Introduction

Nitrate ion is an important chromophore and can undergo photochemical reactions on the surface of atmospheric aerosols,\textsuperscript{1} deliquesced thin films,\textsuperscript{2} ice/snow\textsuperscript{3} and in solution.\textsuperscript{4} Nitrate ion has an absorption maximum at 302 nm ($\varepsilon=7.2$ mol dm$^{-3}$ cm$^{-1}$) in aqueous solution.\textsuperscript{5} In the atmosphere, gas-phase nitrogen oxides readily react with particulate matter (e.g., mineral dust) to yield adsorbed nitrate. Atmospheric nitric acid is the main reservoir species in the NOx cycle. Heterogeneous reactions and possible renoxification mechanisms of tropospheric HNO$_3$ acid have been widely studied on different environmental interfaces and surfaces.\textsuperscript{6} Mineral dust aerosols act as a reactive surface for atmospheric nitric acid adsorption and photochemical reactions of adsorbed nitrate.

The photochemistry of adsorbed nitrate, formed by either exposure to NO$_2$ or HNO$_3$ has been widely studied on the surface of components of mineral dust aerosol.\textsuperscript{7,8} Photoexcitation of adsorbed nitrates forms several gas-phase products like N$_2$O, NO, NO$_2$ and HONO.\textsuperscript{7,8} Additionally, some recent studies on NO$_2$ adsorption and photochemistry on semiconductor metal oxides such as Cr$_2$O$_3$ and TiO$_2$ have shown conversion of adsorbed nitrate to gas-phase NOx species under irradiation conditions.\textsuperscript{9,10} These studies used mass spectrometry and infrared spectroscopy as tools to detect gas-phase photoproducts and infrared spectroscopy and X-ray photoelectron spectroscopy to detect adsorbed photoproducts as well. For adsorbed species, it is sometimes difficult to differentiate adsorbed products due to the fact that there are overlapping absorption bands for different species that contain N-O functional groups.\textsuperscript{11} X-ray photoelectron spectroscopy (XPS), however can detect adsorbate which differ in the oxidation state of nitrogen atom. In this study XPS is used to investigate the surface photochemistry of nitrate adsorbed on hematite particle surfaces.

Hematite is one of the most common iron oxide polymorphs present in the earth’s crust. Iron-containing particles are transferred to the atmosphere from both wind and volcanic activities in the form of iron containing mineral dust and volcanic ash aerosols.\textsuperscript{1} hematite is a semiconductor material with a lower band gap of 2.2 eV that can absorb solar radiation and has the potential to
alter nitrate photochemistry pathways.\textsuperscript{12} Therefore, the surface photochemistry of nitrate adsorbed on hematite is important to further understand atmospheric processes. In this study, photochemistry of adsorbed nitrate on hematite, $\alpha$-Fe$_2$O$_3$ surface is investigated under environmentally relevant relative humidity and molecular oxygen by XPS and FTIR spectroscopic techniques. Due to the importance of iron solubility in iron cycling the impact that this reaction has on iron dissolution is also investigated.

**Experimental Methods.**

**Surface XPS Analysis Chamber Coupled with Transfer and Reaction Auxiliary Chambers:**

The custom-designed Kratos Axis Ultra X-ray photoelectron spectroscopy system for reactions and analysis has been described in detail before.\textsuperscript{13} The experimental setup has capabilities for reacting samples with gas-phase reactants, evacuating the gas-phase and surface product analysis with four different chambers that include: (i) an ultra high vacuum (UHV) surface analysis chamber, (ii) a sample transfer antechamber, (iii) a stainless steel reaction chamber and (iv) a Teflon coated reaction chamber. The transfer antechamber is connected to the analysis chamber, steel reaction chamber and Teflon coated reaction chamber. With this configuration, the transfer antechamber is used to introduce samples into the analysis chamber, and also allows for samples to be transferred directly from the surface analysis chamber to the reaction chambers vice versa. A 500 W Hg lamp (Oriel 66033) was used to irradiate the samples in the steel reaction chamber.

