faujasite (Figure 5.3). Based on the morphology shown in the TEM image (Figure 5.4), the size of the zeolite Y nanoparticles were between 20 and 30 nm, and showed well-formed nanocrystals with the lattice spacing of 14 Å attributed to the (111) planes of the FAU structure. The particle size distribution obtained from DLS analysis is shown in Figure 5.5, indicating the suspension contains particles with a distribution ranging from 15 to 90 nm. The average particle size is 38 nm, which is in a good agreement with the TEM observations.

Taking advantage of the isolated 40 nm zeolite Y nanoparticles, nano-sized CHA crystals were successfully prepared by interzeolite conversion for the first time. XRD patterns were collected from the dried powder sample and consistent with the CHA-type structure (Figure 5.6). Figure 5.7 shows the SEM image of the CHA nanoparticles and the crystal size was around 90 nm. DLS analysis was employed to evaluate the particle size in the colloidal crystalline suspensions. A drop of the colloidal suspensions was diluted with distilled water and subjected to analysis. The result shows the size distribution from 40 to 180 nm with an average particle size of 90 nm (Figure 5.8). The particle size distribution in the nano-size range indicates there is no large particles formed by agglomeration and the suspension consists of isolated nanoparticles.

However, the average size of the 90 nm CHA seed is still larger than the PES pore size of 80-90 nm (Figure 5.14(a)), which makes it difficult to load into PES pores and thus incompatible with the secondary growth of membrane. Since the synthesized CHA
nanoparticles could not be used directly as seeds, an alternate strategy as described in section 5.3.4 was developed for seed loading.

5.3.3 Speeding up synthesis of chabazite powders

Since the polymer support is introduced into hydrothermal reactor under reflux, the synthesis should be complete as quickly as possible regarding the endurance of polymer. The strategy is to investigate possible ways of speeding up the synthesis of chabazite powders first, then adapt the method to chabazite membrane.

There are various established methods of synthesizing chabazite zeolites based on interzeolite conversion or from amorphous aluminosilicate gel (Table 5.1), the reactants are normally heated to 95-170 °C for periods of time extending from 16 h to 120 h.

Based on our experimental results, the conventional hydrothermal synthesis process under reflux took no less than 48 h for the inter-zeolitic conversion method and the sol-gel method to obtain crystalline chabazite (Figure 5.9). The gel was refluxed for several days. Samples were collected at various times during the synthesis process. As demonstrated by the XRD patterns shown in Figure 5.9, the zeolite Y peaks completely disappeared after 24 h and some weak CHA peaks started to appear. There was no sign of the (100) peak at $2\theta=9.4$ degree before 48 h for the HY gel or before 52 h for the aluminosilicate gel. The first evidence of the (100) peak was observed after 72 h of heating without dehydration for the HY gel and 52 h for the aluminosilicate gel.

Zeolite crystallization has a slow induction period, followed by rapid crystallization. Several strategies have been reported for influencing and manipulating the nucleation and
growth characteristics of zeolites including compositional control, seeding, altered heating profile, multiple heating stages, and microwave radiation [52-55]. Our group has reported a zeolite growth process by manipulating the supersaturation via a dehydration-rehydration hydrothermal (DRHT) process. The gel after dehydration is heavily nucleated, and upon readdition of the water (under reflux condition), high quality faujasite crystals are formed within an hour [17]. This procedure is sufficiently general and provides the opportunities to be extended to other zeolite framework structures.

By adapting the DRHT strategy, an aged gel was put through three stages in a reflux apparatus. During stage I, half of the water was removed during reflux over the period of 30 min, and in stage II, the concentrated gel was kept in reflux for 2h, and in stage III, water was added back during the course of 30 min.

With the readdition of H₂O back to the concentrated gel, a diffraction pattern showing the (100) peak at 2θ=9.4 that is consistent with CHA type zeolite is first observed after 10 hours for the sol-gel method (Figure 5.10) and 6 hours for the inter-zeolitic conversion method (Figure 5.11), which are both significant improvements in time required for synthesis. The XRD pattern continues to develop with time, and the peaks increase in intensity until reaching completion.

