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HETEROGENEOUS AND MULTIPHASE CHEMISTRY OF TRACE ATMOSPHERIC GASES WITH MINERAL DUST AND OTHER METAL CONTAINING PARTICLES

by

Aruni Gankanda

A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry in the Graduate College of The University of Iowa

May 2016

Thesis Supervisor: Professor Vicki H. Grassian

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Graduate College The University of Iowa Iowa City, Iowa

CERTIFICATE OF APPROVAL

PH.D. THESIS

This is to certify that the Ph.D. thesis of

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has been approved by the Examining Committee for the thesis requirement for the Doctor of Philosophy degree in Chemistry at the May 2016 graduation.

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To my loving husband and beloved parents

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ABSTRACT

Particulate matter in the atmosphere emitted from various natural and anthropogenic sources is important due to their effects on the chemical balance of the atmosphere, the Earth's climate, human health and biogeochemical cycles. Although there have been many studies performed to understand the above effects, there still remains substantial uncertainty associated with processes involved and thus it is difficult for current atmospheric chemistry and climate models to reconcile model results with field measurements. Therefore, it is important to have better agreement between models and observations as the accuracy of future atmospheric chemistry and climate predictions depends on it.

In this research, a greater understanding of the role of mineral dust chemistry was pursued through focused laboratory studies in order to better understand fundamental processes involved. In particular, studies to further understand the photochemistry of adsorbed nitrate, an important inorganic ion associated with particulate matter exposed to gas-phase nitrogen oxides, were conducted using Al₂O₃, TiO₂ and NaY zeolite to represent non-photoactive components, photoactive components and aluminosilicate respectively, present in mineral dust. These studies reveal that photochemistry of nitrate adsorbed on mineral dust is governed by wavelength of light, physicochemical properties of dust particles and adsorption mode of nitrate. Gas phase NO₂, NO and N₂O are the photolysis products of nitrate on oxide particles under dry conditions. In contrast, nitrate adsorbed on zeolite is converted mainly to adsorbed nitrite upon irradiation. This nitrite yield is decreased with increasing relative humidity. Gas phase N₂O is the main photolysis product of nitrate adsorbed in zeolite in the presence of co-adsorbed ammonia. Water adsorbed on semiconducting TiO_2 can be photochemically converted to hydroxyl radicals. These hydroxyl radicals can be involved in surface mediated as well as gas phase oxidation reactions in the presence of cyclohexane.

Another focus of this dissertation was to investigate the oxidation of sulfur dioxide oxidation in the presence of mineral aerosol, particularly, coal fly ash (FA), γ -Fe₂O₃ and Arizona test dust (AZTD), a model for mineral dust aerosol. Depending on the temporal evolution of Fe(II), we proposed that S(IV) oxidation in the presence of FA and γ -Fe₂O₃ initially occurs through a heterogeneous pathway and a homogeneous pathway is also possible over later time scales. S(IV) oxidation in the presence of AZTD appears to be mostly heterogeneous and does not lead to iron dissolution. Overall, these studies suggest that the rate, extent and products of atmospheric S(IV) oxidation can be highly variable and heavily dependent upon the nature of aerosol sources, thereby precluding simple generalizations about this reaction when modeling atmospheric processes involving diverse mineral dust aerosols.

With the recent development in nanotechnology, nanoparticles are becoming a major fraction of atmospheric particulate matter. These particles can undergo aging under ambient conditions at any stage of their life cycle. This impacts the fundamental properties of these materials and therefore the behavior in the environment and interactions with biomolecules and biological systems. ZnO and CuO nanoparticles form adsorbed carbonate phases upon exposure to CO_2 and water vapor. These carbonates become more solvated as the relative humidity is increased. Presence of carbonate phases on ZnO particles increases their water solubility.

Thus, overall the work reported in this dissertation provides insights into heterogeneous and multiphase atmospheric chemical reactions in the presence of mineral aerosol and atmospheric aging of nanoparticles.

PUBLIC ABSTRACT

Atmosphere or the air surrounding us contains a lot of solid and liquid particles called aerosols. These aerosols include soil particles that get into the atmosphere by wind activity and very small particles of man-made materials. These particles in the atmosphere encounter different gases, water vapor and sunlight, and participate in interesting atmospheric chemistry. Atmospheric gases such as carbon dioxide, nitrogen dioxide and sulfur dioxide interact with these particles and generate coatings of different chemical species. A major focus of this dissertation was to understand the effect of sunlight on the interactions of atmospheric gases with aerosol particles. I found that chemical species on aerosol particle surfaces formed by the interaction with nitrogen containing gases are converted to different chemical species in the presence of sunlight. Mostly, these species formed in the presence of sunlight are gases. Some of the aerosol particles can absorb sunlight and use that energy to split water molecules generating hydroxyl radical. Aerosol particles present in clouds can convert pollutant gas sulfur dioxide into sulfate. I also found that interaction of carbon dioxide with man-made metal containing particles such as zinc oxide and copper oxide lead to changes in the particle surfaces. These changes affect their dissolution in water. Results presented in this dissertation help to better understand the effect of aerosols on the Earth's atmospheric processes and climate.

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CHAPTER 1

INTRODUCTION

1.1 Atmospheric Aerosols

Atmospheric aerosol is defined as either solid or liquid particles suspended in air with particle diameters in the range of 10⁻⁹ -10⁻¹⁴ m.^{1, 2} Therefore the sizes of aerosol particles vary orders of magnitude from nano- to micro-meters in size (i.e. diameter of 1 nm up to 100 µm).³ These particles can originate from a wide variety of natural and anthropogenic sources. Primary particles are directly emitted into the atmosphere by combustion and wind driven processes including biomass burning, fossil fuel combustion, volcanic eruptions, and suspension of blown soils to form mineral dust and sea spray from wave action.^{1, 4} Secondary particles are mainly formed by gas-to-particle conversion.⁵ Other processes including fluctuations in temperature (temperature reduction), reactive uptake via heterogeneous and multiphase processes can also shift species from the gas to particle phase.⁴ Figure 1.1, is a schematic of the major processes contributing to atmospheric aerosols.⁴ An overview of major types and sources of atmospheric aerosol is given in Table 1.1.⁶

The average lifetime of these aerosol particles in the atmosphere vary from less than 1 day for very large particles to 2 to 4 weeks for very small particles.³ During their lifetime in the atmosphere, aerosol particles can be transported long distances before being removed from the atmosphere. During long range transport, aerosol particles encounter sunlight and reactive trace gas species such as nitrogen oxides, sulfur oxides and organics and undergo chemical and photochemical reactions.⁷ These particles can also uptake water and nucleate clouds. Aerosols are removed from the atmosphere by two major processes known as wet deposition and dry deposition.³ Wet deposition processes are associated with precipitation. Dry deposition processes include turbulence collisions and gravitational settling of aerosols.³



Figure 1.1: Illustration of the Earth's atmosphere as a chemical reactor. This figure shows examples of the natural and anthropogenic processes producing gases and particles in the atmosphere. Subsequent processes can transform and age these particles as they are transported through the atmosphere. Adapted from reference 3.

1.1.1 Mineral Dust

Mineral dust aerosol contributes to one of the largest mass fractions of total aerosol emissions. It is estimated that between 1000 and 3000 Tg of mineral dust is emitted into

the atmosphere annually.⁸ Wind-blown soil emitted mainly from the arid and semiarid desert regions that covers approximately 36 % of the Earth's surface is the largest source of mineral dust.⁹

Source	Estimated Flux (Tg yr ⁻¹)				
Natural					
Primary					
Mineral dust					
0.1-1.0 μm	48				
0.1-2.0 μm	260				
2.5-5.0 μm	609				
5.0-10.0 μm	573				
0.1-10.0 μm	1490				
Seasalt	10,100				
Volcanic dust	30				
Biological debris	50				
Secondary					
Sulfates from DMS	12.4				
Sulfates from volcanic SO ₂	20				
Organic aerosol from biogenic VOC	11.2				
Anthropogenic					
Primary					
Industrial dust (except black carbon)					
Black carbon	100				
Organic aerosol	12				
Secondary	81				
Sulfates from SO ₂					
Nitrates from NO _x	48.6				
	21.3				

Table 1.1: Global emissions of major aerosol classes

Source: Seinfeld, J. H.; Pandis, S. N., *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. 2 ed.; John Wiley: New York, 2006.

Much of the global burden of mineral dust is emitted from the so-called "dust belt".

This is the region that extends from North Africa, over Middle East and Central and South

Asia, to China.⁹ In addition, surface land modification by human activities contribute to 30-50 % of the total atmospheric dust loading. ¹⁰ It is expected that mineral dust loading in the atmosphere will continue to increase due to the expansion of arid and semiarid regions due to improper land-use practices driven by economic, social and political circumstances.^{8, 11} Since mineral dust particles are eroded soils mobilized by strong wind currents, they have a similar although not identical composition to crustal rocks. Mineral dust is mainly composed of crustal species including quartz, mica, oxides, carbonates and clay minerals.⁸ However, the exact minerology depends on the source region from which it originates. For an example, dust particles originate from Saudi Arabia, Jordan and Dead Sea contains a high percentage of paligorskite while montmorillonite and mixed-clay minerals dominate in the dust originated from western desserts of the Tibesti mountains.¹² Another study by Krueger et al. revealed that Saharan dust contains a greater amount of iron than China loess.¹³ The abundance of major oxides found in continental crust is given in Table 1.2.^{8, 14} According to that, SiO₂ (60 %) and Al₂O₃ (10-15 %) dominates the oxide fraction. Mineral dust also contain various photoactive semiconductor oxides such as TiO₂ and oxides of iron.¹⁵ Major phases of iron oxide found in dust include hematite (α -Fe₂O₃) and goethite (FeOOH) that imprints a yellowish red color to dust particles.¹⁶

Table 1.2: Abundance of major oxides in the continental crust

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O3	CaO	Na ₂ O	MgO	K ₂ O	TiO ₂	BaO	MnO
%	61.5	15.1	6.28	5.5	3.2	3.7	2.4	0.68	0.0584	0.1

Source: Usher, C. R.; Michel, A. E.; Grassian, V. H. Reactions on mineral dust. *Chemical Reviews* **2003**, *103*(*12*), 4883-4939.

1.1.2 Anthropogenic Aerosol

Tropospheric aerosol loading have substantially increased over the past 150 years as a result of industrial activities.¹⁷ Human activities such as biomass burning and incomplete combustion of fossil fuels create an enormous continuous input of aerosol into the atmosphere with an estimation of 270 Tg yr^{-1.6} Anthropogenic aerosols are composed of inorganic and organic species, elemental carbon and even mineral dust.¹⁸ Fly ash aerosols discharged into the atmosphere due to large amounts of fossil fuel burning is principally inorganic substances composed mainly of oxides.¹⁹ Metallic elements contained in coal, oil and gasoline are also emitted into the atmosphere during combustion processes mainly as components of submicron particles.²⁰ The metal content of fly ash particles is determined by the factors such as design and operating conditions of the combustion chamber, associated air pollution control equipment and the chemical form of the element in the fuel.²⁰ Fly ash particles contain metals, such as Fe, Co, Cd, Ni, Pb, Sb, and Zn.²¹⁻²³ Concentration of these metals in fly ash increases with decreasing particle sizes.²⁴ Fly ash also acts as a source of soluble iron in the atmospheric aqueous phase and bioavailable ion in the open ocean.²⁵⁻²⁷ With the recent development of nanotechnology, nanoparticles from industrial sources have also become a significant anthropogenic source of airborne particulate matter. It has been estimated that 0.1-1.5 % of global engineered nanomaterial production in 2010 ended up in the atmosphere.²⁸

1.2 Impacts of Aerosol

Atmospheric aerosols interact with many atmospheric, terrestrial and oceanic systems during their long range transport to far away locations from the source region due to wind activity. Aerosol affect atmospheric radiative balance and hence climate in three main processes: (*a*) scattering and absorbing solar radiation; (*b*) scattering, absorbing, and emitting thermal radiation; and (*c*) acting as cloud condensation nuclei.^{3, 6, 8} The first two processes are called the direct climate effects and the third one is called indirect climate effect. Direct climate effects are directly related to the optical properties of aerosol particles such as size, shape and chemistry. Inorganic aerosols such as sea spray, sulfate and nitrate and non-absorbing organic aerosol affect climate through direct effect by scattering radiation. Aerosols that absorb radiation such as brown carbon, elemental carbon and even mineral dust affect climate through direct and semi-direct effects. Radiative forcing by mineral aerosol range from -0.60 to +0.40 W m^{-2.8}

Atmospheric aerosols can have significant effects on biogeochemical cycles directly by changing the gain and loss of nutrients through the atmosphere.³ It has been estimated that annually 300-500 Tg of mineral dust is deposited into oceans with 50 % of total deposition occurring in the north Atlantic ocean.⁸ Mineral dust plays a large role by supplying soluble iron to the oceans providing micronutrients to phytoplanktons.^{8, 29}

Studies show that fine air particulate matter and traffic-related air pollution are correlated with severe health effects, including enhanced mortality, cardiovascular, respiratory, and allergic diseases.^{1, 8, 30} Aerosol particle size, morphology, the durability of dust particles and surface chemistry take place during exposure are the important factors determine the toxicity of aerosols.⁸ Because of the negative health effects caused by aerosols, in 1997, U.S. Environmental Protection Agency established the PM (particulate matter) 2.5 standard which recognized the importance of aerosols that have diameters of \leq 2.5 µm in causing health problems.⁸

Heterogeneous and multiphase chemical reactions occur on aerosol particles can influence atmospheric gas phase chemistry as well as the properties of atmospheric particles and their effects on climate and health. Aging upon exposure to inorganic and organic chemical species or exposure to varying amounts of water vapor in the atmosphere can influence the chemical nature of mineral aerosols. Uptake of nitrogen oxides is one of the most important heterogeneous reactions in the atmosphere.³ Further, mineral aerosol convert over half of the atmospheric gas-phase sulfur dioxide into particulate sulfate and gas-phase ammonia into particulate ammonium. As a result of these reactions, mineral dust particles get coated with different particular chemical species. In general, atmospheric aging decrease the reactivity of aerosol particles. Furthermore, aged particles can have increased hygroscopicity and cloud condensation activity and altered optical properties.^{1,8} In this thesis the focus will be the understanding of the role of mineral dust in (a) nitrate photochemistry (b) atmospheric hydroxyl radical generation and (c) aqueous phase SO₂ oxidation. These topics are discussed in detail below. In addition, the atmospheric chemistry of common nanomaterials - ZnO and CuO - with common gas-phase constituents including carbon dioxide and water have also been explored as discussed below.

1.2.1 Photochemistry of Nitrate Adsorbed on Mineral Dust

Mineral dust particles undergo heterogeneous reactions with nitrogen oxides including N_2O_5 , HNO_3 , NO_3 and NO_2 , the main nitrogen oxide reservoir species in the atmosphere, to yield particulate nitrate.^{31, 32} In the northern and southern hemispheres, greater than 40 % of the total particulate nitrate is associated with mineral dust.⁸ Nitrate adsorption on mineral dust particles considered a sink for NO_y (HNO₃). However, recent

studies show that mineral dust nitrate is transformed back to gas phase nitrogen oxides in the presence of solar radiation leading to a potential atmospheric renoxification process.^{15, 33-36} Interaction of mineral dust with oxides of nitrogen is particularly interesting due to its impact on photochemical ozone production because ozone is formed by a complex series of reactions involving NOx in a nonlinear manner.³¹

Recent laboratory studies suggest that heterogeneous photochemical reactions involving NO₂ on mineral dust may be a source of atmospheric HONO formation. HONO is a source of hydroxyl radicals.⁷ As noted below, OH radicals play an important role in the daytime chemistry of the atmosphere. Possible reactions of nitrogen oxides on mineral dust are illustrated in Figure 1.2.⁸



Figure 1.2: Schematic diagram illustrating important gas phase chemistry and photochemistry involving nitrogen oxides in the troposphere. Dashed lines represent potential heterogeneous reactions on mineral dust. Adapted from reference 7.

1.2.2 Hydroxyl Radical Generation on Mineral Dust

The oxidation efficiency of the atmosphere is primarily determined by OH radicals. Therefore, OH radicals are called "the detergent" of the atmosphere.³⁷ Global concentration of hydroxyl radicals is about 10⁶ cm⁻³, corresponding to a tropospheric mixing ratio of ca. 4×10^{-14} .^{37, 38} OH radicals in the atmosphere are mainly formed through photodissociation of ozone by solar UV radiation by producing electronically excited O (¹D) atmos.^{37, 39} This excited state oxygen atom then reacts with water molecules to produces hydroxyl radicals. Some recent field and laboratory studies suggest the potential of semiconductor components in mineral dust aerosol in the atmosphere to produce reactive oxygen species including hydroxyl radical.⁴⁰ These hydroxyl radicals produced in mineral dust surface can diffuse into the gas phase and are involved in SO₂ oxidation to produce H₂SO₄ which ultimately leads to new particle formation in the atmosphere.^{40, 41} Hydroxyl radicals also react with volatile organic compounds to form various oxidation products.³⁹ Hydroxyl radical generation on semiconductor oxides in mineral dust and a summary of reactions involving these photochemically generated hydroxyl radicals in the atmosphere are illustrated in Figure 1.3.³⁹⁻⁴²



Figure 1.3: Illustration of OH radical generation on semiconductor oxides in mineral dust and its involvement in tropospheric chemistry.

1.2.3 Aqueous Phase Oxidation of Atmospheric SO₂

Sulfate aerosols play a key role in radiative forcing by exerting a net cooling effect that partially counters the effect of greenhouse gas warming.^{43, 44} SO₂ oxidation in the atmosphere may take place either in the gas phase or aqueous phase, primarily in cloud droplets. Gas-phase oxidation of SO₂ mainly occurs via its reaction with hydroxyl radical (OH).⁴⁵ Major aqueous phase oxidation pathways include the reaction of dissolved SO₂ with H₂O₂, O₃ and O₂ (catalyzed by transition metal ions).^{43, 46} Most commonly known transition metal ions involved in this catalytic oxidation pathway are iron and manganese.⁴⁶ Some very recent studies suggest the ability of titanium leached from mineral dust may be involved in transition metal ion catalyzed S(IV) oxidation. ⁴⁴ Aqueous phase S(IV) oxidation kinetics are pH dependent. For an example, oxidation by dissolved H₂O₂ is prominent at pH < 5, while oxidation by ozone makes a significant contribution at pH > 5.⁴⁶ Further, the importance of these different S(IV) oxidation pathways has a high seasonal variability (as shown in Figure 1.4).⁴³



Figure 1.4: Seasonality in the different sulfur dioxide oxidation pathways. Adapted from reference 39.

Aqueous phase pathways including transition metal ion catalyzed S(IV) oxidation is most important in winter with weak sunlight whereas the hydroxyl radical driven pathway is more prominent in summer with increased oxidation capacity of the atmosphere with a higher concentration of hydroxyl radicals.⁴³

1.3 Nanoparticle Aging and Transformation in the Environment

Nanomaterials are widely used in a variety of products and applications these days. Some examples are electronic, biomedical, pharmaceutical, cosmetic, energy, environmental, catalytic and material applications.⁴⁷ The increased production and use of engineered nanomaterials have increased their release to natural environments. Therefore, there is great interest in the potential adverse toxicological and health effects to humans and other organisms. In the environment, nanoparticles can get into the air and, like aerosols, ultimately deposit on land and water bodies.⁴⁸ These nanomaterials can interact or enter into the environment at any stage of their product life cycle. As a result of environmental exposure, nanoparticles can undergo atmospheric aging or transformation and change their fate and transport in the environment compared to pristine material. ^{49, 50} Some of these transformations include oxidation and/or photodegradation, aqueous dissolution, being surface coated and passivation by coexisting matter.⁴⁸

1.4 Thesis Overview

The research presented herein focuses on understanding heterogeneous and multiphase chemical and photochemical reactions that occur on aerosol and other metalcontaining particles including engineered nanomaterials. Several different types of reactions have been explored in this research. In particular, photochemistry of nitrate adsorbed on mineral dust, hydroxyl radical formation by semiconductor components of mineral dust, aqueous phase oxidation of dissolved sulfur dioxide in the presence of mineral dust and other metal-containing aerosol including coal fly ash, and atmospheric aging of ZnO and CuO nanoparticles.

A variety of experiment methods were used in these investigations including transmission Fourier transform infrared (FTIR) spectroscopy in combination with a variety of other spectroscopic and microscopic techniques in order to understand gas-phase and particle surface changes due to these chemical and photochemical reactions. In addition, several other techniques were used to characterize the solution phase behavior of particles previously reacted with trace gases. All of the experimental methods used in these studies are described in detail in Chapter 2.

Subsequent chapters of this thesis focus on the different studies conducted in this research. In Chapter 3, the main focus is to understand the photochemistry of nitrate from HNO₃ adsorption in NaY zeolite under different environmental conditions using FTIR spectroscopy. As will be discussed, upon nitrate photolysis under dry conditions (relative humidity (RH) < 1%), surface nitrite is formed as the major adsorbed product. In addition to adsorbed nitrite, low concentrations of gas phase nitrogen-containing products including NO₂, NO, and N₂O are observed at long irradiation times. The amount of nitrite formed via nitrate photochemistry in NaY zeolite decreases with increasing relative humidity. In the presence of gas phase ammonia, ammonium nitrate is formed in NaY zeolite. Photochemistry of ammonium nitrate yields gas phase N₂O as the sole gas phase product. Here, we discuss mechanisms for the formation of these intermediates from nitrate photochemistry as well as possible atmospheric implications.

In Chapter 4, investigations of the photochemistry of nitrate adsorbed on mineral dust were extended to understand the wavelength dependence of nitrate photochemistry. Laboratory proxies of mineral dust aerosol used in this study include Al₂O₃, TiO₂, and NaY zeolite to represent non-photoactive oxides, photoactive semiconductor oxides, and porous aluminosilicate materials, respectively, present in mineral dust aerosol. Results of this study show that nitrate photochemistry on mineral dust particles is governed by the wavelength of light, physicochemical properties of the dust particles, and the adsorption mode of the nitrate ion. Interestingly, nitrate ion adsorbed on semiconductor oxide particles can undergo photochemistry over a broader wavelength region of the solar spectrum compared to nitrate ion in a solution.

In Chapter 5, investigations on atmospheric aging of ZnO and CuO nanoparticles in the presence of atmospheric carbon dioxide under different relative humidity conditions are presented. In these studies, we found that carbon dioxide adsorption can change particle chemical properties by forming adsorbed carbonate on the surface. We also investigated the effect of carbon dioxide adsorption on nanoparticles on their aqueous dissolution behavior.

Chapter 6 presents a study carried out to understand the effect of mineral dust and other metal-containing aerosol on the oxidation of dissolved sulfur dioxide in the aqueous which is representative of cloud chemistry in the atmosphere. Here we investigate the effect of particle phase and dissolved transition metal ion catalysis under different atmospherically relevant temperatures and in the presence of simulated solar radiation. Dissolution of iron in aerosol samples were used as a starting point to understand the mechanisms of transition metal ion catalysis.