For typical XPS analysis, powdered samples were pressed into indium foil and mounted onto a copper stub. After acquiring the initial scans at the surface analysis chamber, the sample was transferred to the Teflon coated chamber via the transfer antechamber by means of sample transfer rod and a hand valve. The sample was then reacted with HNO$_3$. HNO$_3$ reacted $\alpha$-Fe$_2$O$_3$ surfaces were evacuated and transferred to the sample analysis chamber for initial scans. The evacuation removes molecularly adsorbed HNO$_3$. After the initial scans, samples were transferred to the steel
reaction chamber for reactions under environmentally relevant conditions of (1) $\text{H}_2\text{O}$, (2) $\text{O}_2$, (3) $\text{H}_2\text{O}/\text{O}_2$ and UV light. The reacted sample was then evacuated and transferred back to the analysis chamber for post-reaction surface characterization.

Data Processing of Core Photoelectron Spectra: All spectra were calibrated using the adventitious C1s peak at 285.0 eV.$^{13}$ CasaXPS software was used to process the XPS data.$^{14}$ The N1s transition was fit to one peak with a fixed full-width-at-the-half-maximum (FWHM) value of 1.4 eV. The components of the peaks contain a Gaussian/Lorentzian product with 30% Lorentzian and 70% Gaussian character. An error of ±0.2 eV is reported for all peak binding energies.$^{13}$

Transmission FTIR Spectroscopy. For gas-phase product formation measurements, the $\alpha$-$\text{Fe}_2\text{O}_3$ particles were prepared by pressing onto half of a tungsten grid (3 cm × 2 cm, 100 mesh/in., 0.002” wire dia., Accumet). Other half of the grid was left blank for gas-phase measurements. The oxide samples prepared on the tungsten grid are secured inside the Teflon coated infrared cell by Teflon coated sample holder jaws. The infrared cell is connected to a vacuum chamber through a Teflon tube and two consecutive glass gas manifolds with ports for gas introduction and two absolute pressure transducers. Details of the FTIR experimental system have been described before.$^{15}$ Typically, 250 scans were collected with an instrument resolution of 4 cm$^{-1}$ in the spectral range from 4000 to 750 cm$^{-1}$. Absorbance spectra for gas and adsorbed species were obtained by referencing single beam spectra of the blank grid and the oxide coated grid to single beam spectra collected prior to gas exposure.

Iron Dissolution Experiments. HNO$_3$ reacted $\alpha$-$\text{Fe}_2\text{O}_3$ particles prepared in Teflon coated reaction chamber were suspended in optima water (Sigma Aldrich) at a mass loading of 30 mg/50 mL. The suspension was stirred for 24 h. The stabilities of unreacted and reacted particle suspensions were measured using the sedimentation pattern by measuring the extinction with a Perkin-Elmer Lambda 20 UV-visible spectrometer at 510 nm. Dissolved iron concentration was measured using Varian 720-ES inductively coupled plasma-optical emission spectrometer (ICP-OES). Prior to ICP analysis
aliquot from the supernatant suspension was passed through a 0.2 µm PTFE filter to remove particles. All experiments were conducted in triplicate.

**Characterization of \( \alpha\text{-Fe}_2\text{O}_3 \) particles.** Hematite (\( \alpha\text{-Fe}_2\text{O}_3 \), Alfa Aesar) was used as received. X-ray diffraction (XRD), scanning electron microscopy (SEM) and Brunauer-Emmet-Teller (BET) surface area analyzer were used to characterize the \( \alpha\text{-Fe}_2\text{O}_3 \) samples.

**Sources of Chemicals.** Dry gaseous nitric acid was taken from the vapor of a 1:3 mixture of concentrated HNO\(_3\) (70.6% HNO\(_3\), Mallinckrodt) and 95.9% H\(_2\)SO\(_4\), (Mallinckrodt). Distilled H\(_2\)O (Milli-Q) was used. Prior to use, both the distilled water and HNO\(_3\) were degassed several times with consecutive freeze-pump-thaw cycles. Oxygen (ultra-pure grade) was obtained from Airgas.

**Results and Discussion**

**Characterization of \( \alpha\text{-Fe}_2\text{O}_3 \).** XRD pattern of \( \alpha\text{-Fe}_2\text{O}_3 \) shown in Figure 1 (a) agrees well with the standard pattern for hematite. The average particle size of \( \alpha\text{-Fe}_2\text{O}_3 \) was determined by SEM and shows particles (Figure 1 (b)) with diameter of 310 ± 22 nm (200 particles counted). BET analysis showed a specific surface area of 23 ± 2 m\(^2\)/g.

