

Photocatalytic Conversion of Nitric Oxide on Titanium Dioxide: Cryotrapping of Reaction Products for Online Monitoring by Mass Spectrometry

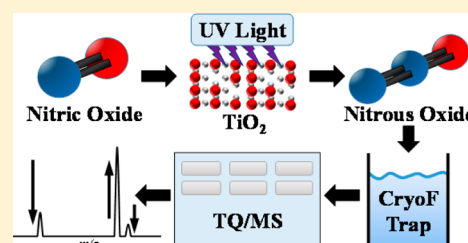
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S Supporting Information

ABSTRACT: Details of coupling a catalytic reaction chamber to a liquid nitrogen-cooled cryofocuser/triple quadrupole mass spectrometer for online monitoring of nitric oxide (NO) photocatalytic reaction products are presented. Cryogenic trapping of catalytic reaction products, via cryofocusing prior to mass spectrometry analysis, allows unambiguous characterization of nitrous oxide (N₂O) and nitrogen oxide species (i.e., NO and nitrogen dioxide (NO₂)) at low concentrations. Results are presented, indicating that the major photocatalytic reaction product of NO in the presence of titanium dioxide (TiO₂) P25 and pure anatase catalysts when exposed to ultraviolet (UV) light (at a wavelength of 365 nm) is N₂O. However, in the presence of rutile-rich TiO₂ catalyst and UV light, the conversion of NO to N₂O was less than 5% of that observed with the P25 or pure anatase TiO₂ catalysts.



1. INTRODUCTION

Photocatalytic processes utilized in the decomposition of organic and inorganic compounds as well as the removal of harmful gases are of great interest in addressing environmental issues associated with air and water pollutants.^{1,2} Nitric oxide (NO) and nitrogen dioxide (NO₂) are among the major air pollutants originating from fossil fuel combustion in automobile engines and industrial burners.³ Various catalytic processes have been developed to convert NO_x gases (i.e., NO and NO₂) into nitrogen (N₂) and oxygen (O₂) or into nitrates (NO₃⁻) for NO_x abatement.^{4–7} However, a majority of the catalysts used in converting NO_x gases into harmless gaseous species (i.e., N₂ and O₂) contain expensive precious metals (e.g., Rh, Pt, or Pd) and perform most efficiently at high temperatures (>200 °C).^{4,8} An ideal catalyst for NO_x conversion is expected to convert or store NO_x gases at lower temperatures (e.g., ambient conditions during the cold start of automobile engines).⁹ Titanium dioxide (TiO₂) is among the major photocatalysts used for catalytic conversion of NO_x gases into nitrous oxide (N₂O) and N₂.^{10,11} Previous studies have shown promising results where TiO₂ catalysts were utilized for NO_x conversion in the presence of solar light.^{12–17}

Photocatalytic efficiencies of TiO₂ catalysts depend on their crystalline phases, surface morphologies, specific surface areas, electronic structures, and thermal treatments.^{18,19} To achieve peak catalytic performance, optimizations of these parameters are necessary.^{18,19} Most of the previously reported studies on conversion of NO_x gases have employed various spectroscopic (e.g., infrared (IR),²⁰ laser absorption,²¹ and chemiluminescence (CL)²²) or electrochemical techniques²³ for detection of

NO_x reaction products. The use of gas chromatography (GC) systems equipped with electron capture detectors (ECDs)²⁴ or mass spectrometers (MS)^{25,26} for identification of NO_x reaction products have been previously reported. In addition, biomedical applications of NO detection, by using high resolution MS²⁷ and, indirectly, semiconducting metal oxides,²⁸ have been reported.

Commercially available NO_x analyzers primarily use either IR or CL for the detection of NO_x species.²² NO_x analyzers based on CL measurement systems often incorporate a heated molybdenum converter for conversion of NO₂ to NO for subsequent CL analysis²⁹ and are limited to the indirect detection of NO₂.²² Therefore, conventional CL NO_x analyzers can only be used for online monitoring of NO and NO₂ during the photocatalytic conversion of NO_x^{30,31} and are not suitable for detection of other potential photocatalytic products such as N₂ or N₂O.^{10–13,32–35} Recently, Bahnemann et al. reported that there may be significant uncertainty in the identity of the detected NO_x species as there could be other nitrogen-containing compounds such as N₂O which are not detected by CL analyzers.^{36,37} N₂O has previously been reported as a primary photocatalytic decomposition product of NO using temperature-programmed desorption measurements.^{13,32,34} Also, N₂O has been shown as a byproduct of NO_x reduction on metal oxides in thermal DeNO_x catalysis.^{38–41}

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MS allows for direct mass-to-charge ratio (m/z) analysis and hence, it can be used for molecular weight determination of NO_x species and other potential NO photocatalytic products.^{10–12,14,35,42,43} In addition, GC/MS systems provide a higher degree of specificity and selectivity for NO_x separation prior to final analysis. The use of conventional open tubular GC columns for analysis of NO_x gas mixtures is challenging due to poor separation of NO from N_2 and O_2 .⁴⁴ To separate NO from N_2 and O_2 , packed GC columns made of molecular sieve polymers, such as poly(vinylbenzene), are more suitable.²⁴ However, due to the reaction of NO_2 with the vinylbenzene molecular sieves, the use of molecular sieve polymers as GC stationary phases hinders the utility of GC for separation and detection of NO_2 .⁷ Moreover, NO_x and N_2O species are often present in the atmosphere at low concentrations (NO : <1 ppb(v) and N_2O : ~0.32 ppm(v))⁴⁵ which limit the use of conventional GC/MS systems for comprehensive detection of NO photocatalysis products. Because of the low NO_x and N_2O concentrations in air, enrichment of pollutants by cryotrapping (cooling with liquid nitrogen) is a useful method for highly sensitive detection of NO_x and N_2O species. Determination of NO_x and N_2O concentrations in air has been previously reported using a “cryotrap enrichment” setup coupled to a GC/MS system.⁴⁵

In this report, we discuss the experimental details of detecting NO and potential NO photocatalytic reaction products using a catalysis unit equipped with mass flow controllers coupled to a liquid nitrogen (LN_2)-cooled cryofocuser/triple quadrupole mass spectrometry (CryoF/TQMS) system. We utilized the CryoF/TQMS system for direct monitoring of catalytic reaction products from a gas stream sample containing 80 ppm of NO in simulated air (i.e., diluted in 80% N_2 and 20% O_2) in the presence of TiO_2 catalysts and ultraviolet (UV) radiation (wavelength maximum, $\lambda_{\text{max}} = 365 \text{ nm}$). We show that the CryoF/TQMS approach allows for detection of the photocatalytic reaction products of NO (e.g., N_2O as the major product) in the presence of high concentrations of O_2 and N_2 . NO concentrations in the range of 10 and 200 ppm have been previously employed to monitor the photocatalytic conversion of NO_x gases using TiO_2 catalysts;^{1,46,47} hence, 80 ppm of NO concentration (i.e., midrange of previous studies) was utilized to demonstrate the catalytic conversion of NO using a unique CryoF/TQMS system. Future studies will employ lower NO concentrations (e.g., <1 ppm) for targeting specific applications such as studying the air purification performance of TiO_2 -based photocatalysts as filters to clean indoor NO_x contaminants. P25 TiO_2 catalyst has been shown to have very high photocatalytic activity for the removal of NO_x gases^{16,48,49} and is a benchmark catalyst for studying the photocatalytic decomposition of NO; hence, we also included P25 TiO_2 in our studies.

