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Photocatalytic oxidation of NO\textsubscript{x} under indoor conditions using a functional wall covering

Abstract

There is an increasing concern about the indoor air environment, where we spend most of our time. The air filling closed spaces is one of the main factors impoverishing health and creating the so-called “sick building syndrome”. Indoor air quality can be affected by microbial contaminants, gases or particulates as well as other energy stressors. The newest tool for achieving depollution is a technology called heterogeneous photocatalytic oxidation, which uses energy from light to activate chemical reactions to degrade indoor air pollutants. This research was carried out to document the performance of a photocatalytic wall-covering under indoor conditions. The experimental results indicate that the photocatalytic oxidation is an effective air purification technology for indoor air pollutants.

Introduction

Indoor air quality (IAQ) has received great attention because of the very important role the indoor environment plays on human comfort and health. Nitric oxides (NO and NO\textsubscript{2}, also written as NO\textsubscript{x}), Sulfur dioxide (SO\textsubscript{2}) and Volatile organic compounds (VOCs), as typical inorganic and organic indoor air pollutants, can be emitted from cooking, combustion, exhaust gases, tobacco smoke, furniture, building materials, even traffic pollutants from outside of buildings, and can cause serious health problems such as drowsiness, headache, sore throat and mental fatigue [1]. So, it is of vital importance to remove these pollutants to improve the indoor air quality.

Heterogeneous photocatalytic oxidation (PCO) has been studied for several decades [2], and shown as an effective method for water or air purification. Although certain progress has been achieved on the air purification employing photocatalytic oxidation, the differences in the findings or conclusions among these studies are still significant [1-6]. Further study is still very necessary, especially in indoor air quality improvement.

The present chapter addresses the indoor air purification applying PCO under indoor conditions. A mixture of NO and NO\textsubscript{2} (NO\textsubscript{x}) is chosen as the target pollutant to investigate the interrelation of the pollutants during the PCO reaction. Visible light (VIS) is used as the light source to simulate the real indoor air conditions, and a modified TiO\textsubscript{2} is used as the photocatalyst, which can be activated by visible light, to produce a photocatalytic material.

Experimental set-up

A PCO set-up was developed following the ISO standard 22197-1: 2007 as a reference here. The set-up is composed of the reactor, visible light source, target gas pollutant supply, transport gas supply, analyzer, mass controller meters, relative humidity valve,
and parameter measurement apparatus such as temperature and relative humidity. The schematic diagram of the PCO set-up is shown in Fig. 1.

Figure 1: Schematic diagram of photocatalytic degradation set-up. 1. NO gas supply. 2. NO\textsubscript{2} gas supply. 3. Synthetic air supply. 4. Mass controller meter. 5. Humidifier. 6. Humidity controller. 7. Temperature and relative humidity sensor. 8/9. Valve. 10. Light source. 11. Reactor. 12. NO\textsubscript{x} analyzer. 13. Computer. 14 Vent.

The reactor, made from non-adsorbing plastic materials with a size of 100 × 200 mm\(^2\) (W × L), allows a flat sample to be embedded. After placing the test sample inside, the top of the reactor is tightly covered with a plate made from borosilicate glass allowing UV and/or visible light to pass through with almost no resistance. The applied visible light source consists of three cool day light lamps of 25 W each (Philips, the Netherlands), emitting a visible radiation in the range of 400-700 nm. The irradiance can be adjusted by a light intensity controller. NO\textsubscript{x} is used as target pollutant. The used gases consist of 50 ppm NO or 10 ppm NO\textsubscript{2} stabilized in nitrogen (N\textsubscript{2}). Because the final target NO\textsubscript{x} concentration ranges in the order of ppb with the maximum concentration of 1.0 ppm, a transport fluid synthetic air which is composed of 20.5 vol.% of oxygen (O\textsubscript{2}) and 79.5 vol.% of N\textsubscript{2} is employed, which is humidified by flowing through a demineralized water bottle. The target concentration of NO\textsubscript{x} is adjusted by the mass controller meters. Pollutants (NO\textsubscript{x}) are analyzed using a chemiluminescent NO\textsubscript{x} analyzer (HORIBA 370, Japan).

