Photoactive Roadways: Determination of CO, NO and VOC Uptake
Coefficients and Photolabile Side Product Yields on TiO₂ Treated Asphalt and
Concrete.

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ABSTRACT

This work reports uptake coefficients and by-product yields of ozone precursors onto two photocatalytic paving materials (asphalt and concrete) treated with a commercial TiO₂ surface application product. The experimental approach used a continuously stirred tank reactor (CSTR) and allowed for testing large samples with the same surface morphology encountered with real urban surfaces. The measured uptake coefficient (γ_{geo}) and surface resistances are useful for parametrizing dry deposition velocities in air quality model evaluation of the impact of photoactive surfaces on urban air chemistry. At 46% relative humidity, the surface resistance to NO uptake was $\sim 1 \text{ s cm}^{-1}$ for concrete and $\sim 2 \text{ s cm}^{-1}$ for a freshly coated older roadway asphalt sample. HONO and NO₂ were detected as side products from NO uptake to asphalt, with NO₂ molar yields on the order of 20% and HONO molar yields ranging between 14-33%. For concrete samples, the NO₂ molar yields increased with the increase of water vapor, ranging from 1% to 35% and HONO was not detected as a by-product. Uptake of monoaromatic VOCs to the asphalt sample set displayed a dependence on the compound vapor pressure, and was influenced by competitive adsorption from less volatile VOCs. Formaldehyde and acetaldehyde were detected as byproducts, with molar yields ranging from 5-32%.

HIGHLIGHTS

- Uptake coefficients for the interaction of ozone precursors and photoactive roadway materials were determined.
- Significant molar yields of radical sources (HONO and aldehydes) were measured during the photocatalytic removal of NO and VOC from asphalt pavement

KEYWORDS

Photoactive roads; titanium dioxide; uptake coefficient; surface resistance; NO, HONO; concrete; asphalt

1. INTRODUCTION

Dry deposition of gases and particles results in formation of grime on urban surfaces. To mitigate the griming process and improve long term appearance and function of building exteriors, self-cleaning materials incorporating photoactive TiO₂ (anatase) are being used in building construction or applied as a surface treatment [1]. A notable commercial use is in self-cleaning window glass for high rise buildings, but anatase TiO₂ is also being incorporated into cement paving blocks, roofing tiles and paints [2]. It has been proposed that a more widespread application to roadway materials and the built environment could be an effective strategy to reduce urban air pollution, particularly at the street level, where multi-pollutant exposure from vehicle exhaust has significant health ramifications. When these materials are exposed to ultra-violet radiation ($\lambda < 387$ nm), HO_x radicals are formed on the surface as the result of the interaction between surface adsorbed water vapor or molecular oxygen and charge carriers that migrate from the bulk of the TiO₂ crystal [1,3,4]. These radicals are thought to be responsible for the observed surface destruction of nitrogen oxides (NO_x) and volatile organic compounds (VOCs) ([5,6] and references therein). In field

experiments, Ballari and Brouwers [7] have shown reduced NO_x mixing ratios along a roadway built with photoactive paving stones while Maggos et al. [8] have shown NO_x reduction in an artificial street canyon. Reductions in NO concentrations over an asphalt parking lot treated with a TiO_2 surface coating have also been reported [9]. In contrast, Gallus et al. [10] did not observe an impact on NO_x levels in a model photoactive street canyon. These differences in field trial results highlight methodological challenges in attributing changes in ambient NO_x mixing ratios to local surface uptake.

Ozone most often exceeds regulatory limits in the US and Europe, and thus any serious adoption of photoactive surfaces as an air quality management strategy would have to quantify potential impacts on ozone. For ozone formation two issues are apparent: the generation of photolabile by-products from photoactive surfaces and potential changes in the NO_x -to-VOC ratio. It has been reported that HONO is formed as a by-product from NO_2 oxidation on TiO_2 treated surfaces [11–13] and that aldehydes may be released from VOC oxidation [14–16]. Enhancing the sources of these HO_x radical precursors might increase O_3 formation rates in urban air sheds [17–23]. The second issue is that potential preferential removal of NO_x over VOCs will change the NO_x -to-VOC ratio and shift the ozone formation chemistry sensitivity [24,25]. Many US urban areas are thought to be NO_x sensitive in the afternoon [26], but in general, urban ozone sensitivity to NO_x or VOC reductions appears to vary widely given differences in urban emissions inventories and UV irradiance in cities around the world [27–30].