The comparison of the crystallization process of CHA powders between the rapid method and the conventional synthesis is demonstrated in Figure 5.12. The relative peak intensity of the (100) peak at 2θ=9.4 is plotted as a function of time. To reach the same peak intensity in the HY gel, the conventional method took 72 h while the rapid process took about 12 h. In the case of aluminosilicate gel, the conventional method took 72 h while
the rapid process took about 17 h. Therefore, the crystallization of zeolite speeded up by a factor of 4-6 as compared to a conventional hydrothermal synthesis using the same composition. The initial dehydration leads to extensive nucleation, maintaining the concentrated state enhances the nucleation, and controlled re-addition of water leads to an overall dramatic increase in the rate of crystal growth.

5.3.4 Synthesis of chabazite membrane on polymer support

The rapid DRHT synthesis procedures was adapted for promoting membrane formation. The concentrated gel left behind in the flask is amorphous, but extensively nucleated. This gel was used as a reactant for membrane formation. Upon readdition of the water, high quality chabazite crystals start to form on the PES support. In order to grow a continuous zeolite layer, there were different synthesis strategies and experimental conditions for optimizing membrane growth.

The CHA gel for membrane growth was synthesized from HY-derived gel by interzeolite conversion. The 40 nm zeolite Y nanoparticles were ion-exchanged with weak acid to make H-form zeolite Y, which can be loaded into the PES pores (80-90 nm) directly as seeds and converted to chabazite along with the HY gel during hydrothermal synthesis. This strategy incorporates the seed conversion procedure into the gel conversion process during the membrane synthesis, which is feasible for the secondary growth of membrane.

The synthetic method involved 0.5 wt% of H-form zeolite Y nanocrystals as seeds and deposited on polyethersulfone (PES) with 80-90 nm pore size, which was used as the support. The coating of the seed on the PES support was carried out by applying vacuum
on the back side of the PES support. With 2h of reflux after removing 30 mL water, the concentrated gel was used as the starting reactant and the seeded support was introduced into the gel by interrupting the reaction. The reaction continued by dripping the water back under reflux conditions for 30 min and heated for another 44h, after which the sample was withdrawn, washed by distilled water and dried in air.

Figure 5.13 exhibits the characteristics peaks of chabazite in the XRD patterns of membrane and gel, both showing the presence of the (100) peak at $2\theta=9.4$ for the pure-phase CHA zeolites. Figure 5.14 displays the top view SEM images of bare PES support and the CHA membrane. A continuous CHA layer involving lots of well-intergrown crystallites with a characteristic geometry is formed, where prismatic edges of columnar crystals coexist with chain-shaped microcrystals. From the cross-section SEM images revealed in Figure 5.15, there exists a dense skin layer on the PES support with an apparent thickness of 4 $\mu$m, which is comparable with the reported CHA membrane prepared at 100 $^\circ$C with a thickness lower than 10 $\mu$m [32].

For the CHA membrane made from 0.5 wt% seed, the PES was dissolved by N-methylpyrrolidone, leaving behind a powder-like white film. Figure 5.16a is a top-view SEM image of the film, which on a closer inspection (Figure 5.16b) is a collection of crystals with the same geometrical features as the original zeolite membrane. There are no cracks in this film, indicating the backbone is strongly supported by the crystals present within the PES. A network of submicron zeolite crystals has grown through the entire PES network that is acting as the template, with a three-dimensional interconnectivity between
the zeolite crystallites. Therefore, there is growth within the porous support, arising from
the penetration of nano HY seeds and subsequent growth.

The effects of a variety of synthetic parameters on the formation of CHA membranes
are investigated in detail.