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In Chapter 7, relative humidity dependence of hydroxyl radical generation by photolysis of water on TiO_2 surface is studied using cyclohexane as the hydroxyl radical scavenger. A discussion of the role of surface and gas-phase hydroxyl radicals in cyclohexane oxidation is presented in this chapter.

Finally, Chapter 8 provides the conclusions and future directions for the research discussed in previous chapters. The results presented here provide insights into heterogeneous and multiphase reactions that occur in the atmosphere in the presence of mineral aerosol and other metal containing particles.

CHAPTER 2

EXPERIMENTAL METHODS

The research presented in this dissertation was carried out using a number of different experimental methods and techniques to investigate the heterogeneous and multiphase reactions of mineral aerosol and metal containing particles in the atmosphere. Laboratory experiments conducted under controlled conditions coupled with particle characterization that can provide comprehensive information about reactions occur in the atmosphere. In this chapter, these experimental methods and techniques are discussed in detail.

2.1 Experimental Design for the Studies on Heterogeneous Reactions

Heterogeneous chemical and photochemical reactions of atmospheric trace gases with mineral aerosol and nanoparticles were investigated using custom made transmission FTIR setups. Infrared spectroscopy provide useful information about the existence of surface adsorbed and gas phase species, structure of surface adsorbed species as well as information about the bonds formed between the surface and the adsorbate. Experiments with nitric acid was conducted using a Teflon coated infrared cell and a glass mixing chamber. Experiments with non-corrosive gases were conducted using a totally stainless steel reaction system.
2.1.1 Teflon Coated FTIR Setup

The modified FTIR cell used in this setup consists of a stainless steel cube with a total inner volume of 197 ± 2 mL. The inside of the cell is coated with Teflon to avoid decomposition corrosive gases on the walls. A schematic of the IR cell is shown in Figure 2.1 (a). Teflon coated stainless steel IR cell has two BaF_2 (ISP Optics) windows. These windows are placed in the stainless steel cube by using two Teflon coated stainless steel holders with rubber O-rings. This infrared cell also has a sample holder with two removable Teflon coated jaws that can hold a tungsten grid ($3 \text{ cm} \times 2 \text{ cm}$, 100 mesh/in., 0.002" wire dia., Alfa Aesar). The infrared cell is mounted on a linear translator. So both the samplecoated or blank grid halves could be positioned into the infrared probe by moving the cell through the IR beam path. The sample cell is connected to a vacuum system comprises a two stage pumping system via a Teflon tube and a glass gas manifold (Figure 2.1(b)) with gas introduction ports and two absolute pressure transducers (MKS instruments) in the range 0.001-10 Torr and 0.1-1000 Torr. The vacuum system consists of a mechanical pump for rough pumping to 10^{-3} Torr (Alcatel) and a turbo molecular pump for further pumping down to 10^{-5} Torr (Alcatel). Volume of the gas handling system including the glass manifold is 1216 ± 4 mL. A commercial air dryer (Balston 75-62) was used to purge the spectrometer and the internal compartment to minimize H₂O and CO₂ concentrations in the purge air.

For the FTIR studies, about 15 mg of mineral dust proxy samples (TiO₂ or zeolite) were sonicated in optima water (Fisher) to form a hydrosol. The hydrosol was then transferred onto one-half of a tungsten grid held in place by removable two Teflon coated jaws. Water was evaporated from the sample at room temperature to create a uniform thin



Figure 2.1: Teflon coated transmission FTIR experimental setup a) Schematic of the IR cell b) Schematic of the gas handling system

film. Al₂O₃ samples were directly mounted on the tungsten grid by approximately pressing the powder. Then the sample coated tungsten grid is placed in the infrared cell. Infrared spectra were collected with a single beam Mattson RS 10000 spectrometer with a narrow band MCT detector. In these experiments, usually 250 scans were collected using WinFirst software with an instrument resolution of 4 cm⁻¹ in the 900 to 4000 cm⁻¹ spectral range. Absorbance spectra for gas phase and surface species were obtained by referencing single beam spectra of blank grid and sample coated grid in the presence of reactant gas or after exposure to reactant gas to single beam spectra prior to gas adsorption.

2.1.2 Stainless Steel FTIR Setup

Basic design of the stainless steel FTIR setup is similar to the reaction system explained previously in 2.1.1. As shown in Figure 2.2, mixing chamber of the stainless steel setup is a braided stainless steel hose. The total internal volume of the premix chamber of this system is 565 ± 9 mL. Stainless steel reaction setup has a special sample holder which is designed to carry out temperature controlled experiments (Figure 2.2(a)). The sample holder contains a tungsten grid (3 cm × 2 cm, 100 mesh/in., 0.002" wire dia., Alfa Aesar) held in position by nickel jaws. Thermocouple wires are spot welded to the tungsten grid to measure the temperature of the sample. Nickle jaws are connected to an external heater that can resistively heat sample coated or pressed on the tungsten grid. Total internal volume of the infrared cell is 310 ± 3 mL. The stainless steel reaction system was coupled to a Mattson Infinity Gold spectrometer for data collection during experiments.



Figure 2.2: Stainless steel transmission FTIR experimental setup a) Schematic of the IR cell b) Schematic of the gas handling system.

2.1.3 Transmission FTIR Spectroscopy: Photochemical Studies

The transmission FTIR experiments described in Section 2.1.1 and 2.1.2 were slightly modified for photochemical experiments. In photochemical studies, 500 Wt mercury arc lamp (Oriel, model no. 66033) was used as a broadband light source that contained ultra-violet, visible, and infrared light. In all the experiments, unwanted infrared radiation coming from the Hg arc lamp was removed using a water filter. Following sample preparation and reactive gas introduction, the valve connecting the FTIR cell to the mixing chamber was closed, letting the gas phase products accumulate inside the cell as the surface was irradiated. Samples were irradiated with either the full broadband irradiation or with the use of long-pass or narrowband filters to cut off unwanted wavelengths of light. Irradiance of the lamp output was measured using a spectroradiometer (model RPS900-R, International Light Technologies). Irradiance profiles of the lamp output in the presence of different filters are shown in Figure 2.3. During the photolysis, infrared spectra of both gas phase and surface were recorded with a single-beam Mattson RS-10000 spectrometer or Mattson Infinity Gold spectrometer in a similar fashion described in section 2.1.1 and 2.1.2.



Figure 2.3: Irradiance profile of the 500 W Hg arc lamp with (a) band pass and (b) broad band filters in place. All the irradiance profiles were measured in the presence of a water filter to remove IR radiation.

2.2 Batch Reactor Studies to Investigate Dissolved Sulfur Dioxide Oxidation in the Presence of Mineral Aerosol

2.2.1 Solution Phase Experimental Apparatus

Atmospheric aqueous phase S(IV) oxidation in the presence of mineral aerosols was investigated using the experimental setup given in Figure 2.4. Solution phase reactor used in these studies is a 70 ml water jacketed glass reactor. The water jacket is connected to a heated/chilled water circulator so that the temperature of the glass vessel can be kept at a constant value throughout the experiments. All solutions were stirred using a magnetic stirrer under atmospheric oxygen exposure during the experiments. 50 mL of 1 ± 0.2 Na₂SO₃ solution at pH = 5 and a solid loading of 1 g L⁴ was used in all experiments. All the experiments were conducted in triplicate and results represent the averages and standard error of three measurements. After addition of the particles into the solution, an appropriate volume of suspension was periodically withdrawn from the vessel using a disposable syringe. The aqueous samples were passed through a 0.2 µm nylon filter and immediately used for the determination of Fe(II), total dissolved iron and sulfite concentrations. To explore the effect of irradiation, a solar simulator with a 150 W xenon lamp (Oriel Corp.) was mounted on the top of the vessels during experiments.

2.2.2 Determination of Dissolved Iron Concentration

Dissolved iron concentrations were colorimetrically determined using 1,10phenanthroline as described previously.⁵¹ For the analysis of Fe(II), first, 50 μ L of 0.43 M ammonium fluoride solution was added to 1 ml of the sample. Then 200 μ L of ammonium acetate buffer and 200 μ L of 5 mM 1,10-phenanthroline were added. The mixture was allowed to sit in the dark for 30 min prior to UV-vis analysis, during which time a reddishorange color developed if Fe(II) was present. Total dissolved iron was determined via the same protocol, except that 20 μ L of 1.44 M hydroxylamine hydrochloride, which reduces Fe(III) to Fe(II), was added to the aqueous sample instead of ammonium fluoride. Absorbance measured at 510 nm was converted to concentrations using aqueous standards prepared from anhydrous beads of ferrous chloride (Sigma Aldrich).



Figure 2.4: Schematic of the custom made glass reactor used for investigating S(IV) oxidation in the atmospheric aqueous phase

2.2.3 Determination of Sulfite Concentration

Sulfite concentration was determined colorimetrically using DTNB $(5,5)^{-1}$ dithiobis(2-nitrobenzoic acid)).⁵² For the analysis of sulfite, 2 mL of 1mM EDTA was added to 1 mL of the sulfite solution. Finally, 5 mL of the DTNB solution was added. The reaction between DTNB and sulfite ion is complete within 2-3 min.⁵² Absorbance measured at 412 nm was converted to concentrations using aqueous standards prepared using Na₂SO₃ solid (Sigma Aldrich).

2.3 Nanoparticle Dissolution Studies

Dissolution studies were used to understand the effect of atmospheric aging of ZnO and CuO nanoparticles on the particle dissolution. Aged nanoparticles in the presence of CO₂ and water vapor was prepared in the stainless steel FTIR reaction chamber. Aged nanoparticles were suspended in Optima water (Fisher) or HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer and stirred for 24 h. After that aliquots of the solution was filtered using Amicon Ultra-4 centrifugal filters (Millipore). The concentration of metal ions was measured using Varian 720-ES inductively coupled plasma-optical emission spectrometer (ICP-OES). Dissolution of unreacted sample was also conducted under the same conditions for comparison. All experiments were conducted in triplicate.

2.4 Complementary Physicochemical Characterization Methods

2.4.1 Powder X-ray Diffraction

Powder X-ray diffraction (XRD) was used to determine the crystalline structure and composition of bulk powder samples. Dry powder samples were placed in the XRD sample holder, and the excess powder was smoothed with a razor until flush with the rim of the holder. A Bruker D8 advance X-ray diffractometer with Cu K α target. XRD powder patterns were collected between 10⁰ to 90⁰ 2 θ angles.

2.4.2 BET Surface Area Measurement

Surface area of mineral samples and nanoparticles were measured by BET surface area analysis. Relative pressures, (P/P₀), of inert gases are introduced into a calibrated sample cell at liquid nitrogen temperature that allows the adsorption of the inert gas, N₂ in the current studies, to be measured, W. Total surface area is calculated using the cross section of the N₂ molecule.

The total surface area is divided by the sample mass to give a surface area per unit mass. The specific surface area of particles used in the research presented in this dissertation was determined from seven point N₂-BET adsorption isotherm measurements performed on a Quantachrome 4200e surface area analyzer by the following equation (Eq. 2.1) in the limited linear range of the BET isotherm,

$$\frac{1}{W\left(\left(\frac{P_0}{P}\right)-1\right)} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \left(\frac{P}{P_0}\right)$$
2.1

where W_m is the weight of adsorbate constituting one monolayer of coverage and C is a constant. Plotting $1/W((P_0/P)-1)$ versus (P/P_0) allows for determination of W_m and C by the slope and intercept of the linear fit. Prior to analysis, samples were degassed overnight at temperatures that would not change the materials' properties.

2.4.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a powerful and sensitive technique that can be used to analyze surface composition of particles. XPS uses X-rays to eject electrons. An electron from a higher energy level, then relaxes down to a lower energy state and simultaneously releases a photoelectron which has a characteristic binding energy. Mean free path of electrons in solid particles is generally about 10 nm. Therefore, XPS inherently probes the surface and near-surface region of the material.

Typically, XPS measures the kinetic energy of the electron. This kinetic energy is related to the binding energy according to the relationship given by the Einstein equation (Equation 2.2). Einstein equation, to a first approximation, can be written as:

where E_B is the binding energy referenced to vacuum level and E_K is the kinetic energy of the electron. The binding energy value obtained from XPS can be used to get the elemental composition of the surface, their oxidation state and also to identify surface functional groups.

A custom-designed Kratos Axis Ultra 41 X-ray photoelectron spectroscopy system (Manchester, UK) was used to investigate the reacted and unreacted metal oxide particles. The powder samples were directly pressed onto indium foil and it was placed on XPS $E_B = hv - E_K$ 2.2 sample holder bar for analysis and placed in the XPS analysis chamber, which had a

pressure maintained at 10^{-9} Torr. Wide energy range survey scans were acquired using the following instrumental parameters: energy range from 1200 to -5 eV, pass energy of 160 eV, step size of 1 eV, dwell time of 200 ms, and an x-ray spot size of ~ 700 × 300 μ m. The data collected were analyzed using CasaXPS data processing software.

2.4.4 Transmission Electron Microscopy

Transmission electron microscopy (TEM) was used to determine the size and surface features of oxide particles. Particles were mounted on lacey carbon TEM grids (LC400-Cu on 400 mesh copper grid) either using a suspension in water or by directly sprinkling samples on the TEM grid. The size of particles was determined by JEOL 1230 transmission electron microscope using the average of at least 200 particles. JEOL 2100F high resolution transmission electron microscope (HR-TEM) was used to analyze the surface features of reacted and unreacted nanoparticles.

2.5 Reagents and Materials

2.5.1 Particle Samples

In the investigations to understand nitrate photochemistry and hydroxyl radical generation on TiO₂, oxide and zeolite particles were used as received. These samples include γ -Al₂O₃ (Degussa), TiO₂ (P25, Degussa), TiO₂ (P25, Sigma Alrdich), NaY zeolite (Sigma Aldrich) and γ -Fe₂O₃ (Alfa Aesar). ZnO (Meliurom) and CuO (Sigma Aldrich) used to investigate atmospheric aging of nanoparticles were calcined at 550 ^oC for 6 hours before using. A fly ash sample (SRM 2690, National Institute of Standards and Technology), and Arizona fine test dust (ISO 12103-1 A2 test dust, Power Technology Inc.) were used in S(IV) oxidation studies.

2.5.2 Liquid and Gas Reagents

Distilled H₂O (Optimal grade) was purchased from Fisher Scientific. Optima water and Cyclohexane (99%, Sigma) used for gas phase experiments were degassed several times with consecutive freeze-pump-thaw cycles prior to use. Dry gaseous nitric acid vapor was introduced from a mixture of H₂SO₄ (96.0%, Fisher) and HNO₃ (79.5%, Fisher) in a 3:1 ratio. This nitric acid solution was degassed with prior to use. Fe(II) and total dissolved iron were performed with 1,10-phenanthroline (\geq 99%) and hydroxylamine hydrochloride (98%) which were purchased from Sigma Aldrich and ammonium acetate (98.5%, Fisher) and glacial acetic acid (99.7%, EMD). Sulfite solutions were prepared from 99.6% Na₂SO₃ solid (Fisher). DTNB (5,5'-dithiobis(2-nitrobenzoic acid)), EDTA, K₂HPO₄ and KH₂PO₄ were purchased from Sigma.

CHAPTER 3

NITRATE PHOTOCHEMISTRY IN ZEOLITE NaY: PRODUCT FORMATION AND PRODUCT STABILITY UNDER DIFFERENT ENVIRONMENTAL CONDITIONS¹

3.1 Abstract

In the atmosphere, mineral dust particles are often associated with adsorbed nitrate from heterogeneous reactions with nitrogen oxides (N₂O₅, HNO₃ and NO₂). Nitrate ions associated with mineral dust particles can undergo further reaction including those initiated by solar radiation. Although nitrate photochemistry in aqueous media is fairly well studied, much less is known about the photochemistry of nitrate adsorbed on mineral dust particles. In this study, the photochemistry of nitrate from HNO₃ adsorption in NaY zeolite under different environmental conditions has been investigated using transmission FTIR spectroscopy. NaY zeolite is used as a model zeolite for studying reactions that can occur in confined space such as those found in porous materials including naturally occurring zeolites and clays. Upon nitrate photolysis under dry conditions (relative humidity, RH, < 1%), surface nitrite is formed as the major adsorbed product. Although nitrite has been proposed as a product in the photochemistry of nitrate adsorbed on metal oxide particle surfaces, such as on alumina, it has not been previously detected. The stability of nitrite in NaY is attributed to the confined three-dimensional structure of the porous zeolite which

¹ This chapter is previously published as Gankanda, A.; Grassian, V. H., Nitrate Photochemistry in NaY Zeolite: Product Formation and Product Stability under Different Environmental Conditions. *The Journal of Physical Chemistry A* **2013**, *117*, (10), 2205-2212.

contains a charge compensating cation that can stabilize the nitrite ion product. Besides adsorbed nitrite, small amounts of gas phase nitrogen-containing products are observed as well including NO₂, NO and N₂O at long irradiation times. The amount of nitrite formed via nitrate photochemistry decreases with increasing relative humidity whereas gas phase NO and N₂O become the only detectable products. Gas-phase NO₂ does not form at RH > 1%. In the presence of gas phase ammonia, ammonium nitrate is formed in NaY zeolite. Photochemistry of ammonium nitrate yields gas phase N₂O as the sole gas phase product. Evidence for an NH₂ intermediate in the formation of N₂O is identified with FTIR spectroscopy for HNO₃ adsorption and photochemistry in NH₄Y zeolite. Here we discuss mechanisms for the formation of these intermediates from nitrate photochemistry as well as possible atmospheric implications.

3.2 Introduction

Mineral dust aerosol plays a critical role in atmospheric chemistry by providing reactive surfaces for trace atmospheric gases.^{8, 53-55} Mineral dust particles undergo heterogeneous reactions with nitrogen oxides including N₂O₅, HNO₃ and NO₂, the main nitrogen oxide reservoir species in the atmosphere to yield particulate nitrate.^{8, 32} In the northern and southern hemispheres greater than 40 % of the total particulate nitrate is associated with mineral dust.⁵⁶ Reactions that can alter NO_x (NO_x = NO + NO₂) concentrations are of great importance in the atmosphere because ozone is formed by a complex series of reactions involving NOx in a non-linear manner.⁵⁷ Additionally, nitrate associated with mineral dust as nitrate coatings, adsorbed nitrate or deliquesced nitrate layers are transported to remote locations by prevailing winds and can undergo various further reactions, causing regional impacts.^{7, 58}

Zeolites are crystalline aluminosilicate that are present in mineral dust aerosol.^{59, 60} These zeolites have a rigid three dimensional internal pore structure of molecular dimensions and a negatively charged framework with charge compensating cations.⁵⁹ Porous materials such as zeolites, as well as swellable clay minerals, can provide a larger internal surface area for atmospheric trace gas adsorption in contrast to mineral oxides such as alumina where the adsorption is limited to the external surface only.^{8, 61, 62} A number of studies have been reported on the application of engineered zeolite materials for selective catalytic reduction of NOx in diesel emissions.^{59, 63-67} Zeolites act as a NOx storage material in the form of adsorbed nitrate and nitrite ions. The mechanism of formation of these adsorbed species is often governed by the structural water content in the zeolite pores. In the presence of water, NOx adsorption occurs via a hydrolysis reaction to yield HNO₃ and HONO (*vide infra*). However, atmospheric implications of the chemistry of gas-phase nitrogen oxides and the continued chemistry of adsorbed nitrate in zeolites as a component of mineral dust aerosol have yet to be fully explored.

Continued chemistry of particulate nitrate includes photochemistry as the nitrate ion is recognized as an important chromophore in natural waters. It shows two dominant absorptions in the UV visible region. A weak adsorption band around 302 nm is due to the $n \rightarrow \pi^*$ transition ($\epsilon = 7.2 \text{ M}^{-1} \text{ cm}^{-1}$) and a stronger adsorption at 200 nm is due to the $\pi \rightarrow \pi^*$ transitions ($\epsilon = 9900 \text{ M}^{-1} \text{ cm}^{-1}$).⁶⁸ Recent studies show the potential importance of photochemistry of nitrate adsorbed on mineral dust in the atmosphere at $\lambda > 300 \text{ nm}$ as a renoxification process that converts surface nitrate to gas phase species including NO, NO₂ and N₂O.^{32, 33} Based on studies on the photochemistry of nitrate adsorbed on alumina surface from adsorption of nitric acid, Rubasinghege and Grassian proposed a reaction pathway for the photochemical conversion of surface adsorbed nitrate to gas phase NO via a surface adsorbed nitrite intermediate.³² In a related study, irradiation of ammonium nitrate layers on alumina lead to the formation of gas phase N_2O via a proposed NH_2 intermediate.⁶⁹

To the best of our knowledge, evidence for the presence of these intermediates (NO_2^-) and NH_2 have not been observed to date. Due to the presence of charge compensating cations, confined structure and larger internal surface area there is the possibility that the zeolite can stabilize these intermediates. Therefore, a major focus of this study is to investigate the photochemical product formation of nitrate photolysis and the stability of intermediates within the unique environment of the zeolite pore structure under different environmental conditions including in the presence of water, molecular oxygen and ammonia. NaY zeolite was used in these studies as a model system to represent zeolite in mineral dust aerosol. Here we report the formation of stable surface nitrate in NaY zeolite formed by adsorption of nitric acid. We also report the formation of adsorbed NO_2^- and adsorbed NH_2 formed from nitrate photolysis in the absence and presence of ammonium ion, respectively, for the first time. Reaction mechanisms involved and environmental implications are discussed.

3.3 Materials and Methods

Commercially available NaY zeolite purchased from Sigma-Aldrich with a total surface area of $646 \pm 8 \text{ m}^2/\text{g}$ and a Si/Al ratio of 1.3 was used in this study. Scanning electron microscopy shows a range of zeolite particle sizes with an average diameter of ~ 1 µm. Zeolite surface areas were measured using an automated BET apparatus (Quantachrome Nova 4200e). Si/Al molar ratio was determined by acid digestion with HF

solution followed by neutralization in NaBO₃, using PerkinElmer Plasma 400 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP/AES). Dry HNO₃ vapor was obtained from a mixture of concentrated HNO₃ (60.03%, Fisher) and H₂SO₄ (95.6%, Mallinkrodt). Optima grade water (Fisher) was degassed before using. Anhydrous ammonia gas was purchased from Matheson Tri Gas.

Surface and gas phase products formed followed by HNO_3 adsorption and irradiation of adsorbed nitrate and ammonium nitrate were probed by transmission FTIR spectroscopy. The modified FTIR cell used in this study consists of a stainless steel cube with two BaF₂ windows. The inside of the cell is coated with Teflon to avoid HNO_3 decomposition on the walls. The sample cell is connected to a vacuum system comprises a two stage pumping system via a Teflon tube and a glass gas manifold with gas introduction ports and two absolute pressure transducers in the range 0.001-10.000 Torr and 0.1-1000.0 Torr. The vacuum system consists of a mechanical pump for rough pumping to 10^{-3} Torr and a turbo molecular pump for further pumping down to 10^{-5} Torr.