Investigating the efficacy of photoactive urban surfaces could potentially be done using chemical transport modeling to determine if the enhanced surface destruction rate for NO_x and VOCs is sufficient to impact near surface concentrations and to investigate the potential impacts on O_3 . Currently, there is a lack of information on surface resistances or uptake coefficients and by-product yields for such materials, which are needed to

parameterize dry deposition rates and impacts on ozone photochemistry for air quality modeling. Engel et al. focused on determining photocatalytic deposition velocities based on the ISO 22179-1 method which requires the use of a plug flow reactor restricting size and shape of photoactive samples [31]. The authors suggests that the use of a continuously stirred tank reactor (CSTR) would allow overcoming such limitations. However, other studies argue that the use of CSTR might result in diffusion limitations if turbulence is not adequately provided [33]. We note that CSTRs were used to determine surface resistances of grasses, soils, and water in the early days of dry deposition studies of ozone. This paper reports uptake coefficients (γ) of NO and selected VOCs onto concrete and asphalt samples treated with a commercially available TiO₂ surface coating using a CSTR. The reported uptake coefficients account for the transport resistance of the CSTR [34,35]. The uptake coefficients determined using a CSTR illustrate what to expect from commercially available treatment products applied to common, real urban surface materials, and they can be used to parameterize dry deposition rates in chemical transport models. Molar yields of HONO from photocatalytic NO removal, and formaldehyde and acetaldehyde from photocatalytic VOC removal are also reported.

2. MATERIALS AND METHODS

2.1. Samples

Two types of conventional paving materials were used as substrate: asphalt concrete (AC) mixtures and Portland cement concrete (PCC) mixtures. Both types of samples were prepared in the laboratory. Details on the preparation are described in the Supplementary Material. The samples obtained had different surface characteristics, with different levels of the binder material exposed to the air. Additionally, a set of samples was obtained from a

cylindrical core taken from a 4 year old asphalt roadway. Figure 1 shows the different samples studied and a front view of the illuminated chamber setup with samples inside:

Figure 1. *Left:* surface view of each type of sample studied. *Right:* front view of illuminated chamber with a set of samples inside.

The samples were sent to a company specializing in spray-on surface applications of TiO_2 . Spray application requires less TiO_2 , simplifies maintenance, and has potentially higher photocatalytic efficiency since more catalyst is exposed to UV compared to applications where the catalyst is embedded on the substrate. However surface coatings are subject to road wear from traffic and performance would be expected to diminish over time. Osborn et al. [36] examined the durability of a TiO_2 surface coating applied to a lightly traveled asphalt and concrete roadway surface. They determined that photocatalytic activity was reduced by 50% after about 2.5 months. The TiO_2 mass loadings used in this study were suggested by the company based on their business experience. The loading of TiO_2 is hypothesized to be directly related to the pollutant removal efficiency, with larger loadings resulting in a greater ability to degrade pollutants. The TiO_2 mass loadings for the samples studied here, and the labeling chosen for each type of sample are described in Table 1.

Table 1. Description of concrete and asphalts sample sets.

Paving Material	Label	Description	TiO_2 loading (kg/m^2)
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Asphalt	AC1	rough surface, binder exposed	0.065
	AC2	smooth cut surface, aggregates exposed	0.097
	AC3	smooth cut surface, aggregates exposed	0.210
	AC4	rough, road sample	0.210
Concrete	PCC1	rough surface	0.097
	PCC2	smooth cut surface, aggregates exposed	0.097
	PCC3	troweled surface, binder exposed	0.065

2.2. Chamber Description

A more detailed description and a schematic of the chamber setup are presented in the Supplementary Material. Briefly, the 148 L chamber was made of 2 mil perfluoroalkoxy polymer resin (PFA) Teflon film with removable Plexiglas ends. Inside the chamber an aluminum support frame held a stainless steel rack where the samples were placed. Test gas mixtures made from humidified zero grade air entered the chamber through a perforated ¼” PFA Teflon tube that extended through the bottom of the chamber below the sample rack. Mixing was provided by two small fans, each rated at 196 L /min. A separate PFA ¼” Teflon tube pulled sample air from the middle of the chamber and was connected to a suite of instruments described in the following section.