5.3.4.1 Optimization of nano zeolite seed loading

Nano zeolite HY dispersions with concentrations of 0.05 and 0.5 wt% were
investigated to coat the PES. XRD of as synthesized membranes with HY gel are shown in
Figure 5.17. The membrane support is made up of a 100 μm PES layer on a thicker
nonwoven fabric support. X-ray diffraction shows that the PES layer is amorphous, but the
backing gives rise to a crystalline structure, as marked in Figure 5.17. The CHA patterns
could be observed on both cases. However, the SEM images in Figure 5.18 reveals that
membrane formation is incomplete by using 0.05 wt% seed. Isolated crystals were
dispersed randomly on the PES support, with a flower like morphology. A close look of
the crystal flower in Figure 5.19 shows that the crystal was penetrated into the pores of
PES, indicating the growth took place within the pores. As zeolite dispersion concentration
increases to 0.5 wt%, more crystals are evident and a membrane-like layer is formed on
the support (Figure 5.14 (b)). The cross-section SEM (Figure 5.15) indicates growth of a
material within the membrane.

Nano CHA zeolite dispersions with concentration of 0.05 wt% was also investigated
to coat the PES and XRD of as synthesized membrane by sol-gel method is shown in Figure
5.20. X-ray diffraction shows that the backing gives rise to a crystalline structure. There is
no evidence of formation of a CHA zeolite membrane because the size of CHA seed (90 nm) is larger than the average pore size of PES (70 nm). They could not enter the pores but were only deposited on the surface and easily fell off during the synthesis.

5.3.4.2 Optimization of synthesis time

The effect of synthesis time was characterized by SEM microscopy. Compared with the SEM image in Figure 5.14b that shows the membrane surface was fully covered with substantial amount of chabazite crystals after 44 h growth, Figure 5.21a shows the surface morphology of the chabazite membrane after 26 h growth. Isolated crystals were observed on the PES surface without intergrowth. With a close inspection (Figure 5.21b), small crystals were filled within the pores which indicates the penetration of nano HY seeds and subsequent growth. Thus the membrane was still under growing after 26 h synthesis.

The fact that the prolonged synthesis time resulted in the formation of chabazite membrane was also illustrated in the literature [33]. The author claimed the obvious voids among crystals were observed in 8 h of synthesis time, while the support surface was fully covered with chabazite crystals after 16 h.

5.3.4.3 Advantage of the interzeolite conversion method

The impact of different starting materials on the fabrication of CHA membranes was explored to find out the suitable membrane growth conditions. The HY derived gel leads to the growth of CHA membrane with distinctive XRD patterns as discussed above. The
aluminosilicate gel under the same experimental conditions shows weak peaks of CHA crystals on PES according to the XRD result (Figure 5.22).

One of the advantages of interzeolite conversion is that the crystallization rates of CHA zeolites upon conversion of FAU type zeolite were notably faster compared to those observed in conventional hydrothermal syntheses utilizing amorphous aluminosilicate gel [41-44]. The characteristic enhancement in the crystallization rate is a result of the generation of locally ordered aluminosilicate species through the decomposition/dissolution of the starting zeolite, resulting in assembly and evolution into another type of zeolite [40]. The aluminosilicate gel may take longer time to form a continuous layer. In addition, this might be a result of the inhomogeneous reactive suspension involved in the aluminosilicate gel, which would give rise to a large concentration gradient along the axial direction of the tubular membranes over the course of hydrothermal reaction. Thus the interaction of gel with nano HY seed within the pores would be weakened and affect the chabazite growth.

We also consider that the nutrition from decomposed zeolite HY crystals is different from the aluminosilicate gel, and contains some species (nanoparts) since the CHA seeds via the same hydrothermal synthesis fails to form chabazite crystals. Although these nanoparts were not observed by XRD, they are considered to be/contain probably composite building units such as D6R. Due to D6R being also the main building unit for chabazite, the decomposed zeolite HY is easy to convert into chabazite crystals. Besides the transformation of zeolite Y themselves, these special species derived from zeolite HY
seeds also help the large amount of amorphous gel forming the CHA framework, probably due to their nuclei role.

Therefore, our results indicate that the interzeolite conversion is an effective way to fabricate metastable zeolite phases that were difficult to make directly from amorphous gel.

5.3.5 Transport properties of CHA zeolite/polymer composite membranes

The advantage of the membranes made by secondary growth is the high flux and the possibility to orient the seed crystals [56]; the drawback is the ease of formation of defects or non-zeolitic pores, which form intercrystalline pathways, larger than the zeolite pores and therefore not selective. Coating of PDMS, commonly used as sealing material, has been reported to seal defects on porous polymeric materials, as well as zeolite membranes [57, 58]. The possibility that PDMS penetrates into the zeolite pores is unlikely, since the size of PDMS is estimated to be 0.8 nm [57], higher than the 0.38 nm CHA pore opening. So, the PDMS is filling up the defects between the crystals.

