Supporting Information:

Gas-Phase Nitrous Acid (HONO) Formation Is Controlled by Surface Interactions of Adsorbed Nitrite (NO$_2^-$) on Common Indoor Material Surfaces

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The supporting information document contains 8 figures, 1 table, and 14 pages in total.
S.1. Mass balance for photo-enhanced NO₂ hydrolysis

Figure S1. Change in gas-phase HONO or NO₂ concentration from photo-enhanced NO₂ hydrolysis reaction in presence of A) kaolinite, B) cement, and C) CH₃COOH exposed cement samples. Thin films were exposed to a fixed quantity of NO₂ (~110 ppb) at 45±5 % RH in the presence of solar light. For kaolinite, NO₂ level depleted by ~15 ppb and approximately makes 5 ppb of gas-phase HONO under steady-state condition. For the cement sample, gas-phase HONO concentrations were below the background HONO mixing ratio.

Along with the condensed-phase products, gas-phase HONO production and NO₂ loss were monitored during surface exposure at lower NO₂ concentration (~110 ppb) in the presence of solar light at 45 ± 5 % RH. Typical uptake profiles of NO₂ on kaolinite and cement surfaces and
subsequent HONO formation under illumination are presented in Figure S1. A large initial uptake of NO\textsubscript{2} was observed that slowly reaches steady-state condition. Heterogeneous reaction of NO\textsubscript{2} on particle surface results in the formation of NO, which was not probed in this study. A total of $3.9 \pm 0.5 \times 10^{16}$ molecules and $9.9 \pm 0.5 \times 10^{16}$ molecules of NO\textsubscript{2} were adsorbed by the kaolinite and cement surfaces, respectively over a period of 16 h. Steady state concentration of HONO was $\sim5$ ppb above the background signal for kaolinite surface which is equivalent to $1.3 \times 10^{16}$ molecules. HONO concentrations from the cement surface film was below the signal to noise ratio. Condensed-phase nitrate and nitrite concentrations are summarized in Table S1. Taking all of this into account, we estimate that approximately 15-20\% of products are other nitrogen-containing products, most likely other gas-phase nitrogen oxides such as NO or N\textsubscript{2}O.

**Table S1.** Mass balance for photo-enhanced NO\textsubscript{2} uptake reaction on kaolinite and cement at lower NO\textsubscript{2} concentration

| Surfaces | NO\textsubscript{2} loss | HONO   | Nitrate + Nitrite |
|----------|--------------------------|--------|-------------------|
| Kaolinite| $3.9 \pm 0.5$           | $1.3 \pm 0.2$ | $1.8 \pm 0.1$    |
| Cement  | $9.9 \pm 0.5$           | -      | $8.4 \pm 0.1$    |

**S.2. HONO uptake**

There are some direct sources of indoor HONO such as gas stove cooking, space heaters usage, and candle burning beside the conversion of NO\textsubscript{2} to HONO. Additionally, Collins et al have suggested that the gas-surface equilibrium of HONO controls the indoor HONO level. Hence, all these surfaces were exposed to $\sim200$ ppb of HONO under the dark condition at RH = 45±5 % to determine their efficiency as a HONO reservoir. Figure S2 shows the condensed-phase nitrite coverage following HONO exposure for 16 h. Like NO\textsubscript{2} exposed samples, nitrite concentration
was significant on zeolite and cement proxy surfaces. This result further supports the conclusions that only some surfaces act as nitrite reservoirs.

![Image showing surface coverage of nitrite ions on different materials.](image)

**Figure S2.** Surface coverage of nitrite ions on four different indoor model surfaces: zeolite, kaolinite, CaO + CaCO₃ as cement proxy, and painted wall following exposure to ~200 ppb of HONO for 16 h in the dark and at RH = 45±5 %. Data points are the average of multiple measurements, and error bars represent uncertainties of ±1σ.