2.3. Instrumentation

NO_x (NO_2 and NO) and NO_y ($\text{NO}_x + \text{HONO} + \text{HNO}_3 + \text{other nitrogen oxides species}$) were measured using a two-channel chemiluminescence detector (Air Quality Design). NO_y was detected in one channel by conversion to NO using a molybdenum converter. NO_x was measured in the second channel by converting NO_2 to NO using a blue light photolytic converter. HONO measurements were made by sampling through a parallel set of custom-made denuders, one coated with NaCl to remove HNO_3 , the other coated with Na_2CO_3 to

remove HONO and HNO₃. HONO was measured as the difference between the NO_y signal measured through the NaCl denuder (NO_x + HONO) and Na₂CO₃ denuder (NO_x) [13]. HONO collection efficiency was determined by preparing HONO by the heterogeneous reaction of HCl with NaNO₂ [37]. VOCs were measured using a PTR-MS instrument (Ionicon Analytik, Austria). The instrument was operated at 80 Townsend (Td) to decrease fragmentation and the sample flow was dehumidified upstream of the PTR-MS inlet to increase the sensitivity to HCHO [38]. CO was measured using a conventional air quality monitor (TECO 48). Relative humidity and temperature were measured at the exhaust vent using a probe (Vaisala Humicap HMP110). H₂O concentrations were measured with a non-dispersive infrared detector (LICOR 840-A). Ultra-violet radiation was measured using a handheld sensor (General, Model UV513AB).

2.4. Lights

Fluorescent black lights (Sylvania BL350, 25W, $\lambda_{\text{max}} = 350 \text{ nm}$) surrounded the chamber and provided controllable levels of UV illumination. The black lamp spectrum compared to that of sunlight is shown in the Supplemental Material. The spectra were measured by a spectroradiometer with 0.5 nm resolution (Meteorology Consult). For the CSTR experiments a hand held UV sensor was used to measure irradiance at the sample surface level inside the chamber. The sensor response function has a range of 290-375 nm resulting in an underestimation of the TiO₂ active UV flux ($\lambda < 387 \text{ nm}$). The underestimation was calculated as 25%, thus the sensor measurements were corrected by a factor of 1.25. The samples were illuminated with an environmentally relevant range of UV intensities.

2.5. Box Model Analysis

The chamber data allows to determine k for the test gas based on the following steady state equation:

$$k = \frac{\eta (C_{in} - C_{ss})}{C_{ss}} \quad (1)$$

where C_{in} corresponds to the concentration entering the chamber, C_{ss} is the concentration at steady-state and η is the air exchange rate (s^{-1}).

The air exchange rate η can be determined from the volume of the chamber and the measured flow rate entering the chamber; however η was determined empirically in test mixtures of NO and CO₂ in an empty chamber. For example, at an inflow of 10 slpm, the measured η for an NO mixture was $1.28 \times 10^{-3} \pm 5.81 \times 10^{-6} s^{-1}$, 1.5% larger than the theoretical η calculated from the flow rate and the chamber volume determined from the nominal dimensions of its cylindrical shape.

2.6. Uptake coefficients

The net gas uptake coefficient (γ) is defined as the ratio between the number of gas kinetic collisions that effectively end in uptake by the surface and the total number of collisions between the gas molecule and the surface. The uptake coefficients can be determined from the measured loss coefficients k , as described in Equation 2. A more detailed derivation of this Equation is shown in the Supplementary Material.

$$\gamma_{geo} = \frac{4kVv_t}{v_{ave}(Av_t - kV)} \quad (2)$$

The net uptake coefficient defined in Equation 2 is a function of the average velocity of the gas molecule (v_{ave}), the geometric area of the sample (A), the volume of the chamber (V), the experimental loss coefficient (k) obtained from the CSTR experiments, and the transport-limited deposition velocity (v_t) [39]. This last parameter represents the influence of mass transport processes and it was determined empirically for our chamber setup (Supplementary