2. EXPERIMENTAL METHODS

2.1. Sample Preparation. Nitric oxide (NO) (100 ppm balanced with nitrogen (N_2)), ultrahigh purity (UHP) oxygen (O_2) (purity: 99.993%), UHP N_2 (purity: 99.999%), and UHP helium (He) (purity: 99.999%) gases were purchased from a commercial source (Praxair, Danbury, CT). Aeroxide P25 titanium dioxide (TiO_2) (average particle size: 21 nm, purity: >99.5%) was purchased from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO). Pure anatase TiO_2 (Nanostructured and Amorphous Materials Inc., Houston, TX) and rutile-rich

TiO_2 (Skyspring Nanomaterials, Inc., Houston, TX) were provided by Dr. Boris Lau (Baylor University, Waco, TX) and were characterized by X-ray diffraction to confirm anatase/rutile ratios. Standard nitrous oxide (N_2O) (purity: 99.99%) gas sample was purchased from Matheson (Basking Ridge, NJ). The nitrogen dioxide (NO_2) standard sample was prepared by reacting copper metal with nitric acid.⁵⁰ 80 ppm of NO in simulated air (80% N_2 and 20% O_2) was prepared online by the controlled mixing of 20 sccm (standard cubic centimeter per minute) of 100 ppm of NO (balanced in N_2) with 5 sccm of UHP O_2 . All other gases (i.e., N_2 , O_2 , and He) discussed in this report were used “as-is” and without further refinement. Unless explicitly stated otherwise, the temperature and relative humidity of the catalytic reaction chamber (measured using a humidity sensor (model HTU21D(F), Measurement Specialties, Hampton, VA) placed inside of the catalytic bed) were $23 \pm 2^\circ\text{C}$ and $24 \pm 2\%$, respectively. During the exposure of the TiO_2 catalysts to UV radiation, the temperature of the catalytic reaction chamber increased by $\sim 2^\circ\text{C}$.

TiO_2 catalysts used in all NO photocatalytic reactions presented in this article were used as provided (i.e., without initial UV preactivation). However, additional experiments were conducted on the photocatalytic conversion of NO in the presence of preactivated (i.e., with 15 h of UV light exposure, $\lambda_{\text{max}} = 365 \text{ nm}$) P25 and pure anatase TiO_2 catalysts (nine experimental trials were performed for each catalyst over a three-day period), but no significant changes to the NO, N_2O , and NO_2 trends (as compared to experiments with the nonactivated P25 and pure anatase TiO_2 catalysts) were observed. The cryofocuser and mass spectrometer were used to continuously monitor gases released before, during, and after the exposure of the TiO_2 catalyst to UV radiation (i.e., UV pretreatment) and no released contaminants from the catalyst were detected. Hence, the TiO_2 catalysts utilized in this report were utilized without any degreening/pretreatment.

2.2. Powder X-ray Diffraction (XRD). Powder X-ray diffraction (XRD) spectra of TiO_2 samples were obtained using a Siemens D5000 diffractometer (formerly Siemens—now a division of Bruker Corporation, Billerica, MA) equipped with a $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$, generated at 40 kV and 30 mA) source and operated in θ – 2θ mode. Verification of anatase/rutile ratios for each TiO_2 catalyst was calculated using the equation:⁵¹

$$x = \left(1 + 0.8 \frac{I_A}{I_R} \right)^{-1} \quad (1)$$

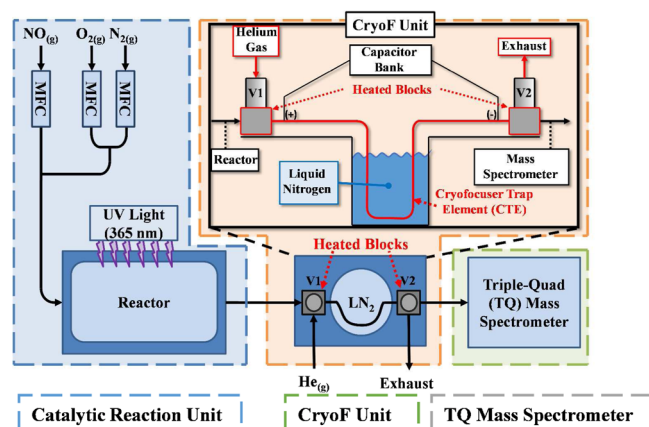
where x is the fraction (by weight) of rutile, I_A is the peak intensity for the anatase (101) peak (labeled “A” in Figure 3), and I_R is the peak intensity for the rutile (110) peak (labeled “R” in Figure 3).

2.3. Transmission Electron Microscopy (TEM). Analysis of average particle diameters was performed using transmission electron microscopy (TEM). Briefly, the pure anatase, rutile-rich, and P25 TiO_2 catalysts were suspended in pure ethanol and sonicated for approximately 30 min. Concurrently, FORMVAR 15/95 (Electron Microscopy Sciences, Hatfield, PA) coated copper grids were glow discharged using an EM ACE600 (Leica Microsystems, Wetzlar, Germany) operating at 10 mA for 10 s at a working distance of 50 mm. Grids were placed for 5 min on drops of suspended titania species and air-dried.

TEM analysis was performed using a JEM-1010 (JEOL, Ltd., Tokyo, Japan) operating at 100 kV equipped with an XR16-ActiveVu camera (AMT, MA, USA) at 50000 $\times$ magnification. Data processing and particle size measurements were performed using the Cell F software package equipped with the particle analysis toolkit (Olympus, Life and Material Science Europa GmbH, Hamburg, Germany).

2.4. Photocatalysis Unit. The design of the catalysis unit was similar to a previously reported photocatalytic flow reactor system equipped with a chemiluminescence NO_x analyzer.³¹ Briefly, the catalysis unit consisted of a reaction chamber made of poly(methyl methacrylate) (length: 7.0 cm; width: 8.0 cm; height: 5.0 cm) transparent thermoplastic material (refer to [Scheme 1](#) for a simplified schematic representation of this unit).

Scheme 1. Simplified Schematic Representation of the Catalysis Unit Coupled to the Cryofocuser/Triple Quadrupole MS System^a



^aNote: GC is not shown in this scheme, as it was only used for experiments confirming the identity of N₂O.

The reaction chamber was equipped with (i) a catalyst bed (length: 4.0 cm; width: 4.0 cm; height: 0.2 cm) and (ii) a quartz window (length: 4.0 cm; width: 4.0 cm; height: 0.2 cm). The quartz window was placed on top of the catalyst bed to allow UV radiation from a UV lamp (model UVGL-2S, UVP, Upland, CA) into the catalyst bed. For the experiments reported herein, the photon power density of the UV lamp positioned over the catalytic bed was 7.2 W/m² (peak λ at 365 nm) per manufacturer's specifications. The reaction chamber was connected to three separate gas inlets via a gas manifold. Each gas inlet was in turn connected to a dedicated gas mass flow controller (MFC) (model GM50A, MKS Instruments Inc., San Jose, CA) for controlled introduction of N₂, O₂, and NO gases into the reaction chamber.

2.5. Cryofocuser (CryoF) Unit. The basic design of the CryoF assembly was similar to the original design of Jacoby et al.⁵³ and our previously reported interface for GC/MS.⁵⁴ The CryoF assembly consisted of a capacitive discharge unit for resistive heating of the CryoF trap element (CTE). The CTE was a 10.16 cm Sulfinert stainless steel tube (inner diameter (i.d.): 0.053 cm; outer diameter (o.d.): 0.074 cm, Restek Corp., Bellefonte, PA) immersed in a Teflon (DuPont, Wilmington, DE) cup capable of holding 100 mL of liquid nitrogen (LN₂). The total resistance of the CTE was 1.2 Ω . Two parallel pairs of 0.1 F capacitors (i.e., a total of four capacitors) were connected in series to produce a total capacitance of 0.1 F in the discharge

unit. The capacitors within the discharge unit were electrically charged using an Agilent 500 W direct current (dc) power supply (model 6554A, Agilent Technologies, Inc., Santa Clara, CA). A dc voltage of 40 V (maximum output current of 4.0 A) was used for flash heating of the trap element. Desorption temperatures in excess of 200 $^{\circ}$ C (measured with careful calibration of the resistance change of the CTE within the LN₂ bath as a function of temperature) could be achieved in the trap element during the flash heating cycle. Two brass heating blocks (length: 2.5 cm; width: 1.8 cm; height: 1.3 cm) were used on both ends of the CTE to avoid "cold spots". The entire length of the transfer lines on both sides of the CTE was continuously heated and kept at 150 $^{\circ}$ C throughout the experiments.

