

Interactive comment on “Is the photochemistry activity weak during haze events? – A novel exploration on the photoinduced heterogeneous reaction of NO₂ on mineral dust” by Tao Wang et al.

Anonymous Referee #2

Received and published: 18 June 2019

Overview. The paper by Wang et al. mostly describes laboratory experiments and some field data exploring the role of heterogeneous chemistry involving nitrogen dioxide (NO₂) on surrogate mineral dust and ambient aerosols. The study is comprised of three parts: (1) an FTIR study of NO₂ adsorption to titanium dioxide (TiO₂; industrial-grade photocatalyst) in the dark and when irradiated with UV-visible light; (2) development of a parameterization of the NO₂ uptake coefficients as a function of light intensity as a potential approach for describing NO₂-to-nitrite and nitrate conversion on mineral dust. This work is based on the abovementioned FTIR studies and Monte Carlo simu-

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lations were used to estimate error (details on this part are scarce); and (3), results of a field campaign showing that nitrate and nitrite concentration in aerosols are positively correlated at night, but inversely related when they are collected during the day. The authors conclude that FTIR study shows that the nitrite:nitrate ratios observed in ambient aerosol are due to heterogeneous chemistry involving NO₂ conversion on mineral dust surfaces containing TiO₂. There are several major issues with this manuscript that make it unacceptable for publication. These are outlined below.

General Comments on the Study.

The authors choose as a surrogate for mineral dust Degussa TiO₂ which is mixture of rutile and anatase that is designed to be highly reactive. However, the photoactive mineral anatase is one of the scarcest Ti minerals in Earth's crust. For this reason, I feel that Degussa TiO₂ is not a suitable surrogate for photochemical studies of mineral dust heterogeneous chemistry. That being said, it is probably as good as SiO₂ or alumina for use as a surrogate for non-photochemically active mineral surfaces.

The FTIR product study of NO₂ adsorption and photochemistry on TiO₂ surfaces is parameterized and used to explain the aerosol field results. However, this presumes that the aerosols collected contain mineral dust containing an appreciable amount of anatase surface sites. Unfortunately, the ambient aerosols have not been characterized (e.g., with elemental analysis and crystallographic methods) and therefore, there is nothing supports the validity of using Degussa anatase to represent the aerosol chemistry occurring in the collected ambient aerosol samples. Indeed, the relationships between nitrate and nitrite for these field samples could as easily be explained through, by now, well established non-TiO₂ chemistry. For example, nighttime data can be explained by uptake of NO₂ into aqueous droplets, or onto non-TiO₂ mineral surfaces, while daytime chemistry can be explained by aerosol phase nitrate photolysis. For example, Xianliang Zhou et al. have published results showing that aerosol nitrate is a major source of nitrite and HONO in aerosols and all evidence suggests that TiO₂ is not necessarily needed for this chemistry.

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Concentrations of NO₂ used for the FTIR study are in the range of 9-21 parts-per-million (ppm). These concentrations are unheard of in the natural or even urban environment unless one considers the chemistry occurring within the engine of a car or a power plant stack. Therefore, such data cannot be extrapolated to environmental conditions where ambient NO_x levels are orders of magnitude lower; for this reason, the parameterizations they develop are only applicable to Degussa TiO₂ under the conditions of their study. By now it has been well established that at high concentrations of NO₂, the heterogeneous mechanism involves dimerization of NO₂ followed by autoionization of N₂O₄ and reaction with water (see the review article by Finlayson-Pitts et al, PCCP, 2003, which the authors seem to not be aware of based on their citations). While this mechanism explains much of the thermal chemistry in the manuscript by Wang et al., under ambient concentrations, it is too slow to explain NO_x-to-nitrite chemistry under ambient levels of NO₂; under ambient conditions, the mechanism likely rather proceeds with the mediation by aerosol components that are more abundant than TiO₂ and can also occur in the absence of mineral dust.

In my opinion, the suggested mechanisms are not thought out carefully and in some cases are inaccurate. For example, the authors suggest that negative OH stretches in the FTIR difference spectrum indicate that NO₂ conversion to nitrite and nitrate on TiO₂ in the dark involves reactivity at the Ti-OH sites (that is involvement of hydride anions), which would imply breaking the Ti-O bond. The energetics of this is likely not favorable based on bond strength considerations; the involvement of water is more likely. Caution should be used in interpreting negative peaks in the OH stretching region in the FTIR difference spectrum as they also develop when the H-bonding environment changes. Again, the authors should refer to the Finlayson-Pitts et al. review article in PCCP (2003) for more discussion for mechanism at such high NO₂ concentrations.