The above-synthesized CHA membranes were spin coated with 2 wt% PDMS and used for CO2/N2 separation. The transport result shows poor separation properties with CO2/N2 selectivity of 1 and CO2 permeance of 8737 GPU, indicating the presence of defects on the membrane. Figure 5.23 shows a few defective spots on the membrane, where the zeolite crystals are peeled off after intense wash and the PES structure reveals. Figure 5.24 shows the top view SEM image of PDMS coated membrane. The thickness of the 2 wt% PDMS layer is of the order of ~200–300 nm [59]. Although this thin silicone cover layer does seal some of these defects, the coverage is not thick enough as shown by the
rough surface morphology. The selectivity was close to 1, which is near the Knudsen factor (0.8) indicating significant mesoporosity.

Higher concentrations of 5 wt% PDMS was then prepared on 0.5 wt% nano HY seeded PES support to investigate the sealing effect. The transport result shows CO$_2$/N$_2$ selectivity of 10 and CO$_2$ permeance of 1005 GPU, which is even better than the membrane with 2 wt% PDMS coating. The 900 μg/mL zeolite Y seeded PES support after coating with 3.5 wt% PDMS shows 810 GPU CO$_2$ permeance with 15.5 CO$_2$/N$_2$ selectivity [16], which is comparable to our result.

5.4 Conclusions

CHA-type nanocrystals are synthesized by interzeolite conversion of H-form zeolite Y nanocrystals. The rapid synthesis approach is applied to crystallization of CHA zeolites, with a 4~6-fold increase in the rate of crystal growth, as compared to conventional hydrothermal process. Chabazite-type zeolite membranes are synthesized via the secondary growth method using a template-free solution. The variables affecting the quality of the resulting chabazite zeolite membranes including starting materials and synthesis time are investigated to determine the optimum conditions for chabazite membrane synthesis.
Reference


Table 5.1. A Comparison of Chabazite Reaction Conditions

<table>
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<tr>
<th>Type</th>
<th>Molar composition</th>
<th>Reaction time (hour)</th>
<th>Reaction temperature (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHA</td>
<td>SiO₂:0.19Al₂O₃:0.39K₂O:0.03Na₂O:40H₂O</td>
<td>96</td>
<td>95</td>
<td>[51]</td>
</tr>
<tr>
<td>CHA</td>
<td>SiO₂:0.08Al₂O₃:0.17K₂O:0.08SrO:0.67KNO₃:65H₂O</td>
<td>18</td>
<td>140</td>
<td>[30]</td>
</tr>
<tr>
<td>CHA</td>
<td>SiO₂:0.2Al₂O₃:0.17K₂O:0.08SrO:0.67KNO₃:65H₂O</td>
<td>16-24</td>
<td>150</td>
<td>[33]</td>
</tr>
<tr>
<td>CHA</td>
<td>SiO₂: 0.05 Al₂O₃: 0.40 Na₂O: 0.09 K₂O: 100 H₂O</td>
<td>24</td>
<td>170</td>
<td>[50]</td>
</tr>
<tr>
<td>CHA</td>
<td>SiO₂:0.05-0.33Al₂O₃:0.39K₂O:0.1-0.5NH₄F:35H₂O</td>
<td>24-120</td>
<td>160</td>
<td>[21]</td>
</tr>
</tbody>
</table>
Figure 5.1. Schematic representation of CHA framework.
Figure 5.2. Synthesis apparatus for the DRHT process.
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Figure 5.18. Top view SEM image of CHA membrane grown with 0.05 wt% seed.
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Figure 5.21. Top view SEM image of CHA membrane after 26 h: (a) low magnification image, (b) high magnification image.
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Figure 5.23. Top view SEM image of defects on CHA membrane.
Figure 5.24. Top view SEM image of 2 wt% PDMS coated CHA membrane.
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