**S.3. The effect of surface nitrate loss over time**

HONO production should be a function of the concentration of surface adsorbed nitrate or nitrite unless it is present in large excess. The effect of surface nitrite or nitrate loss on gas-phase HONO concentration was examined by photolyzing NO₂ exposed surface for a long time at a fixed reaction condition; solar radiation at RH = 45±5 %. As shown in Figure S3, HONO concentration dropped over time for NO₂ exposed painted surface. Gas-phase HONO concentration ([HONO]_{measured}) was fitted to an exponential decay function eq. S1.

\[
[HONO]_{measured} = A \cdot e^{-kt}
\]  

*Eq. S1*
Here parameter $A$ is a proportionality constant, $t = \text{time}$, and $k = \text{decay constant}$. Fitted decay constants for different surfaces are determined to be $0.15 \pm 0.01 \text{ s}^{-1}$ for these surfaces. An average of 15-16% correction in concentration was required due to surface adsorbed nitrate loss over time. The effect of surface nitrate and nitrite loss was countered using eq. S2.

$$[HONO]_{\text{corrected}} = [HONO]_{\text{measured}} \cdot e^{kt}$$  
Eq. S2

Figure S3. Time variation of gas-phase HONO concentration measured (red) from NO$_2$ exposed painted surface under solar illumination at RH = 45\% \pm 5 \%. Greyline represent an exponential fit to equation S1 of the experimentally measured HONO concentration ($[HONO]_{\text{measured}}$) shown in red colored circles. Corrected HONO concentration ($[HONO]_{\text{corrected}}$), obtained using eq. S2, is shown in the wine colored square data points in the figure.

S.4. HONO generation in the dark from surface adsorbed nitrate under humid conditions

RH-dependent HONO production from surface adsorbed nitrate and nitrite was also performed. Figure S4 presents the RH-dependent HONO and NO$_2$ concentrations produced from NO$_2$ exposed surfaces under dark conditions. These concentrations are the average of multiple measurements. Gas-phase product concentrations are significant differences on different surfaces. NO$_2$ is the dominant product from zeolite and cement proxy samples where kaolinite and painted walls
primarily produce HONO. The maximum amount of gas-phase HONO is being generated on the painted surface (10-60 ppb) followed by the kaolinite surface (5-45 ppb). Gas-phase HONO is the major product for these two samples where the HONO mixing ratio increases with the increase of the RH except for the highest RH value. This trend suggests that the adsorbed water plays an important role in the renoxification reaction to produce HONO from NO$_2$ exposed painted walls and kaolinite surfaces. RH-dependent HONO concentration from the cement proxy sample follows the same trend but the overall HONO concentration is significantly lower (5-10 ppb) than the other two surfaces. Similar to the cement sample, a smaller amount (5-15 ppb) of HONO was produced from the zeolite surface which, follows a different RH dependence; an enhancement up to RH = 30% and drops after that. NO$_2$ is the dominant product for zeolite and cement proxy where its concentration remained the same at all RH. This implies NO$_2$ degassing from these surfaces takes place at a fixed rate which is independent of RH. However, a gradual decrease in NO$_2$ concentration was observed for the painted wall surface. This could imply that surface adsorbed water enhances NO$_2$ hydrolysis to increase gas-phase HONO concentrations. RH-dependent NO$_2$ formation on kaolinite follows a complex trend; initial increase up to RH=30% followed by a dip and a small enhancement >60% RH. A combination of two processes might be occurring simultaneously a) replacement of adsorbed NO$_2$ or N$_2$O$_4$ by water molecules and b) increased water adsorption opens up more reactive sites as previously discussed by Liu et al.$^2$
Most strikingly, only a smaller amount of HONO was generated under dark conditions from zeolite and cement proxy surfaces where substantially large amounts of surface adsorbed nitrites are stored. These surface adsorbed nitrites do not readily get protonated to make gas-phase HONO even at a very high RH. In contrast, a notable amount of HONO signal was detected when there was a minimal amount of surface nitrite on kaolinite and painted wall surfaces. This result complements the observations by Abbatt co-workers during the HOMEChem campaign (2018); house floor mopping with vinegar solutions enhances the gas-phase mixing ratio of HONO.
Alkaline surface materials such as grout and concrete are found to be a good reservoir of nitrite and vinegar solution could alter the surface pH to facilitate the protonation step of reaction RS1 and RS2 or the protonation of Ca(NO$_2$)$_2$. Hence, we propose the following reaction mechanism for HONO formation in the dark:

\[
MO^- + NO_2(g) \rightleftharpoons MO - NO_2^-(s) \xrightarrow{+H_2O} MO - OH + HONO(g) \quad RS1
\]

\[
MO + 2NO_2 \rightleftharpoons MO - N_2O_4(s)
\]

