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Standardization methods for testing photo-catalytic air remediation materials: Problems and solution

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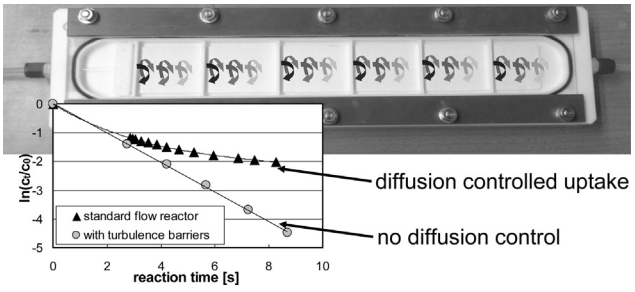
HIGHLIGHTS

- Known photo-catalytic air remediation test methods have severe shortcomings.
- No judgement about the environmental impact of photo-catalytic materials possible.
- A new test method for air remediation by photo-catalytic materials is proposed.
- The concept of the uptake coefficient is used for a modified bed flow photo-reactor.
- The use of environmentally important reactants and products is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, problems of different methods used for quantifying the air remediation activity of photo-catalytic active surfaces are described. It is demonstrated that in bed photo-reactors (e.g. ISO), transport limitations can lead to underestimation of the activity, if fast heterogeneous reactions are investigated. In contrast, in stirred tank photo-reactors (e.g. UNI), complex secondary chemistry may lead to an overestimation of the photo-catalytic remediation of NO_x, if NO_2 is also present. In addition, the quantities, used for ranking the photo-catalytic air remediation activity in the different methods are not independent of the applied experimental conditions, and thus, make any intercomparison between the different methods or the extrapolation to atmospheric conditions very difficult. Furthermore, unrealistic high NO_x levels are used, for which the chemical kinetics may already be affected by surface saturation problems. Finally, it is shown that the use of only nitrogen monoxide (NO) will not enable users to judge about the quality and effectiveness of a photo-catalytic surface for improving air quality, since surfaces which are active toward NO may be completely non-reactive toward other important atmospheric pollutants. A modified method for quantifying the air remediation activity of photo-catalytic surfaces is proposed here to overcome these problems.

1. Introduction

Besides its self-cleaning properties, it is known since almost 100 years that titanium dioxide (TiO_2) acts as a photo-catalyst that can decompose pollutants under UV radiation (Renz, 1921). TiO_2 exists in different modifications of which the anatase form is believed to

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be most active for photo-catalytic reactions (Linsebigler et al., 1995). The absorption of UV radiation of typically <390 nm leads to the formation of an electron in the conduction-band (cb) and a corresponding valence-band (vb) hole:

$$TiO_2 \xrightarrow{+h\nu} h^+_{vb} + e^-_{cb}, \quad (1)$$

which can initiate both, reduction (e^-_{cb}) and oxidation (h^+_{vb}) reactions of adsorbed species, e.g. of oxygen and water. These reactions form highly reactive intermediates such as O_2^-/HO_2 and OH, which can decompose adsorbed pollutants, like nitrogen oxides (NO_x = NO + NO_2) or volatile organic compounds (VOCs). After reaction or recombination of e^-_{cb} and h^+_{vb}, TiO_2 is reverted to its initial form and thus, acts as a catalyst.

During the last two decades several commercial photo-catalytic products have been developed for indoor and outdoor applications, e.g. photo-catalytic concrete, mortar, paint, window glass and roof tile surfaces (Allen et al., 2005; Cassar, 2005; Fujishima, 2005; Guerrini and Peccati, 2007; Maggos et al., 2007, 2008; Salthammer and Fuhrmann, 2007; Auvinen and Wirtanen, 2008; Beeldens, 2008; Hüsken et al., 2009; Mo et al., 2009; Langridge et al., 2009; Ballari et al., 2010; Zhang et al., 2011; Guerrini, 2012). When these products were tested in the atmosphere, very different results were obtained. While for example in model or real street canyon experiments high NO_x air remediation of 26–66% (Guerrini and Peccati, 2007) and 40–80% (PICADA, 2006) was reported, the measured NO_x reduction was below the detection limit in a recent field project using a photo-catalytic noise barrier at a motorway in the Netherlands (IPL, 2010). The contradictory results can be explained by differences in the transport limitation, geometry of the field site, positions of the sampling inlets and prevailing environmental conditions, like irradiance level, humidity or frequency of removal of reaction products by rain wash off. For example, in the PICADA project (PICADA, 2006), the very narrow model street canyon set-up resulted in an unrealistically high surface to volume ratio (*S*/*V*). Since the rate of a heterogeneous reaction is directly correlated to *S*/*V*, extrapolation to typical urban street canyon conditions only results in an expected reduction of a few percent (Laufs et al., 2010). In addition, if pollutants are measured very close to the photo-catalytic surface (Guerrini and Peccati, 2007), gradients may lead to a strong overestimation of the photo-catalytic reduction when compared to typical sampling heights of environmental measurement stations (e.g. 3 m). Accordingly, more studies on the photo-catalytic air remediation under realistic environmental conditions are necessary to determine typical pollution reduction.