During the flash heating cycle, the CTE was resistively heated by discharging the capacitors in the discharge unit onto the trap element. The capacitive discharge event was initiated upon receiving a 5 V logic level signal from the CryoF Unit microcontroller. The CryoF Unit and its associated pulse valves, flash heating cycle, and cryofocusing time were controlled using an in-house developed computer program (written in C/C++, compiled using avr-g++).⁵⁵ The computer program was loaded onto an Arduino Uno R3 microcontroller (Arduino, Torino, Italy) which subsequently controlled pulse valve actuations and flash heating via digitally controlled relay switches on a Relay4 Board (Microelektronika, Belgrade, Serbia).

For the experiments reported herein, various cooling periods (i.e., cryofocusing times) were utilized and the heating cycle time was held constant at 100 ms. It should be noted that heating time was governed by the time constant (τ) of the RC circuit used in the discharge unit of the CryoF, which was $\sim$ 72.8 ms (hence, a 100 ms heating cycle time was sufficient to encompass the full discharge period).

2.6. Gas Chromatography (GC). The heated transfer line from pulse valve #2 (labeled "V2" in [Scheme 1](#)) was directly connected to the injection port (kept at 100 $^{\circ}$ C) of a GC system. The GC column was a Porapak Q (length: 183 cm; i.d.: 0.21 cm; particle size: 80/100 mesh) stainless steel packed column (Restek Corp., Bellefonte, PA) housed in an SRI GC instrument (model 8610C, SRI Instruments, Las Vegas, NV). Helium (He) gas was used as the GC carrier gas with the He head pressure set to 10 psi; the GC oven temperature was isothermal at 60 $^{\circ}$ C. GC effluent was directly sent into the mass spectrometer through a heated transfer line (kept at 150 $^{\circ}$ C). GC was utilized only in experiments aimed at confirming the identity of N₂O and thus was not included in [Scheme 1](#).

2.7. Mass Spectrometry (MS). Mass spectra were collected using a triple quadrupole (TQ) mass spectrometer (Model 1200L, formerly Varian Corp.—now a division of Agilent Technologies, Inc., Santa Clara, CA) equipped with an electron ionization (EI) source operated in positive-ion mode. Electron energy was set to 70 eV. The TQMS system was operated in scan mode (i.e., Q1 $\rightarrow$ scan, Q2 and Q3 $\rightarrow$ no scan) with m/z scan range set between 14 and 100 Th (at a rate of 16 scans/s). MS instrument control and data analyses were performed using the Varian Mass Workstation software (version 6.9.1, formerly Varian Corp.—now a division of Agilent Technologies, Inc., Santa Clara, CA). To ensure optimum instrument performance, standard "autotune" and instrument calibrations were performed on a daily basis prior to all MS measurements. Optimized electron multiplier voltages and standard calibration parameters (from the autotune files)

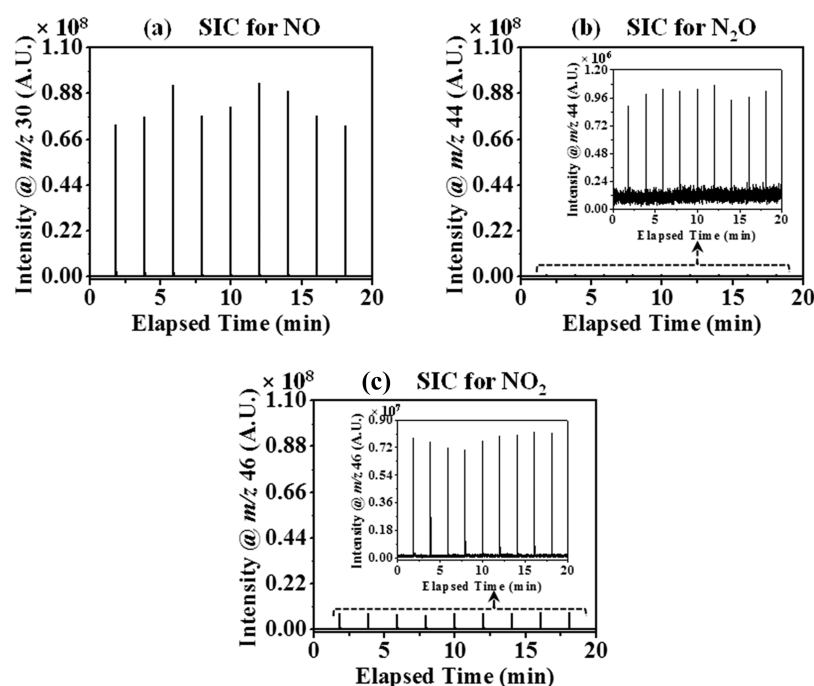


Figure 1. Representative selected ion chromatograms (SICs) for (a) $\text{NO}^{+\bullet}$ (m/z 30), (b) $\text{N}_2\text{O}^{+\bullet}$ (m/z 44), and (c) $\text{NO}_2^{+\bullet}$ (m/z 46) in the absence of TiO_2 catalyst and UV light. NO concentration was 80 ppm in simulated air. Insets in (b) and (c) show the expanded regions of the SIC for $\text{N}_2\text{O}^{+\bullet}$ (m/z 44) and $\text{NO}_2^{+\bullet}$ (m/z 46), respectively.

were used for all subsequent data acquisitions. TQ mass spectrometer ion source and transfer line temperatures were set to 150 °C. For experiments performed without the SRI GC connected, TQ mass spectrometer ion source and main vacuum chamber pressures were generally $<2.5 \times 10^{-3}$ and $<6.0 \times 10^{-7}$ Torr, respectively. Instrument, method, and sample blanks were used to identify potential chemical contaminants for background correction. The ion intensities (i.e., peak areas) for the NO, N_2O , and NO_2 species represented in Figures 1, 2, and 4 were corrected for ionization sensitivity (IS). Previously reported literature values of NO (i.e., 1.17) and N_2O (i.e., 1.66) were utilized for IS correction.⁵⁶ The IS value of 1.39 for NO_2 was calculated based on the relationship between molecular polarizability (α) and IS (i.e., $\text{IS} = 0.36\alpha + 0.30$),⁵⁷ using $\alpha = 3.02 \text{ \AA}^3$ for NO_2 .⁵⁸ Hence, we divided the peak areas of NO, N_2O , and NO_2 by 1.17, 1.66, and 1.39, respectively, to obtain their corrected peak areas.

3. RESULTS AND DISCUSSION

In the following sections, we present results from the use of a cryofocuser (CryoF)/TQ mass spectrometer coupled to a catalytic reaction unit to study nitric oxide (NO) decomposition products in either the absence or presence of TiO_2 catalysts with and without UV radiation.

3.1. Catalysis Reaction Unit Coupled to a Cryofocuser/Triple Quadrupole Mass Spectrometry System. A modular block diagram of the instrumental setup used in this study (for continuous monitoring of the products formed during the photocatalytic conversion of NO) is displayed in Scheme 1. The instrumental setup consists of three modules: (i) the catalytic reaction unit, (ii) the CryoF unit, and (iii) a triple quadrupole (TQ) mass spectrometer. The catalytic reaction unit (labeled as “Reactor” in Scheme 1) operated under continuous flow, enabling photocatalytic reactions to be performed in the presence of a preselected gas composition (via

three independent gas inlets for introduction of NO, O_2 , and N_2). Prior to mixing NO with N_2 and O_2 , the N_2 and O_2 flows could be directed to bubble through or bypass a water bubbler, thus allowing control of humidity in the catalytic reaction chamber. Please note that the data presented in Figures 1, 2, and 4 were obtained using the experimental setup as shown in Scheme 1 and did not utilize GC which will be discussed further in subsequent sections.

