Photocatalytic Concrete Stones Containing TiO₂ for Atmospheric NOₓ Removal

In the present work the degradation of NOₓ compounds employing concrete paving stones provided with TiO₂ to be applied in road construction is studied. The experiments were carried out in a photoreactor designed according to the standard ISO 22197-1 (2007) to assess these kind of photocatalytic materials. A kinetic model is proposed to describe the photocatalytic reaction of NO and NO₂ and the influence of several parameters that can affect the performance of these stones.

Keywords: heterogeneous photocatalysis, air purification, concrete roads, nitrogen oxides, kinetic model.

Introduction

Heterogeneous photocatalysis represents an emerging environmental control option for the efficient removal of chemical pollutants and it can be applied to water and air purification. This process involves a nano-solid semiconductor catalyst, regularly titanium dioxide (TiO₂), which is activated with ultraviolet light of the appropriate wavelength. For various reasons repetitively reported, titanium dioxide in the form of anatase has been the preferred choice due to its strong oxidizing power under UV irradiation, its chemical stability and the absence of toxicity. These reactions are very attractive for treating pollution problems because: (1) in the vast majority of the cases transform pollutants into innocuous products and (2) have very low selectivity, thus permitting the treatment of a wide range of contaminants.

Nitrogen oxides (NOₓ) is the generic term for a group of highly reactive gases, most of them emitted in air in the form of nitric oxide (NO) and nitrogen dioxide (NO₂). Nitrogen oxides form when fuel is burned at high temperatures, as is the case in combustion processes in automobiles. NOₓ causes a wide variety of health and environmental impacts, like the formation of tropospheric ozone and urban smog through photochemical reactions with hydrocarbons. Furthermore, NOₓ together with SOₓ (sulfur dioxide and sulfur trioxide) is the major contributor to the “acid rain”, one of the most serious environmental problems across the world.

The European Union (EU) has taken important steps over the past decade leading to a decrease in the emissions to air and water of a number of pollutants. One of its directives (1999/30/EC) /1/ establishes limit values for concentrations of sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air. Some of the pollutant emissions have since become more or less manageable; however particulates, NOₓ and smog are still problematic.

To date, a number of researchers have investigated the dynamics of the photocatalysis of nitrogen oxides. While some of the NOₓ control methodology is to reduce NOₓ back to N₂ /2/, another approach is to oxidize NO decomposition to NO₂, and then NO₂ to
NO$_3$H through the hydroxyl radical attack generated during the photocatalyst activation stage /3-5/. The development of innovative materials that can be easily applied on structures, with both de-soiling and de-polluting properties, is a significant step towards improvements of air quality. The use of TiO$_2$ photocatalyst in combination with cementitious and other construction materials has shown a favorable effect in the removal of nitrogen oxides /6/.

In the present work, the degradation of NO$_x$ compounds employing concrete paving stones with TiO$_2$ to be applied in road construction is studied experimentally and theoretically. The experiments were carried out in a photoreactor designed according to standard ISO 22197-1 (2007) /7/ to assess these kind of photocatalytic materials employing NO as the pollutant source. Furthermore, a kinetic model is proposed to describe the photocatalytic oxidation of NO$_x$ (NO and NO$_2$). A reaction rate expression for the oxidation of NO as well as for the appearance and disappearance of NO$_2$ are postulated and the kinetic parameters are determined employing the experimental data. In addition, the influence of several parameters that can affect the performance of these stones, such as NO inlet concentration, reactor height and flow rate is studied, for constant relative humidity, temperature and irradiance. Finally, the model predictions with the estimated kinetic constants are compared with the experimental results obtaining a good agreement between them.

**Experimental setup**

The standard ISO 22197-1 (2007) /7/ serves as a sound basis for measurements, its recommendations were largely followed for the practical conduction of the present study. The applied apparatus is composed of a planar reactor cell housing the concrete stone sample, a suitable UV-A light source, a chemiluminescent NO$_x$ analyzer, and an appropriate gas supply (Figure 1).

![Experimental setup](#)

Table 1 shows the main characteristics, dimensions and operating conditions of the experimental setup that were employed to carry out the NO photocatalytic degradation experiments.
The kinetic expression proposed for the NO degradation reaction rate is the corresponding to the Langmuir-Hinshelwood model /4, 5/ which is widely employed for the photocatalytic degradation of a number of contaminants /8, 9/. Nevertheless, only few times the photocatalytic kinetic model includes the reaction dependence with other reactants and/or intermediates concentrations (in this case NO₂) /4/. Moreover, the reaction rate should be expressed as a superficial rate for a gas-solid heterogeneous system /10/. Following this model, applied to a heterogeneous reaction, the Langmuir-Hinshelwood kinetic model for NO disappearance rate and NO₂ appearance / disappearance rate for irreversible reactions, per unit area of active surface and for constant relative humidity and irradiance reads:

\[
r_{\text{NO}} = -\frac{k_1 K_{\text{NO}} C_{\text{NO}}}{1 + K_{\text{NO}} C_{\text{NO}} + K_{\text{NO}_2} C_{\text{NO}_2}}
\]

\[
r_{\text{NO}_2} = -\frac{k_2 K_{\text{NO}_2} C_{\text{NO}_2}}{1 + K_{\text{NO}} C_{\text{NO}} + K_{\text{NO}_2} C_{\text{NO}_2}} + \frac{k_1 K_{\text{NO}} C_{\text{NO}}}{1 + K_{\text{NO}} C_{\text{NO}} + K_{\text{NO}_2} C_{\text{NO}_2}}
\]

