Applied Catalysis B: Environmental 166–167 (2015) 84–90

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

The effectiveness of indoor photocatalytic paints on NO_x and HONO levels

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ARTICLE INFO

Article history:
Received 11 September 2014
Received in revised form 27 October 2014
Accepted 8 November 2014
Available online 15 November 2014

Keywords:
Indoor air
Flow reactor
Heterogeneous reactions
Nitrogen oxides
Nitrous acid

ABSTRACT

There is an increasing concern about the indoor air environment, where we spend most of our time. Common methods of improving indoor air quality include controlling pollution sources, increasing ventilation rates or using air purifiers. Photocatalytic remediation technology was suggested as a new possibility to eliminate indoor air pollutants instead of just diluting or disposing them. Titanium dioxide (TiO_2) is a widely used photocatalyst, which is aimed to eliminate organic and inorganic pollutants.

Here, we demonstrate that indoor photocatalytic paints which contain TiO_2 can substantially reduce the concentrations of nitrogen dioxide (NO_2). We show that the efficiency of nitrogen dioxide (NO_2) removal increases with the quantity of TiO_2 in the range 0–7%. The geometric uptake coefficients increase from 5×10^{-6} to 1.6×10^{-5} under light irradiation of the paints. On the other hand, during the reactions of NO_2 with this paint (7% of TiO_2) nitric oxide (NO) and nitrous acid (HONO) are formed. Nitrous acid (HONO) is an important harmful indoor pollutant and its photolysis leads to the formation of highly reactive OH radicals. Maximum conversion efficiencies of NO_2 to HONO and NO of 15% and 33% were observed at 30% RH, respectively.

A dynamic mass balance model applied to typical indoor environment predicts a steady state mixing ratio of 5.6 ppb of HONO released upon light-induced surface reaction of NO_2 with a photocatalytic paint (7% of TiO_2) and considering the photolysis process as the most important loss of HONO.

The quantity of TiO_2 embedded in the paint is of crucial importance with respect to nitrogen oxides NO_2 remediation, but may also influence the formation of harmful intermediates like nitrous acid (HONO), which should be considered for future optimization of photocatalytic paints aimed for indoor applications.

1. Introduction

The influence of indoor air quality on human health is increasingly considered, since people spend the majority of their life indoors. During the last 20 years the design and construction of buildings was radically modified to improve the building energy efficiency and to lower running costs. On the other hand, the new building advances have resulted in more airtight modern home environments, offices, schools and hospitals among others. Thus, the levels of airborne indoor pollutants can reach much higher values compared to outdoor environments [1]. Regarding the gas-phase pollutant NO_2, indoor mixing ratios in the range between 15 and 200 ppb were reported [2–4]. In some indoor environments such as industrial workplaces and homes equipped with gas stoves, peak NO_2 mixing ratios may reach at 1–2 ppm with a 24-h average NO_2 mixing ratio of up to 500 ppb [5].

Weschler and Shields [6] stated that heterogeneous chemistry may play an important role in the indoor environment because the surface to volume ratios (S/V) (m^{-1}) are much higher within indoor settings [4,7] increasing the importance of NO_2 surface reactions. There are several studies reporting "dark" HONO formation during the heterogeneous reactions between gas-phase NO_2 and water layers adsorbed on indoor surfaces [8]. Two recent studies [9,10] have shown that HONO can be formed upon heterogeneous reactions of NO_2 with indoor surfaces in presence of UV light ($300\,nm < \lambda < 400\,nm$).

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http://dx.doi.org/10.1016/j.apcatb.2014.11.011
0926-3373/

To improve the indoor air quality, photocatalytic materials have been suggested as a new remediation technology, for which titanium dioxide (TiO_2) nanoparticles are either deposited at the surface of the material (such as glass, pavement . . .) or embedded in paints or concrete.

These photo-catalysts, typically activated by UV light (<390 nm) are able to oxidize adsorbed pollutants forming less harmful products, like e.g. CO_2 or adsorbed nitrate. Despite the apparent promise of these materials, extensive trials by authorities across the developed countries have produced relatively little solid evidence in support of their effectiveness for efficient indoor air remediation. Nevertheless, the interest in their extensive application continues to grow [11].

Indeed, several studies claimed the efficiency of TiO_2 nanoparticles to remove the atmospheric pollutants such as nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds (VOCs) [12–18]. Although some promising results have been obtained in the past, also the formation of harmful intermediates has been observed, like for example aldehydes on photocatalytic indoor paints from the decomposition of the organic binder or from reaction of VOCs [17,19] which can certainly affect the durability of the paint. In addition, Langridge et al. [20] have shown that the uptake of NO_2 *on self-cleaning window glass containing* TiO_2 does not represent a permanent sink for gas-phase NO_2, but rather provides a strong daytime source of harmful nitrous acid (HONO). In contrast, Laufs et al. [21] observed a degradation of nitrous acid (HONO) induced by commercial photocatalytic paints aimed for outdoor building facades. Especially, the potential formation of HONO raises important questions regarding the use of photocatalytic materials, because HONO is readily photolyzed leading to OH radical formation [22], which in turn can induce a series of chemical reactions and further aggravate the indoor air quality through formation of secondary pollutants such as ozone and VOCs oxidation products [23]. In addition, HONO is also directly harmful, since its reaction with the amino groups of the nucleotides forms cross-links between the double helix of the DNA leading to mutagenic properties [24–27]. Also, the gas-phase reactions of HONO with amines lead to the formation of nitrosamines in the air [28,29], which are known to exhibit mutagenic and carcinogenic properties [30]. Finally, Sleiman et al. [31] have shown that surface reactions of adsorbed nicotine with gaseous HONO also leads to the formation of nitrosamines. It is noteworthy to mention that HONO was identified and detected for the first time within indoor environments by James N. Pitts, Jr., a prominent scientist in the field of atmospheric chemistry [32,33].