For these FTIR studies, about 20 mg of zeolite were sonicated in optima water (Fisher) for 30 min to form a hydrosol. The hydrosol was then transferred onto one half of a tungsten grid held in place by removable two Teflon coated jaws. Water was evaporated from the sample at room temperature to create a uniform thin film. The zeolite coated tungsten grid was placed in the infrared cell. The infrared cell is mounted on a linear translator. So both the sample-coated or blank grid halves could be positioned into the infrared probe by moving the cell through IR beam path. After overnight evacuation, zeolite samples were exposed to 100 ± 2 mTorr HNO₃ pressure for 30 min followed by overnight evacuation. The valve connecting the sample cell and Teflon tube was closed in

order to accumulate the gas phase products formed upon surface irradiation inside the cell. A 500 W Hg arc lamp (Oriel, model no. 66033), equipped with a water filter to remove IR radiation was used for photochemistry experiments. Additionally in some cases a broadband filter, with λ greater than 300 nm (Oriel filter no. 59425), was used. In a typical experiment HNO₃ was introduced into the infrared cell and Infrared spectra were collected with a single beam Mattson RS 10000 spectrometer with a narrow band MCT detector. In these experiments usually 250 scans were collected using WinFirst software with an instrument resolution of 4 cm⁻¹ in the 900 to 4000 cm⁻¹ spectral range. Absorbance spectra for gas phase and surface species were obtained by referencing single beam spectra of blank grid and zeolite coated grid to single beam spectra prior to HNO₃ adsorption. In some experiments H₂O, O₂ and NH₃ were also introduced into the FTIR cell. The sample was then irradiated with the Hg arc broadband source and products were monitored with FTIR spectroscopy.

3.4 Results and Discussion

3.4.1 HNO₃ adsorption in NaY zeolite

The transmission FTIR spectrum of NaY zeolite exposed to 100 mTorr HNO_3 is shown in Figure 3.1. Although nitric acid adsorption in NaY zeolite has not been previously reported in the literature there have been many studies of NO_2 adsorption in zeolite. Furthermore, in the presence of water nitric acid is formed from the hydrolysis of nitrogen dioxide in NaY zeolite. Thus there are many earlier studies (see Table 3.1) that can be drawn upon in order to assign the spectral features observed in this current studies.^{64-66, 70} Based on previous studies, HNO₃ interacts with the NaY zeolite forming Brønsted acidic OH groups and Na⁺NO₃⁻ species according to Reaction (3.1).⁶⁴

$$Zeo - O^{-} \dots Na^{+} + HNO_{3} \leftrightarrow Zeo - O^{-} \dots H^{+} + Na^{+}NO_{3}^{-}$$
 (3.1)

Figure 1 shows the spectrum of surface species formed in NaY zeolite after exposure to 100 mTorr HNO₃. The most intense feature observed in the spectrum is the strong absorption band centered at 1408 cm⁻¹ which is attributed to NO₃ ions complexed to Na⁺ sites inside the zeolite cage.⁷⁰ The absorption band at 1765 cm⁻¹ is attributed to v_1+v_4 combination vibration of NO₃⁻ ion.⁶⁴ Brønsted acidic O-H groups formed from HNO₃ adsorption are characterized by absorption bands at 3645 and 3550 cm⁻¹ in the O-H stretching region (see inset of Figure 3.1).⁶⁶ Additionally, as shown in the inset of Figure 3.1, an absorption at 3620 cm⁻¹ is most likely due to O-H stretching vibrations of molecularly adsorbed HNO₃.⁶⁶ The absorption band at 1210 cm⁻¹ follows the behavior of nitrate peak centered at 1408 cm⁻¹ for all the experiments discussed in this work. Therefore, this feature may be due to a different absorption mode of nitrate.⁷¹ The negative absorption features for water bending(δ_{HOH}) and stretching(v_{OH}) modes appear at 1640 and 3695 cm⁻ ¹ respectively.⁶⁶ They can be attributed to the formation of strongly hydrogen bonded $H^+(H_2O)_n$ species or complexes of water with newly formed Brønsted acidic hydroxyl groups upon nitric acid adsorption.⁷²⁻⁷⁴ The signature for hydrogen bonding is evidenced by the two broad absorption bands at ~ 2900 and ~ 2450 cm⁻¹.⁷²⁻⁷⁴ A third broad absorption band at ~ 1700 cm^{-1} is more difficult to see in Figure 3.1 because of other absorption bands in this region.⁷²⁻⁷⁴ These three broad absorption bands have been proposed to be characteristic of hydrogen bonded hydroxyls arise due to a Fermi resonance of zeolite OH stretch mode with the overtone of bending vibrations.⁷⁴



Figure 3.1: FTIR spectrum of NaY zeolite after exposing to 100 mTorr HNO₃. The spectrum was referenced to the zeolite surface before HNO₃ introduction. The inset shows the hydroxyl region following 100 mTorr HNO₃ adsorption.

3.4.2 Irradiation of Adsorbed Nitrate in the Absence of Relative Humidity (RH<1%)

After nitric acid adsorption and evacuation of gas-phase species, the zeolite sample with adsorbed nitrate was irradiated with a broadband light source as already described. Surface spectra recorded following 420 min irradiation of nitrate in the zeolite cage without any UV wavelength filters in place are shown in Figure 3.2. FTIR spectra showing the changes of adsorbed species during 420 min irradiation in the 1150 to 1800 cm⁻¹ spectral range are shown in Figure 3.2 (a). Figure 3.2 (b) shows the difference spectra of the same spectral region as in panel (a). These difference spectra are obtained by subtracting the zeolite

spectrum at time = 0 from the spectra obtained at different irradiation times. Difference spectra for the OH stretching are shown in Figure 3.2(c).

	Vibrational Frequency (cm ⁻¹)		Molecular Species and
	Current study	Literature	Vibrational Mode
	1408	1409	$v_3 (NO_3^-)$ on Na^+
	1765	1765	$v_1 + v_4$ combination vibration of
			NO ₃
	3645, and 3550	3640 and 3550	Brønsted acidic OH groups
	3620	3620	O-H stretch of HNO ₃
Surface	1640	1640	δ_{HOH} of adsorbed H_2O
species	3695	3695	ν_{OH} of H_2O
	2910 and 2440	2880-2930, 2400-	hydrogen bonded $H^+(H_2O)_n$
		2510, 1690-1700	or complexes of H_2O with OH
			groups
	1270	1270-1272	NO_2^- on Na^+
	1450	1450 and 1475	$\delta (\mathrm{NH}_4^+)$ of NH_4^+ deformation
Gas-	2224	2224	N ₂ O
phase	1874	1872	NO
species	1614	1614	NO ₂

Table 3.1: Assignment of vibrational frequencies of surface and gas-phase species



Figure 3.2: (a) FTIR spectra showing the changes of adsorbed species in NaY zeolite during 420 min irradiation under dry conditions (RH < 1%) in the spectral region extending from 1150 to 1800 cm⁻¹. (b) Same spectral region as in (a) but now shown as difference spectra. (c) Difference spectra of the O–H stretching region. Irradiation times are 30, 60, 120, 180, 240, 300, 360 and 420.

Upon irradiation, the nitrate band, centered at 1408 cm⁻¹, decreases in intensity as a function of irradiation while another band grows in at 1270 cm⁻¹. This band at 1270 cm⁻¹ ¹ is characteristic of nitrite complexed to Na⁺ ions in NaY zeolite as previously reported.^{65-⁶⁷ The loss of nitrate and the growth of nitrite in the zeolite cage as a function of time is seen as a decrease and increase in the infrared absorption bands at 1408 cm⁻¹ and 1270 cm⁻¹ ¹ respectively as shown in Figure 3.3. These are plotted as normalized amounts of nitrate and nitrite in the zeolite cage as determined by the integrated infrared absorptions between 1297and 1480 cm⁻¹ for nitrate and 1240 to 1296 cm⁻¹ for nitrite. When a broadband UV filter is put in place, with $\lambda > 300$ nm nitrite peak is still observed to form but of lower intensity without the filter. This may be due to the lower irradiance reaching the sample. Other than surface nitrite, very small amount of N₂O, NO and NO₂ are observed in the gas phase with absorption bands at 2224, 1874 and 1614 cm⁻¹, respectively.³²}



Figure 3.3: Surface nitrate loss and nitrite formation in NaY zeolite under dry conditions (RH < 1%) as a function of irradiation time. Error bars represent the standard deviation of three or more measurements. A 1:1 stoichiometry is assumed here as shown in Reaction (3.2) in the text.

Gas-phase product concentrations were insignificant in the presence of wavelength filters as well as at irradiation times shorter than 420 min. Formation of different surface bound and gas phase products in the zeolitic cage upon nitrate irradiation can be explained using well known photochemical reactions of nitrate ion in aqueous media, snowpack and recent studies of adsorbed nitrate.

Reaction (3.2) gives the overall stoichiometry of nitrate irradiation to form nitrite ion under acidic conditions.^{7, 32, 75-77}

$$NO_3^- \xrightarrow{h\nu} NO_2^- + O(^3P)$$
(3.2)

The exact mechanism of this reaction depends on the wavelength of light used for irradiation. At λ >290 nm, nitrate is directly converted to nitrite with an absorption maximum around 305 nm.^{7, 32, 75} But at λ < 290 nm nitrite formation can also take place via photoisomerization of nitrate to peroxynitrite ion as shown in Reaction (3.3).^{68, 75} Peroxynitrite ion can absorb light and reisomerize to nitrate ion under acidic conditions or dissociate to form nitrite.⁷⁸ In the current study we do not observe any absorption bands characteristic of peroxynitrite ion at 721, 815 and 943 cm⁻¹.⁷⁷ This observation may be due to rapid photoiosomerisation of peroxynitrite ion back to nitrate ion around 300 nm, rapid dissociation to nitrite ion in the zeolite cage or the lack of ability to see below 1000 cm⁻¹ due to lattice vibrations of the zeolite.^{77, 78} However it cannot absolutely be ruled out that peroxynitrite does not form in the photolysis of nitrate adsorbed in zeolite under the given experimental conditions.

$$NO_3^- \xleftarrow{h\nu} ONO0^- \xrightarrow{h\nu} NO_2^- + 0$$
 (3.3)

It was found here that the 1270 cm⁻¹absorption band persists even upon overnight evacuation indicating nitrite is highly stable in the zeolite cage. In similar studies done by

Rubasinghege and Grassian and Schuttlefield *et.al.* on the photochemistry of nitrate adsorbed on alumina surfaces, surface nitrite was not detected although its secondary photolysis product, nitric oxide was readily detected in the gas phase.^{32, 34} Rubasinghege and Grassian proposed an adsorbed nitrite intermediate in the reaction. This was based on the observation of NO as a photolysis product of nitrate adsorbed on alumina.³² In the zeolite cage, there is a potential to stabilize nitrite ions through a complex with Na⁺ ions in the confines of the three dimensional pore structure. Thus the presence of stable nitrite in zeolite can be attributed to the three dimensional structure of zeolite with charge compensating cations.

A second major product channel for nitrate photochemistry is the production of gaseous NO₂ around 305 nm according to Reaction (3.4) under acidic conditions.^{75, 79} As a result of this reaction, zeolitic water which formed H_3O^+ ions with H⁺ ions of nitric acid can thus be regenerated (Reaction 3.5). Water regeneration is evidenced by the appearance of 1640 and 3695 cm⁻¹ absorption bands in the difference spectra shown in Figure 3.2(b) and (c).

$$NO_{3}^{-} \xrightarrow{305 nm} NO_{2} + 0^{-}$$

$$O^{-} + H_{3}O^{+} \rightarrow OH + H_{2}O$$

$$O^{-} + H_{2}O \rightarrow OH + OH^{-}$$

$$(3.4)$$

$$(3.5)$$

In the confined space of zeolite with the presence of charge compensating cations the photochemistry favors nitrate to nitrite ion production over NO₂ formation.

NO₂ formed in Reaction (3.4) can further form HNO₃ and HONO through a wellknown hydrolysis reaction as shown below.⁶⁶ Acidic gases formed in this reaction can either release into the gas phase or reabsorb on the zeolite forming surface nitrate and nitrite.

$$2NO_2 + H_2O \leftrightarrow HNO_3 + HONO \tag{3.6}$$

NO₂ is the major irradiation product for shorter photolysis times (≤ 420 min). But for longer irradiation times (660 min) NO also become prominent in the gas phase. Therefore NO may be a secondary photolysis product. Possible reactions for gas phase NO formation by the secondary photolysis of NO₂ and NO₂⁻ are shown in Reaction (3.7) and (3.8).^{32, 80, 81}

$$NO_{2}^{-} + H^{+} \xrightarrow{365 nm} NO + OH$$

$$NO_{2} \xrightarrow{\leq 420 nm} NO + O(^{3}P)$$

$$(3.7)$$

$$(3.8)$$

None of the reaction mechanisms discussed above explains the formation of gas phase N₂O. In previous studies by Weisen *et.al*. it has been proposed that nitrous oxide is produced by the reaction of NO₂ with water under acidic conditions as shown below in the net Reaction (3.9).^{32, 82, 83}

$$8NO_2 + 3H_2O \xrightarrow{H^+} N_2O + 6HNO_3$$
(3.9)

Initial steps of this mechanism are produced to involve HONO as an intermediate via Reaction (3.3). Under acidic conditions HONO is then converted to hyponitrous acid $((HNO)_2 \text{ or } HON = \text{NOH})$ which in turn breaks down to yield N₂O and H₂O.

3.4.3 Effect of Molecular Oxygen and Relative Humidity on Nitrite Formation

Photochemical reactions in the atmosphere are highly affected by ambient conditions including temperature, pressure and the presence of oxygen and water vapor. Therefore, adsorbed nitrate photochemistry inside the zeolite cage was investigated at different relative humidities and in the presence of 150 Torr molecular oxygen.

As shown below, there is a clear effect of oxygen and relative humidity on photolysis product formation and product distribution. The presence of oxygen or an increase in relative humidity considerably slows down and inhibits the production of the observed nitrite. In the presence of oxygen only, the total residual nitrate in the zeolites after 420 min photolysis was 98 ± 1 % while that in the absence of oxygen was 74 ± 11 %. The effect of oxygen on zeolitic nitrite can be explained using the two step reaction mechanism shown in (3.10) and (3.11).^{75, 84}

$$0_2 + 0({}^3P) \to 0_3$$
 (3.10)

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2$$
 (3.11)

The first step of this mechanism is the production of ozone from the reaction of oxygen with triplet oxygen produced by nitrate photolysis. This ozone can then react with nitrite ions to form nitrate ions and molecular oxygen by the transfer of an oxygen atom from ozone to nitrite ion.^{85, 86} As a result of this reaction, nitrite can convert back to nitrate. The confined structure of the microporous zeolite can promote such reactions via trapping intermediates in the three dimensional structure in the proximity of nitrite ion providing a favorable orientation and geometry for the reaction to proceed. Lower surface nitrate loss in the presence of oxygen is a result of nitrate regeneration via Reaction (3.11).

The impact of water vapor on nitrate photochemistry was studied at four different relative humidity conditions, i.e. including 5, 20, 45 and 80 % RH. Surface nitrite was only observed to form at 5 % RH. Unlike under dry conditions, i.e. <1 % RH, gas phase products were more easily observed at higher relative humidity. Upon irradiation under all higher RH values, gas-phase nitric oxide forms. Gas phase N₂O was also observed. Gas phase NO₂ was absent for all the experiments carried out at different RH. Therefore there is a clear effect of relative humidity on nitrate photolysis in NaY zeolite. At higher relative humidities, water adsorbed in zeolite can solvate nitrate ions there by lowering the interactions with Na⁺ ions. Therefore, there is a possibility for zeolitic nitrate or nitrite ions to behave similar to nitrate ions in aqueous media. Moreover, due to the decreased stability of adsorbed nitrite ions they may further photolyse to form nitric oxide. In addition, absorbed water inside the zeolite cage can react with the photolysis product NO₂ to reform nitrate ions thereby hindering its release into the gas phase. Note that a small amount of N₂O and NO were observed in some control experiments as well but at very lower intensity which may be due to wall reactions.

3.4.4 Effect of Ammonia on the Photochemistry of Nitrate

To study the impact of ammonia on nitrate photochemistry, the zeolite sample was reacted with 100 mTorr of HNO₃ and then the infrared cell was exposed to gaseous NH_3 (500, 100 0r 50 mTorr) for 30 min. Upon adsorption of ammonia, a new peak centered at 1450 cm⁻¹ is formed and the nitrate peak centered at 1408 cm⁻¹ is red shifted to 1390 cm⁻¹ (Figure 3.4).



Figure 3.4: (a) FTIR spectra of the zeolite after exposing to 100 mTorr nitric acid in the v_3 nitrate region and (b) subsequent evacuation for 30 min followed by exposure to ammonia to produce ammonium nitrate as indicated by the change in the spectra.

The 1450 cm⁻¹ spectral feature is attributed to $\delta(NH_4^+)$ in the zeolite cage.⁵⁹ A shift of the nitrate vibrational frequencies is possibly due to changes in the interaction of the nitrate ion in the zeolite cage in the presence of both Na⁺ and NH₄⁺ present. Ammonium ions in zeolite are formed by the reaction of ammonia molecules with Brønsted acidic OH groups formed by HNO₃ adsorption.⁵⁹ Another mechanism for ammonia adsorption is the reaction with molecular nitric acid in zeolite forming ammonium nitrate

$$\operatorname{Zeo} - 0^{-} \dots \operatorname{H}^{+} + \operatorname{NH}_{3} \leftrightarrow \operatorname{Zeo} - 0^{-} \dots \operatorname{NH}_{4}^{+}$$
(3.12)

$$NH_3 + HNO_3 \leftrightarrow NH_4NO_3$$
 (3.13)

Changes of the surface nitrate absorption band during 420 min irradiation in the presence of adsorbed ammonia are shown in Figure 3.5(a) and 3.5(b). In the difference spectra in Figure 3.5(b), there is the clear appearance of the water bending mode at ~ 1640 cm⁻¹. Photochemistry of ammonium nitrate in the zeolite cage showed the formation of gas phase nitrous oxide only as determined by the absorption band at 2224 cm⁻¹ as shown in Figure 3.5(c). This observation is consistent with that reported by Rubasinhage *et.al.* on the photolysis of ammonium nitrate salt and ammonium nitrate adsorbed on aluminum oxide particle surfaces.⁶⁹ Based on the literature, the N₂O and H₂O products can be explained according to a three step sequence involving Reactions (3.4), (3.14) and (3.15). That is in the first step, nitrate ions undergo photochemistry to produce NO₂ and O⁻ according to Reaction (3.4), then in a second step the ammonium ion can react with O⁻ produced by the photolysis of nitrate ion and subsequently to produce N₂O as shown below.^{69, 78}

$$NH_4^+ + 0^- \rightarrow NH_2 + H_20$$
 (3.14)

$$NH_2 + NO_2 \rightarrow N_2O + H_2O$$
 (3.15)

During nitrate photolysis, a broad absorption band appears in the N-H/O-H stretching region centered at ~3400 cm⁻¹ in difference spectra of the zeolite surface. In NH₄Y zeolite, this broad absorption has a shoulder at ~3370 cm⁻¹ as shown in Figure 3.6. In NaY, this shoulder appears in the presence of adsorbed ammonia only. Therefore, this may be due to the formation of new species with N-H bonds during irradiation of ammonium nitrate such as NH₂.^{87, 88} The presence of stable NH₂ radical in zeolite pores have been previously reported in literature.^{89, 90} Although a second absorption band due to symmetrical stretching centered at 3290 cm⁻¹ is also reported, it is not noticeable in Figure 3.6.⁸⁸ In Figure 3.6, the

 3662 cm^{-1} absorption band can be attributed to OH stretching vibrations of newly formed H₂O in zeolite cages. Two broad bands centered at 3540 and 3466 cm⁻¹ may be due to (a) vibrations of hydroxyl groups in different chemical environments.



Figure 3.5: FTIR spectra during nitrate photolysis in NaY zeolite in the presence of adsorbed ammonia (a) Changes in nitrate region during 420 min irradiation are shown. Individual spectra were recorded after 0, 30, 60, 120, 180, 300 and 420 min. (b) Same data as shown in (a) but now shown as difference spectra during broadband irradiation. (c) FTIR spectra showing gas-phase products formed during broadband irradiation of adsorbed nitrate in the presence of ammonia. Only nitrous oxide, N₂O, is seen in the gas phase (2224 cm⁻¹ band).



Figure 3.6: Difference spectra of the O-H and N-H stretching region showing the changes of adsorbed species during 420 min irradiation of HNO₃ adsorbed NH₄Y zeolite under dry conditions (RH < 1%). Irradiation times are 30, 60, 120, 180, 300 and 420 min. See text for further details of intermediate species observed.

3.5 Conclusions and Atmospheric Implications

In summary, HNO₃ adsorption in NaY zeolite and chemical and photochemical reactions of nitrate adsorbed zeolite surface at different environmental conditions were studied using FTIR spectroscopy (a summary of chemical and photochemical reactions is presented in Table 3.2). HNO₃ reacts within the NaY zeolite cage to form a $Na^+NO_3^-$ complex with the charge compensating Na^+ cation and Brønsted acidic OH groups. Irradiation of nitrate in NaY zeolite produces nitrite which can be detected by infrared spectroscopy. The presence of stable nitrite in the zeolite can be attributed to the three-dimensional confined structure and the presence of charge compensating cations. Gas

phase N₂O, NO and NO₂ are formed at longer irradiation times and in very low concentrations. In the presence of molecular oxygen, nitrite is reconverted to nitrate. Surface nitrite coverages decrease with increasing relative humidity. Increased solvation of nitrite due to adsorbed water results in more gas phase NO. Gas phase ammonia adsorbed in the zeolite forms ammonium ions leading to NH_4NO_3 when reacted with molecular HNO₃. In the presence of ammonia, the major photolysis product is gas-phase N₂O.