Typically, photo-catalytic air remediation is used to decompose harmful gaseous pollutants (NO_x, VOCs) into less harmful products, which are either adsorbed on the surface (e.g. nitrate, Laufs et al., 2010) or in the gas-phase (e.g. CO_2, Boulamanti and Phillippopoulos, 2009). The photo-degradation of NO_x and VOCs has a positive environmental impact, since both classes of pollutants can be directly harmful (e.g. NO_2 or benzene). In addition, they can also indirectly cause health problems through the formation of harmful reaction products via complex secondary chemistry (e.g. photo-chemical formation of ozone during summer smog, see Finlayson-Pitts and Pitts, 2000). Because of the very large detrimental environmental impact of NO_2, threshold limit values have been implemented for this compound. These limits are, however, typically exceeded in Europe under urban conditions (Carslaw et al., 2007) the reasons of which are still under discussion (Kurtenbach et al., 2012). Accordingly, a major proposed use of photo-catalysis has been its application to reduce, in particular, NO_x in the urban atmosphere.

However, besides the expected positive impacts, also the formation of harmful reaction products is well documented. For example, in the reaction of nitrogen dioxide (NO_2) on pure photo-catalysts or on self-cleaning window glass surfaces, significant formation of nitrous acid (HONO) was observed (Gustafsson et al., 2006; Ndour et al., 2008; Beaumont et al., 2009; Monge et al., 2010), which is even more harmful than NO_2 (Pitts, 1983). In addition, on photo-catalytic indoor paints oxygenated hydrocarbons (e.g. formaldehyde) can be formed under irradiation, which is explained by intermediates of the photo-catalytic degradation of VOCs or the organic binder (Auvinen and Wirtanen, 2008). Thus, careful laboratory work and optimization of commercial photo-catalytic products under relevant atmospheric conditions (irradiance, concentration, humidity) is necessary in order to exclude any negative environmental impacts.

In the present study, currently used or discussed standardization methods to quantify the air remediation activity of photo-catalytic products are presented, problems and uncertainties are discussed and finally, a modified method is proposed which resolves the problems associated with the other methods. Since typically nitrogen monoxide (NO) is used to demonstrate the ability of photo-catalytic surfaces for air remediation, this article also mainly focuses on nitrogen oxides. However, it should be highlighted that also other test methods are available, in which for example, oxidation of different VOCs are tested (see e.g. Mills et al., 2012).

2. Current methods

Different types of photo-reactors have been used in standardization methods, which are partially still under development (UNI, DIN, CEN, ISO) to quantify the photo-catalytic air remediation activity of commercial photo-catalytic materials (Amrhein and Stephan, 2011; Dillert et al., 2012; Mills et al., 2012; Minero et al., 2013). Such a method should be simple to apply by technicians in industry and it should be able to accurately rank a product according to its activity.

Typically, the degradation of nitrogen oxides (NO_x) is studied, since (a) relatively simple and cheap chemiluminescence instruments are available to quantify NO_x (Finlayson-Pitts and Pitts, 2000) and (b) NO_2 is of crucial importance for urban air quality. However, typically only NO is used because of its simpler detection, the typical lower ability to adsorb on reactor surfaces and the slower dark reactions on photo-catalytic surfaces (Sivachandiran et al., 2013), leading to faster response on experimental changes in flow reactors studies. Unrealistically high NO concentrations in the range 500–1000 ppb are applied to reduce the time for establishing the adsorption equilibrium and to increase the precision of the NO_x data obtained from the low-sensitive instruments, which are commonly used. Since the analysis of the reaction products requires more sophisticated analytical instrumentation, typically no reaction products besides NO_2 (e.g. HONO and nitrate) are quantified. Only in the ISO 22197-1 method, adsorbed nitrate is measured after the experiment. Since NO_2 is a typical intermediate during the photo-catalytic oxidation of NO by reaction with O_2^-/HO_2 (Laufs et al., 2010), the photo-catalytic reduction of NO_x and not only of NO is finally quantified by the different methods.

2.1. Bed flow photo-reactors (ISO)

In bed flow photo-reactor experiments, for example in ISO 22197-1 (2007), a humidified NO mixture (50% r.h.) is passed over the flat rectangular sample of typically 5 cm × 10 cm and is irradiated by UV-A light (10 W/m^2 irradiance) through a UV transparent window with a distance to the sample of 5 mm (see