**XPS of HNO\(_3\) Acid Reacted \( \alpha\text{-Fe}_2\text{O}_3 \) in the Presence of Environmentally Relevant Pressures of Relative Humidity and Molecular Oxygen.** The high-resolution spectra of Fe2p, O1s and N1s binding energy regions of unreacted and \( \alpha\text{-Fe}_2\text{O}_3 \) reacted with HNO\(_3\) for 25 minutes are shown in Figure 2. Photoelectrons emitted within the Fe2p region for unreacted \( \alpha\text{-Fe}_2\text{O}_3 \) are at binding energies of 711.2 and 724.7 eV which correspond to Fe2\(_{3/2}\) and Fe2\(_{1/2}\). In the O1s region, photoelectrons at 530.0 and 531.6 eV were observed for the unreacted surface. These are assigned to Fe-O in \( \alpha\text{-Fe}_2\text{O}_3 \) lattice structure and surface hydroxyl groups, respectively. Upon reaction with HNO\(_3\), formation of adsorbed nitrate is observed as well as seen by a new peak in the N1s region. Additionally, there are observed shifts in the O1s and Fe2p levels by ~0.5 eV and ~0.7 eV,
respectively as a result of strong electrostatic interaction between nitrate and the hematite surface. The peak appearing at 532.5 eV in the O1s region after reacting with HNO$_3$ can be assigned to the oxygen atoms in adsorbed nitrate.$^{16}$ The high resolution N1s spectrum of HNO$_3$ reacted $\alpha$-Fe$_2$O$_3$ can be curve fit with one component corresponding to the 407.4 eV peak that is assigned to nitrate ion (NO$_3^-$), adsorbed on the surface.$^{13}$ The formation of adsorbed NO$_3^-$ can be written as follows.

$$\text{HNO}_3(g) \rightarrow \text{NO}_3^-(\text{ads}) + \text{H}^+(\text{ads}) \quad (1)$$

Nitrate formation is governed by dissociative HNO$_3$ adsorption with NO$_3^-$ occupying Fe sites and dissociated proton on lattice oxygen sites according to Reaction 1. The dissociative adsorption of HNO$_3$ acid is presumably an exothermic process and thus thermodynamically favorable process on hematite surface. Upon HNO$_3$ adsorption no features were observed around 403 eV or 406 eV region to surface nitrite (NO$_2^-$) or molecularly adsorbed NO$_2$ species. Formation of such species have been observed in various oxide surfaces including hematite when reacted with NO$_2$.$^{10,13,17}$ Further experiments were performed by adsorbing HNO$_3$ on $\alpha$-Fe$_2$O$_3$ particles and then subsequently exposing this reacted surface to various conditions, i.e. under dry conditions %RH<1 and without and with 100 Torr of O$_2$ as well as 45% RH without and with 100 Torr of O$_2$. Upon post-analysis, no new peaks nor change in the binding energy observed in the N1s upon subjecting HNO$_3$ reacted $\alpha$-Fe$_2$O$_3$ particles for 30 minutes under these different environmental conditions.

**Nitrate Photochemistry on $\alpha$-Fe$_2$O$_3$ in the Presence of Environmentally Relevant Pressures of Water Vapor and Molecular Oxygen.** In order to understand the photochemistry of adsorbed nitrate on $\alpha$-Fe$_2$O$_3$ particle surfaces following reaction with nitric acid, the surface was irradiated and high resolution XPS analysis was performed. The high-resolution spectra in the N1s binding energy region of $\alpha$-Fe$_2$O$_3$ reacted with HNO$_3$ and then irradiated with UV light ($\lambda$ > 300 nm) for 90 minutes are shown in Figure 3. These experiments were performed under different levels of molecular oxygen and water vapor. XPS in the N1s showed only the binding energy peak
corresponding to surface nitrate at 407.4 eV, but with a decreased intensity following UV exposure indicating loss of surface bound nitrate. However, when nitrate was irradiated with UV radiation in the presence of water vapor a broad feature appeared at low binding energy region (Figure 3c and d) and there is also a more significant decrease in the intensity of nitrate peak (vide infra). This broad low binding energy feature was fit to two components, a peak centered at 401.7 and another 400.3 eV. The exact binding energy assignment of reduced nitrogen species between 402 – 399 eV has been controversial as the surface binding sites can change the binding energy slightly. Baltrusaitis and co-workers have discussed these differences in detail and used computational analysis to assign these two features at 401.7 and 400.3 eV to NO and N, respectively. In previous studies, the formation of NO has been observed using FTIR spectroscopy. This has been proposed to occur via short lived NO\textsubscript{2} and/or NO\textsuperscript{−} intermediates according to the Reactions 2 to 4.\textsuperscript{7}