Model pollutant selection

NO\textsubscript{x} are generated from the reaction of nitrogen and oxygen gases in the air during combustion, especially at high temperatures. The two major emission sources are transportation vehicles and stationary combustion sources such as electric utilities and industrial boilers, as well as indoor sources such as cooking, heating and smoking. NO\textsubscript{x} emissions contribute to the formation of fine particulates and ozone smog. Even worse, NO\textsubscript{x} together with SO\textsubscript{x} (sulfur dioxide and sulfur trioxide) are the major contributors to the “acid rain”, one of the most serious environmental problems across the world.

Although great progress on NO\textsubscript{x} degradation by PCO has been achieved, the differences in the findings or conclusions among these studies are still evident. For instance, in Devahasdin et al. [4], the increase of the relative humidity leads to a higher PCO conversion rate while in Ao and Lee [6] it results in a lower PCO conversion rate.
Reaction kinetics of the PCO of NO has been investigated as well; however, as an undesired intermediate, NO₂ is seldom considered in literature. In addition, using NO and NO₂ together as target pollutants as well as their interrelation during the PCO reaction have not been addressed. Thus, further study is still very necessary, especially for indoor air quality improvement.

Hence, with the consideration that NOₓ are typically available in both indoor and outdoor conditions and they are very harmful to human beings, here NOₓ are chosen as the target pollutants with a low concentration of ppb level.

**PCO material development and test**

Photocatalyst plays a key role in the PCO reaction [7]. Also as discussed elsewhere [8], traditional TiO₂ could not be activated under visible light range due to its larger band gap. Accordingly, a modified TiO₂ (carbon-doped TiO₂) was used as the photocatalyst here, which has a cut-off wavelength of 535 nm (band gap of 2.32eV) that corresponds to bluish green light range.

A commercially available wall paper was used as the substrate for the application of the photocatalyst. The used photocatalyst is mixed with water and an inorganic binder. Then the photocatalyst slurry is painted onto the wall covering followed by curing in ambient conditions for at least 2 days before any PCO experiment was carried out.

<table>
<thead>
<tr>
<th>Table 1: Experimental conditions employed in the tests.</th>
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<tr>
<td><strong>Description</strong></td>
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<tr>
<td>Photocatalyst dosage (mg cm⁻²)</td>
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<tr>
<td>Volumetric low rate Q (L min⁻¹)</td>
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<tr>
<td>Relative humidity RH (%)</td>
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<tr>
<td>Light intensity E (W m⁻²)</td>
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<tr>
<td>NO inlet concentration (ppb)</td>
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<tr>
<td>NO₂ inlet concentration (ppb)</td>
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The experiments were carried out under the test conditions as described in Table 1, and using a standard procedure illustrated as follows. The first step is to warm up the NOₓ analyzer to a stable condition for about 1-3 hours. In the meantime the reactor is prepared, including the preparation of the testing sample, placing the sample into the reactor, sealing the reactor and placing the reactor into the reaction chamber with the reactor covered by an opaque material. Then the gas is allowed to flow through the system using a bypass (with valve 9 open and valve 8 closed, see Fig. 1), and the concentration is adjusted with the mass controller meter to the desired value while monitored by the NOₓ analyzer. Then the visible light lamp is switched on to get a stable radiation and adjusted to the desired experimental light intensity value with the lamp control valve while the reactor remains covered, followed by the adjustment of the relative humidity to the desired value with the humidity control valve.

When these experimental conditions become stable, the photocatalytic oxidation reaction can be started first by opening valve 8 and then closing valve 9, while keeping the reactor covered. The NOₓ concentration decreases immediately when it flows...
through the reactor because of the adsorption of NO\textsubscript{x} onto the surface of the sample. Then the concentration increases again to the initial concentration within several minutes, 5 - 10 minutes is usually enough here, although it can be influenced by the NO\textsubscript{x} initial concentration, flow rate, and the surface structure of the tested sample. This phenomenon also indicates that no photocatalytic oxidation reaction takes place in the dark. After this the photocatalytic oxidation reaction is started by uncovering the reactor to allow the visible light to irradiate the sample. The PCO reaction lasts for 30 minutes and is ended by covering the reactor to stop the light irradiation.

