CHEMICAL ENGINEERING TRANSACTIONS
VOL. 32, 2013
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet
Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-23-5; **ISSN** 1974-9791
DOI: 10.3303/CET1332060

Smart Tiles for the Preservation of Indoor Air Quality

Diana Sannino*, Vincenzo Vaiano, Giuseppe Sarno, Paolo Ciambelli

University of Salerno, Department of Industrial Engineering, Via Ponte Don Melillo, 84084 Fisciano (SA), Italy
dsannino@unisa.it

Tiles functionalized with titanium dioxide (TiO_2) for the elimination of air pollutants were prepared by the dip-coating process with titanium alkoxide solution.
The synthesis of the coating solution consist of a chemical method employing polyethylene glycol (PEG) to obtain better dispersion and adhesion of TiO_2 particles onto the ceramic substrates.
Nitrogen oxides (NO_x), hazardous air pollutants, were found to be efficiently removed by the thin film of photocatalyst.
The effectiveness of tiles, functionalized with TiO_2 thin films, has been studied in the degradation of NO_x at very low concentration in continuous flow reactors.

1. Introduction

Indoor air quality (IAQ) has become a critical community concern due to increased personal time spent in indoor environment, such as home, office, car and shopping centre. Unfortunately, IAQ was suggested to be even worse than outdoor environment, attributing to the continuously emitting sources of combustion by-products, cooking, construction materials, office equipment, and consumer products. The detected pollutants from such sources mainly include nitrogen oxides (NO_x), carbon oxides (CO and CO_2), particulates, and volatile organic compounds (VOCs) (Sun et al., 2011).
For air purification, traditional devices such as air purifiers typically employ filters or adsorbant (e.g., granular activated carbon) to remove particulate matters and gaseous pollutants. However, these techniques allow the transfer of the contaminants to another phase rather than eliminating them. Photocatalytic oxidation is a promising alternative technology for air purification. It has been demonstrated that organics or NO_x can be transformed to carbon dioxide, water or N_2 and other harmless compound at ambient temperature by heterogeneous photocatalytic nanomaterials (Lasek et al., 2013). A wide range of potential applications of photocatalysis to air purification have been reported (Ollis, 2000). TiO_2 is the most used photocatalyst because of its non toxicity, stability and availability in large amounts (Segota et al., 2011). Being a semiconductor with photocatalytic capacity, when TiO_2 is submitted to UV rays (320 - 400 nm), in the presence of water molecules, it leads to the formation of hydroxyl radicals (OH) and superoxide ions (O^{2-}) (Wu and Cheng, 2006). Those highly oxidative compounds react with dirt and inorganic substances promoting their decomposition.
For air purification of already emitted indoor pollutants, the photocatalyst can be fixed on a substrate, e.g. tiles profiting also of the solar light to promote oxidation reactions. The immobilization method is more convenient for practical use since the main problem in the usage of TiO_2 suspended in an aqueous solution is the separation of TiO_2 nanoparticles after the photocatalytic reaction and their reuse (Segota et al., 2011). Different methods have been used to prepare TiO_2 films: chemical vapour deposition, sputtering, pulsed laser deposition (PLD) (Yamamoto et al., 2001), hydrothermal method (Lee et al., 2002) and sol-gel deposition (Ling et al., 2004). Sol–gel process is considered as one of the most promising alternatives because it presents a number of advantages such as low sintering temperature, versatility of processing and good homogeneity at low cost.
The aim of this research was to prepare titania films, with the addition of PEG, on a ceramic tiles substrate by using the sol–gel dip-coating method and to verify their photocatalysts for the degradation of NO_x at low concentration in continuous flow according to a standard method, UNI-EN-ISO 11247. Moreover, their

Please cite this article as: Sannino D., Vaiano V., Sarno G., Ciambelli P., 2013, Smart tiles for the preservation of indoor air quality, Chemical Engineering Transactions, 32, 355-360 DOI: 10.3303/CET1332060

efficiency has been tested in different operating conditions and in a modified continuous photoreactor, to verify the catalyst efficiency and the influence of the reactor configuration.