\[
\text{NO}_3(\text{ads}) + H^+ + \text{hv} \rightarrow \text{NO}_2(\text{ads}) + \text{OH}^* \quad (2)
\]

\[
\text{NO}_3(\text{ads}) + \text{hv} \rightarrow \text{NO}_2(\text{ads}) + \text{O}_2(\text{P}) \quad (3)
\]

\[
\text{NO}_2(\text{ads}) + H^+ + \text{hv} \rightarrow \text{NO}(\text{ads}) + \text{OH}^* \quad (4)
\]

The newly formed adsorbed NO and NO\textsubscript{2} can subsequently desorb into the gas phase. Photolysis of adsorbed nitrate on alumina reported NO and NO\textsubscript{2} as the major gas phase species.\textsuperscript{7} It has also been shown that NO has a relatively high electron affinity and can easily trap free electron thus forming a negatively charged NO\textsuperscript{−} anion adsorbed on metal cationic sites on the surface according to reaction 5 resulting band at 401.7 eV.\textsuperscript{13}

\[
\text{NO}(\text{ads}) + \text{e}^- \rightarrow \text{NO}^- (\text{ads}) \quad (5)
\]

\[
\text{O(\text{vacancy})}^- + \text{NO}(\text{ads}) \rightarrow \text{N}^-(\text{ads}) + \text{O}(\text{ads}) \quad (6)
\]

In addition, adsorbed NO can decompose on some surfaces to produce atomic N and O on the surface as reported by NO\textsubscript{2} adsorption studies on several metal oxide surfaces.\textsuperscript{18} Iron oxide surfaces have been reported as being materials rich with oxygen vacancies. Higher population of point defects have been reported for hematite surface compared to the bulk.\textsuperscript{19} Furthermore, oxygen
vacancies on other semiconductor surfaces like TiO$_2$ have shown negative charge associated with trapped electrons and similar sites has been proposed on iron oxide surfaces in previous studies.$^{20}$ The electrons generated from band gap excitations of hematite can be trapped in oxygen vacancy sites and increase the availability of negatively charged oxygen vacancy sites. Therefore, in the current study, newly formed NO decomposition on negatively charged O vacancy can be expected resulting N$^-$ according to the reaction 6.

More reaction pathways (reaction 7 - 9) are available for nitrate photolysis via a nitrate radical intermediate forming reduced NO and NO$_2$ on a semiconductor surface as evident by the nitrate photochemistry studies on TiO$_2$.\textsuperscript{21} These reactions, initiated by electron-hole ($e^-/h^+$) pairs, can also play a significant role on hematite surface.

\begin{align*}
\text{NO}_3^-(\text{ads}) + h^+ & \rightarrow \text{NO}_3^- \quad (7) \\
\text{NO}_3^- + \text{hv} & \rightarrow \text{NO(ads)} + \text{O}_2 \quad (8) \\
\text{NO}_3^- + \text{hv} & \rightarrow \text{NO}_2(\text{ads}) + \text{O}^- \quad (9) \\
\text{NO}_2(\text{ads}) + e^- & \rightarrow \text{NO}_2^- \quad (10)
\end{align*}

Newly formed NO$_2$(ads) from reaction 9 can either react with photogenerated electrons forming adsorbed NO$_2^-$ which undergoes continued photoreactions to yield adsorbed NO according to reaction 4 or desorb to the gas phase. We have no evidence for NO$_2$(ads) or NO$_2^-$(ads). Therefore, NO$_2$(ads) conversion to NO(ads) via NO$_2^-$ may be a very fast reaction. Additionally, the electron attachment, reaction 10, is more feasible on hematite surface due to the availability of photogenerated electrons. Reduced-nitrogen, surface-species formation did not show any difference in the presence of molecular oxygen (spectra not shown). In the presence of water vapor, hydroxyl radicals formed on hematite surface upon UV irradiation (reaction 11) can initiate following reactions in competition with the nitrate photolysis reactions leading to secondary pathways.