Condensed-phase nitrate and nitrite concentration were measured after humidity treatment for 6 h. Figure S5 presents the change in surface coverage of nitrite and nitrate ions after humidity treatment. Surface coverage of nitrate was depleted for all four surfaces to make gas-phase HONO formation more favorable.
and NO$_2$. An enhancement of nitrite concentration was observed for zeolite and cement samples. HONO generated through reactions RS1 and RS2 could be stabilized as nitrite on the surfaces.

**S.5. Photo-enhanced gas-phase HONO production**

Changes in the HONO concentration as a function of RH for NO$_2$ exposed samples in the presence of solar radiation are shown in Figure S6. Total HONO and NO$_2$ concentrations are the sum of products from two different mechanism: some produced in the dark as explained in the previous sections (sec. S.4) and some from nitrate photochemistry. Figure 4 in the main text presents the photo-enhanced fraction (ΔHONO and ΔNO$_2$) of the gas-phase products. Photo-enhanced HONO concentration increases with the increase of RH as surface adsorbed water facilitates NO$_2$ hydrolysis or protonation of nitrite. It is to point out that multilayer water uptake or liquification on the surface can hinder the water-to-air exchange rate of HONO as previously seen on gypsum surfaces.$^1$ Additionally, a greater wall loss of highly water-soluble HONO can reduce the gas-phase photo products. For zeolite, cement proxy, and painted wall, enhancement is higher than suppression. Kaolinite surface follows a complex trend; initial increase up to RH=45% followed by a dip and a small enhancement $>$70% RH. This could be the result of two compensating factors that are operating in kaolinite as discussed in the previous section. A combination of two processes might be occurring simultaneously as previously discussed by Liu et al. a) reduction of gas-surface exchange due to surface adsorbed water molecules and b) increased water adsorption opens up more reactive sites.$^2$ For the cement material, HONO percentage increases with RH except at the lowest RH condition. This can be argued that the surface $-$OH determines the reaction rate of NO$_2$ hydrolysis at dry conditions. As RH increases, water starts to condense on the surface and makes NO$_2$ hydrolysis more feasible in the liquid phase. Additionally, NO$_2$ hydrolysis at the photoactive
site makes HNO₃ which can change the pH of the surface locally and can enhance the protonation of nitrite.

**Figure S6.** Gas-phase HONO (red) and NO₂ (cyan) concentrations as a function of RH for solar-irradiated NO₂–exposed thin films (A) zeolite, (B) kaolinite, (C) CaO + CaCO₃ as cement proxy, and (D) painted wall in the presence of solar simulator. Data points are the average of triplicate measurements, and error bars represents a sigma uncertainty.
S.6. Condensed-phase measurements of NO$_2$ exposed samples after broadband irradiation.

![Figure S7](image-url)

**Figure S7.** Change in surface coverage of nitrite (red) and nitrate (black) ions for NO$_2$ exposed surfaces after broadband irradiation for 6 h under humid conditions. A negative value represents the depletion of nitrite or nitrate. A positive value signifies growth.