In the CryoF unit, reaction products from the photoreactor were preconcentrated in the trap element. After removing most of the residual N_2 and O_2 with a He gas purge, cryofocused reaction products were flash-heated and introduced into the TQ mass spectrometer. Two miniature three-way pulse valves (labeled as “V1” and “V2” in Scheme 1) (Model VAC-250, Parker Hannifin Corp., Cleveland, OH) were used to control gas flow pathways during the cryofocusing and He gas purge periods. The valve “V1” operating in “normally open” mode (i.e., not actuated) allowed gas to flow from the reaction unit into the CryoF trap element (CTE) for preconcentrating reaction products; when valve “V1” was “closed” (i.e., actuated), He purge gas flowed into the CTE. The valve “V2” operating in “normally open” mode directed CTE gas flow into an exhaust vacuum pump; once valve “V2” was “closed”, the gas flow containing the desorbed preconcentrated analytes (after resistive heating of the CTE) was directed into the TQ mass spectrometer.

In the TQ mass spectrometer, the photocatalytic reaction products were detected in real time following the CryoF and subsequent He purge times. A typical sequence of events used in this study was as follows: (1) photocatalytic reaction products were transferred into the trap element for a predefined period of time (e.g., typically 60 s cryofocusing time to preconcentrate analytes), (2) “V1” was energized and He (back-pressure of 5 psi) was introduced to purge the trap element for 60 s, (3) the CTE was flash-heated for 100 ms and

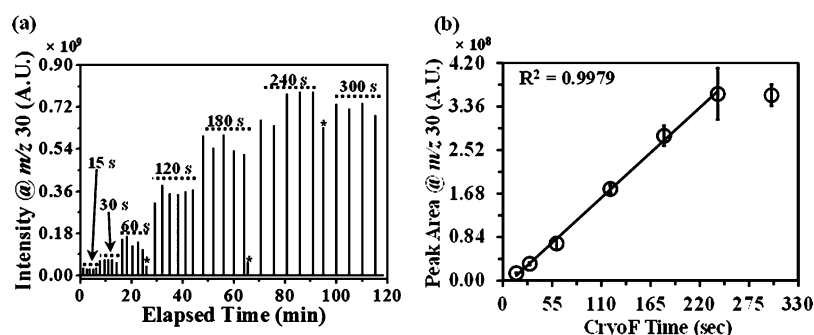


Figure 2. (a) Selected ion chromatogram (SIC) for $\text{NO}^{+\bullet}$ (m/z 30) at varied cryofocusing times (15–300 s). (b) Plot of average peak area as a function of cryofocusing time at 80 ppm of NO concentration. Error bars are reported at the 95% confidence level for $n = 5$ experimental trials.

“V2” was immediately energized to transfer the trapped compounds into TQ mass spectrometer for 100 ms, (4) TQMS data (continuous acquisition) were acquired, and (5) “V1” and “V2” were de-energized to return to step 1. These steps were repeated continuously for the entirety of each experimental run.

3.2. Detection of NO, N_2O , and NO_2 in the Absence of TiO_2 Catalyst and UV Light. Figure 1 shows the representative selected ion chromatograms (SICs) for (a) $\text{NO}^{+\bullet}$ (m/z 30), (b) $\text{N}_2\text{O}^{+\bullet}$ (m/z 44), and (c) $\text{NO}_2^{+\bullet}$ (m/z 46), in the absence of TiO_2 catalyst and UV light, collected after a cryofocusing time of 60 s and inlet NO concentration of 80 ppm. Results from the CryoF/TQMS showed sharp, symmetric, and reproducible MS peaks that yielded SIC peak widths of ~ 2 s (measured at peak base). In Figure 1a, the MS signal intensity for $\text{NO}^{+\bullet}$ (m/z 30) is ~ 90 - and ~ 16 -fold higher than the MS signal intensities for $\text{N}_2\text{O}^{+\bullet}$ (m/z 44) (Figure 1b, inset) and $\text{NO}_2^{+\bullet}$ (m/z 46), respectively (Figure 1c, inset). The larger MS signal intensity for $\text{NO}^{+\bullet}$ was expected, as the final gas composition was primarily NO in simulated air. Although N_2 and O_2 were still detectable by the mass spectrometer, N_2 and O_2 signals were low compared with that of NO due to the He purge segment of the experiment (which allowed for N_2 and O_2 gases to escape to the exhaust system through “V2”, as shown in Scheme 1). The presence of N_2O was a result of trace N_2O impurity in the NO gas composition (confirmed using GC-MS), potentially generated in the copper^{59,60} transfer line between the gas tank and MFC. The presence of NO_2 likely results from minor noncatalytic oxidation reaction of NO in the presence of oxygen.⁶¹ In order to examine the effects of cryofocusing time on the signal response of NO, we performed MS experiments measuring NO signal intensity as a function of cryofocusing time.

Figure 2a shows the SIC for $\text{NO}^{+\bullet}$ (at m/z 30) at increasing cryofocusing times (from 15 to 300 s). The NO gas composition for the data shown in Figure 2 was the same as that used in Figure 1. A linear increase in signal intensity for $\text{NO}^{+\bullet}$ was observed as the cryofocusing time was increased (e.g., an ~ 4 -fold increase in $\text{NO}^{+\bullet}$ signal intensity was observed when the cryofocusing time was increased from 30 to 120 s). It is important to note that the flash heating temperature must be sufficient to desorb all trapped analytes at each cryofocusing cycle. For the experiments reported here, we utilized an optimized flash heating time of 100 ms to ensure complete desorption of all NO_x and N_2O species. No significant changes in $\text{NO}^{+\bullet}$ signal intensity was observed after 240 s cryofocusing time (i.e., the $\text{NO}^{+\bullet}$ signal intensities at 240 and 300 s cryofocusing time are similar) due to the saturation of the EM

detector. The peaks denoted with asterisks in Figure 2a were of lower intensity (due to a system reset upon changing cryofocusing time that resulted in premature analyte release from the CTE) and were not used for the calculations in Figure 2b.

Figure 2b shows the calibration line for $\text{NO}^{+\bullet}$ signal intensity (measured as the chromatographic peak area for m/z 30) detected as a function of cryofocusing time using data from Figure 2a. Each data point (denoted with empty circles) in Figure 2b corresponds to an average of five experimental trials with error bars reported at the 95% confidence level. The R -squared (R^2) value (0.9979) was obtained using the linear regression function in Microsoft Excel (Microsoft Office 7, Microsoft Corporation, Redmond, WA) for data acquired over a cryofocusing time range of 15–240 s (deemed to be the “linear range”⁶² for this setup). MS Data at 300 s cryofocusing time was not utilized for determining the R^2 value because the $\text{NO}^{+\bullet}$ signal intensity was outside the linear range of the MS detection system. In the absence of analyte standards, internal calibrants can be used to calculate unknown concentrations. To estimate the concentrations of N_2O and NO_2 , we used NO as the internal calibrant and corrected for detector response factor (i.e., IS differences between NO, N_2O (1.66), and NO_2 (1.39)).^{56,57} Because the freezing points for NO, N_2O , and NO_2 are all above liquid nitrogen temperature (i.e., >77 K), cryofocusing efficiencies for these analytes were assumed to be similar.

