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Report on photocatalytic materials: Studies on byproducts, intermediates and secondary emissions

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Table of contents

0 Executive summary

One of the objectives of workpackage 3 is the development and testing of photocatalytic construction materials able of improving indoor air quality under (indoor) illumination conditions. According to the description of work the potential formation of byproducts during the use of the new developed photocatalytic materials has to be addressed and delivered in form of report (D3.13) that should be reviewed by the ethics and safety board prior to circulation. The present report is based on experiments carried out at JRC premises (Annex 1). A summary of the objectives pursuit and results obtained is given below.

The objective of the research studies carried out at JRC and presented here is to assess the potential formation of by-products during the photocatalytic degradation of priority indoor organic (i.e. toluene) or inorganic (i.e. NO) pollutants using photocatalytically active construction materials in indoor environments. It is known that NO_2 is formed as an intermediate product by the incomplete degradation of NO to nitrate (Ohko et al, 2009), while carbonyl compounds have been described to be formed both as intermediates by the degradation of organic pollutants and as secondary emissions by the degradation of organic constituents/additives in the supporting material (Salthammer et al, 2009; Auvinen et al, 2008; Salthammer et al, 2007) and released to indoor air.

Various types of substrates/materials manufactured by the partners of the consortium have been received and tested at JRC premises. Samples included doped TiO_2 powders, and small (25 x 25 cm^2) and large (1 x 1 m^2) panels of building materials containing various amounts of TiO_2-based photocatalysts. The corresponding materials without photocatalyst additions were also received and tested.

The photocatalytic experiments were carried out in air tight environmental chambers (0.45 m^3 glass exposition chamber and the 30 m^3 environmental chamber -Indoortron-) with controlled atmospheres of inorganic (NO) and organic (toluene) target pollutants at two concentration levels. The photocatalytic materials were irradiated for 6 hours with a Philips Master TL-D Super80 18W/840 lamp to simulate indoor-like illumination conditions. Temperature and relative humidity were fixed at 23 °C and 50%, respectively. Prior to the irradiation of the samples, they were conditioned inside the chambers for 24 h under ventilation (0.5 ach – air change per hour), 23 °C and 50% relative humidity. After conditioning of the sample, the chamber was turned into the static mode to perform the photocatalytic experiment.

Formation of both NO_2 and carbonyl compounds as by-products during the photocatalytic experiments was monitored. An automatic NOx analyzer (Thermo Environmental Instruments Inc. model 42C) was used for the online monitoring of NO and NO_2. Carbonyl compounds were determined by air sampling using SEP-PAK DNPH cartridges and analysis by HPLC-UV.

The study shows that all the tested materials form by-products during the photocatalytic degradation of the target pollutants to a different extent. The amount of originated byproducts depends on several factors such as irradiation intensity, photocatalytic activity and material composition. Under the test conditions of this study formation of NO_2 ranges from 2 to 25 ppbv while formaldehyde concentrations up to 40 $\mu g/m^3$ have been measured.

The concentrations measured are below the guideline values for NO_2 (200ppbv and 40ppbv ppb for short-term and long-term respectively) and formaldehyde (100 µg/m^3 for short term) established recently by WHO (WHO 2010) for public health protection.

Indoor environments are characterized for the coexistence of multiple emission sources responsible of the overall chemical level in the air. Formaldehyde is a well known strong indoor pollutant (USEPA, 2011; Salthammer et al, 2010) emitted from a wide variety of indoor sources such as household products, furniture or smoke. Similarly NO_2 is commonly found in indoor environments and originated mainly from combustion and gas appliances. Reported formaldehyde and NO_2 indoor concentrations in private houses range 15-20 µg m^{-3} (Geiss et al, 2011) and 15-50 µg m^{-3} (WHO 2010) respectively. Considering actual chemical values underlines the necessity to avoid additional sources which might contribute to exceed guideline values. In this sense the formation of NO_2 and/or carbonyl compounds as by-products is an undesirable effect, contributing to the chemical load in indoor environments that should thus be eliminated or minimized as much as possible.

Possible approaches to minimize the formation of such by-products have been considered and illustrated, such as the selection of more stable ingredients used in the preparation of the supporting material in which the photocatalyst is embedded or the irradiation of the final product in the industry prior to its commercialisation.

1 Annex 1: Studies on byproducts, intermediates and secondary emissions from photocatalytic materials.