\begin{align*}
\text{H}_2\text{O} + h^+ & \rightarrow \text{H}^+ + \text{OH}^- \quad (11) \\
\text{NO}_2^- + \text{H}^+ & \rightarrow \text{HONO} \quad (12)
\end{align*}
\[
\text{NO}_2^- + \text{OH}^* \rightarrow \text{NO}_2 + \text{OH}^- \quad (13)
\]
\[
\text{NO}_3^- (\text{ads}) + \text{OH}^* \rightarrow \text{NO}_3^* + \text{OH}^- \quad (14)
\]

These alternative pathways can dominate in the presence of relative humidity according to the reactions 12 and 13 converting \(\text{NO}_2^-\) intermediate to the gas phase HONO and \(\text{NO}_2\) and converting \(\text{NO}_3^- (\text{ads})\) to nitrate radical (reaction 14). Surface product formation under irradiation was investigated as a function of water vapor pressure. Left panel of Figure 4 shows the N1s region of \(\text{HNO}_3\) reacted \(\alpha\text{-Fe}_2\text{O}_3\) after 90 minute UV irradiation at different water vapor pressures. The right panel of Figure 4 shows the total nitrate loss after 90 minute UV irradiation calculated from initial and final N1s:Fe2p speciation ratio using the adsorbed nitrate N1s peak at 407.4 eV. In the absence of water vapor, reduced nitrogen species were not observed. This can be due to the low nitrate loss under irradiation in the absence of water vapor and low availability of electrons due to higher electron hole recombination. The total nitrate loss is ~3 times higher in the presence of water vapor. This confirms the important role of water vapor in nitrate photolysis on hematite and the increase in nitrate loss due to increase ability to react and new mechanisms available for reactions giving rise to a significantly greater loss of nitrate and the observed increase in surface-bound products at 5 and 11.5 Torr water exposures. Additionally, in the presence of water vapor photo-generated holes react with water molecules and that decreases the \(e^-/h^+\) recombination leaving more electrons to form reduced nitrogen surface species. In the presence of water vapor, around 60% nitrate loss was observed for all three %RH experiments. Reduced-nitrogen, surface-species were not observed at the highest water vapor exposure. This suggest that surface sites for \(\text{NO}^-\) and \(\text{N}^-\) adsorption are available only at 5 and 11.5 Torr water exposures (24 and 55 %RH) and potentially covered at the highest water vapor pressure of 17 Torr (81% RH). Mogili et. al. have previously reported that the water adsorption is not uniform on hematite surfaces and water adsorption results water patches leaving some of the surface sites available up to 60% RH water vapor exposure. Since the percentage nitrate loss did not show much difference for three water vapor pressures the
disappearance of NO\(^{-}\) and atomic N\(^{-}\) species at the highest water vapor exposure can be possibly due to the occupation of water molecules on adsorption sites at the highest relative humidity that are then blocked for further reactions. Figure 5 shows schematics of the summary of reactions for nitrate photochemistry on hematite and reduced nitrogen surface species and gas-phase NO, NO\(_2\) formation under different water vapor exposures.

The gas-phase products formed during photolysis of nitrate adsorbed on \(\alpha\)-Fe\(_2\)O\(_3\) particles were also monitored using the FTIR system described under experimental methods. Surface FTIR spectra were consistent with data reported for HNO\(_3\) adsorption on \(\alpha\)-Fe\(_2\)O\(_3\).\(^{15}\) Figure 6 show the gas-phase product formation recorded as a function of UV exposure time in the presence of 45% RH of water vapor. Three peaks appeared at 1616, 1874 and 2223 cm\(^{-1}\). These vibrational modes can be attributed to the gas-phase NO\(_2\), NO and N\(_2\)O species respectively. Gas phase NO\(_2\) appeared at longer irradiation times of 120 and 420 minutes. The dominant gas-phase species in the presence of water vapor was NO at all the irradiation times agreeing with the presence of adsorbed NO\(^{-}\) on the surface. Identical experiments performed to monitor the gas-phase products under wet condition, in the presence of molecular oxygen showed higher gas phase NO\(_2\) amounts (data not shown). The N\(_2\)O formation in the presence of 45% RH that can be due to secondary pathway according to the reaction 15 under acidic conditions in the presence of water vapor.\(^{23}\) Furthermore, reactions 16 and 17 can be sources for N\(_2\)O as well.\(^{24}\)

\[
\begin{align*}
8\text{NO}_2 + 3\text{H}_2\text{O} & \rightarrow \text{N}_2\text{O} + 6\text{HNO}_3 \\
\text{NO} + \text{NO}_3^- & \rightarrow \text{N}_2\text{O} + 5/4\text{O}_2 + 1/2\text{O}^2- \\
\text{NO}_2 + \text{NO}_3^- & \rightarrow \text{N}_2\text{O} + 7/4\text{O}_2 + 1/2\text{O}^2-
\end{align*}
\]