3.3. Compositional and Structural Analysis of TiO_2 Catalysts. TiO_2 crystals have three naturally occurring polymorphisms including anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic).⁶³ Anatase and rutile structured TiO_2 are the primary constituents of the P25 catalyst.⁶⁴ To verify the purity and characterize the TiO_2 catalysts (i.e., P25, “pure anatase”, and “rutile-rich”) utilized in this work, we analyzed each catalyst using powder XRD. In Figure 3, normalized intensities from the P25, pure anatase, and rutile-rich TiO_2 catalysts are plotted against scattering angle. Based on the XRD data (calculations using eq 1),⁵¹ anatase and rutile compositions (by mass) were obtained for P25 (Figure 3a) as 85.9% anatase/14.1% rutile, for pure anatase (Figure 3b) as 96.9% anatase/3.1% rutile, and for rutile-rich (Figure 3c) as 25.2% anatase/74.8% rutile. The XRD data were insufficient to determine 100% compositional purity for the pure anatase catalyst sample due to signal-to-noise limitations. No rutile peaks were observed in the XRD spectra; hence, we presumed the sample to be “pure” anatase. Additionally, calcination of the pure anatase TiO_2 , using the procedure outlined by Li et al.,⁶⁵ did not result in any significant change in the appearance of

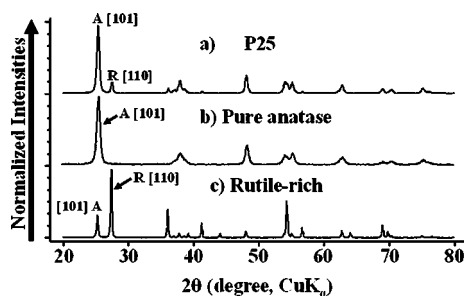


Figure 3. XRD spectra of (a) P25, (b) pure anatase, and (c) rutile-rich TiO_2 catalysts. Letters “A” and “R” represent the anatase and rutile peaks utilized in the catalyst composition calculations, respectively.

XRD spectra or photocatalytic reactivity, supporting the assumption that any rutile fraction was minimal. Commercially available P25 titania photocatalyst composition has been previously reported as 78 wt % anatase, 14 wt % rutile, and 8 wt % amorphous phases.⁴⁹ Amorphicity of the pure anatase and rutile-rich catalysts is unknown at this time.

TEM images of pure anatase particles (Figure S1a) showed homogeneous short rod-shaped nanoparticles (average diameter: 28.14 ± 13.16 nm, $n = 400$). Rutile-rich nanoparticles (Figure S1b), however, showed three distinct particle size distributions (average diameter: 81.09 ± 51.53 nm, $n = 400$) possibly representing the separate anatase, rutile, and amorphous components. P25 nanoparticles (Figure S1c), despite also being a biphasic mixture like the rutile-rich nanoparticles, were observed to be mostly spherical and of uniform size (average diameter: 26.04 ± 8.68 nm, $n = 400$).

3.4. Photocatalytic Reaction of NO in the Presence of TiO_2 . We used the instrumental setup depicted in Scheme 1 to analyze the products of the previously reported photocatalytic reaction of NO in the presence of P25, pure anatase, and rutile-rich TiO_2 photocatalysts when exposed to UV radiation.³¹ When TiO_2 is exposed to incident UV radiation at 365 nm, an electron is excited to yield an electron–hole (e^- – h^+) pair. This excited electron can relax back (i.e., recombination) into the unoccupied molecular orbitals of the adsorbed species on the TiO_2 ’s surface.⁶⁶ However, if this electron–hole pair is localized at the surface, it can also act as an individual electron donor and electron acceptor and impact NO decomposition.³¹ In this study, the conventionally used standard photocatalyst, P25 TiO_2 , was investigated for its ability to catalyze the reduction of NO into N_2O . P25 TiO_2 used in this experiment was a biphasic mixture of anatase and rutile nanoparticles (Figure 3a) with an average diameter of 21 nm.⁶⁴ Furthermore, the photocatalytic efficiency of pure anatase TiO_2 and rutile-rich TiO_2 were compared with that of the P25 TiO_2 catalyst. It is believed that the electron–hole pairs from the excited TiO_2 form primarily on the anatase nanoparticles and the smaller rutile nanoparticles function to facilitate charge transfer to the anatase nanoparticles and slow down the electron–hole recombination.⁶⁷ The efficient electron–hole separation with lower recombination rates observed in P25 TiO_2 (possessing mixed anatase–rutile phase ratios) has made P25 TiO_2 a benchmark for photocatalytic reaction studies.⁶⁷ However, the increased photoactivity of P25, due to proximal rutile and anatase particles, has been argued against.⁴⁹

Figure 4 shows the temporal plots of normalized ion intensities for the NO, N_2O , and NO_2 species at 80 ppm of NO (in simulated air) and a cryofocusing time of 60 s in the

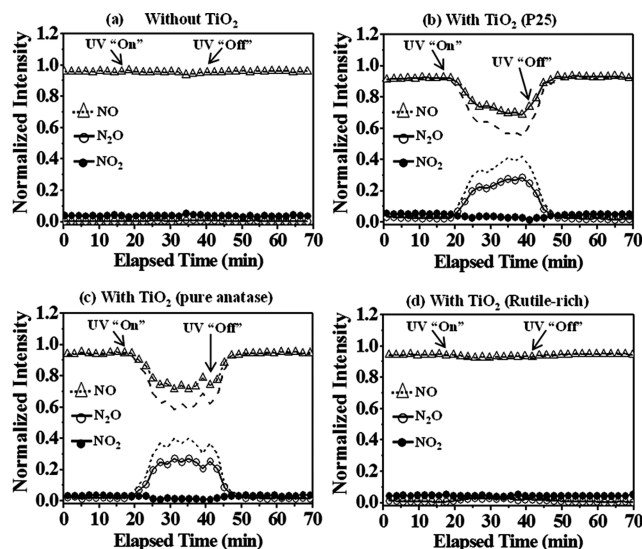


Figure 4. Temporal plots of normalized ion intensities (i.e., peak areas) for NO, N_2O , and NO_2 (a) without TiO_2 catalyst, (b) with TiO_2 (P25), (c) with TiO_2 (pure anatase), and (d) with TiO_2 (rutile-rich) catalysts. NO concentration was 80 ppm in simulated air. Dashed and short dashed lines represent NO and N_2O normalized ion intensities, respectively, corrected for the NO^{*+} fragment ion contribution from the parent N_2O^{*+} ion as a result of EI fragmentation.

presence/absence of UV light and TiO_2 catalysts. In Figure 4, symbols denoted by empty triangles, empty circles, and solid circles represent NO, N_2O , and NO_2 ion intensities, respectively. The plots shown in dashed and short dashed lines in Figures 4b and 4c correspond to the normalized ion intensities of NO and N_2O corrected for NO^{*+} fragment ion contribution from EI fragmentation of N_2O^{*+} , respectively. Normalized ion intensities for the NO, N_2O , and NO_2 species were obtained by dividing the total ion intensity of each NO, N_2O , and NO_2 species by the sum of the total ion intensities from NO, N_2O , and NO_2 species at each time (or data) point. UV radiation was applied (indicated by the arrow symbol and UV “On”) at an elapsed time of 17 min and stopped (indicated by the arrow symbol and UV “Off”) at an elapsed time of 42 min. Hence, the catalytic reaction chamber was exposed to UV radiation for 25 min and was manually covered with aluminum foil to keep the chamber dark outside the UV exposure period.

In Figure 4a, the normalized ion intensities for NO, N_2O , and NO_2 were obtained without any TiO_2 catalyst in the reaction chamber to determine the variation of the NO, N_2O , and NO_2 species as a result of UV radiation (control). The temporal plot in Figure 4a shows that ion intensities for the NO, N_2O , and NO_2 species do not change significantly throughout the duration of the experiment and are independent of UV radiation exposure. As expected, NO ion intensities were consistently higher than N_2O and NO_2 ion intensities, and the observed ion intensity trends for the NO, N_2O , and NO_2 species corroborate with the results observed in Figure 1. The lack of any significant change (i.e., >5%) in ion intensities for the NO, N_2O , and NO_2 species suggests that in the absence of the TiO_2 catalyst UV radiation does not play an important role in the conversion of NO.