Material). Our reported γ_{geo} is defined in terms of the geometric surface area, which can be much smaller than the specific surface area for rough surfaces. The reported γ_{geo} values are thus upper limits to γ . The surface resistance can also be calculated from the measured flux and the transport resistance (Supplementary Material). The usefulness of γ_{geo} and the surface resistance is that it can be directly applied in chemical transport models to represent dry deposition to real urban surfaces, such as roads and buildings, where geometric surface areas are known.

2.7. General Procedure

For each type of material studied, a set of 6 disk-shaped samples was placed on the stainless steel rack inside the chamber. The total planar sample area for each experiment was 0.11 m². Each disk-shaped sample was enclosed in aluminum foil to expose only the top surface of the sample. NO test gas mixtures were prepared by dynamically diluting compressed gas standards (Scott Marrin, CA) into a 10 slpm zero air flow to produce a ~120 ppbv NO mixing ratio. VOC test gas mixtures of alkylbenzene compounds in the range of 50-60 ppbv were prepared by dynamic dilution of a very low flow liquid infusion of the neat compound (or equal molar mixture of the compounds) into a heated 10 slpm zero air flow (Supplementary Materials). With the chamber filled and mixing ratios at steady-state, the UV lights were turned on and the experiment proceeded until reaching a new steady-state condition. For each set of conditions, the procedure was repeated at least 3 times sequentially, and the average values were reported. The chamber was constantly flushed with zero air (RH≈15%) while not in use. To illustrate the nature of the experimental data, Figure 2 shows experiments comparing NO uptake to treated and untreated asphalt and concrete samples under UV illumination. For NO, the loss is larger on both treated and untreated concrete material samples compared to asphalt. The TiO₂ surface treatment clearly enhances surface

uptake upon irradiation with UV. Uptake of NO by untreated concrete may be due to the potential presence of TiO₂ in the fly ash. At 41 W/m² of TiO₂ active UV irradiance, the NO loss coefficient k for untreated asphalt samples was $1 \times 10^{-5} \text{ s}^{-1}$, the approximate lower bound for our measurement sensitivity. For the treated concrete sample PCC2, the average k value was $4.19 \times 10^{-3} \text{ s}^{-1} \pm 1\%$, which is slightly less than the transport limited uptake of $4.6 \times 10^{-3} \text{ s}^{-1} \pm 6\%$, determined experimentally for this CSTR.

Figure 2. Example of CSTR data showing uptake of NO to untreated and TiO₂ treated samples upon UV illumination. Treated samples are AC2 and PCC2. UV=41 W/m², H₂O=2 mmol mol⁻¹ (~RH=10%). The percentage shown represents the net uptake of NO by each set of samples.

As k approaches the transported limited rate, the uncertainty in γ_{geo} rapidly increases given the uncertainty in A , V , k , and $v_{t,}$. The derived γ_{geo} is also very dependent on the accuracy of the v_t determination. Such high uptakes were observed for NO under dry conditions with the concrete samples, and with some VOC's to the asphalt sample tested. For the purpose of illustrating trends and to discuss experimental limitations with the CSTR approach, we report uptake coefficients for these cases with the caveat that these values are more uncertain than implied by experimental precision and simple error analysis. At the point where the surface resistance to chemical uptake is the same as the transport resistance the resulting γ_{geo} is 5.4×10^{-5} , which could be considered a reasonable upper limit for a well constrained γ_{geo} determination for this CSTR.

3. RESULTS AND DISCUSSION

3.1. NO uptake and the influence of water vapor

The measured k values for NO uptake to the concrete and asphalt samples as a function of water humidity are displayed in Figure 3a, and the corresponding γ_{geo} are presented in Figure 3b. The AC1 sample set was not included as they showed significantly lower photocatalytic activity (less than 5% NO removal) compared to the other samples. The low uptake of NO by the AC1 sample may imply that the TiO_2 treatment didn't adhere as well to the bitumen binder as it does to the exposed aggregate.

