Journal of Photochemistry and Photobiology A: Chemistry 222 (2011) 304–306

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Short note

Studies on photo-induced NO removal by Mn-doped TiO_2 under indoor-like illumination conditions

C. Cacho[a], O. Geiss[a], J. Barrero-Moreno[a,*], V.D. Binas[b], G. Kiriakidis[b], L. Botalico[c], D. Kotzias[a]

[a] European Commission, Joint Research Centre, Institute for Health and Consumer Protection, Chemical Assessment and Testing Unit, Via E. Fermi 2749, I-21027 Ispra (VA), Italy
[b] Institute of Electronic Structure and Laser, Foundation for Research & Technology-Hellas, 100, N. Plastira St., Vasilika Vouton, 70013 Heraklion, Crete, Greece
[c] CTG Italcementi, Via Gabriele Camozzi 124, I-24121 Bergamo (BG), Italy

ARTICLE INFO

Article history:
Received 2 March 2011
Received in revised form 26 April 2011
Accepted 26 April 2011
Available online 6 May 2011

Keywords:
Photocatalysis
NO degradation
Indoor-like illumination
Mn-doped TiO_2

ABSTRACT

Mn-doped amorphous TiO_2 photocatalyst powders containing 0.1% and 1% Mn (w/w) were tested for oxidation of NO under indoor-like illumination conditions. Only the catalyst containing 0.1% Mn was able to degrade NO efficiently upon irradiation with the indoor-like source (visible light), whereas the one containing 1% Mn was active under solar-like irradiation. Preliminary results from addition of the 0.1% Mn–TiO_2 photocatalyst to calcareous filler commonly used in the formulation of building products demonstrate its ability, in this form too, to degrade NO at concentration levels typically found in indoor environments.

1. Introduction

Since the discovery of the Honda–Fujishima effect in 1972 [1], TiO_2 and ZnO have been extensively investigated as catalysts for photochemical degradation of numerous pollutants [2–8]. However, due to their wide energy band gap (>3 eV), they can only be activated by UV irradiation. In an attempt to use photocatalysis for remediation of indoor air pollution, nowadays research is directed towards development of additives that would reduce the band gap of TiO_2 and ZnO, leading to activation by visible light so that they will then be useful for applications in indoor environments.

Among the different strategies to obtain photocatalysts activated by indoor-like illumination, the most promising results have been achieved by doping photocatalysts with either non-metals (e.g. N, C or S) [9–11] or transition metals (e.g. Fe, Co, Cu, Mn or Au) [12–15].

Ullah and Dutta [16] described preparation of ZnO doped with 1% Mn. The doped photocatalyst proved to be 50 times more efficient than undoped ZnO for degradation of an aqueous suspension of methylene blue using visible light. On the other hand, Hu et al. [17] recently evaluated the photocatalytic activity of TiO_2 co-doped with Mn and N for oxidation of rhodamine B, demonstrating that co-doping was significantly more efficient than just doping TiO_2 with N. This study reports on the efficiency of TiO_2 doped with manganese to degrade inorganic priority pollutants, e.g. NO, upon irradiation with a commonly used indoor light.

2. Methods

0.1% and 1% doped Mn–TiO_2 powders were prepared in accordance with the procedure described in patent GR-20090100724 and patent application PCT/EP2010/070872. Further details on the procedures for synthesis of the powders applied are given elsewhere [18]. Thirty grams of the photocatalyst powder was spread homogeneously in a 0.1 m radius Petri dish and placed in a 0.45 m^3 environmental test chamber in which a controlled atmosphere containing approximately 200 ppbv NO was created. The loading factor achieved under these conditions was around 0.07 m^2/m^3. Furthermore, samples of calcareous filler containing 0%, 5% or 10% of the 0.1% doped Mn–TiO_2 photocatalyst were deposited on 0.25 m × 0.25 m glass panels, giving a loading factor of around 0.14 m^2/m^3 when placed in the 0.45 m^3 test chamber. Prior to irradiation, the photocatalytic material was conditioned for 18 h in the chamber by passing synthetic air at an air change rate of 1 per hour.