2. Experimental

2.1 Preparation of sol-gel TiO_2 films

TiO_2 films were deposited on ceramic tiles with dimensions 100 mm X 100 mm X 12 mm. The substrates were carefully cleaned prior to the process of deposition. First, the substrates were ultrasonically cleaned in surfactant and rinsed with water. Then, they were ultrasonically cleaned in acetone for 10 mins. For the preparation of solution (TiO_2 sol), the following components were used:

- Titanium (IV) isopropoxide, TIP ($Ti(C_3H_7O)_4$, M_r = 284.25, purity 97 %, Sigma Aldrich) as a titanium precursor;
- Ethanol, (C_2H_5OH, M_r = 46.07, purity >99.8 %, Fluka Analytical) as a solvent;
- Acetic acid (CH_3COOH, M_r = 60.05, purity 99.8 %, Aldrich Chemistry) as a catalyst;
- Acetylacetone ($CH_3(CO)CH_2(CO)CH_3$, M_r = 100.12, purity ≥ 99 %, Sigma Aldrich) as a chelating agent;
- Bidistilled water (H_2O, M_r = 18.02) for gelation;
- Polyethylene glycol, PEG ($HO(C_2H_4O)_nH$, M_r = 5,000–7,000, Aldrich Chemistry) as an organic additive.

Sol 1 was prepared by dissolving titanium isopropoxide in ethanol. A magnetic stirrer was used to continuously mix the liquid. Then, acetylacetone and acetic acid were slowly added. The resulting sol was stirred for 15 min and after that it was sonicated for 20 min. In a different flask, 5 g of polyethylene glycol (PEG) were added to bidistilled water under continuous stirring. The obtained solution was mixed with sol 1 and stirred vigorously. The obtained clear solution was sonicated for 15 min. The molar ratios of components used to prepare titania coating solutions are shown in Table 1.

Tiles were dipped into the sol at a rate of 12 mm/min, were kept there for 10 min, and then removed at the same rate with an home-made system. All coated substrates were dried at 120 °C for 60 min and then calcinated at 450 °C for 2 h. The process (dipping – calcination) was replicated three times.

Table 1: Composition of coating solution and molar ratios

Component	$Ti(C_3H_7O)_4$	C_2H_5OH	$CH_3(CO)CH_2(CO)CH_3$	CH_3COOH	H_2O	$HO(C_2H_4O)_nH$
Molar Ratio	1	40	1.3	0.9	12.5	0.0008

2.2 Characterizations of TiO_2 films

Chemical-physical characterisation of the samples was performed by different techniques.

Laser Raman spectra were obtained at room temperature with a Dispersive MicroRaman (Invia, Renishaw), equipped with 514 nm diode-laser, in the range 100 - 800 cm^{-1} Raman shift. X-Ray fluorescence spectroscopy (XRF) was performed using a ThermoFischer ARL QUANT'X EDXRF spectrometer equipped with a rhodium standard tube as the source of radiation and with Si-Li drifted crystal detector.

2.3 Photocatalytic tests

Photocatalytic tests were carried out at ambient temperature and atmospheric pressure feeding an air stream with different total air flow rate (90 NL/h and 30 NL/h) containing 0.55 ppm of NO_x in two continuous photoreactors, irradiated by UV-lamp, emitting at 365 nm with a light intensity of 20 W/m^2. The outlet gas composition was continuously measured by an on-line chemiluminescence analyzer.

Two different reactors were tested: (i) a pyrex cylindrical photocatalytic reactor (volume 3 L) realized according to UNI-EN-ISO 11247 standard; (ii) a photocatalytic plate reactor (volume 0.2 L) realized in steel with a pyrex window (90 mm X 90 mm). This window was illuminated by the UV lamp. In order to control the reaction temperature, a heater system was used to set the reactor temperature.

3. Results and discussion

3.1 Materials characterization

Raman spectroscopy has been extensively used to study TiO_2 (Felske and Plieth, 1989); it is a rapid way of obtaining the surface crystal structure of the titania, which is believed to be important in the efficacy of the NO_x photocatalytic removal (Ohtani et al., 1997).