$Zeo - O^- \dots Na^+ + HNO_3 \leftrightarrow Zeo - O^- \dots H^+ + Na^+NO_3^-$	(3.1)
$NO_3^- \xrightarrow{h\nu} NO_2^- + O(^3P)$	(3.2)
$NO_3^- \xleftarrow{h\nu} ONOO^- \xrightarrow{h\nu} NO_2^- + O$	(3.3)
$NO_3^- \xrightarrow{305 nm} NO_2 + O^-$	(3.4)
$0^- + H_30^+ \rightarrow 0H + H_20$	(3.5)
or	
$0^- + \mathbf{H}_20 \rightarrow 0\mathbf{H} + 0\mathbf{H}^-$	
$2NO_2 + H_2O \leftrightarrow HNO_3 + HONO$	(3.6)
$NO_2^- + H^+ \xrightarrow{365 nm} NO + OH$	(3.7)
$NO_2 \xrightarrow{\leq 420 \text{ nm}} NO + O(^3P)$	(3.8)
$8NO_2 + 3H_2O \xrightarrow{H^+} N_2O + 6HNO_3$	(3.9)
$0_2 + 0(^3\mathbf{P}) \rightarrow 0_3$	(3.10)
$NO_2^- + O_3 \rightarrow NO_3^- + O_2$	(3.11)
$Zeo - O^- \dots H^+ + NH_3 \leftrightarrow Zeo - O^- \dots NH_4^+$	(3.12)
$NH_3 + HNO_3 \leftrightarrow NH_4NO_3$	(3.13)
$NH_{4}^{+} + O^{-} \rightarrow NH_{2} + H_{2}O$	(3.14)
$\underbrace{\mathbf{NH}_2^2 + \mathbf{NO}_2 \rightarrow \mathbf{N}_2\mathbf{O} + \mathbf{H}_2\mathbf{O}}_{\mathbf{NH}_2\mathbf{O}}$	(3.15)

 Table 3.2: Summary table of chemical and photochemical reactions

The main focus of this study was to investigate nitrate photochemistry in the confined environment of a zeolite cage to demonstrate the impact of the physical structure of mineral dust particles on photochemical product formation and stability. NaY zeolite was used as a model system for these studies. Here we showed the photochemical product formation and product stability is affected by the physical structure. This study provides evidences for the formation of stable surface nitrite in mineral dust components upon irradiation of adsorbed nitrate, especially at low relative humidities. Nitrite adsorbed in the zeolite acts as an ozone scavenger showing the role of mineral dust in the coupling of NOx cycle with atmospheric ozone level. N₂O produced in nitrate photolysis, mainly in the presence of ammonia is an important greenhouse gas. Studies presented in this paper, which were done under controlled conditions, provide some insights into fundamental processes and mechanistic details of potentially important heterogeneous photochemical pathways.

3.6 Acknowledgement

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CHAPTER 4

NITRATE PHOTOCHEMISTRY ON LABORATORY PROXIES OF MINERAL DUST AEROSOL: WAVELENGTH DEPENDENCE AND ACTION SPECTRA²

4.1 Abstract

Nitrate ion adsorbed on mineral dust particles from reaction of nitric acid, nitrogen pentoxide and nitrogen dioxide with the particle surface, is thought to be a sink for nitrogen oxides but in fact it has the potential to release gas-phase nitrogen oxides back into the atmosphere when particle surfaces are irradiated with UV light. In this study, the wavelength dependence of nitrate ion photochemistry when adsorbed onto model laboratory proxies of mineral dust aerosol including Al₂O₃, TiO₂ and NaY Zeolite has been investigated using FTIR spectroscopy. These proxies represent non-photoactive oxides, photoactive semiconductor oxides and aluminosilicate materials, respectively, present in mineral dust aerosol. Nitrate photochemistry on mineral dust particles is governed by the wavelength of light, physicochemical properties of the dust particles and the adsorption mode of the nitrate ion. Most interestingly, in some cases, nitrate ion adsorbed on oxide particles can undergo photochemistry over a broader wavelength region of solar spectrum compared to nitrate ion in solution. As shown here, gas-phase NO_2 is the major photolysis product formed from nitrate adsorbed on the surface of oxide particles under dry conditions. The NO_2 yield and the initial rate of production is highest on TiO_2 indicating that nitrate photochemistry is more efficient on photo-active oxides present in

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mineral dust. Nitrite ion complexed to Na⁺ sites in aluminosilicate zeolite pores is the major photolysis product found in nitrate photochemistry in zeolites. Mechanisms for the formation of gas-phase and surface-adsorbed products and a discussion of the wavelength dependence of nitrate ion photochemistry are presented as is a discussion of the atmospheric implications.

4.2 Introduction

Mineral dust aerosol in the atmosphere provides reactive surfaces for heterogeneous reactions of nitrogen oxides including nitrogen dioxide, nitric acid and nitrogen pentoxide to form particulate nitrate.⁹¹⁻⁹⁶ Although the formation of particulate nitrate is often considered a sink for atmospheric nitrogen oxides, recent studies have shown that this particulate nitrate can be re-converted to nitrogen oxides in the presence of solar radiation leading to potential renoxification similar to nitrate in snowpack.^{91, 96} Atmospheric processes affecting NO_x concentrations are of great significance because ozone is formed by a complex series of non-linear reactions involving NO_x and volatile organic compounds.^{92, 93, 96} Therefore, studies focused on understanding the mechanism and kinetics of chemical and photochemical reactions involving particulate nitrate is of great importance.

It has been estimated that 1000 to 3000 Tg of mineral dust is annually emitted into the atmosphere.⁹² A large fraction of mineral dust is composed of oxides and aluminum silicates contributing to approximately 8% by mass of the total atmospheric dust loading.^{92,} ⁹⁶ Oxide fraction of mineral dust is dominated by SiO₂ (60%) and Al₂O₃ (10-15%).⁹² Aluminosilicate fraction is mainly composed of clays as well as some minor components including zeolite.^{92, 97} There are exchangeable cations (eg. Na⁺ and K⁺) often associated
with these aluminosilicate minerals to maintain a net neutral charge within the negatively charged framework.^{94, 98} Another important component in the oxide fraction is photo-active semiconductor oxides such as titanium dioxide and iron oxides which have the ability to photocatalyze reactions with solar light.⁹⁹ Given the complexity of composition, nitrate photochemistry on mineral dust aerosol can only be understood if materials representing the different components are investigated. In this study we choose three different model systems including aluminum oxide, titanium dioxide and sodium Y zeolite as representative non-photoactive oxides, photoactive semiconductor oxides and aluminosilicate materials to investigate details of nitrate photochemistry.

Nitrate ion shows two dominant absorptions in the UV region including an intense $\pi \rightarrow \pi^*$ transition around 200 nm and a weak $n \rightarrow \pi^*$ transition around 310 nm.¹⁰⁰ This weak $n \rightarrow \pi^*$ transition overlaps with the solar spectrum reaching the atmosphere (λ >290 nm) thus making nitrate ion an important chromophere in atmospheric chemistry. Recently, several laboratory studies have been carried out to understand the complex chemistry and kinetics of the photochemical reactions of nitrate associated with different mineral dust proxies.^{91, 96, 101-104} Titanium dioxide due to its semiconductor and photocatalytic properties can initiate interesting chemistry in the presence of solar light. Rosseler *et al.* and Ndour *et al.* have shown that nitrate adsorbed on TiO₂ can be converted to NO₂, NO and other reduced nitrogenous species upon irradiation.^{91, 104} Schuttlefield *et al.* and Rubasinghege and Grassian found that nitrate adsorbed on Al₂O₃ can be converted to NO, NO₂ and N₂O during broad band irradiation at $\lambda > 300$ nm. In another study, Rubasinghege *et al.* found that NO₂ is the major product formed from nitrate during 310 nm narrow band irradiation under a range of conditions.¹⁰² Previously, we showed that during broad band irradiation,

 $Na^+NO_3^-$ in NaY zeolite is converted to $Na^+NO_2^-$.¹⁰³ Thus, these studies noted above clearly show that photochemistry of surface adsorbed nitrate can significantly differ on different materials that may represent the range of activities that can occur for mineral dust aerosol.

There have been few studies on the wavelength dependence of nitrate photochemistry on mineral dust. Therefore, this current study is focused on understanding the wavelength dependence of the photochemistry of nitrate adsorbed on mineral dust particles using Al₂O₃,TiO₂, and NaY zeolite as mineral dust proxies. A major goal of the current study is to obtain action spectra for nitrate photolysis on these different proxies to better understand the wavelength dependence. Using nitric acid as the gas-phase precursor to adsorbed nitrate, these different mineral dust proxies were exposed to HNO₃ vapor and then the wavelength dependence was investigated by irradiating adsorbed nitrate with low pass or band pass optical filters. Additionally, previous studies on nitrate photochemistry using broadband irradiation on mineral dust surfaces suggest the existence of different intermediates leading to NO formation including surface adsorbed nitrite and HONO. However, broadband irradiation used in most previous studies can promote secondary photodecomposition of primary photoproducts thereby making their detection challenging. Therefore, another goal of this study is the investigation of the existence of intermediates formed in nitrate photochemistry on mineral dust surfaces proposed in previous studies in order to verify previously proposed reaction mechanisms.

4.3 Materials and Methods

Three different materials were used in these studies. These include TiO_2 , $\gamma - Al_2O_3$, and NaY zeolite. Average particle sizes for these were determined using the

images obtained by JEOL-1230 Transmission electron microscope and Hitachi S4800 scanning electron microscope. BET surface area of these samples was measured with a Quantachrome Nova 4200e BET apparatus. Si/Al ratio of zeolite was determined by acid digestion method using PerkinElmer Plasma 400 Inductively Coupled Plasma Optical Emission Spectrometer. Rutile/Anatase molar ratio of the TiO_2 sample was calculated using peak intensities of the X-ray diffraction pattern according to the method proposed by Spurr and Myers.^{105, 106} HNO₃ vapor was obtained from a 1:3 mixture of concentrated HNO₃ (60.03%, Fisher) and H₂SO₄ (96.0%, Fisher).

FTIR spectroscopy was used to probe the surface and gas phase products formed during photolysis of adsorbed nitrate on mineral dust model systems. The custom made FTIR setup with a Teflon coated IR cell used in the study is completely described in our previous work.¹⁰³ For FTIR studies, samples of mineral dust proxies were prepared either by pressing $(\gamma - Al_2O_3)$ or coating the hydrosol (TiO₂ and NaY zeolite) on one-half of a tungsten grid. Then the sample coated Tungsten grid attached to Teflon coated jaws on the upper lid is placed in the infrared cell and evacuated for seven hours down to 10⁻⁵ Torr. After evacuation, the samples are exposed to 100 mTorr HNO₃ vapor for 25 min and evacuate overnight at 10^{-5} Torr to remove all the weakly adsorbed species. Then, in order to accumulate gas phase products formed during irradiation, reaction chamber is isolated from the rest of the system by closing the valve between the infrared cell and gas handling system. In photochemistry experiments, sample inside the infrared cell was irradiated with the light emitted by a 500 W Hg arc lamp (Oriel, model no. 66033) equipped with a water filter to remove IR irradiation and a narrow band (254, 289, 310, 326 or 350 nm) or a broad band light filter with $\lambda > 295$ (Newport), > 320 (Edmunds optics) and > 335 nm (Newport)

cut off wavelengths as required. The 310 nm band pass filter was purchased from Andover Corporation and the others were purchased from Edmund Optics. Intensity dependent studies at 310 nm were carried out using neutral density (ND) filters of 0.6 and 0.3 optical density (25% and 50% nominal transmission respectively) purchased from Edmunds Optics. Irradiance and intensity profiles of the Hg lamp output with and without narrow band filters measured with RSP900-R spectroradiometer (International Light Technologies). In these experiments, which focused on the nitrate ion in the absence of coadsorbed water, all experiments were carried out under dry conditions (relative humidity, RH < 1%). Infrared spectra were collected using a single beam Mattson RS10000 spectrometer with a narrow band MCT detector. In a typical experiment, 250 scans were collected using WinFirst software with an instrument resolution of 4 cm⁻¹ in the spectral range of 900 to 4000 cm⁻¹. Surface and gas phase absorbance spectra were obtained by referencing the sample coated and blank grid single beam spectra at time = t to single beam spectra collected prior to gas adsorption (t = 0). In all experiments, changes for both the gas phase and surface were simultaneously monitored. All the data presented in this paper are the average of multiple replicate measurements (two or three).

4.4 **Results and Discussion**

4.4.1 HNO₃ Adsorption on Al₂O₃, TiO₂ and NaY Zeolite

 Al_2O_3 and TiO_2 and NaY zeolite surfaces were exposed to 100 mTorr HNO₃ vapor in order to form surface adsorbed nitrate. After exposure, the nitric acid vapor was evacuated overnight. The spectra following this procedure are shown in Figure 4.1a and b. Spectral features observed in these spectra can be assigned to adsorbed nitrate ion based on previous work (Table 4.1).^{93, 95, 107} On Al_2O_3 and TiO_2 , nitric acid adsorption results in predominantly oxide coordinated nitrate under the conditions used in this study with different modes of coordination to the surface. These include monodentate, bidentate and bridging adsorption modes to the surface. Other than oxide coordinated nitrate, infrared absorption bands characteristic of water solvated nitrate and molecularly adsorbed nitric acid were also identified in the surface spectrum for Al_2O_3 . Interaction of nitric acid with Al_2O_3 and TiO_2 can be described by reaction 4.1, where M stands for aluminum or titanium surface atoms.⁹³ In this reaction, nitric acid reacts with surface hydroxyl groups on oxide surfaces forming adsorbed nitrate and water molecules. Consumption of surface hydroxyl groups were observed as negative features in the OH stretching region of Al_2O_3 and TiO_2 surface spectra.

$$HNO_3 + M(OH) \rightarrow MNO_3 + H_2O \tag{4.1}$$

Nitric acid interacts with NaY zeolite forming Na⁺NO₃⁻ species according to reaction 4.2 as the main adsorbed product. Na⁺NO₃⁻ is characterized by the infrared absorption band centered at 1408 cm⁻¹ corresponding to v₃ mode of NO₃⁻ on Na⁺ sites (Figure 4.1c).^{70, 108} The negative feature observed in the spectrum is for water bending mode at 1640 cm⁻¹ which is proposed to be due to the formation of the hydronium ion or strongly hydrogen bonded species with water as described in our previous publication.¹⁰³

$$\text{Zeo} - 0^{-} \dots \text{Na}^{+} + \text{HNO}_{3} \leftrightarrow \text{Zeo} - 0^{-} \dots \text{H}^{+} + \text{Na}^{+} \text{NO}_{3}^{-}$$
(4.2)



Figure 4.1: FTIR spectra of oxide samples after exposing to 100 mTorr HNO_3 followed by overnight evacuation (a) Al_2O_3 (b) TiO_2 and (c) NaY zeolite. These spectra have been referenced to the clean surface prior to HNO_3 exposure. Assignment of absorption features are given in Table 4.1.

Surface description	Assignment .	Al_2O_3		TiO ₂		NaY	
		Literature	Current study	Literature	Current study	Literature	Current study
Monodentate	v_3 (high)	1565/1532107	1563/1537	1510107	1507	-	-
	$v_3^{}$ (low)	1306 ⁹³	1309	1283107	1285	-	-
Bidentate	$v_3^{}$ (high)	1587 ⁹⁵	1587	1584 ¹⁰⁷	1584	-	-
	v_3 (low)	1292/1306 ^{93,} 95	1309	1238	1233	-	-
Bridging	$v_3^{}$ (high)	1625 ⁹⁵	1627	1637 ¹⁰⁷	1637	-	-
	$v_3^{}$ (low)	1260 ⁹⁵	-	1230107	1233	-	-
	v_1	-	-	1005 ⁹³	1002	-	-
Solvated nitrate		1411 ⁹⁵	1415	-	-	-	-
		130795	1309	-	-	-	-
Ion complexed Na ⁺ NO ₃	v ₃	-	-	-	-	1409 ⁷⁰	1408
	$\nu_{1^+}\nu_4$	-	-	-	-	1765 ¹⁰⁸	1765

Table 4.1: Assignment of vibrational frequencies of surface adsorbed nitrate on oxide

 and Zeolite particles

4.4.2 Photochemistry of Nitrate Adsorbed on Oxide Particles

Broad band irradiation of adsorbed nitrate on Al_2O_3 with the full output of a Hg arc lamp yields an initial production of gas phase NO_2 (1614 cm⁻¹). The intensity of the NO_2 absorption band increases and is highest in these spectra after 15 min of irradiation. The intensity then decreases as a function of time after that as shown in Figure 4.2.⁹⁶ Concomitant with the loss of NO₂ from the gas phase, two other IR features appear at 1874 and 2224 cm⁻¹ which are characteristic of gas-phase NO and N₂O, respectively.⁹⁶ On Al₂O₃, adsorbed NO has an infrared absorption frequency of 1721 cm⁻¹, which is also detected in these experiments.⁹⁶ Broadband irradiation of adsorbed nitrate on TiO₂ under dry conditions show some similarities to Al₂O₃, however, surface adsorbed NO was not detected on TiO₂.

The wavelength dependence of nitrate photochemistry on these mineral dust proxies were investigated using the light output of the Hg lamp with 254, 289, 310, 326 and 350 nm filters in place. In narrow band irradiation, gas phase NO_2 is the only photolysis product detected on both Al_2O_3 and TiO_2 (Figure 4.3a and b). In contrast to broad band irradiation, the concentration of gas phase NO_2 produced from photolysis of adsorbed nitrate on oxide particles increased with time at all five wavelengths investigated.

Action spectra for the production of gas phase NO_2 by nitrate adsorbed on oxide particles are given in Figure 4.4. These action spectra are clearly different between the two oxides. These action spectra show a significantly higher NO_2 production for TiO₂ compared to Al_2O_3 . More interestingly, NO_2 production on Al_2O_3 is near zero at 350 nm probably caused by photodissociation at near threshold wavelength for UV absorption by nitrate adsorbed on alumina.¹⁰⁹ In contrast, on TiO₂, although the NO_2 yield is decreased towards 350 nm, it still remains noticeably high due to the semiconductor properties of this oxide (*vide infra*). The action spectrum for nitrate adsorbed on Al_2O_3 is in good match with the UV/Vis diffuse reflectance spectrum for nitrate adsorbed on Al_2O_3 reported by Goodman *et al.* especially near the threshold wavelength¹⁰⁹



Figure 4.2: Gas phase species produced during broad band irradiation of nitrate adsorbed on oxide particles with the full Hg lamp output (a) on Al_2O_3 and (b) on TiO₂.

(a) $Al_2 0_3$



Figure 4.3: Gas phase species formed in narrow band irradiation of adsorbed nitrate at different wavelengths including: 254, 289, 310, 326 and 350 nm. Gas-phase spectra after 90 min irradiation of nitrate (left panel) and time dependent variation of NO_2 product concentration formed from nitrate (Right panel) adsorbed on (a) Al_2O_3 and (b) on TiO₂. Blank experiments shown here were performed in order to explore if there is any NO_2 production in the absence of irradiation. All NO_2 concentrations have been normalized to the highest gas-phase NO_2 concentration.

Action spectra for the production of gas phase NO_2 by nitrate adsorbed on oxide particles are given in Figure 4.4. These action spectra are clearly different between the two oxides. These action spectra show a significantly higher NO_2 production for TiO₂ compared to Al_2O_3 . More interestingly, NO_2 production on Al_2O_3 is near zero at 350 nm probably caused by photodissociation at near threshold wavelength for UV absorption by nitrate adsorbed on alumina.¹⁰⁹ In contrast, on TiO₂, although the NO_2 yield is decreased towards 350 nm, it still remains noticeably high due to the semiconductor properties of this oxide (*vide infra*). The action spectrum for nitrate adsorbed on Al_2O_3 is in good match with the UV/Vis diffuse reflectance spectrum for nitrate adsorbed on Al_2O_3 reported by Goodman *et al.* especially near the threshold wavelength¹⁰⁹



Figure 4.4: (a) Action spectra for NO_2 production from nitrate adsorbed on oxide particles for 90 min irradiation (b) Variation of intensity normalised NO_2 concentration with wavelength. All the NO_2 concentrations have been normalized to the highest gas-phase NO_2 concentration.

Although the intensity of 310 nm narrow band light is approximately four times higher than that at other wavelengths, NO_2 production does not show a complementary increment as seen in Figure 4.4a which is more prominent in the action spectrum for TiO₂. This feature is clearer in the intensity normalized NO_2 concentration vs wavelength plot shown in Figure 4.4b. Observed results for the irradiation of nitrate adsorbed on oxide surfaces at 350 nm clearly show that wavelength is the limiting factor of surface nitrate photolysis. Intensity signal of 254 nm light was very low to be distinguished from the background signal. Therefore NO_2 production at 254 nm was not included in Figure 4.4b. Additionally, it was found that the initial rate of NO_2 production from adsorbed nitrate on TiO₂ is always higher than Al_2O_3 (Table 4.2).

Table 4.2: Relative rates of NO_2 formation from nitrate adsorbed on oxide particles atdifferent wavelengths

Relative rate of $NO_2(g)$ production (TiO ₂ / Al ₂ O ₃)					
254 nm	289 nm	310 nm	326 nm	350 nm	
3	6	7	7	80	

In a previous study by Ndour *et al.*, the photochemistry of nitrate on pure SiO₂ and TiO₂/SiO₂ mixed films⁹¹ showed gas-phase NO_x production only for nitrate adsorbed on TiO₂/SiO₂ films. Therefore they concluded that observed NO_x production arise from photocatalytic properties of TiO₂. In agreement with Ndour *et al.*, the TiO₂ action spectra obtained in this current study show that the dissociation of nitrate is significantly enhanced for the semiconductor oxide (TiO₂) compared to the non-semiconductor (Al₂O₃). Although the shape of the curve is currently not well understood with a dip in the yield seen at 310

nm for TiO₂, the intensity normalized spectrum is much higher for TiO₂ compared to Al_2O_3 at all wavelengths (Figure 4.4b). Additionally, all the NO₂ concentrations present in this work were normalized to the total surface area of oxide sample to eliminate the effect of sample mass and particle surface area.

It should be noted that several control experiments were carried out using full output of the Hg arc lamp in the absence of oxide or zeolite samples confirmed that there is no contribution from wall reactions of the Teflon coated FTIR cell for the reported NO_2 yield. Although there is some NO_2 background observed over longer time periods, experiments presented here were carried out only for 90 min to eliminate background effects. This study clearly shows that wavelength is the limiting factor for NO_2 production from adsorbed nitrate. Additionally, intensity dependence of NO_2 production was studied at 310 nm from nitrate adsorbed on Al_2O_3 surface and the results of this show a linear relationship between NO_2 production and light intensity. This observation confirms that NO_2 product observed in the current study is generated in a photochemical reaction and not due to a thermal reaction.