During the experiments an atmosphere of 200 ppbv NO was generated in the 0.45 m^3 environmental test chamber with controlled conditions of temperature (23 °C) and relative humidity (50%) in static mode (thorough mixing of the atmospheric constituents in the chamber, using a fan). The lamps selected to activate photocatalysis were an OSRAM UltraVitalux 300 W lamp to simulate solar irradiation and a Philips TL-D Super80 18W-840 lamp to simulate indoor-like illumination. Light intensities over the material surface

---

* Corresponding author. Tel.: +39 0332789863.
E-mail address: josefa.barrero-moreno@jrc.ec.europa.eu (J. Barrero-Moreno).

1010-6030/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2011.04.037

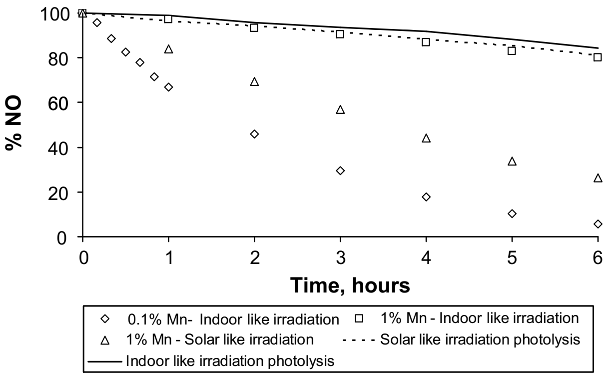

Fig. 1. Comparison of photolytic and photocatalytic decomposition of NO with Mn-doped TiO_2 catalysts containing 0.1% and 1% Mn under indoor- and solar-like illumination.

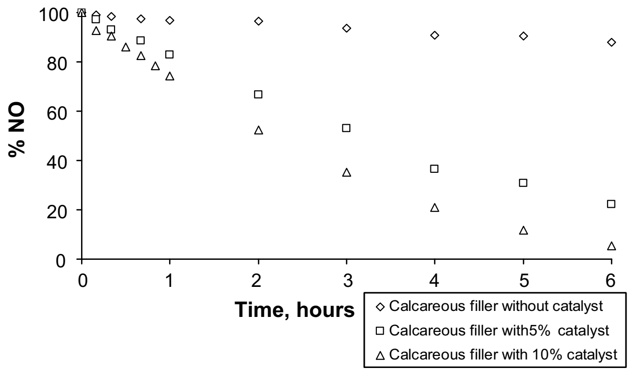

Fig. 2. Photocatalytic decomposition of NO by calcareous filler panels containing 0.1% Mn–TiO_2 photocatalyst. Influence of the amount of the catalyst (PC).

in the visible and UV-A spectral regions, measured with a Delta Ohm HD9021 radiometer, were 31 and 4 W/m^2 for the OSRAM lamp and 3 and 0.038 W/m^2 for the Philips lamp.

The photocatalytic tests were carried out by irradiating the photocatalyst for 6 h, both in powder form and embedded in the calcareous matrix. During this period, the concentration of both NO and NOx in the chamber was analyzed on a periodic basis. To do so, around 1 l of air was sampled from the chamber at selected times (once every hour) and both NO and NOx were analyzed by means of a chemiluminescence NO/NOx gas analyser from Thermo Environmental Instruments.

3. Results

The ability of the Mn-doped TiO_2 photocatalysts to degrade NO was evaluated under both solar- and indoor-like illumination. In order to assess the influence of other depletion mechanisms that could affect the NO concentration inside the chamber, each experiment followed four steps: (1) evaluation of the chamber sink in the absence of the photocatalytic material and in the dark; (2) evaluation of the NO adsorption on the photocatalytic material in the presence of the photocatalyst and in the dark; (3) evaluation of NO photolysis in the absence of the photocatalyst and under irradiation with the same lamps used in the photocatalysis experiments; and (4) evaluation of NO photocatalysis in the presence of the photocatalyst and under irradiation.