To examine the effects of the TiO_2 catalyst on the conversion of NO to N_2O and NO_2 , ~0.50 g of P25, pure anatase, or rutile-rich TiO_2 photocatalysts was individually loaded into the

reaction chamber. Figures 4b–d show the normalized ion intensities for the NO, N₂O, and NO₂ species in the presence of the P25, pure anatase, and rutile-rich TiO₂ catalysts during separate experiments. As shown in Figure 4b, the normalized ion intensities of NO, N₂O, and NO₂, prior to the application of UV radiation (from elapsed time of 0 to 17 min), were stable and followed a similar trend to that observed without the catalyst (as in Figure 4a). Upon exposure of the P25 TiO₂ catalyst to UV radiation (starting at an elapsed time of 17 min), a significant (i.e., >5%) decrease in NO ion intensities and an associated increase in N₂O ion intensities were observed. However, when the exposure of P25 TiO₂ photocatalyst to UV radiation was terminated or turned “off” (at 42 min elapsed time), NO and N₂O ion intensities returned to their initial levels after a 5–10 min delay (i.e., comparable to their respective ion intensities prior to exposure to UV radiation).

The notable changes in NO and N₂O ion intensities, in response to the P25 TiO₂ photocatalysts exposure to UV radiation, suggest that N₂O was the major photocatalytic product of NO. No significant (i.e., >5%) changes were observed in NO₂ ion intensity in either the presence or absence of P25 TiO₂ photocatalyst exposed to UV radiation.

The pure anatase TiO₂ photocatalyst showed trends similar to the P25 TiO₂ photocatalyst for variations in NO, N₂O, and NO₂ ion intensities during the UV radiation “on” period. In Figure 4c, ion intensity for NO decreased and ion intensity for N₂O increased when NO was exposed to the pure anatase TiO₂ photocatalyst in the presence of UV radiation, and no significant (i.e., >5%) change in NO₂ ion intensity was observed.

Photocatalytic activity of the rutile-rich TiO₂ catalyst was considered insignificant (~2% decrease in NO ion intensity), in comparison to the P25 (~32% decrease in NO ion intensity) and pure anatase TiO₂ (~31% decrease in NO ion intensity) catalysts, for the conversion of NO to N₂O. For example, in Figure 4d only minor (i.e., <5%) changes were seen for the ion intensities of NO and N₂O during the exposure of NO to UV radiation in the presence of the rutile-rich TiO₂ photocatalyst. Low photocatalytic activity of rutile TiO₂ catalyst for conversion of NO to N₂O in the presence of UV radiation has been previously reported.⁶⁷

It is known that NO₂ dimerizes to dinitrogen tetroxide (N₂O₄) at lower temperatures (i.e., <–10 °C), but at temperatures >140 °C, N₂O₄ converts back to NO₂ gas.^{68,69} To verify if NO₂ is detected intact (i.e., not partially lost due to degradation or dimerization) in the mass spectrometer after trapping (at ~–196 °C, i.e., LN₂ temperature) and desorption (at >150 °C), we performed cryofocusing experiments utilizing pure NO₂ samples to monitor the effects of cryofocusing on NO₂. Under identical experimental conditions (i.e., He purge period, cryofocusing duration, flash heating duration and temperature, and mass spectrometry parameters) to other photocatalytic experiments reported in the article, the standard NO₂ sample was detected in the mass spectrometer with no detectable NO₂ degradation products other than its fragment ions (e.g., ion at *m/z* 30 from fragmentation of NO₂ and potential residual NO (see Figure 5)).

Also, N₂O₄^{•+} (the ionized dimer of NO₂ at *m/z* 92) was not detected (at either 70 or 20 eV electron energies) by the mass spectrometer during any of the experiments involving the photocatalytic reaction of NO.

Summation of NO and N₂O signals was higher during UV radiation exposure in the presence of TiO₂ (Figures 4b and

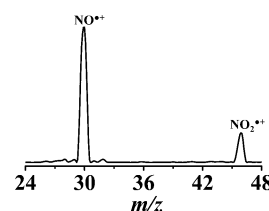


Figure 5. EI (at 70 eV) mass spectrum for standard NO₂ (at *m/z* 46) showing its major fragment ion at *m/z* 30.

Figure 4c) than in the absence of TiO₂ (Figure 4a). It might initially be expected that the summation of NO and N₂O ion intensities should in fact be less during photocatalytic conversion as the stoichiometry of NO → N₂O is 2:1, respectively. However, it should be noted that NO^{•+} is a commonly observed fragment ion of N₂O (in the EI mass spectrum)⁷⁰ and will contribute to the overall NO^{•+} signal intensity. To correct for the contribution of NO^{•+} resulting from the fragmentation of N₂O^{•+} during EI (at 70 eV) to the overall NO^{•+} signal intensity, we performed EI experiments using a standard N₂O sample under similar experimental (i.e., CryoF and MS) conditions as the data presented in Figure 4. The calculated NO^{•+} to N₂O^{•+} ratio (i.e., 0.474) from the standard N₂O was used to obtain the ion intensity contribution of NO^{•+} from N₂O^{•+} fragmentation. The calculated intensity of NO^{•+} from N₂O^{•+} fragmentation was then subtracted from the total NO^{•+} signal intensity (data shown in dashed lines in Figures 4b and 4c) and added to the total ion intensity for N₂O^{•+} (data shown in short dashed lines in Figures 4b and 4c). Another potential method to eliminate the contribution of NO^{•+} from the fragmentation of N₂O^{•+} to the overall ion intensity of NO^{•+} is to perform EI experiments at lower electron energies (e.g., <24 eV) and avoid NO^{•+} fragment ion formation. Conducting EI at lower electron energy minimizes fragmentation but results in an overall reduction in sensitivity.⁷¹ We conducted EI experiments at 20 eV (the lowest electron energy available on our MS system) on the standard N₂O sample and continued to observe NO^{•+} signal from the fragmentation of N₂O^{•+} but with approximately 1 order of magnitude loss in sensitivity. Thus, we utilized the calculated NO^{•+} to N₂O^{•+} ratio (obtained with EI at electron energy of 70 eV) to correct for the contribution of NO^{•+} (resulting from the fragmentation of N₂O^{•+}) to the overall NO^{•+} signal intensity.

In a separate experiment, a GC system was used to confirm the identity of the N₂O produced during the catalytic decomposition of NO. A transfer line was inserted from valve 2 (“V2” in Scheme 1) into a GC injection port to introduce the cryogenically trapped catalysis reaction products into the GC before MS detection. The GC effluent was then introduced into the MS system for *m/z* analysis. Retention time of the N₂O generated during photocatalysis was then compared to the retention time of a standard N₂O gas sample. The standard N₂O gas sample was placed into a sealed 40 mL glass vial and transferred to the CTE element of the CryoF Unit (using a transfer line connected to valve #1 (labeled as “V1” in Scheme 1)) for cryofocusing and subsequent desorption and introduction into the GC injection port. No other experimental parameters for the catalysis unit, CryoF, or mass spectrometer were modified for the aforementioned GC experiments.

The GC retention time of N₂O (from the photocatalysis of NO in the presence of P25 TiO₂ and UV light) was 2.004 ± 0.004 min (at 95% confidence level; *n* = 3) (see Figure 6). The

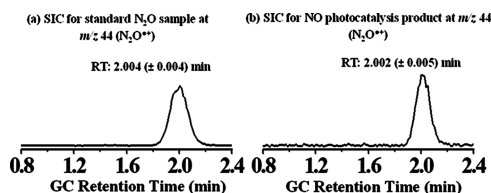


Figure 6. Selected ion chromatograms (SICs) of (a) standard N_2O sample at m/z 44 (N_2O^+) and (b) NO photocatalysis product at m/z 44 (N_2O^+) obtained from GC/MS analyses. The values on top of the peaks are the average retention times (RTs) for the SIC peak maxima at m/z 44 from triplicate experiments (the error at 95% CL is included in parentheses for each value).