**Results analysis**

The photocatalytic oxidation reaction takes place immediately when the sample is exposed to the visible light. After reaching the maximum degradation rate, the process will slightly slow down and reach a stable conversion condition finally. NO\textsubscript{2} is generated during the oxidation reaction of NO. However, not all the produced NO\textsubscript{2} can be oxidized to HNO\textsubscript{3} because a small part of it is released into the air due to desorption. So, the NO\textsubscript{x} conversion is calculated as the PCO efficiency indicator of the samples:

\[
\text{NO}_x,\text{conv} (\%) = \frac{C_{\text{NO}_x, \text{in}} - C_{\text{NO}_x, \text{out}}}{C_{\text{NO}_x, \text{in}}} \times 100\%
\]  

where \(C_{\text{NO}_x, \text{out}}\) is defined as the average NO\textsubscript{x} concentration during the last 5 minutes of the measurement (ppb).

The PCO tests are performed using different initial concentration proportions of NO\textsubscript{x}, but always with a total amount of 500 ppb. Fig. 2 left shows the influence of varying the initial pollutant concentration on the outlet concentration of both nitrogen oxides.

![Fig. 2: Left: Effect of the initial pollutant concentration on the NO\textsubscript{x} conversion; right: NO\textsubscript{x} conversion versus NO\textsubscript{x} concentration.](image)

Increasing the initial concentrations results in higher removal rates for NO and NO\textsubscript{2}, indicating that the PCO process does not privilege the degradation of one molecule over the other. This is one characteristic of the hydroxyl radicals, as they can oxidize a wide number of chemicals. Nevertheless, there is one difference between the PCO of the two molecules: increasing the NO concentration yields more NO\textsubscript{2}, up to a point where the
outlet concentration of NO$_2$ is higher than at the inlet. This behavior reduces significantly the overall NO$_x$ conversion, as shown in the Fig. 2 right. This happens because the complete oxidation of NO takes two intermediate steps of first to NO$_2$ [8], which then can either be oxidized to NO$_3^-$ or be desorbed into the carrier gas.

Another difference can be noticed from Fig. 2 left when the inlet air stream carries only NO or NO$_2$. When there is only NO at the inlet, there is a significant production of NO. When the inlet air stream carries only NO$_2$ at 500 ppb, there are still traces of NO at the inlet. The initial amount of NO appears due to the fact that the NO$_2$ supply cylinder contains trace amounts of NO, and is shown in the analyzer as well as confirmed by the certificate from the gas provider. However, the outlet NO concentration slightly increases from 10.3 to 16.3 ppb. The generation of NO may occur because NO$_2$ can react with water vapor producing nitric oxide as well as nitric acid:

$$3\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{NO} + 2\text{HNO}_3 \tag{2}$$

Although the formation of NO by the homogeneous reaction shown in Equation (2) may occur, it is very small compared to the photocatalytic reactions [8].

The water adsorbed on the photocatalyst reacts with the hole and generates hydroxyl radicals (OH$^-$), which then oxidizes pollutants. It has been reported that the PCO reaction is typically governed by the generation of the hydroxyl radicals [9], although reactions that generate other radicals, like chlorine, could also display high reaction rates [10]. When there is an absence of water vapor, the PCO is seriously retarded, for instance when the target pollutant is formaldehyde [11] or acetone [12]. However, it has also been stated that an excessive amount of water vapor on the catalyst surface will inhibit the reaction rate, because the water vapor competes with pollutants for adsorption sites on the photocatalyst, thus reducing the pollutant removal rate [6].

The ASHRAE standard 55-2004 specifies that to decrease the possibility of discomfort due to low humidity, the dew point temperature should not be less than 2.8°C, which equals to 31% RH in 21°C. The upper dew point limit is specified to 16.7°C, which equals to 76% RH in 21°C. Therefore, here the relative humidity is varied between 40% and 70% to investigate its effect on the PCO behavior.