This demonstrated that competing depletion mechanisms in the form of adsorption of NO onto the chamber walls or the sample were negligible compared with the degradation due to photocatalysis. The contribution made by the chamber sink or adsorption on the samples was in the 5–10% range in every case. NO photolysis, on the other hand, led to 20% depletion of NO under the OSRAM lamp and 8% under the Philips lamp.

The results (see Fig. 1) clearly indicate that the photocatalyst doped with 0.1% Mn was able to degrade NO by up to 95% under indoor-like illumination, whereas the material doped with 1% Mn was active under solar-like illumination only. According to this result, not only the nature of the dopant material, but also its concentration plays a very important role in the capability of a certain photocatalyst to be active in the visible region. Further research would nonetheless be required in this field in order to better understand how the dopant concentration influences the band-energy gap in order to better design visible active photocatalysts.

Partial inactivation (around 10% per cycle) of both photocatalysts was observed after consecutive photocatalytic cycles. This can be attributed to the adsorption of HNO_3 formed during the photocatalysis of NO onto the catalyst occupying active photocatalyst centres. This effect had already been observed by Ohko et al. for photocatalysis of NO and NO_2 using pure anatase TiO_2 [19,20].

After confirming the photocatalytical activity of the 0.1% Mn-doped TiO_2 powder under indoor-like illumination, two small (0.25 m × 0.25 m) glass panels were prepared containing 5% and 10% (w/w) of the 0.1% Mn-doped TiO_2 photocatalyst embedded in calcareous filler. As can be observed from the data in Fig. 2, when added to a building material matrix, the photocatalyst still remains active for degradation of NO. The activity of these preparations is directly correlated with the amount of catalyst added. After irradiation for 6 h with the Philips lamp, NO was degraded efficiently in the presence of panels containing 5% and 10% of photocatalyst, by up to 80% and 95% respectively. NO_2 equivalent concentration, calculated as the difference between the concentrations of NOx and NO inside the chamber, was maximum after 4–5 h of irradiation, and showed a very slowly decrease during the rest of the photocatalytic experiments.

As previously described [19], first-order kinetics was followed for photocatalysis of NO. Photocatalytic rates, expressed as micrograms of NO converted per square metre of material per second, were calculated as 0.08 and 0.12 during the first hour (Table 1). It is worth adding that the inactivation observed in the pure Mn-doped TiO_2 powders was demonstrated to be negligible when they were added to the calcareous filler.

Table 1
Photocatalytic rates (μg/m^2 s) and photocatalytic (after 6 h of irradiation) degradation (%) of NO under the different experimental conditions.

% Mn in photocatalyst	% doped photocatalyst embedded in calcareous filler	Irradiation type	Photocatalytic rate (μg/m^2 s)	% NO photodegraded (6 h)
1	Pure powder	Solar like	0.09	88
		Indoor like	0.02	11
0.1	Pure powder	Indoor like	0.18	95
	0	Indoor like	0.02	12
	5	Indoor like	0.08	80
	10	Indoor like	0.12	95

4. Conclusions

A Mn-doped TiO_2 photocatalyst containing 0.1% Mn (w/w) was successfully applied for photocatalytic degradation of NO under indoor-like illumination conditions. After it was added to a calcareous matrix, the photocatalyst was able to degrade up to 95% of NO after 6 h of irradiation, without any significant photocatalyst inactivation.

Results from these experiments demonstrate that, with selection of both the appropriate dopant and its concentration, the photo-assisted elimination of air pollutants is a promising technique for remediation purposes in indoor environments too.

Acknowledgements

The authors wish to acknowledge the funding received under the FP7 NMP ‘Clear-up’ IP project no. 211948.

References

[1] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (1972) 37–38.

[2] J. Zhao, X.D. Yang, Photocatalytic oxidation of indoor air purification: a literature review, Build. Environ. 38 (2003) 645–654.