Figure 3. Panel (a) shows NO loss coefficients for photoactive asphalt (circles) and concrete (squares) sample sets as a function of relative humidity. Error bars represent 1 sigma uncertainty. Dashed line indicates transport limited uptake determined using $\text{O}_3 + \text{KI}$ with shading representing 1 sigma uncertainty. Panel (b) shows corresponding uptake coefficient. Shaded region indicates where the surface resistance to chemical uptake is less than the transport resistance and calculated γ_{geo} is thus more uncertain. For TiO_2 mass loadings see Table 1. $\text{UV}=41 \text{ W/m}^2$.

For the concrete samples at the lowest relative humidity the first order loss coefficient (k) approaches the transport limit, resulting in large uncertainty in the derived γ_{geo} . These γ_{geo} values are very sensitive to the measured k value for NO uptake and the transport limit k ; small differences in these values yield large changes in gamma and so these values are not

well determined. The data are shown to illustrate, for completeness, the apparent strong influence of RH on concrete surface chemistry. Uptake to the concrete samples increased significantly with decreasing humidity. The impact of water vapor on photoactive concrete samples is similar regardless of the TiO₂ loading or surface characteristics; there was no significant difference between the three samples at each water vapor concentration studied. In contrast, the NO uptake to the asphalt sample sets remained relatively constant with RH, with the exception of the AC4 samples that displayed a 50% lower uptake at the highest RH. In general the AC4 samples are were 2-3 times more effective in removing NO than AC3 samples, even though they have the same TiO₂ loading. The distinction between the two sets of samples is that the AC4 set was from a 4 year old road surface constructed from limestone aggregate and had a rough surface, while AC3 samples were made in the laboratory with a basalt aggregate and had a smooth cut surface from slicing the sample core. The AC4 samples thus likely have a higher specific surface area than AC3 samples and thus a larger γ_{geo} . Note the AC3 sample set, with twice the TiO₂ mass loading of the AC2 set displayed on average an 80% larger uptake than the AC2 set.

We attempted to measure NO₂ uptake to the AC4 sample set but NO₂ photolysis and enhanced chamber uptake of NO₂ at higher RH severely limited the usefulness of this CSTR. A better system for NO₂ uptake has been described [40]. It was apparent, however, that for dry conditions NO₂ uptake was about a factor of 10 less than that of NO. This factor of 10 difference has been reported on uptake to Aeroxide P25 briquettes [31] and from inferred deposition velocities of NO and NO₂ to a photoactive commercial bitumen membrane product in an outdoor experiment [41]. In contrast uptake of NO and NO₂ to a commercial photoactive cementitious product showed similar uptakes of NO and NO₂, with a reported γ of $\sim 3.3 \times 10^{-5}$ [10], similar to what we measured for NO at 46%RH to the concrete and AC4 sample sets.

There is a surprising absence of reported NO and NO₂ uptake coefficients or surface resistance measurements to concrete or asphalt to despite the attention that such materials receive for air pollution abatement. From the 46% RH test condition the PCC sample sets displayed an average surface resistance of $\sim 1 \text{ s cm}^{-1}$ and the AC4 sample set $\sim 2 \text{ s cm}^{-1}$. For comparison, the surfaces resistances for NO, NO₂ and HNO₃ used in regional chemical transport models for dry deposition parameterization in an urban environment during summer are $2 \times 10^8 \text{ s cm}^{-1}$ (dry deposition is thus insignificant for NO), 30 s cm^{-1} , and 0 s cm^{-1} (HNO₃ has no surface resistance) [42]. Dry deposition for compounds with very small surface resistances are thus largely determined by the transport resistance (the aerodynamic and the quasi laminar sublayer resistances). The turbulence properties of photocatalytic street canyons could be the limiting factor in determining NO dry deposition.