**Aqueous Phase Behavior of HNO\(_3\) Reacted Hematite Particles.** Sedimentation plots of HNO\(_3\) reacted and unreacted \(\alpha\)-Fe\(_2\)O\(_3\) showed fast settling down with no difference between the two.
Dissolved Fe concentration was below the limit of detection of ICP(OES). The data explains HNO$_3$ reaction does not change particle aggregation or enhance Fe dissolution from $\alpha$-Fe$_2$O$_3$ particles.

**Conclusions and Atmospheric Implications**

HNO$_3$ adsorption on hematite surface under different environmental conditions of relative humidity and molecular oxygen was explored in the presence and absence of UV irradiation. Ex and in-situ analyses were used to follow the surface and gas-phase species that form in these reactions. Surface nitrate was found to be the predominant species in the absence of UV irradiation. Irradiation with UV light resulted in the formation of surface-bound, reduced-nitrogen species. Furthermore, XPS analysis indicates that reduced species are observed only with the presence of co-adsorbed water except at the highest pressures of water vapor, and thus highest coverage, during the UV irradiation. Thus, these data show a relative humidity dependent extent of reaction and the stability of reduced surface species that form. FTIR studies confirm that irradiation with the UV light resulted the reduction of the adsorbed nitrate to form gas-phase N$_2$O, NO and NO$_2$ species. The distribution of surface-bound and gas-phase products depends on the presence of water vapor. Additionally, HNO$_3$ acid adsorption does not change the dissolution and solution phase behavior of these $\alpha$-Fe$_2$O$_3$ particles.

The data presented here support the role that iron-containing aerosol surfaces in the atmosphere can facilitate the conversion of adsorbed nitrate to gas-phase NO$_2$, NO and N$_2$O as well as adsorbed NO$^-$ and N$^-$ during heterogeneous photochemistry. The effect of relative humidity in the formation of highly reduced nitrogen species on iron oxides has not been shown previously and represents another role of adsorbed water in the reaction chemistry of environmental interfaces.

**Acknowledgments:** This material is based on the work supported by the National Science Foundation under grant CHE-0952605.
Figures

Figure 1. (a) X-ray diffraction pattern and (b) scanning electron microscope image of $\alpha$-Fe$_2$O$_3$.

Figure 2. High-resolution X-ray photoelectron spectra of $\alpha$-Fe$_2$O$_3$ particles in the Fe2p, O1s and N1s binding energy regions (a) prior to and (b) after saturation exposure of HNO$_3$.

Figure 3. High resolution X-ray photoelectron spectra of $\alpha$-Fe$_2$O$_3$ particles in the N1s binding energy regions following exposure to HNO$_3$ to saturation coverages and subsequent UV irradiation for 90 minutes in the presence and absence of water vapor and molecular oxygen. (a) %RH < 1 without O$_2$, (b) %RH < 1 with 100 Torr O$_2$, (c) %RH = 45 without 100 Torr O$_2$, (d) %RH = 45 with 100 Torr O$_2$ at $T = 296$ K. Black and green lines represent the experimental data acquired and the total fit respectively. Different surface species obtained by peak fitting are shown in red and blue lines. The fitted curve for the nitrate peak overlaps with the total fit.
Figure 4. High-resolution X-ray photoelectron spectra of α-Fe₂O₃ particles in the N₁s binding energy regions following exposure to HNO₃ to saturation coverages and subsequent UV irradiation for 90 min in the presence of (a) 0 Torr H₂O, (b) 5 Torr H₂O, (c) 11.5 Torr H₂O, and (d) 17 Torr H₂O at T = 296 K (left panel) and the percentage loss of nitrate after 90 min of UV irradiation in the presence of different water vapor pressures (right panel). In the left panel, black and green lines represent the experimental data acquired and the total fit, respectively. Surface species obtained by peak fitting are shown as red and blue lines. The fitted curve for nitrate peak overlaps with the total fit.