[3] A.G. Agrios, P. Pichat, Study of the art and perspectives on materials and applications of photocatalysis over TiO_2, J. Appl. Electrochem. 35 (2005) 655–663.

[4] S. Wang, H.M. Ang, M.O. Tade, Volatile organic compounds in indoor environment and photocatalytic oxidation: state of the art, Environ. Int. 33 (2007) 694–705.

[5] T. Maggos, J.G. Bartzis, P. Leva, D. Kotzias, Application of photocatalytic technology for NO_x removal, Appl. Phys. A 89 (2007) 81–84.

[6] U.I. Gaya, A.H. Abdullah, Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems, J. Photochem. Photobiol. C 9 (2008) 1–12.

[7] J. Mo, Y. Zang, Q. Xu, J.J. Lamson, R. Zhao, Photocatalytic purification of volatile organic compounds in indoor air: a review, Atmos. Environ. 43 (2009) 2229–2246.

[8] S. Rehman, R. Ullah, A.M. Butt, N.D. Gohar, Strategies of making TiO_2 and ZnO visible active, J. Hazard. Mater. 170 (2009) 560–569.

[9] E.M. Rockafellow, L.K. Stewart, W.S. Jenks, Is sulphur-doped TiO_2 an effective visible light photocatalyst for remediation? Appl. Catal. B 91 (2009) 554–562.

[10] W.K. Jo, J.T. Kim, Application of visible light photocatalysts with nitrogen-doped or unmodified titanium dioxide for control of indoor-level volatile organic compounds, J. Hazard. Mater. 164 (2009) 360–366.

[11] Y. Ao, J. Su, D. Fu, C. Yuan, Synthesis of C, N, S-tridoped mesoporous titania with enhanced visible light induced photocatalytic activity, Micropor. Mesopor. Mater. 122 (2009) 1–6.

[12] H.M. Song, J.M. Ko, J.H. Park, Hybrid photoreactive magnet obtained from Fe_3O_4/TiO_2 composite nanoparticles, Chem. Lett. 38 (2009) 612–613.

[13] N. Bengtsson, M. Castellote, M.J. López-Muñoz, L. Cerro, Preparation of co-doped TiO_2 for photocatalytic degradation of NO_x in air under visible light, J. Adv. Oxid. Technol. 12 (2009) 55–64.

[14] L. Andronic, B. Hristache, A. Enesca, M. Visa, A. Duta, Studies on titanium oxide catalyst doped with heavy metals (cadmium, copper and nickel), Environ. Eng. Manage. J. 8 (2009) 747–751.

[15] A. Kafizas, S. Kellici, J.A. Darr, I.P. Parkin, Titanium dioxide and composite metal/metal oxide titania thin films on glass: a comparative study of photocatalytic activity, J. Photochem. Photobiol. A 204 (2009) 183–190.

[16] R. Ullah, J. Dutta, Photocatalytic degradation of organic dyes with manganese-doped ZnO nanoparticles, J. Hazard. Mater. 156 (2008) 100–194.

[17] Y. Hu, Z. Zhang, C. Wei, Simple preparation of Mn–N-codoped titania photocatalyst with visible light response, Res. Chem. Intermed. 36 (2010) 95–101.

[18] V.D. Binas, G. Kiriakidis, Synthesis and properties of titanium dioxide–manganese dioxide composite nanostructured powder for photocatalytic application in the UV and VIS, Catalysis Today (2011).

[19] Y. Ohko, Y. Nakamura, N. Negishi, S. Matsuzawa, K. Takeuchi, Photocatalytic oxidation of nitrogen monoxide using TiO_2 thin films under continuous UV light irradiation, J. Photochem. Photobiol. A 205 (2009) 28–33.

[20] Y. Ohko, Y. Nakamura, A. Fukuda, S. Matsuzawa, K. Takeuchi, Photocatalytic oxidation of nitrogen dioxide using TiO_2 thin films under continuous UV light irradiation, J. Phys. Chem. C 112 (2008) 10502–10508.