Reaction Mechanisms

Mechanisms of gas-phase product formation for the photolysis of nitrate adsorbed on Al_2O_3 has been extensively discussed in previous work done by Shuttlefield *et al.* and Rubasinghege and Grassian.^{96, 101} Gas-phase NO₂ can be formed by direct photolysis of surface adsorbed nitrate ion on Al_2O_3 under acidic conditions as shown in reaction 3.^{96, 100, ¹⁰¹ There are two possible routes for NO formation including the secondary photolysis of NO₂ and via nitrite ion intermediate according to reaction 4.4 to 4.6.^{80, 96, 100, 101}}

$$NO_3^- + H^+ \xrightarrow{h\nu} NO_2 + OH$$
(4.3)

$$NO_2 \xrightarrow{\leq 420 \text{ nm}} NO + O(^3P) \tag{4.4}$$

$$NO_3^- \xrightarrow{h\nu} NO_2^- + O(^3P)$$
(4.5)

$$NO_{2}^{-} + H^{+} \xrightarrow{365 \text{ nm}} NO + OH$$

$$(4.6)$$

In addition to the mechanisms and reactions provided above, the photochemistry on semiconductor photocatalysts such as TiO₂ can also be initiated by the generation of electrons in the conduction (e_{cb}^-) band and holes (h_{vb}^+) in the valence band through absorption of UV radiation at wavelengths less than 390 nm.¹¹⁰ In this mechanism, the h_{vb}^+ generated by light absorption can react with surface adsorbed nitrate to form nitrate radical (NO₃) which has a very short lifetime.^{110, 111} The nitrate radical absorbs visible light and can then go on to form NO₂ and NO in the wavelength range of $\lambda \le 640$ nm and 585 nm \le $\lambda \le 640$ nm respectively.¹¹²⁻¹¹⁵ Therefore, the NO₃ \rightarrow NO₂ channel is more prominent at shorter wavelengths.¹¹⁶ It has also been reported that reaction 4.9 is much faster than reaction 4.10 with photolysis rate constants of ~0.18 s⁻¹ and ~0.022 s⁻¹ respectively.¹¹⁵

$$\mathrm{TiO}_{2} + \mathrm{hv} \xrightarrow{<390 \,\mathrm{nm}} \mathrm{e}_{\mathrm{cb}}^{-} + \mathrm{h}_{\mathrm{vb}}^{+} \tag{4.7}$$

$$NO_3^- + h_{vb}^+ \to NO_3^{\bullet}$$

$$\tag{4.8}$$

$$NO_3^{\bullet} \xrightarrow{\leq 640 \text{ nm}} NO_2 + 0^{\bullet}$$
(4.9)

$$NO_3^{\bullet} \xrightarrow{585 \text{ nm} \le \lambda \le 640} NO + O_2$$
(4.10)

The approximately ten times faster rate of reaction 4.9 compared to reaction 4.10 accounts for the absence of NO in the spectra collected after 15 min during broad band irradiation. Although NO₃[•] is formed on TiO₂ in the presence of UV light at any $\lambda < 390$ nm, its photolysis is limited to the visible region as given above. Therefore, reaction 4.9 and 4.10 are unlikely to occur in narrow band irradiation with UV light especially at shorter wavelengths. Another pathway for NO_3^{\bullet} loss is its self-reaction to produce NO_2 and O_2 as shown in reaction 4.11.¹¹⁷⁻¹¹⁹ Enhanced NO_2 production observed on TiO₂ in the UV range compared to Al₂O₃ is probably due to this self-reaction.

$$\mathrm{NO}_3^{\bullet} + \mathrm{NO}_3^{\bullet} \to 2\mathrm{NO}_2 + \mathrm{O}_2 \tag{4.11}$$

 NO_3^{\bullet} can also react with NO_2 to produce NO (reaction 4.12). However, this NO can rapidly react with NO_3^{\bullet} according to reaction 4.13 cancelling out the contribution of reaction 4.12 for the total NO budget. ¹¹⁸

$$NO_3^{\bullet} + NO_2 \rightarrow NO + NO_2 + O_2$$

$$NO_3^{\bullet} + NO \rightarrow 2NO_2$$

$$(4.12)$$

$$(4.13)$$

Other than reaction 4.5, on TiO_2 , NO_2 formed in above photodecomposition reactions can also produce nitrite ions by the reaction with e_{cb}^- in the conduction band.¹¹⁰

Further, in the presence of H⁺ ions, nitrite formed by direct photolysis of nitrate ion on

$$NO_2 + e_{cb}^- \rightarrow NO_2^- \tag{4.14}$$

oxide surfaces by reaction 4.5 and/or by the reaction of NO_2 with e_{cb}^- on TiO_2 can form HONO as shown below in reaction 4.15.¹¹⁰ The HONO product can also photodecompose to NO at wavelengths shorter than 400 nm.

 $NO_2^- + H^+ \to HONO \tag{4.15}$

 $HONO \xrightarrow{\lambda < 400 \text{nm}} \text{NO} + \text{OH}$ (4.16)

Similar to previous studies, adsorbed nitrite or HONO were not detected during photolysis of adsorbed nitrate on oxide particles. Interestingly, NO production was absent even at 254, 289, 310 and 326 nm where nitrite photolysis does not occur. Prompt NO₂ formation and the absence of nitrite suggest that reaction 4.3 is the major photolysis pathway of nitrate adsorbed on Al_2O_3 under dry conditions. Therefore, photochemically formed NO₂ is the main source of gas phase NO observed in broad band irradiation of nitrate adsorbed on Al_2O_3 and not adsorbed nitrite or nitrous acid. Other than reaction 4.3, NO_2 can also be formed via NO_3^{\bullet} on TiO₂, as discussed above. Although there is no direct evidence for the formation of NO₃, enhanced NO₂ production on TiO₂ compared to Al₂O₃ provides indirect evidence for the existence of another product channel. Considerably higher NO₂ production from nitrate adsorbed on TiO₂ at higher wavelengths including 326 and 350 nm where nitrate photolysis via reaction 4.3 is lowest may be due to the overlap of narrow band light with the NO₃ absorption spectrum. Significantly low gas phase NO₂ concentration and lower irradiation reaching Al₂O₃ and TiO₂ surfaces may be responsible for the absence of NO during narrow band irradiation of nitrate on oxide particles. Other than these reasons, hindrance of reaction 4.10 in the UV range can also responsible for the absence of NO in narrow band irradiation of nitrate adsorbed on TiO_2 .

The above discussion does not describe the formation of gas phase N_2O observed in broad band irradiation. As reported previously, N_2O formation can be explained using dark reactions proposed by Malecki and Malecka in their studies on thermal decomposition of d-metal hydrate nitrates.^{96, 110, 120} The prompt appearance of N_2O with the depletion of NO_2 suggests that reaction 4.17 is the most likely reaction to occur in the current study. Further, Bedjanian and Zein, in their work on the interaction of NO_2 with TiO₂ surface under UV irradiation also claim the plausibility of the above reaction over other mechanisms suggested by Malecki and Malecka.¹¹⁰

$$NO_2 + NO_3^- \rightarrow N_2O + \frac{7}{4}O_2 + \frac{1}{2}O^{2-}$$
 (4.17)

Rusu and Yates have found that NO is converted to gas phase N_2O on TiO₂ surface even at sub band gap photon energies less than 3.2 eV (387 nm) which can be given by the overall reaction 4.18.¹²¹ Further, Rosseler *et al.* has also been reported the conversion of adsorbed nitrate on TiO₂ to N_{red} during irradiation under dry condition at 365 nm.¹⁰⁴

$$2NO(a) \xrightarrow{h\nu} N_2 O(g) + O(a)$$
(4.18)

4.4.3 Nitrate Photochemistry in NaY Zeolite

In order to study the wavelength dependence, nitrate ion adsorbed in zeolite was irradiated with a series of band pass (254, 289, 310, 326 and 350 nm) and broad band (>295. >320, >335 nm) filters in place for 420 min. In contrast to oxides, surface nitrite ions complexed to Na⁺ sites (Na⁺NO₂⁻) are the major photolysis product formed in broad band irradiation of nitrate in zeolite (Figure 4.5). Formation of surface nitrite is characterized by an absorption band centered at 1270 cm⁻¹ in surface spectra.^{66, 103, 122, 123} It was observed that at lower coverage this absorption band shifts to higher wavenumbers. Stability of surface nitrite formed during irradiation was confirmed by the presence of nitrite absorption feature in the surface spectra obtained after overnight evacuation. In addition to nitrite, formation of water molecules was also observed during irradiation of nitrate on the zeolite surface which is characterized by water bending vibrations at 1637

cm⁻¹ in the surface spectra. Formation of surface nitrite during photolysis can be explained using reaction 4.3.

In broad band irradiation experiments, surface nitrite formation was decreased with increasing cut off wavelength of broad band light and was no longer produced with $\lambda > 335$ nm (see Figure 4.5). According to the action spectrum shown in Figure 4.6a for surface nitrite formation during broad band irradiation, nitrate in zeolite shows the highest photoactivity in the wavelength range from 295 to 320 nm. Further endorsing the above statement, in irradiation with band pass filters in place, nitrate was formed only at 310 and 326 nm with minimal detectable surface adsorbed nitrite at 326 nm.



Figure 4.5: Changes of surface species on NaY zeolite during irradiation with broad band light

This lower yield for nitrate adsorbed in the zeolite may be due to cage effects and/or the stabilization by complexation to the charge compensating Na⁺ ions.¹⁰³ Action spectra obtained for surface adsorbed nitrite formation in narrow band irradiation are shown in Figure 4.6b. Variation of intensity normalized surface nitrite concentrations showed a similar trend to oxides (inset of Figure 4.6b). In these experiments, Gas phase products were not observed during irradiation of nitrate adsorbed in zeolite.



Figure 4.6: Action spectra for nitrite production from nitrate adsorbed on NaY zeolite (a) broad band irradiation (b) narrow band irradiation. The inset of figure 6b shows the variation of intensity normalized surface nitrite concentration with wavelength. All the surface nitrite concentrations have been normalized to the largest surface nitrite concentration.

Action spectra obtained for irradiation of nitrate adsorbed on Al₂O₃, TiO₂, and NaY Zeolite clearly show that the photoactivity of the nitrate ion is significantly different among these three materials. First, the products formed are different (gas-phase NO_2 for TiO_2 and Al₂O₃ compared to adsorbed nitrite in NaY). Second, nitrate adsorbed on oxide particles are photoactive over a much wider range of wavelengths compared to NaY zeolite. This may be due to the heterogeneity of the surface and the different adsorption sites for nitrate. This leads to broadening of the UV absorption spectrum.¹²⁴ In contrast, the nitrate ion in NaY zeolite exists as $Na^+NO_3^-$ within a crystalline cage which is a more homogeneous environment. The action spectrum for nitrate photolysis in zeolite is complementary to the UV/Vis diffuse reflectance spectra for NaNO₃, formed by NO₂ adsorption on NaCl, as reported by Goodman *et al.*¹⁰⁹ Furthermore, Goodman *et al.* reports a red shift of $n \rightarrow \pi^*$ transition of nitrate when coordinated to oxide surfaces compared to that found for NaNO₃.¹⁰⁹ Therefore, nitrate complexed to sodium ions in NaY zeolite in the confined zeolite cage may be potential reasons for the difference of nitrate photolysis at longer wavelengths.

4.4.4 Comparison of Nitrate Photochemistry on Mineral Dust with Aqueous Solution

For the comparison of nitrate photochemistry on mineral dust with aqueous nitrate, 0.01 M aqueous HNO_3 were irradiated with narrow band light emitted by a 500 W Hg arc lamp with 254, 310 and 350 nm narrow band filters in place for 420 min. Photoactivity of aqueous nitrate was monitored by measuring the nitrite ion concentration using Griess reagent (Life technologies). These studies showed that aqueous nitrate photolysis stops at

350 nm where the UV absorption of aqueous nitrate ion approaches zero (Figure 4.7). Comparison of the action spectra for nitrate photolysis on oxide particles and solution reveals an extension of photo-activity to longer wavelengths in some cases due to surface adsorption and the semiconductor properties of some of the dust particles (TiO_2) . The shorter wavelength region, which is not relevant to the tropospheric photochemistry, also differs between the solution phase action spectrum and the adsorbed nitrate action spectra. Reasons for this may include differences in quantum yields, cage effects and the formation mechanisms for different photoproducts. Further, studies in the shorter wavelength regime are warranted to understand these differences.



Figure 4.7: Action spectrum for nitrite ion production in aqueous nitric acid solutions. The inset shows the absorption spectrum for the solution.

4.5 Conclusions and Atmospheric Implications

In summary, the wavelength dependence of the photochemistry of nitrate adsorbed on mineral dust were studied using Al₂O₃, TiO₂ and NaY zeolite as proxies to represent non-photoactive oxides, photoactive oxides and aluminosilicate, respectively. In particular, a comparison of photoproduct yields and rates were compared for nitrogen-containing products for nitrate adsorbed on these different materials and nitrate in solution. This study shows that nitrate photochemistry on mineral dust particles are governed by the wavelength of light, physicochemical properties of the dust particles and the adsorption mode of the nitrate ion. Although wavelength is the limiting factor of nitrate photolysis, product concentration is governed by light intensity. Further substantial differences observed between aqueous nitrate and mineral dust nitrate photochemistry in the current study clearly shows that nitrate photochemistry is highly altered upon surface adsorption. Recent studies using cavity ringdown spectroscopy have clearly shown changes in gas-phase nitric acid photolysis compared to that for adsorbed nitric acid, this current study compares nitrate photochemistry in solution versus adsorbed and also shows significant differences and changes.^{38,39} Taken together, these studies indicate that surface photochemistry and heterogeneous photochemistry of mineral dust aerosol are important areas for further study.

According to this study, surface adsorbed nitrate on mineral dust shows the highest photo-activity to produce NO_2 in 300 – 350 nm region under dry conditions which overlaps well with the atmospheric window (300-800 nm) of the solar spectrum.¹¹¹ Further it has been found that over 90% of the NO_2 molecules in the atmosphere is dissociated in to NO and O between 300-370 nm region.¹¹¹ Therefore a larger fraction of NO_2 generated from nitrate adsorbed on mineral dust surfaces should be finally converted to gas phase NO.

Additionally, nitrite ions formed from nitrate adsorbed on aluminosilicate components in mineral dust can act as a source of daytime HONO which can also be dissociated into NO at $\lambda < 400$ nm. Therefore, mineral dust nitrate photochemistry has a great impact on atmospheric NO concentration. These activities of mineral dust nitrate and nitrogen oxides occurs mainly in troposphere in the 300-400 nm wavelength region can cause a significant impact altering the solar radiation spectrum of the earth's atmosphere similar to O_2 and O_3 . The formation of gas phase nitrogen oxide photoproducts which include NO_2 , NO and $\mathrm{N}_2\mathrm{O}$ during irradiation for the oxide materials investigated indicate the importance of mineral dust nitrate photochemistry as a source of potential renoxification. Nitrate adsorbed on mineral dust can be transported long distances with wind currents thereby affecting the NO_x levels in remote locations as well. NO_x is a major component responsible for photochemical smog formation. N₂O produced by surface mediated reactions on oxide surfaces is an important greenhouse gas. Studies presented in this paper which were done under controlled laboratory conditions provide important insights into understanding atmospheric reactions of nitrate associated with mineral dust particles which, although important, may be difficult to isolate in actual atmospheric settings.

4.6 Acknowledgement

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CHAPTER 5

ROLE OFATMOSPHERIC CO2 AND H2O ADSORPTION ON ZnO AND CuO NANOPARTICLE AGING: FORMATION OF NEW SURFACE PHASES AND ITS IMPACT ON NANOPARTICLE DISSOLUTION

5.1 Abstract

Heterogeneous reactions of atmospheric gases with metal oxide nanoparticle surfaces have the potential to cause changes in their physicochemical properties including their dissolution in aqueous media. In this study, gas-phase carbon dioxide adsorption on ZnO and CuO nanoparticle surfaces has been studied as a function of relative humidity in order to better understand the role of CO₂ and H₂O on nanoparticle aging and the increased mobilization of metal ions in these nanoparticles when in contact with these atmospheric gases. In particular, temporal variations of surface adsorbed species upon exposure to atmospherically relevant pressure of CO2 under different relative humidity (RH) conditions were monitored using transmission infrared spectroscopy. The adsorption of CO_2 on these two oxide nanoparticles shows interesting changes with increasing relative humidity. Under dry conditions, gas phase CO_2 readily reacts with surface hydroxyl groups present on the nanoparticle surface to form adsorbed bicarbonate whereas the interaction of CO₂ with surface defect sites and lattice oxygen gives rise to surface adsorbed monodentate and bidentate carbonate species as well as adsorbed carboxylate. With increasing relative humidity from 0 to 70 %, surface speciation gradually changes to that of water-solvated adsorbed carbonate. At the highest relative humidity, 70 % RH, water-solvated adsorbed carbonate was the only detectable surface species. Further analysis of reacted ZnO and CuO nanoparticles with high resolution TEM shows considerable surface restructuring consistent with precipitation of carbonate phases in the presence of adsorbed water. Furthermore, although the reactivity of ZnO and CuO nanoparticles with CO₂ is limited to the near surface region, there are significant changes in their dissolution when placed in aqueous media. Thus, this work provides insights into reactions of atmospheric gases, CO₂ and H₂O, on ZnO and CuO nanoparticle surfaces and the irreversible changes in surface properties and behavior in aqueous media.

5.2 Introduction

The extremely small size of nanoparticles results in a very high percentage of surface atoms compared to larger size particles, which leads them to have novel physicochemical properties and high reactivities.¹²⁵⁻¹²⁷ Because of these and other unique features, nanoparticles are increasingly used in a variety of technological applications.¹²⁵ ZnO nanoparticles are widely used in personal care products, coatings, paints, textiles and optical and electronic materials.¹²⁸⁻¹³¹ According to a modeling study by Sun *et al.*, the total ZnO nanoparticle production in Europe itself was more than one thousand metric tons in 2012 and approximately 80 % of it has been used for cosmetics and the rest in paints and plastic or polymers.^{132, 133} Nanoscale CuO is also used in a variety of industrial applications such as gas sensors, photovoltaic cells, heat transfer nano fluids and catalytic processes.^{50, 128, 129} Rapid growth in the production of engineered nanomaterials and their use in consumer products and industrial applications has also increased the potential release of nanoparticles into the environment and human and ecological exposure risks.^{125, 134}

Once released into the environment, engineered nanomaterials can undergo aging or corrosion in the presence of trace atmospheric gases. It is an important phenomena leading to modification of nanoparticle surfaces. This aging process due to the interaction

with atmospheric gases could start almost immediately after the synthesis and continue to occur during their pre-use i.e. storage and transport and also in the fabrication of products.¹³² There have been several studies on atmospheric aging of nanomaterials. Pan *et.al.* have reported the formation of $ZnCO_3$ on ZnO nanowires exposed to atmospheres containing CO₂ in the presence of a small amount of moisture.¹³⁵ Turber and coworkers have shown that pure and Fe-doped ZnO nanoparticles show both magnetic and structural changes due to aging in ambient conditions.¹³⁶ In another study, Mudunkotuwa et.al. showed that copper nanoparticles form a surface oxide coating that increases upon atmospheric aging which results in completely different solution phase chemistry compared to the pristine nanoparticles.⁵⁰ Aging can cause increased dissolution of metal oxide nanoparticles, resulting in greater amount of metal ions in aqueous suspensions. It is well known that particle chemical composition and surface properties are two important factors governing the dissolution of nanoparticles which in turn regulates the persistence of nanoparticles in the environment and biological response of living organisms to nanoparticles.¹³⁷

Toxicity of metal-based nanoparticles through dissolution is said to be more common for Class B soft metal cations such as the cations of Ag, Zn and Cu.¹²⁷ It has been found that nanoparticles of CuO are up to 50 times more toxic than bulk CuO particles to crustacians.¹³⁸ Solubility of CuO and ZnO nanoparticles to release Cu²⁺ and Zn²⁺ is one of the key reasons for their enhanced toxicity.¹³⁸ Furthermore, some studies show that surface functionalization of carbon nanotubes and sulfidation of silver nanoparticle surfaces due to aging in the atmosphere.^{132, 139, 140} It has also been reported that this atmospheric transformation of carbon nanotubes significantly alter their toxicity by lowering its redox activity and cytotoxicity.¹³⁹ Additional studies show that nanoparticles interact with atmospheric gases such as oxygen, carbon dioxide, hydrogen sulfide, nitrogen dioxide, sulfur dioxide, chloride and airborne moisture which results in changes in nanoparticle surface composition, morphology, crystallinity, fate and toxicity relative to pristine nanomaterials.^{50, 127, 135, 141, 142}

Here we present a systematic investigation of potential aging processes for ZnO and CuO nanoparticles mediated by the surface adsorption of CO₂ and H₂O under atmospherically relevant conditions. Nanoparticle aging under controlled conditions was monitored *in situ* using FTIR spectroscopy. These particles were also analyzed after exposure to CO₂ at various relative humidities using powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) in order to understand the effect of aging on the formation of other phases that may play a role in particle physicochemical properties. As such, the dissolution of aged nanoparticles was also investigated using inductively coupled plasma optical emission spectroscopy (ICP-OES), in order to understand the effect of aging of nanoparticles on the release of dissolved Zn²⁺ and Cu²⁺ which are known to be toxic to organisms.

5.3 Materials and Experimental Methods

5.3.1 Materials

ZnO nanoparticle samples were purchased from Meliorum Technologies. CuO nanoparticles and HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer

were obtained from Sigma Aldrich. Research grade carbon dioxide gas was purchased from Praxair. Optima water was purchased from Fisher scientific.

5.3.2 Nanoparticle Characterization

Bulk crystalline phase of the nanoparticles were examined using powder X-ray diffraction (XRD) patterns collected using Bruker D8 advance X-ray diffractometer. Nanoparticle sizes were determined with at least two hundred randomly selected particles using TEM images obtained by JEOL 1230 transmission electron microscope and JEOL 2100F high resolution transmission electron microscope (HRTEM). Total surface areas of ZnO and CuO were determined using a Quantachrome Nova 4200e multipoint BET surface area analyzer. All the samples were heated overnight at 120 °C under vacuum prior to surface area analysis. Surface area measurements on each sample were done in triplicate. Surface composition of nanoparticles were analyzed using Kratos Axis Ultra X-ray photoelectron spectrometer. All the XPS spectra were calibrated using C1s adventitious carbon peak at 285.0 eV.¹⁴³

5.3.3 Transmission FTIR Studies of CO₂ (g) Adsorption on ZnO and CuO Nanoparticles

The adsorption of gas phase CO₂ on ZnO and CuO nanoparticle surfaces at different relative humidity conditions was studied using transmission FTIR spectroscopy. The experimental setup has been described in detail elsewhere.¹⁴⁴ FTIR spectra were collected using a Mattson Galaxy 6000 spectrometer equipped with a liquid nitrogen cooled MCT (mercury-cadmium-telluride) detector. All the nanoparticle samples were calcined at 550 ^oC for 6 hours prior to adsorption experiments and stored in a nitrogen purged glove box until use. Approximately 25 mg of ZnO or CuO samples were mixed with optima water

and sonicated for 1 minute in order to form a hydrosol. This hydrosol was then transferred on to one half of a tungsten grid held in position by nickel jaws using a pipette. The sample coated tungsten grid was attached to thermocouple wires. The sample holder was then placed in the stainless steel infrared reaction chamber.

The infrared reaction chamber is connected to a gas handling system consists of a mixing chamber, gas introduction ports and a two stage vacuum system. FTIR cell sits on a linear translator which allows to move the sample coated or the blank half of the tungsten grid into the infrared beam path. FTIR spectra were recorded using WinFirst software at a resolution of 4 cm⁻¹ in the 800 to 4000 cm⁻¹ spectral region. Typically, spectra recorded using WinFirst software was the average of 250 scans and for Macros it was the average of 4 scans. Prior to adsorption experiments, sample coated on the tungsten grid was heated to 200 ⁰C for one hour under vacuum of 10⁻⁵ Torr in order remove adsorbed water. After that, samples were further evacuated for five more hours under vacuum to obtain a clean surface for adsorption studies.