Fig. 3: Influence of relative humidity on the NO$_x$ conversion (Left: $C_{\text{NO,in}} = 400$ ppb, $C_{\text{NO}_2,\text{in}} = 100$ ppb; right: $C_{\text{NO}_2,\text{in}} = 400$ ppb, $C_{\text{NO},\text{in}} = 100$ ppb).
Fig. 3 shows the influence of the relative humidity on the outlet concentrations of both nitrogen oxides. The relative humidity however, within the range specified, does not have any significant influence on the outlet concentration of NO: the NO conversion remains at stable levels of 9.5% at 40% RH to 9.4% at 70% RH when the initial concentration is 400 ppb. In the case of NO initial concentration of 100 ppb, the NO conversion very slightly varies from 8.3% at 40% RH to 8.8% at 70% RH. For NO₂, the relative humidity indeed influences its conversion: at 400 ppb, NO₂ degradation decreases from 11.1% at 40% RH to 7.4% at 70% RH. This behavior could be explained by the fact that water molecules compete with NO₂ for the adsorption of active sites, decreasing the reaction efficiency. However, when NO₂ is at 100 ppb, something different happens: the NO₂ conversion is always negative, meaning there is more production of the nitrogen dioxide rather than its degradation. This is explained by the generation of more NO₂-intermediate molecules. The conclusion from this phenomena is that at increasing RH, the water vapor is inducing desorption of the NO₂ molecules from the surface.

The degradation rate is always higher when NO₂ is the abundant molecule in the mixture. The slope of the abundant-NO₂ trend line is steeper than the one with abundant NO, which also confirms the higher influence water vapor plays on NO₂ than on NO degradation. This generalized decrease in the NOₓ conversion has also been reported [5,6]. Hüskens et al. [5], for instance, reported a linear decrease in the NO conversion, within an investigation range of 10% to 80% RH. They also reported that the RH values higher than 45% result in higher NO₂ concentrations, which is exactly the same behavior as found here. What could be explained here is that the authors used a higher concentration of pollutants, so the pollutant molecules have a larger chance of reaching the active sites, decreasing the molecular competition and increasing the reaction rates. The difference of results in literature may be due to the influence of different substrates used. Martinez et al. [13] compared the photo-degradation of NO using glass and mortar as substrates and found different results: within a RH range of 0-74%, the optimal humidity level for the degradation of NO using glass as the substrate is found to be 32%. Using mortar, no optimal humidity level could be identified due to the fact that the excess water is absorbed by the substrate, reducing molecular competition. In this research a paper-based wall covering is used, which could be the reason why the decrease in the NOₓ concentration is small when varying the RH: when NO is the dominant pollutant, the NOₓ conversion decreases from 6.8% at 40% RH to 4.9% at 70% RH. When NO₂ is the dominant pollutant, the NOₓ conversion decreases from 10.6% at 40% RH to 7.7% at 70% RH. While in both cases there is a decreasing trend of the NOₓ conversion, the variation is small, and may indicate that the adsorption of excess water on the substrate decreases the impact of the molecular competition on active sites.

After reviewing the influence of certain variables on the NOₓ conversion, it is clear that in every case, the conversion is considerably higher when the NO₂ is the dominant nitrogen oxide in the mixture. The purpose of maintaining the concentration of NOₓ fixed at 500 ppb every time while varying the pollutants proportions is more to assess mixture variations rather than to assess the absolute bulk concentration of pollutants. The result is clear that NO₂ is degraded more efficiently than NO. The pathway to a
nitrate oxidation takes just one reaction step, while the oxidation of NO has first to undergo a conversion to NO₂.

Conclusions

This paper addresses the indoor air purification using heterogeneous photocatalytic oxidation. A photocatalytic oxidation test set-up was developed following the ISO standard 22197-1:2007 as a reference. A novel functional photocatalytic wall covering was produced. Using NOₓ as the target pollutant, the PCO experiments were carried out in indoor air conditions. The following conclusions are drawn:

- The experimental results indicate that the PCO is an effective indoor air purification technology. All PCO experiments were carried out at ambient conditions under visible light, which shows its convenience for the indoor air purification.
- Lower initial NO concentration shows a higher NOₓ conversion. However, a longer reaction time is needed for the photocatalytic oxidation of NO with a very low initial concentration.
- Water plays a very complex role in the PCO process. It is the source of the hydroxyl radical generation, but it also competes with other reactants for the active surface occupation.
- The overall NOₓ conversion is always higher when NO₂ is the abundant pollutant no matter which test parameter is varied, which is a favorable outcome since NO₂ is more toxic than NO. The difference in conversion occurs because NO₂ only needs to undergo, during the PCO reaction, one oxidation step to reach the nitrate form, while NO is oxidized via the intermediate NO₂ to nitric acid. Also, when NO₂ is the only pollutant in the stream, there is a slight generation of NO, indicating the possible presence of homogeneous reactions.

Acknowledgements


References:


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