GC retention time of the standard N_2O sample was 2.002 ± 0.005 min (at 95% confidence level; $n = 3$) (see Figure 6). Under the same GC/MS conditions, retention time for CO_2 (which also generates an ion at m/z 44) was 1.488 ± 0.035 min (at 95% confidence level; $n = 3$). The retention time for the N_2O product of the photocatalytic reaction of NO statistically matched with the retention time of the standard N_2O (based on student t test at 95% confidence level) and, combined with its mass spectral pattern, allowed us to confirm the identity of the N_2O photocatalytic product.

Additional sets of experiments were performed (to deduce the role of O_2 gas), where only NO and N_2 (i.e., no O_2) were introduced into the photocatalytic reaction chamber; similar trends for NO and NO_2 profiles (i.e., decrease in both NO^+ and NO_2^+ intensities) were observed in the presence and absence of O_2 gas. However, we did not observe any conversion of NO to N_2O in the absence of O_2 .

Figure 7 shows the ion intensities for the NO, N_2O , and NO_2 species in the presence of the P25 TiO_2 catalyst and nitrogen gas (i.e., without any O_2 gas). Upon exposure of the P25 TiO_2 catalyst to UV radiation (indicated by UV “on” and the dashed closed arrow symbol at an elapsed time of 16 to 47 min), a significant (i.e., >5%) decrease in NO and NO_2 ion intensities

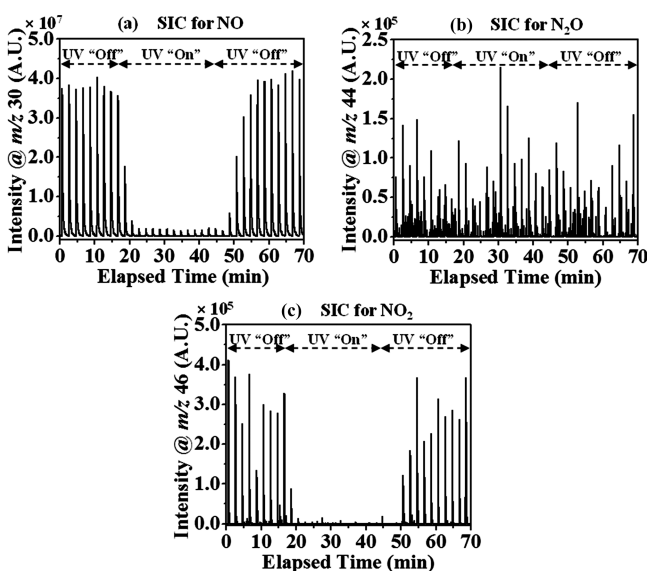
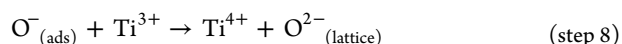
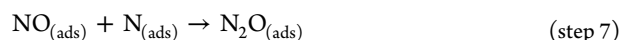
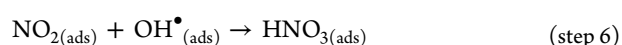
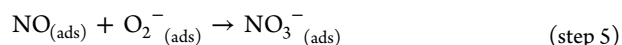
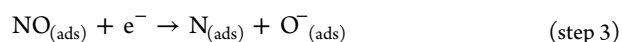
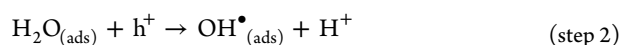


Figure 7. Representative selected ion chromatograms (SICs) for (a) NO^+ (m/z 30), (b) N_2O^+ (m/z 44), and (c) NO_2^+ (m/z 46) in the presence of P25 TiO_2 catalyst and UV light. NO concentration was 80 ppm in nitrogen environment. Arrows indicating UV “off” and “on” durations are placed on top of the SICs.

was observed and no change in N_2O ion intensity was detected. When the exposure of P25 TiO_2 photocatalyst to UV radiation was terminated (indicated by UV “off” and the dashed closed arrow symbol at initial elapsed time of 47 min), NO and NO_2 ion intensities returned to their initial levels and N_2O ion intensity remained unchanged. It is possible that NO is being converted into N_2 species though we did not notice any significant increase in N_2^+ intensity. N_2 is still a potential product from the photocatalytic decomposition of NO in the absence of O_2 , but results remain inconclusive due to the inherent limitations of trapping N_2 gas using a LN_2 cryofocuser. Future experiments with the use of NO gas balanced in helium will be performed to verify this hypothesis.

One of the major features of the TiO_2 photocatalyst is the availability of oxygen vacancies on its surface. Two Ti^{3+} sites are present at each oxygen vacancy, which are the primary locations for NO adsorption. Based on a previously reported mechanism,^{2,12} the photocatalytic conversion of NO to N_2O on Ti^{3+} might potentially involve the following suggested reaction steps:



Briefly, the photocatalytic conversion of NO to N_2O involves the adsorption of gas-phase NO molecules to the oxygen vacancies on the TiO_2 surface to form adsorbed NO molecules (i.e., $\text{NO}_{(\text{ads})}$). Oxygen (O_2) and water (H_2O) molecules also adsorb to the surface of TiO_2 to form $\text{O}_{2(\text{ads})}$ and $\text{H}_2\text{O}_{(\text{ads})}$, respectively. An electron generated from TiO_2 's exposure to incident UV radiation (step 1) cleaves the N–O and O–O bonds in $\text{NO}_{(\text{ads})}$ and $\text{O}_{2(\text{ads})}$ to form an adsorbed nitrogen atom (i.e., $\text{N}_{(\text{ads})}$) and an adsorbed oxygen anion (i.e., $\text{O}^-_{(\text{ads})}$) (step 3) and $\text{O}_2^-_{(\text{ads})}$ (step 4), respectively. The electron hole (i.e., h^+) generated in step 1 reacts with $\text{H}_2\text{O}_{(\text{ads})}$ molecules to form adsorbed hydroxyl radical ($\text{OH}^{\bullet}_{(\text{ads})}$) and hydrogen ion (H^+) (step 2). $\text{OH}^{\bullet}$ can also form when hydroxyl anion (i.e., OH^-) reacts with h^+ (i.e., $\text{OH}^-_{(\text{ads})} + h^+ \rightarrow \text{OH}^{\bullet}_{(\text{ads})}$). The oxygen anion (i.e., $\text{O}_2^-_{(\text{ads})}$) may react with $\text{NO}_{(\text{ads})}$ or $\text{NO}_{2(\text{ads})}$ to form $\text{NO}_3^-_{(\text{ads})}$ which stays bound to the surface of TiO_2 (step 5).² Adsorbed NO_2 (i.e., $\text{NO}_{2(\text{ads})}$) reacts with $\text{OH}^{\bullet}_{(\text{ads})}$ to form $\text{HNO}_3^{\bullet}_{(\text{ads})}$ which remains on the TiO_2 surface (step 6).² An additional $\text{NO}_{(\text{ads})}$ reacts with $\text{N}_{(\text{ads})}$ to form adsorbed N_2O (i.e., $\text{N}_2\text{O}_{(\text{ads})}$) (step 7) which can in turn lose its oxygen atom