Recently, a new generation of photocatalytic indoor paints containing TiO_2 nanoparticles, has been launched on the market. As these new paints have not yet been rigorously tested, in the present study, optimum conditions with respect to NO_x remediation and HONO formation on photocatalytic paints were studied. For this purpose, in collaboration with the industrial partner ALLIOS we tested new photocatalytic paints with different quantities of TiO_2 nanoparticles aimed for indoor application which are sensitive to UV light in the region between 300 and 400 nm.

2. Materials and methods

2.1. Preparation of photocatalytic paints

The photocatalytic paints were produced by the manufacturer ALLIOS. The type of the photocatalyst used is TITANE P2 in anatase form with a TiO_2 nanoparticles content of ~85%.

TITANE P2 represents a very high purity ultrafine TiO_2 powder with specific surface of 350 m^2/g. In all paints photocatalytically inactive TiO_2 particles in micrometric size are present at the same quantity of 13.4% (w/w). A mixture of grinded additives, called slurry, was prepared with a mass fraction of 35% (w/w) active TiO_2 nanoparticles.

Then, 10, 15 and 20% of this slurry was mixed with the other paint constituents (micrometric TiO_2, and architectural constituent of the paint, i.e. calcium carbonate, $CaCO_3$) to reach 3.5, 5.25 and 7% of photocatalytic active TiO_2 nanoparticles (w/w), respectively. Note that, the photocatalyst in the paint is sensitive to the UV light. The replacement of $CaCO_3$ with the slurry induces a change in the density which in turn has an impact on the paint stability. Therefore, the maximum allowed mass fraction of TiO_2 nanoparticles in the paint is 7%. Note, that the slurry is absent in the paint without TiO_2 nanoparticles.

The prepared paint was then applied *on one side of* glass plates with dimensions 29 cm × 1.9 cm (length × width) by a well-established *drying* procedure developed by the manufacturer. This procedure allows homogeneous, uniform and reproducible wet film with 100 μm thickness. The glass plates were stored during 21 days in an oven ventilated by clean air at 23 °C and 55% relative humidity. The prepared glass plates were then delivered to our laboratory in order to assess the impact of the photocatalytic paints on NO_x and HONO levels. The latter was achieved by studying the NO_2 heterogeneous reactivity in a flow tube photo-reactor.

2.2. Flow tube photo-reactor

The experimental set-up was previously described in detail [9,10]; hence, here only a brief description is given.

The kinetic experiments were performed in a double-wall flow tube photo-reactor connected to a thermostatic bath which allowed operation at different temperatures. The dimensions of the flow reactor were chosen to ensure conditions for gas-phase laminar flow. The flow tube is a cylinder of 131 cm^3 made of borosilicate glass. The glass plate was inserted into the flow tube reactor with the painted side upward oriented. The length of the glass plate is almost identical with the dimension of the flow reactor which allows to be perfectly fitted into the reactor without perturbation of the laminar flow. Inside the flow tube, a movable injector is inserted which allows to vary the exposed length of the paint. The flow tube and six lamps (Philips TL-D 18 W, 340–400 nm, λ_{max} = 368 nm, length = 60 cm) that could be operated individually were placed in a stainless steel box. Because the paints were applied only on one side of the glass plate, the lamps were placed in the following manner: four lamps were mounted on the box above the reactor and two were placed in the upper left and right corner of the box. The spectral irradiance of these lamps was already characterized in our previous study [10] and compared to the solar light intensity which could penetrate indoors which allows to perform the experiments under relevant indoor conditions.

A certified mixture of NO_2 (100 ppm) in Helium (Praxair) was connected to a mixing loop fed by synthetic air (Linde gas 5.0, flow controller, Brooks SLA, 0–500 ml/min) to allow a first dilution before the introduction of the NO_2 through the movable injector (flow controller, Brooks SLA, 0–20 ml/min). In order to simulate realistic indoor conditions all the experiments were performed at 40 ppb of NO_2. A sheath flow of 980 ml/min (Linde gas 5.0, flow controller Brooks SLA 0–1 l/min) was fed to a humidification system before its introduction in the reactor. Humidity was adjusted by splitting this sheath flow in two fluxes controlled by needle valves, one of dry air flow and the other humidified by bubbling through deionised water. A mixing of these two flows at different ratios generated a carrier gas at controlled relative humidity. Downstream of this device, a hygrometer "Hygrolog NT2" (Rotronic) with a