Measurements of the surface coverage of nitrate and nitrite were also performed on the same NO$_2$ exposed surfaces at the end of the gas-phase photolysis experiments. Figure S7 presents the change in surface coverage by subtracting the surface coverage measured using ion chromatography before and after photolysis where each sample was exposed to light and humidity for 6 h. A negative value represents the loss of surface coverage. Nitrate loss is apparent for zeolite, kaolinite, and painted surface. For zeolite and painted surfaces, nitrate concentration reduces upon irradiation along with a small growth of nitrite coverage. Nitrate photolysis under humid conditions makes nitrite which can be stabilized by zeolite or porous painted surface. Therefore, the loss of nitrate resulted in the growth of nitrite concentration. Alternatively, nitrate can directly convert to nitrite; photoisomerization to peroxy nitrite followed by rapid dissociation.$^5$

\[
NO_3^-(s) \xrightleftharpoons{hv} ONOO^-(s) \xrightarrow{hv} NO_2^-(s) + O(^3P) \quad RS3
\]
A drastically different result was found for the cement proxy surface; loss of nitrite coverage and rise of nitrate coverage. This implies that some of the nitrites were converted to nitrate upon photolysis. Here we propose the following pathway which involves the photolysis of nitrite. Nitrite has three distinct UV absorption bands: a $\pi \rightarrow \pi^*$ transition around 220 nm and two bands peaking near 318 nm and 354 nm, corresponding to $n \rightarrow \pi^*$ transition.\(^6\)

\[
\text{RS4} \\
NO_2^- + h\nu \rightarrow NO + O^- \\
3\text{NO} \rightarrow N_2O + NO_2 \\
\text{RS5} \\
\text{RS6} \\
NO_2 + O^- \rightarrow NO_3^- \\
No_2^- + O(3P) \rightarrow NO_3^- \\
\text{RS7}
\]

Nitrite photochemistry makes NO which could lead to the formation of N\(_2\)O and NO\(_2\) in a secondary reaction. Although NO and N\(_2\)O were not probed in this work, previous nitrate photolysis studies reported N\(_2\)O and NO as gas-phase photoproducts. Alternatively, nitrite can be directly converted to nitrate by the oxygen atom generated in reaction R16B. Most importantly, nitrite to nitrate conversion upon illumination is significant on the alkaline cement surface. Thus, photochemistry under humid condition is complex and associated with loss of nitrate and nitrite along with nitrite to nitrate conversion.

**S.7. Implications for indoor air environments**

To estimate the concentration of HONO resulting from irradiated kaolinite clay surfaces, following equation can be used.\(^7\)

\[
C_{\text{HONO}}(t) = \frac{E_{\text{HONO}} \times S}{k_{AER} V + J_{\text{HONO}} V_1} [1 - e^{-(k_{AER} J_{\text{HONO}}) t}] \quad \text{Eq. S3}
\]
where $C_{HONO}(t)$ is the gas-phase HONO concentration (mg m$^{-3}$) in a room, $E_{HONO}$ is the emission rate of HONO in mg m$^{-2}$ h$^{-1}$, $S$ is the surface area of the room (m$^2$), $V$ is the room volume (m$^3$), $k_{AER}$ is the air exchange rate (h$^{-1}$), and $J(HONO)$ is the photolysis rate of indoor HONO. It is worth mentioning that outdoor HONO levels are usually lower than indoor levels and it assumed to be zero in the above expression.

![Figure S8](image_url) **Figure S8.** The estimated (Eq. S3) HONO concentration from NO$_3^-$ photochemistry on kaolinite surface in an indoor air environment when one-fifth of the indoor volume is directly illuminated by sun light and at RH = 45 ± 5 %. HONO concentration is calculated considering 100% (black), 50% (red), and 30% (blue) of surface materials available for reaction.

Consider an unfurnished room with a total volume of $V = 50$ m$^3$, total surface area of $85$ m$^2$ (S/V = 1.7 m$^{-1}$), and total wall and ceiling area made of kaolinite $S = 55$ m$^2$. Assuming only one fifth of the room volume is irradiated by direct solar light $V_1 = 10$ m$^3$, an average air exchange rate $k_{AER} = 0.56$ h$^{-1}$, and HONO photolysis rate $J(HONO) = 0.26$ h$^{-1}$, HONO concentration is predicted in Figure 5 in the main text. In this calculation and in the condensed-phase data analysis, it is assumed that the entire surface materials were involved in the reaction. Indoor HONO concentration is
calculated considering 100%, 50%, and 30% of surface materials being reacted for kaolinite sample.

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