and diffuse as N_2 gas (i.e., $\text{N}_2\text{O}_{(\text{g})} + \text{e}^- \rightarrow \text{N}_{2(\text{g})} + \text{O}^-_{(\text{ads})}$). In addition, the oxygen anion (i.e., $\text{O}^-_{(\text{ads})}$) generated from NO dissociation (step 3) remains in the filled oxygen vacancy as $\text{O}^{2-}_{(\text{lattice})}$ (step 8). The adsorbed superoxide, $\text{O}_2^-_{(\text{ads})}$ (formed in step 4), dissociates to form adsorbed peroxide ($\text{O}^-_{(\text{ads})}$) and adsorbed atomic oxygen ($\text{O}_{(\text{ads})}$) (step 9). Adsorbed peroxide ($\text{O}^-_{(\text{ads})}$) loses its electron (e^-) to form adsorbed atomic oxygen ($\text{O}_{(\text{ads})}$) (step 10). Consequently, the adsorbed oxygen atom ($\text{O}_{(\text{ads})}$) reacts with two adsorbed nitrogen atoms ($2\text{N}_{(\text{ads})}$) to form adsorbed $\text{N}_2\text{O}_{(\text{ads})}$ according to the reaction mechanism proposed by Larson et al.⁷² Steps 7–9, while speculative, provide a potential explanation for the notable lack of observable N_2O formation in the absence of O_2 gas. However, the loss of an oxygen atom requires a sufficiently long N_2O residence time at an oxygen vacancy; otherwise, it can desorb as $\text{N}_2\text{O}_{(\text{gas})}$ (step 12). Kim et al.¹⁴ reported that N_2O does not dissociate on TiO_2 surface to form N_2 and O. Moreover, it has been reported that N_2O molecules are only weakly bound to the TiO_2 surface with an adsorption energy of 7.73 kcal/mol;¹³ thus, it is likely that in this photocatalyzed reaction most of the $\text{N}_2\text{O}_{(\text{ads})}$ were desorbed as $\text{N}_2\text{O}_{(\text{gas})}$ to yield the observed MS signal at m/z 44.

The importance of water in the photocatalytic decomposition of NO in the presence of TiO_2 catalysts has previously been demonstrated.^{2,73} To explore the role of H_2O in the NO photocatalysis mechanism, we conducted experiments identical to the aforementioned experiments (i.e., the photocatalytic conversion of NO using P25 TiO_2 catalyst) in the absence of water (i.e., 0% relative humidity) and in the presence of varying concentrations of water (0–23% relative humidity) (Figure 8). Initial experiments (as shown in Figure 8) displayed an increase in signal intensities for $\text{NO}^{+\bullet}$, $\text{NO}_2^{+\bullet}$, and $\text{N}_2\text{O}^{+\bullet}$ as humidity was increased. More notably, the increase in $\text{N}_2\text{O}^{+\bullet}$ (Figure 8b) signal intensity occurred separately (i.e., ~40 min prior) from the increases in signal intensity for $\text{NO}^{+\bullet}$ (Figure 8a) and $\text{NO}_2^{+\bullet}$ (Figure 8c). However, after the exposure of the P25 TiO_2 catalyst to 80 ppm of NO and UV radiation in the absence of humidity (i.e., 0% relative humidity), the subsequent introduction of humidity resulted in similar releases of $\text{NO}^{+\bullet}$, $\text{NO}_2^{+\bullet}$, and $\text{N}_2\text{O}^{+\bullet}$ (even in the absence of UV radiation). Thus, the trends observed in Figure 8 are due to an initial increase in humidity facilitating the release of already formed N_2O (from TiO_2 surface) and followed by further humidity increases releasing bound NO and NO_2 from the TiO_2 surface.

In the presence of high concentrations of H_2O (i.e., at $70 \pm 2\%$ relative humidity), we observed similar trends (i.e., decrease in $\text{NO}^{+\bullet}$ and $\text{NO}_2^{+\bullet}$ and increase in $\text{N}_2\text{O}^{+\bullet}$ intensities) to the results obtained at lower relative humidity (i.e., at $24 \pm 2\%$, data shown in Figure 4b) during the photocatalytic decomposition of NO in the presence of P25 TiO_2 catalyst but with a 15% lower overall NO conversion efficiency (shown in Figure S2). Although it is known that H_2O provides hydroxyl radicals ($\text{HO}^\bullet$) which play a key role in the photocatalytic oxidation of NO (formation of NO_2 and HNO_3), some reports have also stated that increases in humidity levels reduce the catalytic conversion efficiency of NO in the presence of P25 TiO_2 photocatalysts.^{74,75} For example, Ao et al. reported that H_2O vapor competes with NO adsorption sites on the TiO_2 surface; thus, increasing the H_2O vapor pressure reduces the availability of TiO_2 active sites for NO photocatalysis.^{74,75} Hence, we surmise that the reduction in overall NO conversion efficiency observed in our experiments (in the presence of high

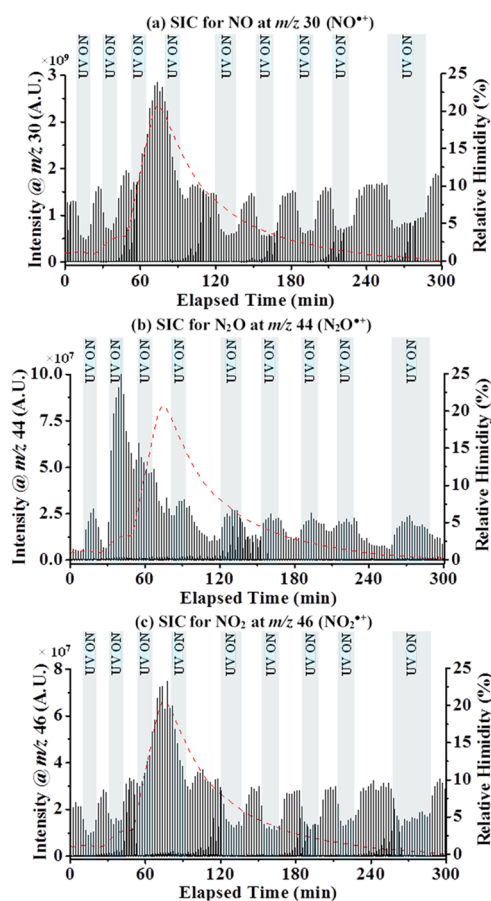


Figure 8. Representative selected ion chromatograms (SICs) for (a) $\text{NO}^{+\bullet}$ (m/z 30), (b) $\text{N}_2\text{O}^{+\bullet}$ (m/z 44), and (c) $\text{NO}_2^{+\bullet}$ (m/z 46) in the presence of P25 TiO_2 catalyst, UV light (shown in blue-colored rectangular boxes and “UV ON”), and increasing relative humidity (0–23%). NO concentration was 80 ppm in simulated air. The red dotted lines overlaid on the SIC represent the relative humidity (%) of the catalytic reaction chamber during the experiment.

H_2O vapor pressure) is because of the competition between H_2O and NO for adsorption sites on the TiO_2 surface.

4. CONCLUSION

We designed and constructed a novel photocatalytic reaction chamber coupled to a custom-built liquid nitrogen cryofocusing unit for mass spectrometry analysis and monitoring of nitrogen oxide species. Results from the detection of NO in the absence of TiO_2 catalyst indicate that NO ion intensity increases linearly with cryofocusing time. We also showed that the major photocatalytic reaction product of the decomposition of NO in the presence of P25 TiO_2 and pure anatase TiO_2 is N_2O . We anticipate the use of the cryofocusing/mass spectrometry unit coupled to the photocatalytic reaction chamber for further examination of the photocatalytic decomposition of NO in the presence of different photocatalysts and with varying experimental conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b10631.

Figure S1: representative TEM images of (a) pure anatase, (b) rutile-rich, and (c) P25 TiO_2 nanoparticles

used in this study; Figure S2: temporal plots of normalized ion intensities for NO, N₂O, and NO₂ with P25 TiO₂ catalyst at 70 ± 2% relative humidity (PDF)

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Notes

The authors declare no competing financial interest.

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