Because the majority of the roads in the US are made of asphalt, further investigations were performed only on asphalt roadway samples (AC4). The response of γ_{geo} to different levels of UV irradiance for NO is presented in Figure 4. The final values are corrected for dark uptake, represented by the uptake of NO to the chamber setup. The dark uptake of NO was measured as the difference in NO concentration between the CSTR inlet and outlet flows at steady state. The photocatalytic destruction rate depends on the UV photon flux ($< 387 \text{ nm}$) and it has been proposed that the destruction rate scales as a power law function of the UV photon flux [43]. This is thought to originate from the competition between active sites reacting with the absorbed compound and active site decay through charge carrier recombination reactions [1,43]. For our experimental conditions, γ_{geo} displayed a non-linear dependence on UV irradiance with a power law fit to the data yielding an exponent of 0.59 (see equation in figure caption). Note that the uptake coefficient at $\sim 40 \text{ Wm}^{-2}$ is roughly a factor of 2 greater than for the equivalent test condition for the same sample presented in Figure 3 performed a year earlier. This difference is likely attributable to changing sample

surface conditions with time, in this case becoming more active, presumably due to TiO_2 particles oxidizing away encapsulating binder as has been observed for paints.

Figure 4. NO uptake coefficients as function of TiO_2 active UV irradiance for the asphalt roadway sample (AC4) at 8% RH. Shaded region indicates where the surface resistance is less than the transport resistance. Error bars are 1 sigma uncertainty. Fit corresponds to a function $\gamma = a \cdot I^b$, where the coefficient a is the product of the concentration of adsorbed species and the first-order rate constant and the coefficient b is the order of the reaction with respect to light intensity (I) [1]. Fit to data: $a = 8 \times 10^{-6} \pm 5.5 \times 10^{-7}$ and $b = 0.59 \pm 1.7 \times 10^{-2}$.

3.2. VOC uptake

An example of the behavior observed for a mixture of VOCs interacting with AC4 sample set is shown in Figure 5. The decrease in mixing ratio is different between each of the components of the mixture, with 1,2,4-trimethylbenzene displaying the greatest change and benzene the least. Formaldehyde and acetaldehyde increased consistently during each UV exposure period. Auvinen and Wirtanen [15] studied removal of VOC by photocatalytic paints and also observed generation of aldehydes during illumination which was attributed to degradation of the paint and VOCs. No significant increase in aldehydes was observed when illuminating the chamber containing asphalt samples previous to the injection of VOCs. Thus the aldehyde production is associated with the VOC degradation. It is apparent from the figure that uptake is less pronounced with each cycle, presumably as a result of surface

passivation by photoproducts, and it took many hours for the sample set to reach an equilibrium. For determining uptake coefficients the experiment was run overnight until a reasonably consistent set of three sequential uptake experiments was achieved.

Figure 5. Mixture of benzene (black), toluene (red), *p*-xylene (blue) and 1,2,4-trimethylbenzene (green) interacting with photoactive asphalt (AC4). Shaded areas correspond to periods with UV illumination. Formaldehyde (orange) and acetaldehyde (light blue) are photolabile side products produced during illumination.

We observed that VOC uptake for single component mixtures was greater than for multicomponent mixtures. This effect was particularly distinctive for benzene. Figure 6a illustrates the differences in the calculated uptake coefficients for VOCs studied individually and as part of a mixture with other VOCs. In the figure, γ_{geo} is plotted as a function of the gas phase bimolecular OH rate constant to discern kinetic trends. VOC destruction of aromatics is thought to be initiated by the OH radical [44], thus the gas phase OH rate constant for each VOC serves as proxy for reactivity. The difference between single compounds and compounds forming part of a mixture suggests a competitive adsorption mechanism driving the interaction between the photoactive surface and pollutants in a mixture; less volatile compounds are more likely to be physically adsorbed at the surface.

Plotting γ_{geo} obtained from single component test mixtures against their vapor pressure (a proxy for adsorption enthalpy) results in a clear trend for aromatic compounds (Figure 6b). As the vapor pressure of the compound increases, the uptake coefficient decreases exponentially. Such relationships might be useful for parametrizing uptake in air quality models. However, VOC uptake will depend on the abundance and adsorption enthalpies of other VOCs present in the urban mix, and could be much lower than determined here. This is the essential problem for characterizing VOC uptake for dry deposition modeling to photoactive surfaces and may also impact NO uptake. To account for competitive adsorption effects future studies should test vehicle exhaust to more accurately assess NO and VOC uptake to photocatalytic urban materials.