The work is also not novel. The TiO₂-NO_x system has been exhaustively studied by numerous groups over the years in both the catalysis and atmospheric chemistry community. Previous papers presented detailed mechanisms that are not accurately

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considered or interpreted in the current manuscript. One interesting discussion is that of how adsorbed nitrite can be oxidized to nitrate by the reaction of NO_x on the surface, an observation that is nonetheless well documented in the literature (see numerous papers by Szyani et al.) and is shown to occur under high NO_x concentrations by researchers studying catalytic converter technology.

Conclusions are made that are not supported by the results and overstate the importance of the results. For example, starting on line 297 the authors state, "Generally, higher NO₂ concentrations suggest broader influence scope of illumination. Hence, current serious NO₂ pollution may increase the participation of solar irradiation in the formation of secondary aerosols." It is not clear how this work actually addresses formation of secondary aerosol since most of the work looked at NO₂ chemistry on TiO₂ and a rather limited study of nitrite and nitrate levels in ambient aerosols. In another example, on line 322, the authors state, "However, the nitrate formation on mineral dust is found to be more dependent on weak sunlight, indicated that photochemistry processes are still crucial in heavy haze." They further state as one of the main conclusions of the paper is that nitrate formation on mineral dust is "more dependent on weak sunlight." Unfortunately, it was unclear to me how the authors can extract this conclusion from their data. It is well known that nitrate formation is driven by photochemical oxidation that converts NO₂ to nitric acid/nitrate in a radical termination step. This photochemical pathway is directly proportional to light intensity, which drives both OH and NO_x production rates. The nitrate formation rate on TiO₂ is also shown to increase with light intensity as shown in Figure 1G.

The authors also suggest there is a "nitrite burst accompanied by low nitrate concentrations" that has not been considered by the atmospheric community. It is not clear what burst they are referring to, as this part of the discussion was quite unclear. The conclusion appears to come from the correlations observed in Figure 3, but those observations are expected and can be interpreted using known chemistry. For example the positive correlation between nitrite and nitrate at evening/night is expected since

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both stem from adsorption of N₂O₅ and NO₂ to particles, while a negative correlation is expected during the day since high photon flux generates high concentrations of more photochemically stable nitric acid/nitrate, but effectively photolyzes nitrite.

In summary, The paper is poorly organized and written; there is no experimental evidence that the ambient aerosol N chemistry is driven by or can be linked to TiO₂ (anatase) chemistry; the TiO₂ study is not conducted under atmospherically relevant conditions on a substrate that is not atmospherically relevant; and some of the main mechanisms proposed are either inaccurate or lack experimental support and can rather be explained using well-established chemistry. For this reason, I do am unable to recommend this manuscript for further consideration. Moving forward, I would suggest that the authors place all of the TiO₂ data (which appears to be of good quality) into a concise manuscript (break the multi-panel figures up into more digestible figures) focused on the topic of photocatalytic reactions of N on TiO₂ surfaces, which could be submitted to a more specialized journal in the area of catalysis or environmental remediation.

Specific Comments: Too many figures are shown in Figure 1. These figures can easily be broken up in a way to make a separate manuscript on its own (see above comment).

line 62: The authors state that some researchers have studied the effect of radiation on NO₂ uptake on TiO₂ but have ignored the reaction mechanism behind the trends in reactivity. However, after reading the papers cited and some that are not cited, I disagree.

line 229-230. In figure 2c, the authors fit a polynomial function to the experimental data collected for NO₂ uptake coefficients plotted as a function of light intensity. They then provide an inset showing a near perfect correlation between experimental uptake coefficients and those making up the line they fit to it. This is unnecessary. I recommend omitting the inset and simply reporting the R-squared value for the polynomial fit.

237-238: The polynomial fits lack any physical meaning and are only applicable to the

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substrate and conditions of the experiment, which are not necessarily environmentally applicable (see above).

Figure 3: It is entirely unclear what the rightmost column is depicting. What do the authors mean by "nitrite classification?" What do the color codes mean?

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-315>, 2019.

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