Where \( r_{\text{NO}} \) and \( r_{\text{NO}_2} \) are the superficial reaction rate (mole dm\(^{-2}\) min\(^{-1}\)) of the NO disappearance and NO₂ appearance/disappearance. \( C_{\text{NO}} \) and \( C_{\text{NO}_2} \) are the corresponding molar concentration (mole dm\(^{-3}\)) of NO and NO₂ (which are related to the NO and NO₂ concentrations in ppm through the air volume under normal condition of 1 bar and 20º C). \( k_1 \) and \( k_2 \) are the corresponding reaction rate constants (mole dm\(^{-2}\) min\(^{-1}\)) for NO and NO₂. \( K_{\text{NO}} \) and \( K_{\text{NO}_2} \) are the adsorption equilibrium constant (dm\(^3\) mole\(^{-1}\)) for NO and NO₂ respectively, assuming that these species compete for the same active sites.

The NO and NO₂ balance equations for a plug flow reactor read:
\[
v_{\text{air}} \frac{dC_{\text{NO}}}{dx} = a_v r_{\text{NO}}
\]  
\[
v_{\text{air}} \frac{dC_{\text{NO}_2}}{dx} = a_v r_{\text{NO}_2}
\]  

Where \( v_{\text{air}} \) is the air velocity (dm min\(^{-1}\)) in the reactor and \( a_v \) is the active surface area per unit reactor volume (dm\(^{-1}\)). The reactor inlet conditions are:

\[
C_{\text{NO}}(x = 0) = C_{\text{NO,in}}
\]  
\[
C_{\text{NO}_2}(x = 0) = 0
\]

**Results**

To solve the coupled NO and NO\(_2\) mass balance with the complete kinetic expression, a discretization of the differential equation can be applied (Euler method). The optimization of all kinetic parameters present in the obtained algebraic equations can be achieved employing the “solver” tool of Excel. The result of this estimation and the 95% confidence intervals of the parameters are shown in Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>95% Confidence Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(k_1) (mole dm(^{-2}) min(^{-1}))</td>
<td>0.47×10(^{-7})</td>
<td>0.01×10(^{-7})</td>
</tr>
<tr>
<td>(K_{\text{NO}}) (dm(^3) mole(^{-1}))</td>
<td>3.40×10(^7)</td>
<td>0.08×10(^7)</td>
</tr>
<tr>
<td>2(k_2) (mole dm(^{-2}) min(^{-1}))</td>
<td>15.38×10(^{-7})</td>
<td>0.02×10(^{-7})</td>
</tr>
<tr>
<td>(K_{\text{NO}_2}) (dm(^3) mole(^{-1}))</td>
<td>1.24×10(^7)</td>
<td>0.13×10(^7)</td>
</tr>
</tbody>
</table>

(*\(^\) number of data

It is possible to analyze the effect of different operating variables on the system by resorting the estimated kinetic parameters from the complete model. This analysis can include a comparison between simulated values obtained with the model and experimental measurements.

Figure 2 shows the model predictions and the experimental data corresponding to the NO and NO\(_2\) outlet concentration in function of the NO inlet concentration to the reactor for two different flow rates. When the inlet concentration of NO increases, both NO and NO\(_2\) outlet concentration rise as well. However, as expected, decreasing the initial concentration of the pollutant the final conversion of the reacting system increases.
The effect of the flow rate is possible to analyze comparing Figures 2 and 3. When the flow rate is increased, the resident time in the reactor decreases. Therefore, for low flow rates, a larger conversion of the pollutant is observed.

**Fig. 2**

Model predictions vs. experimental data. NO and NO2 outlet concentration in function of the NO inlet concentration. RH = 50%, E = 10 W m⁻². Q = 3 l min⁻¹.

**Fig. 3**

Model predictions vs. experimental data. NO and NO2 outlet concentration in function of the NO inlet concentration. RH = 50%, E = 10 W m⁻². Q = 5 l min⁻¹.

**Conclusions**

In the present work, a kinetic study of the photocatalytic degradation of nitrogen oxides was conducted. A heterogeneous kinetic expression for the NO degradation and for the NO2 appearance/disappearance was proposed. Several experiments were carried out according to a suitable ISO standard for photocatalytic materials assessment employing only NO as a contaminant. Different operating conditions were selected to carry out the experiments (NO inlet concentration, reactor height, flow rate) remaining constant relative humidity, temperature, and irradiance (50%, 20° C and 10 W m⁻²). Employing these experimental data and the kinetic expressions, the kinetic parameters for NO and NO2 were estimated for a complete solution of the governing equations in the reactor. In all cases, a very good correlation between the experimental data and the computer simulation with the estimated kinetic parameters was obtained, allowing to explain the degradation of NO and the apparition of NO2 in this kind of systems.
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Literature


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