Figure 6. a) Uptake coefficients plotted against their reactivity with OH for a mixture (filled circle) and single component tests (open circle) with photocatalytic asphalt (AC4). Error bars represent 1 sigma uncertainty. Shaded region indicates where the surface resistance is less than the transport resistance. Linear fit shown for mixture data. OH rate constants obtained from Calvert [45]. b) Uptake coefficients from single component tests plotted against compound vapor pressure. Exponential regression fit is shown. UV=41 W/m², 8% RH.

3.3. HONO and NO₂ production

The photocatalytic removal of NO produced HONO and NO₂ as products. Table 3 summarizes HONO and NO₂ molar yields for different humidity conditions. Each water vapor value represents an average of all the experiments performed for all the samples at those conditions. Molar yields are defined as moles of product formed per mole of NO removed. No HONO formation was detected for any of the concrete samples.

Table 2. Average molar yields of HONO and NO₂ measured during NO removal

% RH)	AC2		AC3		AC4		PCC1	PCC2	PCC3
	NO ₂	HONO	NO ₂	HONO	NO ₂	HONO	NO ₂	NO ₂	NO ₂
8	0.20	0.14	0.14	0.01	0.09	0.01	0.07	0.03	0.06
	±0.03	±0.01	±0.02	±0.00	±0.01	±0.00	±0.00	±0.01	±0.01
24	0.22	0.16	0.21	0.06	0.14	0.02	0.21	0.11	0.11
	±0.01	±0.00	±0.01	±0.01	±0.01	±0.00	±0.10	±0.02	±0.01
46	0.20	0.33	0.23	0.06	0.18	0.03	0.30	0.22	0.21
	±0.02	±0.03	±0.01	±0.01	±0.01	±0.00	±0.03	±0.04	±0.02
73	0.22	0.14	0.26	0.03	0.20	0.01	0.34	0.34	0.32
	±0.02	±0.02	±0.02	±0.00	±0.02	±0.00	±0.02	±0.01	±0.03

For the asphalt samples, NO₂ production was similar across all RH conditions, with an average molar yield of 19±5%. HONO was found to be higher for the sample set AC2, with molar yields ranging between 14-33%. Sample sets AC3 and AC4, with larger TiO₂ mass loading, resulted in molar yields ranging between 1-6%. For concrete samples, NO₂ generally showed an increasing trend with increase in water vapor that could be associated with the decrease in photocatalytic efficiency observed (see section 3.1). Molar yields averaged 5% at the driest conditions and 33% at the highest water vapor levels. HONO was not observed as a side product from the concrete samples. It has been noted that HONO formation on TiO₂ treated surfaces is strongly dependent on pH and humidity conditions [4] with strongest production at low pH. Ca(OH)₂ and other hydroxides forming concrete confer a basic pH to the concrete surface.

3.4. Aldehyde production

Formaldehyde and acetaldehyde were observed as products during the photocatalysis of all the VOC studied. Figure 7 describes molar yields and the composition of the aldehyde mixture obtained during the removal of each VOC studied interacting as a single component test mixture with photocatalytic asphalt (AC4). Molar yields are defined as moles of aldehydes per mol of VOC removed. The composition of the aldehydes released was essentially a mixture of formaldehyde and acetaldehyde. The exception was benzene which produced only formaldehyde. The production of aldehydes started immediately as the samples were illuminated, suggesting that the byproducts measured result from oxidation in the surface and not from other processes, such as photolysis of first generation oxidation products that migrate to the gas phase.

The proportion of aldehydes varies between the different methyl-substituted benzenes. The highest relative yield of acetaldehyde was from toluene oxidation, while the smallest was from mesitylene. The proportion of acetaldehyde increased linearly with compound volatility. On the other hand, *n*-propylbenzene produced a larger fraction of acetaldehyde than formaldehyde.

Figure 7. Removal percentages, yields and yields composition for each VOC studied interacting with photocatalytic roadway asphalt (AC4). UV=41 W/m², 8%RH.