In a typical experiment, samples were exposed to 300 mTorr of CO₂ (g) or a mixture of CO₂ (g) and H₂O (g). Relative humidity was controlled by adjusting the water vapor pressure. Typically, infrared spectra were collected every 6.9 s. In the experiments carried out under irradiation, a 500 W mercury arc lamp (Oriel, model no. 66033) equipped with a water filter to remove infrared radiation and a $\lambda > 295$ nm low pass filter (Newport) was used to simulate solar radiation. In these experiments, infrared spectra were manually collected at 300, 600 and 1200s time intervals. A deconvolution procedure was used to peak fit the broad infrared absorption bands for adsorbed carbon dioxide on ZnO and CuO surfaces.

5.3.4 Dissolution Studies

Immediately after nanoparticle surfaces were exposed to CO₂ and H₂O mixture, 3 mg of ZnO or 5 mg of CuO were transferred into glass vials containing 10 ml of Optima water or pH 7.4 HEPES buffer in order to study the dissolution of reacted particles. These vials were placed on a circular rotator (Cole-Palmer) for 24 h. Following this 24 h time period, 4 ml of this solution was transferred into Ultracel- 3k centrifugal filter units (Millipore) and centrifuged at 7500 rpm for 30 min. Then the filtrate was analyzed for dissolved zinc and copper ions using a Varian inductively coupled plasma optical emission spectrometer (ICP-OES).

5.3.5 Characterization of Nanoparticles Samples Exposed to CO₂ and H₂O

After the CO₂ and H₂O adsorption experiments, these nanoparticle samples were characterized again using XRD and HRTEM in order to probe particle crystallinity and size to see if any changes occurred during simulated atmospheric aging.

5.4 Results

5.4.1 Characterization of Nanoparticles

Surface area and average particle size for ZnO and CuO nanoparticles are given below.

		ZnO	CuO		
	Original	After	Original	After	
	sample	calcination	sample	calcination	
BET surface area	21±5	8 ± 0.1	21 ± 0	10 ± 0.2	
(m^{2}/g)					
Particle size (nm)	44 ± 15	67 ± 25	24± 9	61 ±23	

 Table 5.1: Characterization of ZnO and CuO nanoparticles

After calcination, ZnO and CuO nanoparticles showed an average primary size of 67 ± 25 and 61 ± 23 nm, respectively. TEM images and particle size distribution of these particles are given in Figure 5.1. XRD patterns of ZnO nanoparticles obtained after calcination show the presence of zincite and calcined CuO nanoparticles show the presence of tenorite (Figure 5.2).



Figure 5.1: Transmission electron microscopy (TEM) images and corresponding size distribution of ZnO and CuO nanoparticles after calcination at 550 ⁰C for 6 h.



Figure 5.2: Characterization of ZnO and CuO nanoparticles after calcination at 550 ^oC for 6 h by X-ray diffraction (XRD).

The infrared spectrum of the clean ZnO nanoparticle surface obtained prior to adsorption studies is given in Figure 5.3.



Figure 5.3: Infrared spectra of clean ZnO and CuO nanoparticle surface before exposing to CO_2 (g).

Assignment	Wavenumber (cm ⁻¹)
OH on ZnO $(10\overline{1}0)$ with co adsorbed water	3672
OH on ZnO ($10\overline{1}0$) with co adsorbed water	3639
OH on ZnO $(000\overline{1})$	3620
OH on defect sites	3564
	3445

Table 5.2: Assignment of surface hydroxyl groups on ZnO nanoparticle surface

Absence of any infrared absorption features in the 1500 cm⁻¹ region in these spectra confirm the presence of clean ZnO and CuO surfaces prior to CO₂ adsorption. The hydroxyl group stretching region, around 3600 cm⁻¹, clearly shows the presence of surface hydroxyl groups on these oxide nanoparticle surfaces. Assignment of hydroxyl groups in ZnO is given in Table 5.2. Surface composition of nanoparticles were analyzed using XPS spectra (Figure 5.4). XPS spectra of Zn2p region has two peaks at 1021.1 and 1044.4 eV which are assigned to Zn²⁺ ions in ZnO.¹³¹ XPS spectra of CuO show the presence of absorption peaks at 933.6 and 953.8 eV which corresponds to Cu 2p3/2 and Cu 2p1/2 photoelectrons in CuO, respectively.⁵⁰ Shakeup satellite peaks characteristic of ground state Cu²⁺ with d⁹ electronic configuration in the ground state are also present at 941.2, 943.6 and 962.1 eV.^{50,} ¹⁴⁵ XPS data in the O 1s and region show the presence of hydroxyl functional group.^{50, 131} In contrast to infrared spectra of the pretreated nanoparticles in the vacuum, C 1s region of XPS spectra shows the presence of carbonate and acetate which is probably a result of the reaction of atmospheric CO₂ during transport and sample preparation for XPS analysis.^{50,} 131



Figure 5.4: Surface analysis of ZnO and CuO nanoparticles by X-ray photoelectron spectroscopy (XPS). XPS data in the Zn 2p or Cu 2p, C 1s and O1s binding energy regions for calcined a) ZnO and b) CuO nanoparticles.

5.4.2 CO₂ Adsorption on Nanoparticles

In adsorption experiments, ZnO and CuO nanoparticles were exposed to 300 mTorr of CO_2 (g) to mimic atmospherically relevant carbon dioxide partial pressure. Relative humidity is an important factor affecting surface reactions under atmospheric conditions. Therefore, the adsorption studies were done under a range of environmentally relevant relative humidity conditions from 0 to 70 %. Infrared spectra of ZnO and CuO nanoparticle surfaces exposed to CO₂ (g) at 0 % RH as a function of time are shown in Figure 5.5. Panel b of Figure 5.5 shows the deconvoluted absorption peaks in ZnO and CuO surface spectra after exposure to CO_2 (g) for 1200 s, using Gaussian-Lorentzian line shape. A summary of the assignment of infrared absorption features in ZnO and CuO surface spectra observed in this study along with previously reported values in literature are given in Table 5.3. In the ZnO surface spectra, initially three intense absorption features appear at 1219, 1415 and 1638 cm⁻¹ wavenumbers which can be assigned to surface adsorbed bicarbonate species.¹⁴⁶⁻¹⁴⁸ With the increase of exposure time, the surface spectra become more complex and infrared absorption bands become broader. This is due to the formation of adsorbed carbonate and carboxylate species as a result of the adsorption of CO_2 with the ZnO nanoparticle surface. Carbonate absorption bands at 1474, 1386, 1580, 1552 and 1285 cm^{-1} in ZnO spectra can be assigned to v_3 (O-C-O)_{as} and v_3 (O-C-O)_s vibrational modes of monodentate and bidentate carbonate species respectively. Infrared absorption bands at 1523 and 1336 cm⁻¹ in ZnO surface spectra can be assigned to adsorbed carboxylate (M - CO_2^-). Interaction of CO_2 (g) with CuO surface at 0% RH shows similar observations to ZnO.



Figure 5.5: FTIR spectra of a) nanoparticles reacted with CO_2 (g) in the absence of gas phase water vapor (0% RH) recorded at 7, 60, 120, 300, 600, 900 and 1200 s b) deconvoluted absorption bands in the spectra collected in 1200 s. All the spectra shown in Figure 2a is the average of 4 scans and the spectra presented Figure 2b is the average of 250 scans.

However, the adsorbed bicarbonate features at 1229, 1424 and 1618 cm⁻¹ in the CuO surface spectra are very well resolved even after 20 min exposure time compared to ZnO. Although adsorbed carbonate (1305, 1368, 1480 and 1581 cm⁻¹) and carboxylate (1535 and 1204 cm⁻¹) species are also present in CuO surface spectra, their absorption bands are not
very prominent. Upon increase of relative humidity of the gas mixture from 0 to 70 % RH, speciation of CO_2 adsorbed products show a clear and systematic change on both ZnO and CuO surfaces (Figure 5.6).

Assignment	ZnO – this study	CuO – this study	Literature Reference Data	
	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	
Bicarbonate				
v_3 (O-C-O) _{as}	1638	1618	1623 and 1650^{146}	
v ₃ (O-C-O) _s	1415	1424	1410 and 1435^{146}	
δ_4 (COH)	1219	1229	1222 and 1228^{146}	
Monodentate carbonate				
v ₃ (O-C-O) _{as}	1474	1480	1480-1520 ^{146, 149,} 150	
v ₃ (O-C-O) _s	1386	1368	1380-1395 ¹⁴⁶	
Bidentate carbonate				
v ₃ (O-C-O) _{as}	1580,1552	1581	1553-1644 ^{146, 149}	
v ₃ (O-C-O) _s	1285	1305	1243-1355 ^{146, 149}	
Carboxylate				
v3 (O-C-O)as	1523	1535	$\underset{151}{1510}\text{-}1670^{146, 150, }$	
v ₃ (O-C-O) _s	1336	1204	$1210-1330^{146, 150, 151}$	
Solvated carbonate				
	1490	1481	1496-1520 ¹⁴⁷	
	1385	1350	1345-1402 ¹⁴⁷	

Table 5.3: Assignment of the infrared absorptions on ZnO and CuO nanoparticle surfaces following exposure CO_2 (g)

a) ZnO





Figure 5.6: FTIR spectra of a) ZnO and b) CuO nanoparticles reacted with CO_2 (g) at 5%, 20% and 40% and 70% relative humidity after 1200 s.



Figure 5.7: FTIR spectra showing the changes in hydroxyl regions of ZnO and CuO nanoparticles after exposing to CO_2 (g) for 20 min at different relative humidity conditions and/or in the presence of simulated solar radiation.

Formation of surface adsorbed bicarbonate is decreased with increasing RH on both nanoparticle surfaces and bicarbonate formation was no longer observed after 20% RH. On ZnO, there is a very clear transition of adsorption species from 0 to 70% RH. At 70% RH, all the CO₂ molecules adsorb on ZnO forming solvated carbonate which is characterized by the infrared absorption bands at 1490 and 1385 cm⁻¹. In contrast, on CuO, CO₂ adsorption forming only solvated carbonate was occured at a RH as low as 20%. Irradiation of ZnO surface favors the formation of more carboxylate species than in the absence of light. Other than that, any significant change in speciation of adsorbed CO₂ was not observed on both ZnO and CuO surfaces under irradiation compared to dark experiments.

Consumption of surface hydroxyl groups present on both ZnO and CuO were observed in all the CO_2 adsorption experiments as shown in infrared spectra of the hydroxyl stretching region of nanoparticle surfaces given in Figure 5.7.

The rate of CO₂ adsorption on ZnO and CuO nanoparticles was calculated using a plot of time vs integrated absorbance of the carbonate region of infrared spectra. For ZnO, integration was done over the entire area extending from 1751.6 to 1243.8 cm⁻¹ and for CuO, the wavelength region used for integration was from 1737.2 to 1150.1 cm⁻¹. In the presence of gas phase water vapor, water molecules adsorbed on ZnO and CuO giving rise to water bending absorption bands around 1640 cm⁻¹ which falls within the range used for integration. Therefore, for all the experiments carried out at RH > 0%, this water bending absorption band was subtracted from surface spectra before integration. Relative rates of CO₂ adsorption are given in Table 5.4. According to Table 5.4, in general, the rate of CO₂ adsorption on ZnO nanoparticles shows an increase with increasing RH. In contrast, rate of CO₂ adsorption on CuO nanoparticles is highest at intermediate RH.

PCO ₂ (mTorr)	RH (%)	Relative rate of adsorption ([Rate] _{% RH} /[Rate] _{0% RH})		
	-	ZnO	CuO	
300	0	1	1	
300	5	1.4	2.6	
300	20	2.6	2.5	
300	40	3.9	1.9	
300	70	4.1	1.5	

Table 5.4: Kinetic analysis of CO₂(g) adsorption on ZnO and CuO

5.4.3 Characterization of Reacted Nanoparticles and Dissolution Studies

FTIR spectroscopy clearly shows the formation of carbonate upon exposure of ZnO and CuO nanoparticles to CO_2 under all the conditions used in this study. These reacted ZnO and CuO nanoparticles were analyzed using XRD in order to further investigate the nature of carbonate formed on nanoparticle surfaces. They were also analyzed using high resolution TEM (HRTEM). All the XRD patterns obtained for ZnO and CuO resemble the standard XRD patterns of zincite and tenorite respectively. However, interestingly, HRTEM images of some of the reacted ZnO nanoparticles show the presence of new surface features after the reaction compared to unreacted particles as shown in Figure 5.8. These features, especially those reacted with CO_2 at 40% RH shows some crystallinity with a d spacing of 3.0±0.1 Å (Figure 4c). The d spacing value obtained from the analysis of HRTEM images were compared with standard values given by International Center for Diffraction Data (ICDD). This d- spacing value is close to the d-spacing of 020 (3.1 Å) planes of hydrozincite (ICDD, PDF 00-019-1458). Therefore, these crystalline features on ZnO surface can probably be some form of hydrozincite.¹⁵² In a study by Falk *et al.* on the role of carbon dioxide in the atmospheric corrosion of zinc, it has been found that less ordered $Zn_4CO_3(OH)_6.H_2O$ is the more likely product at lower CO_2 pressures than Zn₅(CO₃)₂(OH)₆.^{152, 153} Hydrozincite formation has been previously observed on ZnO samples exposed to both gas phase CO_2 and water vapor as well as in aqueous solutions saturated with CO₂.^{154, 155} HRTEM images of reacted CuO samples also show some new surface features that are absent in unreacted particles (Figure 5.9).

a) Unreacted 5 nm 10 nm b) Reacted with CO₂ at 0% RH 5 nm 5 nm c) Reacted with CO_2 at 40% RH 5 nm 5 nm → 3.0±0.1 Å 2 nm

Figure 5.8: High Resolution TEM images of ZnO nanoparticles a) unreacted b) exposed to CO_2 in the absence of gas phase water vapor c) exposed to CO_2 at 40% relative humidity.



b) Reacted with CO_2 at 0% RH



c) Reacted with CO₂ at 40% RH



Figure 5.9: High Resolution TEM images of CuO nanoparticles a) unreacted b) exposed to CO_2 in the absence of gas phase water vapor c) exposed to CO_2 at 40% relative humidity.

Analysis of HRTEM images revealed that these features show several different d-spacing values including 2.3, 2.5, 2.7 and 3.0 Å. First three lattice spacing values are common for both CuO and copper carbonate phases (ICDD, PDF 04-007-1375, 01-080-8575, 01-080-4957). However 3.0 Å is present only in copper carbonate phases such as malachite and azurite. Therefore, these new surface features might be due to carbonate formation. Formation of crystalline copper carbonate phases on copper nanoparticles dipped in distilled water has been previously observed.¹⁵⁶ Here, the carbonate is formed by reacting Cu^{2+} ions in the outer oxide layers of copper nanoparticles with dissolved carbonate ions.¹⁵⁶

A larger fraction of nanoparticles released into the environment during production, use or transport can at some point enter into water bodies. Additionally, during occupational exposure or when nanoparticles are released into the atmosphere, these particles can also get into human/animal bodies in breathing and dissolve in body fluids. Therefore, the dissolution of reacted ZnO and CuO particles were studied using both optima water and HEPES buffer to mimic human body pH (pH 7.4). Dissolution of both nanoparticles is considerably higher in HEPES than optima water as shown in Figure 5.10a. Generally, ZnO nanoparticles reacted with CO₂ showed an increase in dissolution in water compared to unreacted particles. This dissolution of ZnO was found to be further enhanced in the presence of surface adsorbed water and under the irradiation with broadband light (λ > 295 nm). Overall, dissolution of reacted CuO is very low compared to ZnO. CuO dissolution in optima water is negligible as shown in Figure 5.10a with no signal apparent from these measurements. It should be noted that the concentration of dissolved copper in optima water is close to the instrument detection limit for Cu (~ 5 ppb).¹⁵⁷ Dissolution of both ZnO and CuO in HEPES does not show any systematic variation with different

reaction conditions used in this study. Dissolved metal ion concentrations obtained in ICP-OES measurements in this study was used to quantify the extent of dissolution of nanoparticle surfaces in 24 h in water and HEPES buffer. In these calculations, all the nanoparticles were assumed to be perfectly spherical and the density of the reacted particles were assumed to be similar to pristine nanoparticles. Further, the thickness of one surface layer was assumed to be equal to the distance between Zn^{2+} or Cu^{2+} and O^{2-} in perfectly crystalline nanoparticles which is 1.95 Å.^{158, 159} As shown in Figure 5.10b, these calculations suggest that nanoparticle dissolution in water and HEPES is limited to the near surface region, within the first monolayer mainly with the exception for ZnO dissolution in HEPES which appears to be several layers dissolved.



Figure 5.10: a) Dissolution of ZnO and CuO nanoparticles in water and pH 7.4 HEPES buffer. b) Number of surface layers of ZnO and CuO nanoparticles dissolved in 24 h. Thickness of one layer was assumed to be equal the bond distance between Zn/Cu and O in ZnO and CuO nanoparticles respectively.

5.5 Discussion

In the absence of water vapor, CO_2 molecules interact with surface hydroxyl groups in metal oxide to form bicarbonate as the major adsorbed product according to Reaction 5.1, where M = Zn or Cu.¹⁴⁷

$$M_2 - OH + CO_2 \leftrightarrow M_2 - O_2COH \tag{5.1}$$

The role of surface hydroxyl groups as adsorption sites is confirmed by the negative adsorption features observed in the hydroxyl region of ZnO and CuO surface spectra. Surface adsorbed bicarbonate formation on oxide particles upon exposure to CO₂ has been previously studied in detail by Baltrusaitis et al.^{146-148, 160} Their isotope labeling experiments suggests that CO₂ molecule interact with hydroxyl groups on the oxide surface leading to the formation of bridged bicarbonate structure according to a Langmuir-Hinshelwood type mechanism.¹⁴⁸ In this mechanism, first CO₂ undergo nucleophilic attack by surface oxygen atom of hydroxyl group followed by rearrangement of the surface by an intermolecular proton transfer.¹⁴⁸ Further, it has been found that basic hydroxyl groups are more likely to be involved in initial nucleophilic attack.^{148, 151} Formation of surface adsorbed carbonate and carboxylate species, especially on ZnO at 0% RH is probably due to the direct interaction of CO_2 with surface oxide anions and oxygen vacancy sites. Bidentate carbonate species formed on ZnO is probably a result of reactive interaction of CO_2 with O vacancies on ZnO (0001) surface.¹⁴⁹ This surface has a high density of O vacancies (33%) that exhibits very high reactivity for reactive adsorption.¹⁴⁹ Monodentate carbonate species are generated by the interaction of CO₂ molecules with defect sites.¹⁴⁹

$$M - 0^{2-} + CO_2 \to M - 0CO_2^{2-}$$
(5.2)

$$\Box - M - 0^{2-} + CO_2 \to M_{0}^{0} C = 0$$
 (5.3)

Carboxylates are formed by a charge transfer from surface metal ions to the CO₂ molecules.¹⁵¹

$$-\mathbf{M} - +\mathbf{CO}_2 \rightarrow \mathbf{M} - \mathbf{CO}_2^- \tag{5.4}$$

Comparable to the observations of the current study, surface bound carboxylate formation on TiO₂ surface under the illumination with light emitted by a mercury arc lamp has been previously detected by infrared spectroscopy.^{161, 162} In a study by Liu *et al.* on photocatalytic CO₂ reduction with H₂O on TiO₂, it has been found that there is an association between carboxylate formation and the presence of defect sites.¹⁶³ Their diffuse reflectance Fourier transform infrared spectroscopic studies suggest that carboxylate is unlikely to be formed in the absence of defect surfaces.¹⁶³ In the presence of broad band light, surface defect site are formed as shown in Reaction 5.5 to 5.8.¹⁶⁴ These defect sites formed in the presence of light can facilitate the production of more carboxylate. That may be the reason for the slight increase in carboxylate formation in the reaction of CO₂ with ZnO surface under irradiation conditions with noticeable decrease in adsorbed bicarbonate formation. Although the bidentate carbonate yield should also be increased with increased oxygen vacancy site, carboxylate formation may be more favorable than bidentate carbonate formation.

$$ZnO + h\nu \rightarrow h^+ + e \tag{5.5}$$

$$0^{2-} + h^+ \rightarrow 0^-$$
(surface trapped holes) (5.6)

$$0^{-} + h^{+} \rightarrow \frac{1}{2}0_{2} + \Box \text{ (oxygen vacancy)}$$
(5.7)

$$\operatorname{Zn}^{2+} + e \rightarrow \operatorname{Zn}^{+}_{s}$$
 (surface trapped electron) (5.8)

Considerably higher intensity of bicarbonate adsorption bands and very low intensity of the infrared absorption bands responsible for carbonate and carboxylate species in CuO surface spectra are probably due to the higher density of surface hydroxyl groups and low density of defect sites present on CuO surface compared to ZnO.

In the presence of gas phase water vapor, CO_2 adsorption is thought to occur via carbonic acid intermediate.¹⁴⁷

$$H_2O(a) + CO_2(g) \leftrightarrow H_2CO_3(a)$$
(5.9)

$$\mathrm{H}_{2}\mathrm{CO}_{3}(\mathrm{a}) \leftrightarrow \mathrm{H}\mathrm{CO}_{3}^{-}(\mathrm{a}) + \mathrm{H}^{+} \tag{5.10}$$

$$\mathrm{HCO}_{3}^{-}(\mathrm{a}) \leftrightarrow \mathrm{CO}_{3}^{2-}(\mathrm{a}) + \mathrm{H}^{+}$$

$$(5.11)$$

Then this carbonic acid or its dissociation products can interact with surface hydroxyl groups on ZnO and CuO surfaces forming adsorbed carbonate.¹⁴⁷

$$MOH + H^+ \leftrightarrow M - OH_2^+ \tag{5.12}$$

$$MOH + H_2CO_3(a) \leftrightarrow M - OH_2^+ + HCO_3^-(a)$$
 (5.13)

$$MOH + HCO_3^-(a) \leftrightarrow MOCO_2^-(a) + H_2O(a)$$

$$(5.14)$$

However, Reaction 5.12 to 5.14 is only possible at lower relative humidity where surface coverage of water is low. At lower relative humidity, there will be a competition between direct CO_2 (g) molecules and H_2CO_3 and HCO_3^- intermediates for surface adsorption sites. Existence of this type of a competition is evidenced by systematic conversion of surface adsorbed carbonate to solvated carbonate with RH in ZnO and CuO surface spectra. With the increase of relative humidity, water to CO_2 molar ratio increases in the gas phase there

by increasing the probability of water molecules to interact with oxide surfaces. This process increases adsorbed water coverage on oxide surfaces which acts as a barrier for direct CO_2 adsorption to form bicarbonate and carbonate species. Therefore, at higher RH, formation of solvated carbonate is the major reaction pathway. Increased rate of adsorption of CO_2 with RH may be due to rapid formation of solvated carbonate in the presence of adsorbed water layer.