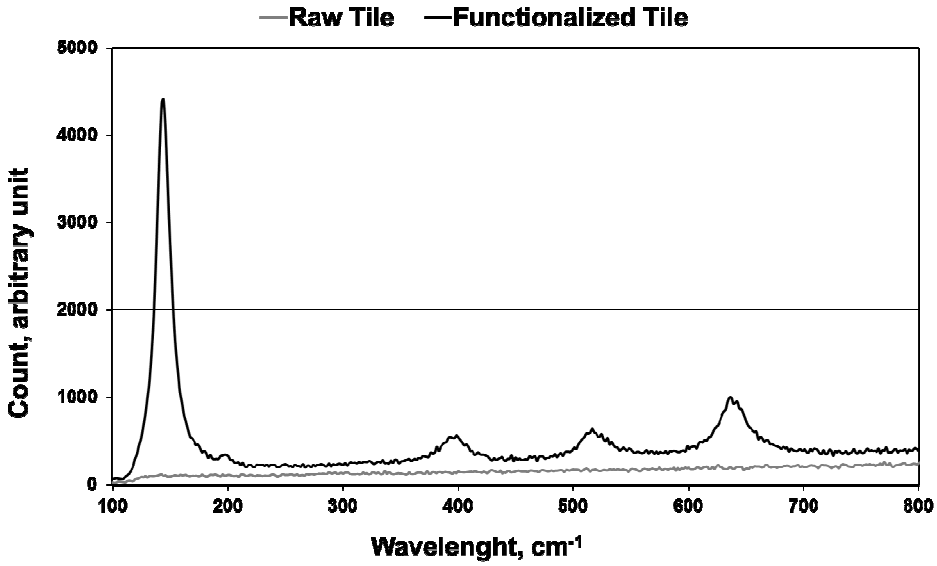

Figure 1: Raman spectra of functionalized and raw tile in the range 100 – 800 cm^{-1}

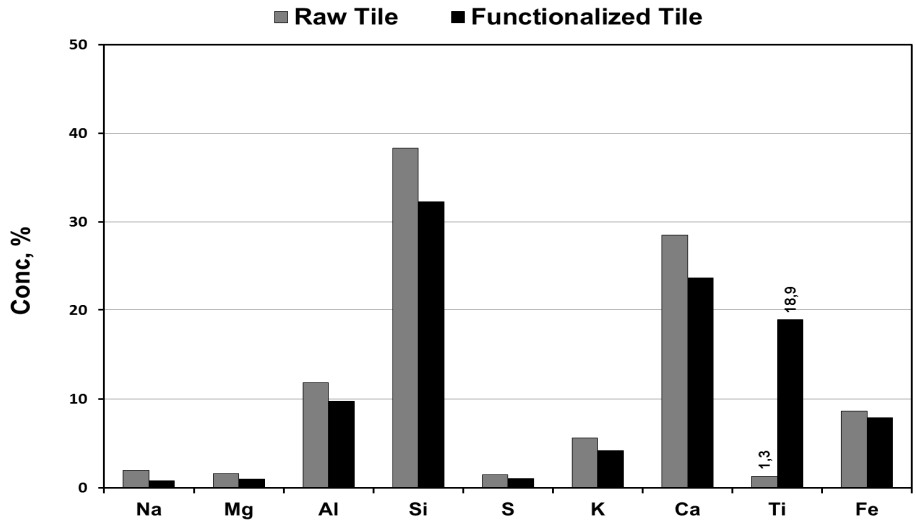

Figure 2: XRF analysis of tiles surface

The Raman spectra of the functionalized tile in comparison with raw tile in the range 100 - 800 cm^{-1} is shown in Figure 1. Functionalized tile display bands at 144, 396, 514 and 637 cm^{-1} and a weak shoulder at 195 cm^{-1}, due to the Raman-active fundamental modes of titania (Ciambelli et al., 2008); these characteristic bands giving evidence for the crystalline form of anatase rather than rutile or brookite (Felske and Plieth, 1989).
XRF results for the samples are shown in Figure 2. As it can be seen, the total amount of titanium in the functionalized sample reached a value of about 19 wt% indicating a high yield for the deposition process under the experimental conditions employed.

3.2 Photocatalytic activity tests

In Figure 3 the results of photocatalytic activity of functionalized tile in comparison with raw tile are reported. The tests were realized employing the UNI-EN-ISO 11247 reactor. At the run starting time the air stream containing 0.55 ppm NO_x, was passed through the reactor in the absence of irradiation at ambient temperature.

At that time the lamps were switched on NO_x degradation immediately increased to about 43 % of the inlet value and then slightly decreased with run time, reaching a steady state value corresponding to about 37 % after about 30 min of irradiation time. This result was obtained in presence of the functionalized tile. When titania is absent on the tile, no photocatalytic activity was observed.
Figure 4 shows NO_x conversion as a function of irradiation time on functionalized tile in the plate reactor and in the UNI-EN-ISO 11247 reactor. In the latter, as reported above the NO_x conversion reached a maximum value (43 %), then the activity decreased approaching a steady state conversion (37 %).
The behavior is quite similar when the plate reactor is used. In this case, when the lamps were switched on, the NO_x conversion immediately increased reaching a maximum of 68 % after about 12 min. At fixed reaction time the conversion in plate reactor was higher than that obtained with the other reactor. This result evidences the importance of the reactor configuration in the NO_x photocatalytic degradation.
The influence of total flow rate on the photocatalytic NO_x conversion was examined by using plate reactor and the obtained results are reported in Figure 5. The performances of the photocatalyzed tiles were strongly influenced by the selected total gas-flow rate.
By decreasing it from 90 to 30 NL/h, NO_x conversion reached 100 % and it was stable during the entire irradiation time.