Figure 5. Schematic of adsorbed nitrate photochemistry on α-Fe₂O₃; (a) in the absence of water vapor, adsorbed nitrates present on the hematite surface in different coordination modes undergo limited nitrate photochemistry due to electron and hole pair recombination, (b) in the presence of 5 and 11.5 Torr water vapor pressure (24 and 55 %RH), there is higher nitrate conversion due to lower electron/hole recombination rates, thus NO⁻ and N⁻ form on cationic sites and O vacancy sites, (c) in the presence of 17 Torr (81 %RH) of water vapor pressure, there is high nitrate conversion, similar as in (b), however cationic sites and O vacancy sites are not available to form NO⁻ and N⁻.

Figure 6. Transmission FTIR spectra of gas-phase product formation from UV illumination of adsorbed nitrate under 45% RH in the absence of O₂ at T = 296 K.
References

D’Anna, B.; Harmon, C. W.; Johnson, S. N.; Finlayson-Pitts, B. J. Nitrate Ion Photochemistry at Interfaces: A
(3) Jacobi, H. W.; Annor, T.; Quansah, E. Investigation of The Photochemical Decomposition of Nitrate,
(4)udson, P. K.; Schwarz, J.; Baltrusaitis, J.; Gibson, E. R.; Grassian, V. H. A Spectroscopic Study of
(5) Goldstein, S.; Rabani, J. Mechanism of Nitrite Formation by Nitrate Photolysis in Aqueous Solution
(6) Mashburn, C. D.; Frinak, E. K.; Tolbert, M. A. Heterogeneous Uptake of Nitric Acid on Na-Montmorillonite
Salmeron, M.; Destaillats, H. Chemistry of NO$_3$ on TiO$_2$ Surfaces Studied by Ambient Pressure XPS: Products,
(8) Hadjiivanov, K.; Knozinger, H. Species Formed After NO Adsorption and NO$^+$O$_2$ Co-adsorption on TiO$_2$:
(9) Schwertmann, U.; Cornell, R. M. Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses (2nd
(10) Baltrusaitis, J.; Jayaweera, P. M.; Grassian, V. H. XPS Study of Nitrogen Dioxide Adsorption on Metal
Oxide Particle Surfaces Under Different Environmental Conditions. Phys. Chem. Chem. Phys. 2009, 11, 8295-
(11) Rodriguez, J. A.; Jirsak, T.; Liu, G.; Hrbek, J.; Dvorak, J.; Maiti, A. Chemistry of NO$_3$ on Oxide Surfaces:
Formation of NO$_3$ on TiO$_2$(110) and NO$_2$$^+$O Vacancy Interactions. J. Am. Chem. Soc. 2001, 123, 9597-9605.
(12) Haubrich, J.; Quiller, R. G.; Benz, L.; Liu, Z.; Friend, C. M. In Situ Ambient Pressure Studies of the
(13) Overbury, S. H.; Mullins, D. R.; Huntley, D. R.; Kundakovic, L. Chemisorption and Reaction of NO and N$_2$O
On Oxidized and Reduced Ceria Surfaces Studied by Soft X-Ray Photoemission Spectroscopy and Desorption
Near the Hematite (0001) Surface: An Atomic Model of Oxygen Vacancies. J. Am. Ceramic Soc. 2002, 85, 213-
(15) Rodriguez, J. A.; Irsak, T.; Liu, G.; Hrbek, J.; Dvorak, J.; Maiti, A. Chemistry of NO$_3$ on Oxide Surfaces:
Formation of NO$_3$ on TiO$_2$(110) and NO$_2$$^+$O Vacancy Interactions. J. Am. Chem. Soc. 2001, 123, 9597-9605.
(16) Baltrusaitis, J.; Cwiertny, D. M.; Grassian, V. H. Adsorption of Sulfur Dioxide on Hematite and Goethite
(17) Baltrusaitis, J.; Cwiertny, D. M.; Grassian, V. H. Adsorption of Sulfur Dioxide on Hematite and Goethite
Conversion of NO$_3$ into HONO and N$_2$O on Acid Surfaces. Faraday Discussions 1995, 100, 121-127.
(19) Malecki, A.; Maleka, B. Formation of N$_2$O During Thermal Decomposition of d-metal Hydrates Nitrate.