Both ZnO and CuO are semiconducting materials with a band gap of \sim 3.2 and 1.2 eV.^{164, 165} Under irradiation conditions, water adsorbed on semiconductor surfaces can scavenge photogeneated h⁺ forming hydrogen ions according to Reaction 5.15.¹⁶⁶

$$MO + 2H_2O + 2h^+ \rightarrow M(OH)_2 + \frac{1}{2}O_2 + 2H^+$$
 (5.15)

Hydrogen ion generated from this reaction can further dissolve metal oxides in a dark reaction and/or can be involved in further photo-corrosion reactions.^{166, 167}

$$MO + 2H^+ \rightarrow M^{2+} + H_2O$$
 (5.16)

$$MO + h^{+} + H^{+} \rightarrow \frac{1}{2}H_{2}O_{2} + M^{2+}$$
 (5.17)

According to these reactions, presence of adsorbed water can dissolve semiconductor metal oxides to form solvated metal cations under irradiation conditions. Very wide band gap of ZnO may be more favorable for these reactions than CuO with a very narrow band gap due to lower possibility of electron-hole recombination in ZnO. However, in the presence of dissolved CO_2 , this reaction mechanism can be more complex than the mechanism given in Reaction 5.15 – 5.17.

Metal oxide nanoparticles dissolve in water releasing metal cations to the aqueous medium as shown in (5.18):¹⁶⁸

$$MO + H_2O \longleftrightarrow^{K_{sp}} M^{2+} + 2OH^-$$
 (5.18)

The solubility constant of $Zn(OH)_2$ (1.2 x 10⁻¹⁷) is higher than $Cu(OH)_2$ (2.2 x 10⁻²⁰) and therefore dissolution of ZnO in water produces more dissolved cations than CuO. However, after the reaction with nanoparticles, their surfaces are covered by adsorbed CO₂. Therefore the dissolution of reacted particles initially depends on the solubility of adsorbed CO₂ in the form of carbonate and bicarbonate. Moreover, both ZnCO₃ and CuCO₃ have higher solubility products than their hydroxides. Increase in nanoparticle dissolution after the reaction with CO_2 is probably due to the presence of surface adsorbed carbonate. Once these carbonate layers are dissolved revealing the nanoparticle surface underneath, dissolution of oxides can also contribute to the total dissolved cation concentration. In the presence of simulated solar radiation and adsorbed water, ZnO dissolution can also be enhanced due to the generation of H^+ ions (Reaction 5.15) as shown in Reaction 5.16 and 5.17. In the presence of adsorbed water, photo-generated Zn^{2+} can get dissolved in that water layer and further interact with solvated carbon dioxide. However, due to the presence of many kinetic factors affecting dissolution, it is hard to exactly rule out the individual effect of each factor. pH of optima water did not show any significant increase after dissolving ZnO for 24 h. The average pH of optima water used for dissolution studies of ZnO is 6.5 ± 0.6 and the average pH of aqueous solution after dissolution of ZnO for 24 h is 6.8 \pm 0.5. At pH 6.5, all the dissolved zinc in water exist in the form of Zn²⁺(aq) cations.¹⁶⁹ Dissolution of CuO in water was minimal and did not show a significant variation similar to ZnO. Both ZnO and CuO showed increased dissolution in HEPES

buffer compared to optima water. This is may be related to chelating effects of HEPES buffer.¹³⁷

5.6 Conclusions

In the current study, atmospheric aging of ZnO and CuO nanoparticles was investigated in the presence of CO_2 , water vapor and simulated solar radiation. A number of important conclusions about nanoparticle aging and its effect on dissolution were derived from this study. Transmission FTIR studies carried out at 0% RH suggest that CO₂ (g) molecules first interact with surface hydroxyl groups on the nanoparticle surface leading to the formation of adsorbed bicarbonate. Surface adsorbed carbonate and carboxylate species are also formed due to the interaction of CO_2 with surface sites other than hydroxyl groups, including metal cations and oxygen vacancies. With the increase of relative humidity from 0 to 70%, nanoparticle surface sites are increasingly blocked by adsorbed water molecules, thereby decreasing the bicarbonate yield. Furthermore, adsorbed water acts as a barrier for CO₂ molecules to reach surface sites to form adsorbed carbonate and bicarbonate. Therefore, solvated carbonate is the only species present on nanoparticle surfaces at RH > 20%. Effect of simulated solar radiation on CO_2 adsorption is important only for ZnO and under very low relative humidity close to 0%. The presence of adsorbed water hinders the effect of simulated solar radiation. Further analysis of reacted ZnO and CuO nanoparticles with HRTEM shows considerable surface restructuring consistent with precipitation of carbonate phases in the presence of adsorbed water. A schematic explaining the formation of crystalline carbonate phases is given in Figure 5.11. CO_2 adsorption clearly increases the dissolution of nanoparticles both in water as well as in pH 7.4 buffer. However, the dissolution of CuO nanoparticles is significantly lower in

any medium than ZnO nanoparticles. Nanoparticle dissolution in HEPES buffer was always higher than water, possibly due to ligand promoted dissolution by buffer molecules.¹³⁷



Figure 5.11: Schematic of the mechanism of crystalline carbonate formation.

This study provides evidence that ZnO nanoparticles are more susceptible to release dissolved cations to water or in the presence of ligands than CuO nanoparticles of the same diameter and surface area. Overall, the work presented here reveals the importance of atmospheric aging of nanoparticles in their dissolution which ultimately affect the bioavailability and nanoparticle toxicity.

5.7 Acknowledgement

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CHAPTER 6

SULFATE FORMATION CATALYZED BY ATMOSPHERICALLY RELEVANT PARTICLES INCLUDING COAL FLY ASH, MINERAL DUST AND IRON (III) OXIDE: VARIABLE EFFECTS OF TEMPERATURE AND LIGHT

6.1 Abstract

Transition metal ion (TMI) catalyzed oxidation is an important in-cloud oxidation pathway of sulfur dioxide. Here we investigated the effect of temperature and simulated solar radiation on TMI catalyzed aqueous S(IV) oxidation to S(VI) (i.e., sulfite to sulfate) in the presence of several TMI-containing, atmospherically relevant particles including coal fly ash (FA), Arizona test dust (AZTD) and iron oxide (y-Fe₂O₃). The effect of temperature and light on S(IV) oxidation is found to be very different for these three samples. In the presence of FA and γ -Fe₂O₃, we propose that S(IV) oxidation initially occurs through a heterogeneous pathway although a homogeneous catalytic pathway also contributes to S(IV) oxidation over later timescales due to the formation and accumulation of dissolved Fe(III). The temporal evolution of Fe(II) is shown to correlate with S(IV) oxidation in the presence of FA and Fe_2O_3 , whereas S(IV) in the presence of AZTD appears to be mostly heterogeneous and notably does not lead to iron dissolution. The overall higher rate of S(IV) loss in the presence of AZTD compared to FA and y-Fe₂O₃ suggests that other factors, including greater adsorption of sulfite, TMI catalysis by other metal ions or different species of iron in AZTD, play a role. Overall these studies suggest that the rate, extent and products of atmospheric S(IV) oxidation can be highly variable and heavily dependent upon the nature of aerosol sources, thereby precluding simple generalizations

about this reaction when modeling atmospheric processes involving diverse mineral dust aerosols.

6.2 Introduction

Sulfate aerosol in the atmosphere has a strong impact on climate due to their effect on direct radiative forcing and their ability to act as cloud condensation nuclei (CCN).^{43, 46, 170, 171} Anthropogenic SO₂ emitted by industrial activities including fossil fuel burning is the main precursor of sulfate in submicrometer particles.⁴⁶ It has been estimated that approximately 50% of global atmospheric SO₂ is ultimately oxidized to sulfate.⁴³ Understanding atmospheric sulfate formation pathways has recently attracted a considerable amount of attention due to very high sulfate levels observed in severe haze conditions in China that cannot be explained using current atmospheric mechanisms and models.¹⁷²⁻¹⁷⁴ Some of the recent studies suggest that the magnitude of this discrepancy can be reduced by incorporating sulfate formation reactions involving mineral dust aerosol in atmospheric models.^{172, 173}

Sulfur dioxide oxidation by O₂ in the presence of transition metal ion (TMI) catalysts is an important S(IV) oxidation pathway in cloud/fog water,^{44, 175} estimated to contribute 9-17 % of global sulfate production.¹⁷⁶ Fe(III) and Mn(II) are the most studied TMIs for aqueous phase S(IV) oxidation.^{44, 176} Recent studies show that this TMI catalyzed oxidation pathway is more important in winter relative to summer due to lower atmospheric oxidation capacity because of weaker sunlight.^{173, 176} Unfortunately, this aqueous phase sulfur dioxide oxidation pathway has been excluded from most atmospheric chemistry models. This is mainly due to the uncertainties and limitations in the availability of

chemical and kinetic data relevant to real atmospheric conditions for different meteorological and climate regimes.^{173, 176}

In the current study, we have begun an investigation of the effect of low temperature and simulated solar radiation on aqueous S(IV) oxidation to sulfate in the presence of atmospherically relevant iron containing mineral particles including a reference material for coal fly ash (FA), a pure iron(III) oxide (formula/symbol) and Arizona test dust (AZTD), which represents a proxy for mineral dust. Previous studies involving these samples have shown that they contain iron-bearing solid phases that can produce dissolved iron in certain aqueous solutions. Our main focus is here is to begin to develop an understanding as to the effect of different atmospherically relevant conditions, particularly, low temperature and solar radiation, on S(IV) oxidation by structural and leached Fe from particles with different phases and mineralogy.

6.3 Materials and Methods

6.3.1 Mineral Aerosols

FA standard reference material (SRM 2690, National Institute of Standards and Technology), Arizona test dust (ISO 12103-1 A2 test dust, Powder Technology Inc.) and γ -Fe₂O₃ (Alfa Aesar) were used as received. Specific surface areas of solid samples were characterized using Quantachrome Nova 4200e BET surface area analyzer.

6.3.2 Simulated In-Cloud Aqueous Phase S(IV) Oxidation in the Presence of Atmospherically Relevant Particles

All S(IV) oxidation experiments were carried out in glass vessels with a water jacket containing an appropriate volume of S(IV) solution and mineral aerosol sample. In a typical experiment, 2 mM (or 1.5 mM in low temperature experiments) aqueous S(IV) solution was prepared by dissolving Na₂SO₃ solid (Fisher) in Optima water (Fisher) at 25 $^{\circ}$ C or 15 $^{\circ}$ C as appropriate (pH~8.3). Then the pH of this solution was adjusted to pH=5 using dilute HCl and NaOH. The final concentration of S(IV) in pH adjusted solutions was 1±0.2 mM, where the decrease in S(IV) during pH adjustment results from elimination of gas-phase SO₂. In all experiments, a solid loading of 1 g L⁻¹ was used. All solutions were constantly stirred in the presence of atmospheric oxygen during the experiment.

Experiments were initiated by adding the solid samples into glass vessels containing 50 mL of 1 mM sulfite solution. Subsequently, aliquots of the reaction mixture were periodically withdrawn over time and filtered with a 0.2 μ M nylon filter (Xpertek). This filtered solution was immediately used to analyze for S(IV) concentration, dissolved Fe(II), total dissolved iron (Fe(III) + (Fe(II)), and to measure pH. Experiments with FA and γ -Fe₂O₃ were carried out for 120 min and the reactions with ATD were carried out for 60 min. All results represent the average and standard error of three replicate experiments. Control experiments in the absence of any particles were also conducted at 25^oC and 15 ^oC, as well as under simulated solar irradiation.

In order to determine the effect of simulated solar radiation on S(IV) oxidation, reaction mixtures at 25 0 C were irradiated with a 150 W xenon arc lamp (Oriel Corp.). All

other experiments were conducted inside a dark room in order to avoid any reactions promoted by room light.

6.3.3 Analytical Methods

The S(IV) concentrations were determined using the method described by Humphrey et al. using DTNB (5,5'-dithiobis(2-nitro-benzoic acid)) as the colorimetric agent.^{52, 175} Fe(II) and total iron concentrations were determined with 1,10-phenanthroline as described in detail previously.^{51, 177}

6.4 **Results and Discussion**

6.4.1 Characterization of FA, AZTD and γ-Fe₂O₃

Specific surface areas of FA, AZTD and γ - Fe₂O₃ are 3.8 ± 0.1, 4.2 ± 1.0 and 56 ± 1 m²/g respectively. Iron content and speciation of FA and AZTD particles used in this study have been characterized in detail previously using digestion methods and Mossbauer spectroscopy.^{25, 26, 51} FA contains 3.57 ± 0.006 wt% iron, while iron content in AZTD is 1.98 ± 0.08 wt%. Both FA and AZTD contain significant amount of iron associated with aluminosilicate.^{25, 26} However, in FA these aluminosilicates are dominantly in a glassy state formed via high temperature combustion followed by fast cooling.²⁶ In FA, iron speciation included 38% Fe(III) and 17% Fe(II) in aluminosilicate glasses, as well as 45% Fe(III) in oxides.²⁶ In AZTD, Fe(III) exists both in crystalline aluminosilicates and oxides, whereas Fe(II) is present as Fe(II)-substituted aluminosilicate.^{25, 26} According to the XRD pattern, γ -Fe₂O₃ is 100% crystalline.

6.4.2 Effect of Temperature and Simulated Solar Radiation on S(IV) Oxidation in the Presence of FA, AZTD and γ-Fe₂O₃

Changes in S(IV) concentration and the corresponding variation of total dissolved iron and Fe(II) over time in the presence of FA and γ –Fe₂O₃ particles are shown in Figure 6.1a and b. Analysis of filtered reaction mixture in the presence of FA and γ –Fe₂O₃ with ATR-FTIR spectroscopy revealed that this S(IV) loss accompanies the formation of solution phase sulfate ions characterized by infrared adsorption band around 1100 cm⁻¹. S(IV) loss is decreased when the temperature is lowered from 25 °C to 15 °C in the presence of both FA and γ –Fe₂O₃. Similarly, iron dissolution was also decreased with lowering temperature. These trends simply reflect the slower reaction kinetics typical of most thermal dissolution processes at lower temperature in the presence of FA and γ -Fe₂O₃. Simulated solar radiation considerably increases the rate of S(IV) loss in the presence of FA and γ -Fe₂O₃. However, S(IV) loss in the presence of FA under irradiation does not show such a difference compared to dark experiments, although iron dissolution was significantly increased in the presence of simulated solar radiation.

 HSO_3^- is the dominant S(IV) species in the aqueous medium at pH=5. Iron in mineral particles can participate in the observed sulfate formation from HSO_3^- either by homogeneous catalysis pathway or heterogeneous catalysis pathway according to the following mechanism given in reactions 6.1 to 6.5.¹⁷⁸

$$Fe(III) + HSO_3^- \rightarrow Fe(II) + SO_3^- + H^+$$
(6.1)

$$SO_3^- + O_2 \rightarrow SO_5^- \tag{6.2}$$

$$SO_5^- + Fe(II) + H^+ \rightarrow HSO_5^- + Fe(III)$$
 (6.3)

$$HSO_5^- + Fe(II) \rightarrow SO_4^- + OH^- + Fe(III)$$
(6.4)

$$SO_4^- + Fe(II) \rightarrow SO_4^- + Fe(III)$$
 (6.5)



Figure 6.1: Variation of a) normalized S (IV) concentration b) absolute dissolved Fe (II) and T(Fe) (total dissolved iron) concentrations with time in the presence of FA, γ –Fe₂O₃ and AZTD under different reaction conditions. In these figures, normalized S(IV) concentrations were obtained by taking the ratio of the S(IV) concentration at some time t ([S(IV)]) to the initial S(IV) concentration ([S(IV)]₀) of each experiment.

Reaction condition -	Rate x 10 ⁻³ (S ⁻¹)			
	FA	γ-Fe ₂ O ₃	AZTD	
25 °C	8	6	15	
15 °C	3	2	17	
25 °C, Irradiated	9	12	16	

Table 6.1: Rate of S(IV) loss in the presence of FA, γ -Fe₂O₃ and AZTD

In homogeneous catalysis, Fe(III) in mineral particles first dissolve in aqueous medium and then react with S(IV) ions to form sulfite radical (Figure 6.2).



Figure 6.2: Schematic of the mechanisms of S(IV) oxidation in the presence of mineral aerosol

In the heterogeneous catalysis pathway, S(IV) species are first adsorbed on the particle surface and get oxidized by an electron transfer reaction between Fe(III) and adsorbed S(IV).¹⁷⁵ In the presence of O₂, this sulfite radical can be further oxidized to form sulfate

ion via a series of chemical reactions. Fe(II) formed by heterogeneous reaction pathway on particle surfaces can be more soluble than Fe(III). As a result, this Fe(II) can be released into the aqueous medium after the oxidation reaction. This is called reductive dissolution of iron. S(IV) oxidation in the presence of FA and γ -Fe₂O₃ acidifies the reaction mixture. The decrease in pH in the presence of FA and γ –Fe₂O₃ ranges between 1-1.5 pH units for the 120 min reaction time (Table 6.2). This acidification of the reaction mixture is also favorable for Fe(II) dissolution.

Table 6.2: Initial and Final pH of CFA, γ -Fe₂O₃ and AZTD and their Comparison with Control

Reaction		pH variation			
condition ⁻	FA (120 min)	γ-Fe ₂ O ₃ (120 min)	Blank (120 min)	AZTD (60 min)	Blank (60 min)
25 °C	5.0-4.0	5.1-3.5	5.1-4.5	5.1-6.1	5.1-4.6
15 °C	5.1-3.8	5.0-4.2	5.1-4.9	5.0-5.8	5.1-5.3
25 ^{°C} , Irradiated	5.1-4.1	5.0-3.4	5.1-4.4	5.0-6.1	5.1-4.5

The observation that Fe(II) and total Fe are equivalent at early timescales for all the experiments with FA and for dark experiments with γ -Fe₂O₃ suggest that observed iron dissolution is reductively driven. This also provides indirect evidence for the dominance of a heterogeneous catalysis pathway for S(IV) oxidation, at least initially. Since the stability constants for FeSO₄⁺ and FeSO₃⁺ are 10^{2.0} M⁻¹ 10^{8.8} M^{-1 179}, respectively, S(IV) is capable of displacing sulfate ions from surface coordination sites after their production.

This may explain our observation of solution phase sulfate ions in the aqueous solution via infrared spectroscopic analysis. At longer timescales, total iron concentration is greater than Fe(II) concentrations in all experiments with FA and all dark experiments with γ -Fe₂O₃, indicating the gradual accumulation of Fe(III) in the aqueous phase. Therefore, once sufficient dissolved iron is generated in solution, a homogeneous reaction pathway becomes viable at later times. A previous study by Rani *et al.* on S(IV) oxidation in the presence of atmospheric dust also suggested the initial heterogeneous catalysis was followed by homogeneous catalysis at later times.^{180, 181} This higher Fe(III) concentration of Se(II) in the solution phase and *ii*) oxidation of Fe(II) to Fe(III) by the mechanism given in reaction 6.3 – 6.5.

During irradiation, light absorption by iron oxide particles leads to the formation of electron (e⁻)- hole (h⁺) pairs. These electron-hole pairs can lead to one electron oxidation of adsorbed sulfite to SO_3 .¹⁷⁵ Furthermore, these electrons can reduce particulate Fe(III) to Fe(II) which is then subsequently released into the aqueous medium. Higher rates of both of these processes may be responsible for considerably more S(IV) loss and iron dissolution observed with γ -Fe₂O₃ under irradiation. Similarly, iron oxide in FA is possibly responsible for the enhanced iron dissolution under irradiation. Furthermore, increased iron dissolution in the presence of FA without a significant change in S(IV) loss compared to the dark experiment at 25 ^oC suggest that S(IV) loss is dominated by sorption rather than reaction, and that sorption primarily occurs on sites other than those iron sites involved in photoreductive dissolution. In the presence of photoactive components and O₂ under acidic conditions (pH= 5 to ~4 in this study), simulated solar radiation can lead to the formation

of reactive oxygen species O_2^{\bullet} , HO_2^{\bullet} and H_2O_2 ,¹⁷⁷ and these species can in turn oxidize Fe(II) to Fe(III). This is proposed to be the main reason for the very high Fe(III) concentration observed with γ -Fe₂O₃ during irradiation experiments.

Variation of S(IV) concentration in the presence of AZTD under different reaction conditions are shown in Figure 6.1c. Notably, unlike FA and γ –Fe₂O₃, iron dissolution was not observed in the presence of Arizona test dust. Most interesting is the fact that the loss of S(IV) in the presence of AZTD is similar under all three experimental conditions used in this study. The presence of sulfate in the ATR-FTIR spectra of the solution phase indicates that S(IV) oxidation takes place even in the presence of AZTD (Figure 6.3).



Figure 6.3: Infrared absorption spectra of the solution phase during S(IV) oxidation in the presence of AZTD. These solution phase spectra were collected for the reaction mixture withdrawn at 0, 10, 20, 30, 40 and 60 min time intervals. Infrared absorption band at 1100 cm⁻¹ corresponds to solution phase sulfate.

Absence of any dissolved iron in the presence of AZTD suggest that S(IV) oxidation in AZTD suspensions is entirely heterogeneous in nature. Fe(II) generated in catalytic reaction in the presence of AZTD likely remains as structural Fe(II), unable to be released to the aqueous solution. This might be expected if Fe(III) in aluminosilicates were the primary oxidant, as Fe(II) would be expected to remain tightly bound in the aluminosilicate lattice after formation. Alternatively, iron dissolution in the aqueous phase may also be inhibited by the increase of pH, arising from S(IV) solution in the presence of AZTD. Finally, TiO₂ present in AZTD or Ti leached into the aqueous phase from TiO₂ may also play a role in very high rates for S(IV) oxidation observed in these experiment.^{44, 171} Previous studies by Harris *et al.* also indicate that Ti is leached form mineral dust with an efficiency comparable to iron and it can also participate in TMI catalyzed oxidation.^{44, 171}

Collectively, these results demonstrate the complexity of sulfur oxidation on different iron-containing samples and, to the best of our knowledge, this is the first study to show these very different effects of temperature and light in the presence of iron containing authentic mineral aerosol and mineral dust proxies. Most importantly, this study shows large differences in mechanisms that can occur for S(IV) oxidation depending on source and characteristics of particles and their transition metal ions. The effect of temperature and light on S(IV) oxidation to sulfate is quite different for FA, γ -Fe₂O₃ and AZTD. Catalyzed S(IV) oxidation in the presence of mineral aerosol, at least partly occurs via a heterogeneous pathway. Therefore, both particle phase as well as solution phase sulfate should be simultaneously quantified in order to accurately understand the S(IV) oxidation pathway. The temporal evolution of iron into the aqueous phase, Fe(III) as well as Fe(II), provides useful information about the S(IV) oxidation pathway. Although these

same kinetic studies suggest a heterogeneous reaction pathway at initial times may also be operative. Furthermore, these new data for AZTD indicates that TMI catalyzed S(IV) oxidation in fact cannot be explained using Fe catalysis. Therefore, this study clearly shows the importance of further investigations that involve other less studied TMI such as Ti and Cr and synergistic interactions among TMI leading to enhanced S(IV) oxidation. These studies are sorely needed for atmospheric models if they are to accurately predict sulfate formation, especially in severe winter haze conditions in China where current models under predict such values.