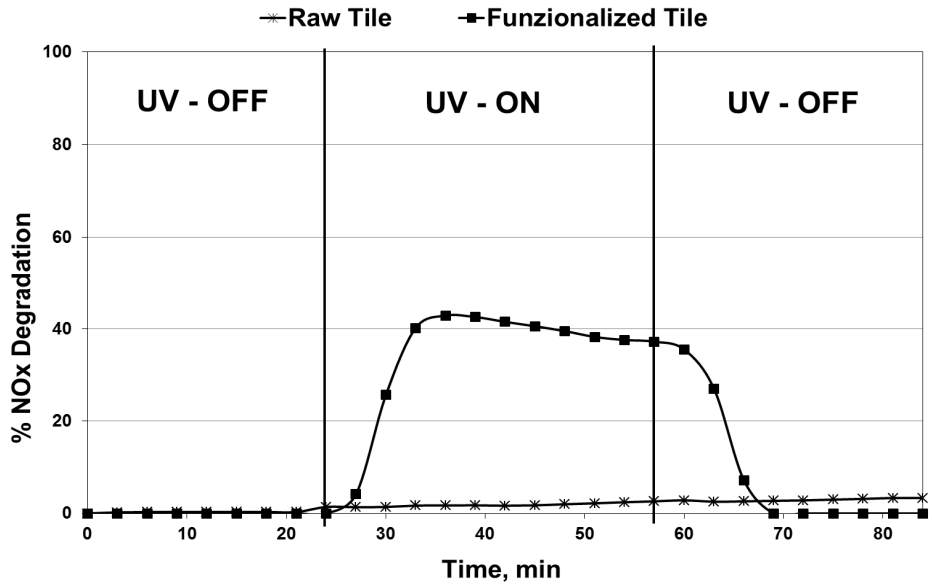

Figure 3: Photocatalytic activity results with UNI-EN-ISO 11247 reactor; total flow rate 90 NL/h

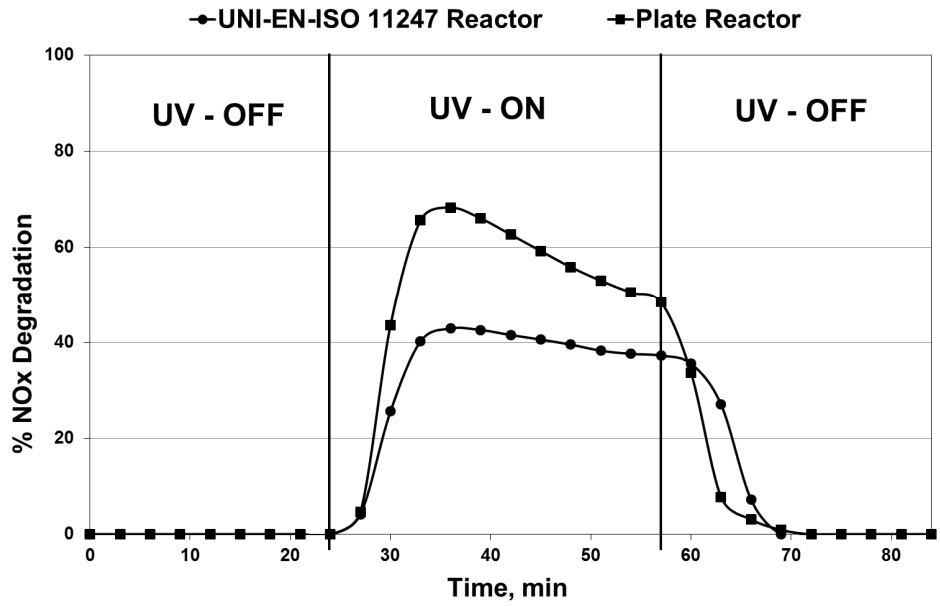

Figure 4: NO_x conversion as a function of irradiation time on functionalized tiles using UNI-EN-ISO 11247 reactor and plate reactor; total flow rate 90 NL/h