3.6. CO uptake

Figure 8 shows the observed changes in CO and NO mixing ratios illustrating insignificant loss of CO to photoactive concrete. During periods with UV exposure, there was no removal of CO while NO removal efficiencies reached on the order of 75%. We note that in several reported field trials evaluating the effectiveness of photoactive roads or building materials the change in NO or NO_x mixing ratios was used as the metric of performance. Spatial and temporal variability of mixing ratios are of course subject to dispersion rate variability (wind speed, wind direction, mixing heights) and vehicle emissions rate variability and typically display log-normal distributions. A better metric would be to measure changes in the CO to NO_x molar ratio, which displays significantly less variability in the urban environment [46, 47]. For example daytime CO to NO_x ratios of 5.2 ± 0.5 were measured for a US near roadway site over a month long period [47]. Significant changes in the CO to NO_x molar ratio would be a better measure of NO_x uptake in local field evaluations since CO would serve as a conserved tracer and account for emissions rate variability and dispersion. Assuming the 1 sigma variation of $\sim 10\%$ in the molar ratio might be typical for a given location, an increase in the average molar ratio of more than 20% (2 sigma) would be required to observe any impact of NO uptake. Published field experiments with photoactive roads have been small in spatial scale and atmospheric mixing tends to wash out local dry deposition impacts on ambient mixing ratios. This has been noted by Palacios et al. [41] who reported that NO concentration gradients above a 700 m² photocatalytic surface in an urban setting were difficult to observe from sequential sampling at 3 heights (16 cm, 85 cm, and 270 cm). Measuring gradients in CO to NO_x molar ratios with high performance instruments would provide a clearer picture of surface uptake.

Figure 8. Comparison of CO and NO responses to UV illumination in the presence of photocatalytic concrete samples. UV=41 W/m², RH = 8%, TiO₂=0.097 kg/m². Each circle represents 1-min average data.

4. CONCLUSIONS

A continuously stirred tank reactor was used to determine uptake coefficients based on the planar surface area (γ_{geo}) of NO, CO, and aromatic VOCs to concrete and asphalt samples treated with a commercially available photoactive TiO₂ surface application (Pureti Clean). The mass transport resistance of the CSTR was determined by measuring the loss of O₃ to samples treated with KI, where the surface resistance to uptake is negligible compared to the transport resistance. CO was found to be unreactive with photoactive concrete. Uptake of NO to concrete was very efficient. For the concrete samples at 46% RH and 41 mW cm⁻² UVA irradiance, the surface resistance was $\sim 1 \text{ s cm}^{-1}$, corresponding to a γ_{geo} that ranged between 6×10^{-5} and 8×10^{-5} for the different concrete sample sets. Under dry conditions uptake was even more efficient and became significantly smaller than the transport resistance of the CSTR. Uptake of NO to the asphalt samples was less efficient and displayed no dependence on relative humidity. The surface resistance to a freshly coated used asphalt roadway sample that had exposed aggregate was 2 s cm^{-1} . These surface

resistance values can be used for dry deposition modeling and are significantly lower than used for NO₂ dry deposition in an urban landscape.

Photolabile side products were observed in all experiments. In particular, HONO and NO₂ were detected during NO removal onto photoactive asphalt with yields of 20% and 14-33%, respectively. Only NO₂ was measured from the interaction of NO with photoactive concrete, with an average molar yield of 20%. The efficient uptake of NO and significant conversion to NO₂ could potentially be problematic in reducing roadway NO₂ levels and would also enhance O₃ formation. Indications from our experiments suggest that NO uptake is much larger than that of NO₂ but this observation needs to be verified by a system better designed to measure NO₂ uptake.

The uptake of monoaromatic VOCs on the freshly treated asphalt roadway sample set (AC4) showed a correlation with vapor pressure and displayed competitive adsorption effects where uptake of the more volatile compounds was reduced in the presence of less volatile compounds. Formaldehyde and acetaldehyde were detected during the removal of all the VOCs studied with molar yields ranging from 8 to 32%. Both compounds are carcinogens and formaldehyde photolysis can enhance ozone production rates. The impact of releasing aldehydes into the atmosphere should be taken into account in any public health benefits reckoning of this technology.

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