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CHAPTER 7

CYCLOHEXANE OXIDATION BY OH RADICALS GENERATED FROM PHOTOLYSIS OF WATER ON TiO₂ SURFACE

7.1 Abstract

In this study, we investigated the effect of relative humidity on the oxidation of cyclohexane by photogenerated •OH radicals on TiO₂ surface. At zero relative humidity (RH), only surface adsorbed oxidation products are present. In the presence of gas phase water vapor at higher relative humidities, gas phase cyclohexanone was also detected as an oxidation product. This gas phase cyclohexanone concentration was increased with increasing RH until 40%. This gas phase cyclohexanone product is absent at 73% RH. There are two possible sources of gas phase cyclohexanone; a) reaction of •OH radicals diffused into the gas phase with cyclohexane molecules b) diffusion of cyclohexanone molecules formed on the TiO₂ surface to the gas phase. Absence of any gas phase products at 73% RH is probably due to limitations in the diffusion of •OH radicals or cyclohexanone product formed on the surface to the gas phase due to thicker adsorbed water layer.

7.2 Introduction

TiO₂ is widely present in airborne particulate matter coming from both natural and anthropogenic sources.¹⁴ Wind-blown mineral dust is the main natural source of atmospheric TiO₂. With the recent development in nanotechnology, TiO₂ nanoparticles emitted by industrial sources have also become an important source of TiO₂ in the atmosphere. TiO₂ is a photocatalyst that is known for its ability to efficiently produce

reactive oxygen species (ROS) including OH, H_2O_2 , HO_2 and O_2^- by photo-activating H_2O and O_2 under ambient conditions.^{14, 182-184}

Until recently, it was assumed that the reactions of reactive oxygen species generated on TiO₂ are limited only to the surface. However, some of the recent studies show the ability of reactive oxygen species generated on TiO₂ surface such as OH, H₂O₂ and OH₂ to diffuse into the gas phase and participate in chemical reactions.^{42, 182-186} According to a study by Dupart *et al.*, OH radicals diffused from photoactive metal oxides in dust particles can oxidize SO₂ to H₂SO₄ in the vicinity of the particle surafce.⁴¹ Nie and coworkers also observed dust-surface mediated new particle formation initiated by reactions of diffused OH radicals during a field study in south China.⁴⁰ These OH radicals are the main oxidant of volatile organic compounds (VOC) in the atmosphere.¹⁸⁷ Due to high reactivity with OH radicals, VOC are widely used to scavenge OH radicals in atmospheric chemistry laboratory studies. One of such compounds is cyclohexane which reacts with OH radicals in the gas phase to produce cyclohexanoe.^{188, 189}

In this study, we investigated the effect of relative humidity on OH radical generation on TiO_2 surfaces and its diffusion to the gas phase using cyclohexane as the OH radical scavenger.

7.3 Experimental Methods

Relative humidity dependent oxidation of cyclohexane by photogenerated OH radicals was studied using transmission FTIR spectroscopy. These experiments were carried out using a custom made stainless steel reaction set up. The experimental setup has been previously described in detail.¹⁹⁰ FTIR spectra were collected using a Mattson Galaxy 6000 FTIR spectrometer with a mercury-cadmium-telluride detector. In a typical

experiment, 20 mg of TiO_2 (P25, Sigma Aldrich) sample was dissolved in optima water and sonicated for 2 min. to form a hydrosol and transferred onto one half of a tungsten grid. The sample holder was placed in the stainless steel reaction chamber and the infrared reaction chamber was evacuated under vacuum in order to clean the surface. This infrared cell sits on a linear translator which allows us to move the sample coated or blank half of the tungsten mesh towards the IR beam in order to obtain surface and gas phase spectra respectively. Then the TiO₂ surface was exposed to a mixture of 3 Torr of anhydrous cyclohexane (Sigma) vapor, 100 Torr O₂ and water vapor. Relative humidity of the gas phase was controlled by adjusting the water vapor pressure of the gas mixture. After exposing to the gas mixture, sample was irradiated using a 500 W Hg arc lamp (Oriel, model no. 66033) equipped with a 300 nm broadband UV filter (Edmunds) and a water filter to remove IR irradiation. In this study, FTIR spectra of the surface and gas phase were recorded using Winfirst software every 15 min for 60 min at a resolution of 4cm⁻¹. Single beam spectra collected in this study are the average of 250 scans from 800 to 4000 cm⁻¹. Single beam spectra obtained during irradiation were referenced to the surface or gas phase obtained before gas exposure in order to identify surface adsorbed and gas phase species.

7.4 **Results and Discussion**

Adsorption of cyclohexane in the initial gas mixture on TiO_2 surface is highest at 0% relative humidity as shown by the intensity of the infrared absorption band at 1451 cm⁻¹ in Figure 7.1.¹⁹¹ Surface adsorbed cyclohexane shows another weak absorption band around 1257 cm⁻¹ due to CH₂ bending vibrations which is not shown in this figure.¹⁹¹ Lower adsorption in the presence of gas phase water vapor might be due to competitive

adsorption of more polar water on the TiO_2 compared to non-polar cyclohexane molecules that do not partition into the particle phase to a larger extent.⁴¹



Figure 7.1: Adsorption of cyclohexane on TiO₂ surface upon exposure to a mixture containing 3 Torr Cyclohexane, 100 Torr O₂ and water vapor.

After initial exposure of the surface to a gas mixture containing 3 Torr Cyclohexane, 100 Torr O₂ and water vapor, the infrared cell was isolated form the rest of the system and TiO₂ surface was irradiated with the output of 500 W Hg arc lamp with a λ >300 nm broadband filter. During irradiation at 0% relative humidity, different surface adsorbed species formed form cyclohexane oxidation was observed in the surface spectra (Figure 7.2). Gas phase products were absent at this relative humidity. This indicates that cyclohexane oxidation in the absence of gas phase water vapor is confined to the surface.



Figure 7.2: Variation of surface adsorbed cyclohexane oxidation product concentration with time on TiO_2 surface at 0% relative humidity upon exposure to light. Surface spectra were collected every 15 min for 60 min time period

Cyclohexanone is the major absorption product formed in the oxidation of cyclohexane on TiO_2 as indicated by the absorption bands at 1725, 1700, 1680, 1313 and 1278 cm⁻¹ that can be assigned to different absorption modes of cyclohexanone (Table 7.1).^{191, 192} Infrared bands at 1725, 1700 and 1313 cm⁻¹ are due to desorbed or bulk cyclohexanone molecules in surface water layer and the other two are due to surface adsorbed cyclohexanone.^{191, 192} The absorption band at 1642 cm⁻¹ is due to surface adsorbed water on TiO_2 .¹⁴ Absorption bands at 1575, 1520, 1424 and 1357 cm⁻¹ are probably due to adsorbed carboxylate and cyclohexyl peroxide.¹⁹¹⁻¹⁹³ The absorption bands at 1520 and 1424 cm⁻¹ are only visible in the spectra collected at higher relative humidity (Figure 7.3).

	Assignment	This study (cm ⁻¹)	Literature (cm ⁻¹)
Cyclohexane	CH ₂ bending	1451	1449 ¹⁹¹
	CH ₂ bending	1257	1257 ¹⁹¹
Cyclohexanone	C=O stretching (dissolved in water)	1692,1700,1725	$1690^{192},1712^{191},$ 1720^{192}
	C=O stretching (adsorbed)	1680	1683,1680 ¹⁹¹
	CH ₂ bending	1313	1313 ¹⁹¹
	Twisting (cyclohexyl ring)	1278	1278
Carboxylate	C=O stretching(monodentate)	1575	$1565^{192}, 1575^{191}, 193$
	C=O stretching (monodentate)	1424	1424 ¹⁹²
	C=O stretching (bidentate)	1520	1520 ¹⁹²
Cyclohexyl hydroperoxide	bending	1357	1367 ¹⁹¹
Adsorbed water		1642	1642 ¹⁹²

Table 7.1: Assignment of infrared absorption bands in TiO₂ surface spectra

Formation of above surface species can be explained using the reactions between cyclohexane and ROS generated on the TiO₂ surface upon irradiation. Upon irradiation of TiO₂ with light ($\lambda < 387$ nm), electron-hole pairs (e⁻/h⁺) are generated in the valence and conduction bands.^{42, 183}

$$\mathrm{TiO}_2 + \mathrm{h}\nu \to \mathrm{h}^+ + \mathrm{e}^- \tag{7.1}$$



Figure 7.3: Variation of surface adsorbed cyclohexane oxidation product concentration with time on TiO_2 surface at a) 5% b) 20% c) 40% d) 73% relative humidity. Surface spectra were collected every 15 min for 60 min time period.
These photochemically generated h^+ can react with surface hydroxyl groups on TiO₂ forming •OH radicals (reaction 2).¹⁹⁴ Surface adsorbed water molecules can regenerate the surface hydroxyl groups consumed in •OH radical generation according to reaction 7.3.¹⁹⁴

$$Ti - OH + h^+ \rightarrow Ti - + \bullet OH \tag{7.2}$$

$$Ti - + H_2 0 \rightarrow Ti - 0H + H^+$$
 (7.3)

These e^- and h^+ can also react with water molecules and O_2 leading to the formation of ROS such as •OH, HO₂• and H₂O₂ as shown below from reaction 7.4 to 7.11.¹⁸³

 $h^+ + H_2 0 \rightarrow 0H + H^+ \tag{7.4}$

$$O_2 + H^+ + e^- \rightarrow HO_2 \bullet \tag{7.5}$$

$$2 \bullet 0H \to H_2 O_2 \tag{7.6}$$

$$HO_2 + e^- + H^+ \to H_2O_2$$
 (7.7)

$$2\mathrm{HO}_2 \bullet \to \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2 \tag{7.8}$$

$$0_2 + e^- \to 0_2^-$$
 (7.9)

$$H_2 O_2 + O_2^- \to OH + OH^- + O_2$$
 (7.10)

$$\bullet 0H + HO_2 \bullet \to H_2O + O_2 \tag{7.11}$$

Cyclohexane molecules (RH_2) react with •OH radicals to form cyclohexyl radical (•RH) which leads to the formation of cyclohexanone (RO) and other oxidation products.^{191, 195}

•
$$OH + RH_2 \rightarrow \bullet RH + 2H^+$$
 (7.12)

•
$$\operatorname{RH} + \operatorname{O}_2^- \to \operatorname{RO} + \operatorname{OH}^-$$
 (7.13)

•
$$\operatorname{RH} + \operatorname{HO}_2 \bullet \to \operatorname{RO} + \operatorname{H}_2 \operatorname{O}$$
 (7.14)

Cyclohexanone can also be formed via cyclohexanol (RHOH) intermediate formed by the reaction of •OH with cyclohexyl radical.¹⁹⁵

•
$$OH + eRH \rightarrow RHOH$$
 (7.15)

$$RHOH + 2 \bullet OH \rightarrow RO + 2 H_2 O \tag{7.16}$$

•
$$\operatorname{RH} + \operatorname{HO}_2 \bullet \to \operatorname{RO} + \operatorname{H}_2 O$$
 (7.17)

Cyclohexyl radical reacts directly with O_2 forming cyclohexyl peroxy radical (RHOO•) which then interacts with photo- generated e⁻ to form cyclohexanone.¹⁹⁵ Carboxylates are formed by further oxidation of cyclohexanone.^{191, 192}

•
$$\operatorname{RH} + \operatorname{O}_2 \to \operatorname{RHOO} \bullet$$
 (7.18)

$$\mathsf{RHOO} \bullet + \mathsf{e}^- \to \mathsf{RO} + \mathsf{OH}^- \tag{7.19}$$

$$RO + \bullet OH \to R'COO^{-} \tag{7.20}$$

In contrast to zero relative humidity, both surface and gas phase oxidation products were detected in the experiments conducted at 5%, 20% and 40% relative humidity. Surface spectra collected for cyclohexane oxidation in the presence of gas phase water vapor are given in Figure 7.3.

Surface adsorbed cyclohexanone absorption bands at 1680 and 1313 cm⁻¹ are decreased in intensity with increasing relative humidity. This trend is much clearer in TiO_2 surface difference spectra given in Figure 7.4. Difference spectra presented in Figure 7.4 were obtained by subtracting the initial surface spectrum of TiO_2 collected before irradiation from the spectra obtained after 60 min of irradiation. Further, in general, the concentration of surface adsorbed species are decreased with increasing relative humidity.



Figure 7.4: Difference spectra of the TiO_2 surface after 60 min exposure to cyclohexane at under different relative humidity conditions in the presence of simulated solar radiation.

Gas phase cyclohexanone, characterized by an IR absorption band around 1730 cm⁻¹ was also observed in the experiments carried out at 0 to 40% relative humidity.¹⁹⁶ Figure 7.5 shows the gas phase spectra for cyclohexanone obtained for 60 min at 5%, 20% and 40% relative humidity. In contrast to the trend in surface products, gas phase product

concentration was increased with relative humidity until 40% as shown in Figure 7.6. Gas phase products were absent in the experiment conducted at 73% relative humidity.



Figure 7.5: Gas phase spectra obtained after exposing the TiO_2 surface to 3 Torr cyclohexane at 5%, 20% and 40% relative humidity in the presence of simulated solar radiation.



Figure 7.6: Variation of gas phase cyclohexanone product concentration with time at different relative humidity conditions

There are two possible sources of gas phase cyclohexanone. First is the diffusion of cyclohexanone formed on the particle surface into gas phase. In the second mechanism, •OH radical diffused into gas phase react with gas phase cyclohexane molecule to form

cyclohexanone. In this gas phase reaction pathway, cyclohexane molecules first react with •OH radical to form cyclohexyl radical and water (reaction 7.21).¹⁸⁹ The cyclohexyl radical can then lead to the formation of cyclohexanone by reaction 7.15, 7.16 and 7.17. Cyclohexyl peroxy radical formed in reaction 7.18 can also lead to the formation of cyclohexanone via reaction 7.22 and 7.23.¹⁸⁹

$$\mathrm{RH}_2 + \bullet \mathrm{OH} \to \bullet \mathrm{RH} + \mathrm{H}_2\mathrm{O} \tag{7.21}$$

$$2 \operatorname{ROO} \bullet \to 2 \operatorname{RO} \bullet + O_2 \tag{7.22}$$

$$2 \operatorname{RO} \bullet + \operatorname{O}_2 \to \operatorname{RO} + \operatorname{HO}_2 \bullet \tag{7.23}$$

Decrease in surface product concentration and increase in gas phase product concentration with increasing relative humidity can be due to; a) fast desorption of cyclohexanone formed on the TiO₂ surface into the gas phase or b) increased production and diffusion of •OH radicals into the gas phase with increased surface water content. Further studies are warranted to understand the exact mechanism of this gas phase cyclohexanone formation. Absence of gas phase cyclohexanone at 73% relative humidity is probably due to hindered diffusion of •OH radicals and/or cyclohexanone molecules into the gas phase due to higher water activity on the TiO₂ surface.

7.5 Conclusion

In this study, oxidation of cyclohexane by •OH radicals generated from photolysis of water on TiO_2 was studied under atmospherically relevant conditions. Reaction of •OH radical with cyclohexane lead to the formation of cyclohexanone, cyclohexanol and its dissociation products. In the current study, both cyclohexanone and its dissociation products were observed on the TiO₂ surface. However, gas phase cyclohexanone was the only gas phase product detected. There are two sources for gas phase cyclohexanone. The first one is cyclohexanone formed by the reaction of gas phase cyclohexane with •OH radicals diffused into the gas phase from TiO₂ surface. The other source is cyclohexanone diffused from TiO₂ surface to the gas phase. Gas phase cyclohexanone concentration is increased with increasing relative humidity until 40%. This gas phase cyclohexanone was absent at 0% relative humidity implying that water vapor is necessary for the gas phase cyclohexanone at 73% relative humidity is probably due to limited diffusion of cyclohexanone or •OH radicals.

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CHAPTER 8

CONCLUSIONS AND FUTUREWORK

Mineral aerosol particles in the atmosphere can alter the atmospheric chemical balance via heterogeneous and multiphase atmospheric reactions. Understanding the chemistry of mineral aerosols is vital in order to develop models for accurate climate predictions. Therefore, the primary focus of this dissertation is on understanding the heterogeneous and multiphase chemistry and photochemistry of atmospheric trace gases in the presence of mineral aerosol particles. With recent industrial development, engineered nanomaterials have become a major class of environmental pollutants. These nanomaterials react with atmospheric trace gases and undergo transformation or aging which affects their environmental fate and bioavailability. Another focus of this dissertation research is understanding the aging of metal oxide nanoparticles upon atmospheric exposure and its effects on particle physicochemical properties including dissolution.

In Chapter 2, details of the spectroscopic techniques used to study gas phase reactions, solution phase experimental techniques and sample characterization techniques are described. All of the infrared spectroscopic studies presented in this dissertation were conducted in custom-designed infrared reaction chambers coupled to two stage vacuum systems.

In Chapter 3, photochemistry of nitrate acid adsorbed in NaY zeolite under environmentally relevant conditions is discussed. FTIR spectroscopy was used to probe the change in surface and gas phase composition upon irradiation. Nitric acid reacts within the NaY zeolite cage to form a Na⁺NO₃⁻ complex with the charge compensating Na⁺ cation. Irradiation of nitrate in NaY zeolite produces surface adsorbed nitrite which can be detected by infrared spectroscopy. The presence of stable nitrite in the zeolite can be attributed to the three-dimensional confined structure and the presence of charge compensating cations. Gas phase N₂O, NO and NO₂ are formed at longer irradiation times and in very low concentrations. In the presence of molecular oxygen, nitrite is reconverted to nitrate. Surface nitrite coverages decrease with increasing relative humidity. Gas phase ammonia adsorbed in the zeolite forms ammonium ions leading to NH₄NO₃ when reacted with molecular HNO₃. In the presence of ammonia, the major photolysis product is gas-phase N₂O.

In Chapter 4, the wavelength dependence of the photochemistry of nitrate adsorbed on different mineral dust surfaces was studied using Al_2O_3 , TiO_2 and NaY zeolite as proxies to represent non-photoactive oxides, photoactive oxides and aluminosilicate, respectively. This study shows that nitrate photochemistry on mineral dust particles are governed by the wavelength of light, physicochemical properties of the dust particles and the adsorption mode of the nitrate ion. Although wavelength is the limiting factor of nitrate photolysis, product concentration is governed by light intensity. Nitrate adsorbed on photoactive components of mineral dust shows an extended photo activity compared to aqueous nitrate.

Atmospheric aging of ZnO and CuO in the presence of CO_2 and water vapor was investigated in Chapter 5. A number of important conclusions about nanoparticle aging and its effect on dissolution were derived from this study. When the relative humidity is very low, CO_2 molecules directly interact with surface hydroxyl groups, leading to the formation of adsorbed bicarbonate. Surface adsorbed carbonate and carboxylate species are also formed due to the interaction of CO₂ with surface sites other than hydroxyl groups, including metal cations and oxygen vacancies. At higher relative humidity, solvated carbonate is the only species present on nanoparticle surfaces. CO₂ adsorption increases the dissolution of ZnO nanoparticles in water. However, the dissolution of CuO nanoparticles is significantly lower in any medium than ZnO nanoparticles. Nanoparticle dissolution in HEPES buffer was always higher than water, possibly due to ligand promoted dissolution by buffer molecules. This study provides evidence that ZnO nanoparticles are more susceptible to release dissolved cations to water or in the presence of ligands than CuO nanoparticles of the same diameter and surface area. Findings of this study reveal the importance of atmospheric aging of nanoparticles in their dissolution, which ultimately affect nanoparticle toxicity.

In Chapter 6, oxidation of dissolved sulfur dioxide in the atmospheric aqueous phase in the presence of iron containing mineral particles as a function of temperature and light is discussed. S(IV) oxidation in the presence of coal fly ash (FA), γ -Fe₂O₃ and Arizona test dust (AZTD) show significant differences. S(IV) oxidation in the presence of FA and γ -Fe₂O₃ lead to reductive iron dissolution. Iron dissolution patterns suggest that this oxidation reaction initially occurs via a heterogeneous pathway, a homogeneous pathway is also possible in later times. S(IV) oxidation in the presence of AZTD does not show any iron dissolution suggesting that it is mostly a heterogeneous pathway. Higher rate of S(IV) loss in the presence of AZTD compared to FA and γ -Fe₂O₃ suggests that other factors, including higher adsorption of sulfite, TMI catalysis by other metal ions or enhanced surface-catalyzed processes in AZTD, play a role. Overall these studies suggest that important differences occur in the atmospheric oxidation of S(IV) depending on aerosol sources.

Photochemistry of water to generate hydroxyl radicals on TiO₂ surfaces were studied in Chapter 7. Relative humidity dependent hydroxyl radical generation was monitored using cyclohexane as the hydroxyl radical scavenger. Hydroxyl radicals generated on TiO₂ surface by photolysis of water lead to the formation of surface adsorbed as well as gas phase products. Cyclohexanone was the major gas phase product observed. Cyclohexanone product has two possible origins; a) reaction of hydroxyl radicals diffused into the gas phase with gas phase cyclohexane b) diffusion of cyclohexanone formed on the surface to the gas phase. Gas phase cyclohexanone product is present only at relative humilities higher than 0% indicating the dependence of this reaction on gas phase or loosely bound water vapor. Cyclohexanone product is absent at 73% relative humidity probably due to limited diffusion of hydroxyl radicals and/or cyclohexanone to the gas phase.

Accuracy of future climate predictions depends on the extent to which we understand the atmospheric chemical processes and their kinetics. The research presented in this dissertation provides an important contribution to our understanding of the role of mineral aerosols in the atmosphere and the effect of atmospheric trace gases components on nanoparticle aging and transformation. However, there still remain many unexplored areas that need to be investigated in order to fully understand these processes, which can be done through combined laboratory and field studies and modeling analysis. Some future directions and challenges include the following.

1. Conducting laboratory studies under atmospherically relevant conditions of gas phase concentrations, relative humidity and solar radiation flux.

- 2. Development of more sensitive instruments to simultaneously probe gas phase and surface adsorbed concentrations of atmospheric chemical species
- 3. Experiments to understand atmospheric chemistry and photochemistry should be carried out with model proxies rather than single components to simulate real mineral aerosol.
- 4. Systematic laboratory studies are needed to validate field measurements.
- 5. Experimental studies to understand the effect of atmospherically relevant pH, temperature, dissolved metal ion concentrations and synergistic effects of different transition metal ions on atmospheric sulfur dioxide oxidation to sulfate.
- Modeling analysis are necessary to understand the effect of the reactions of mineral aerosol on climate.
- 7. Experimental studies to understand the effect of atmospheric trace gases on the aging and transformation of most widely used nanomaterial.

The results presented here provide insights into the role of mineral aerosol in the atmosphere and the role of atmospheric gases on the aging of engineered nanomaterials.

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