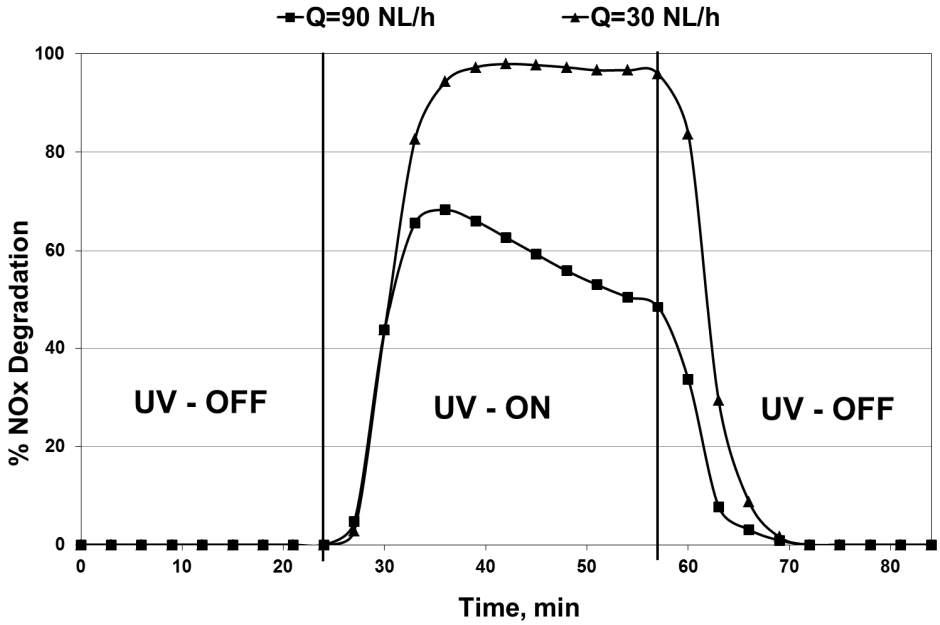

Figure 5: Influence of total flow rate on NO_x photocatalytic conversion with plate reactor

4. Conclusion

In this work, the effectiveness of tiles, functionalized with TiO_2 film, prepared through a coating procedure has been studied in the degradation of NO_x at very low concentration in two continuous flow reactors. The characterization results of functionalized tile showed that the coating method is able to induce the formation of an anatase TiO_2 strongly interacting with tile surface. Photocatalytic activity results evidenced

the importance of the reactor configuration and of operative conditions on the overall removal efficiency. By optimizing the operating conditions it was possible to obtain the complete removal of NO_x from air stream without deactivation of the TiO_2 film.

References

Ciambelli P., Sannino D., Palma V., Vaiano V., Bickley R.I., 2008, Reaction mechanism of cyclohexane selective photo-oxidation to benzene on molybdena/titania catalysts, Applied Catalysis a-General, 349, 140-147.

Felske A., Plieth W.J., 1989, Raman-spectroscopy of titanium-dioxide layers, Electrochimica Acta, 34, 75-77.

Lasek J., Yu Y.-H., Wu J.C.S., 2013, Removal of NO_x by photocatalytic processes, Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 14, 29-52.

Lee J.C., Kim M.S., Kim B.W., 2002, Removal of paraquat dissolved in a photoreactor with TiO_2 immobilized on the glass-tubes of UV lamps, Water Research, 36, 1776-1782.

Ling C.M., Mohamed A. R., Bhatia S., 2004, Performance of photocatalytic reactors using immobilized TiO_2 film for the degradation of phenol and methylene blue dye present in water stream, Chemosphere, 57, 547-554.

Ohtani B., Ogawa Y., Nishimoto S., 1997, Photocatalytic activity of amorphous-anatase mixture of titanium(IV) oxide particles suspended in aqueous solutions, Journal of Physical Chemistry B, 101, 3746-3752.

Ollis D.F., 2000, Photocatalytic purification and remediation of contaminated air and water, Comptes Rendus De L Academie Des Sciences Serie Ii Fascicule C-Chimie, 3, 405-411.

Segota S., Curkovic L., Ljubas D., Svetlicic V., Houra I.F., Tomasic N., 2011, Synthesis, characterization and photocatalytic properties of sol-gel TiO_2 films, Ceramics International, 37, 1153-1160.

Sun H., Ullah R., Chong S., Ang H.M., Tadé M.O., Wang S., 2011, Room-light-induced indoor air purification using an efficient Pt/N-TiO_2 photocatalyst, Applied Catalysis B: Environmental, 108–109, 127-133.

Wu J.C.S., Cheng Y.T., 2006, In situ FTIR study of photocatalytic NO reaction on photocatalysts under UV irradiation, Journal of Catalysis, 237, 393-404.

Yamamoto S., Sumita T., Sugiharuto, Miyashita A., Naramoto H., 2001, Preparation of epitaxial TiO_2 films by pulsed laser deposition technique, Thin Solid Films, 401, 88-93.

.