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INDOOR AIR QUALITY IMPROVEMENT BY PHOTOCATALYTIC OXIDATION

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SUMMARY

The present study aims to analyze the potential of a developed functional wallcovering applying the technology of photocatalysis for the indoor air quality improvement. The effect of the amount of layers of the coating and nano-silica incorporation in the formulation of the coating on the air pollutants removal efficiency is evaluated.

The photocatalytic efficiency is assessed on the lab scale by the degradation of an inorganic pollutant - nitric oxide - using a plug-flow experimental set-up. Experimental conditions to simulate indoor air environment are applied. A pre-treatment method is found to be necessary in order to promote the photocatalytic efficiency.
All coatings exhibited high photocatalytic efficiencies for nitric oxide degradation under applied experimental conditions. The photocatalytic efficiency is positively affected by the nano-silica addition and by the number of layers of the coating. The best performing coatings, able to degrade 69% of nitric oxide, are those containing nano-silica applied in two layers. This work confirms the potential of the photocatalysis for the indoor air quality improvement.

INTRODUCTION

The increased public concern about the environmental pollution has led to the development of effective pollutants removal technologies, which are better known as advanced oxidation processes (AOPs). Among these AOPs, a great interest has been paid to photocatalytic oxidation (PCO) due to its potential to degrade a wide range of inorganic and organic pollutants in the air (or in the water) under ambient conditions without significant additional energy demands.

Pure or modified anatase form of titanium dioxide (TiO_2), a semiconductor photocatalyst, proved to be an efficient material in degrading organic and inorganic air pollutants (Sleiman et al. 2009; Debono et al. 2011; Yu & Brouwers 2009; Dillert et al. 2012). Among various TiO_2-anchoring methods, such as sol-gel, thermal treatment, chemical vapor deposition, electro-deposition, etc., the direct incorporation method has been extensively considered because of its convenience in operation, comparatively low cost and suitability for massive production (Zhao et al. 2011).

Nano-fillers and polymer supporters are in this case prepared separately and then are mixed in a solution or emulsion form.

The development of coatings with immobilized TiO_2 appears to be a perfect economical solution for the application of photocatalysis, because of the low material consumption. However, thin coatings might not possess optimal properties, due to the low number of active sites, because of the lower amount of total immobilized or exposed photocatalytic material. Increasing the film thickness and/or roughness can, to some extent, lead to an enhanced utilization of the immobilized photocatalytic material (Mills et al. 2005; Wu et al. 2013; Chen & Dionysiou 2006). In these cases, the particle size, distribution and level of the exposure of the immobilized TiO_2 play an essential role in production of a functional photocatalytic product (Hüsken et al. 2009; Allen et al. 2008). Moreover, the protection of the organic part of the coating against the oxidative nature of the photocatalyst is important to secure proper service life.

MATERIALS AND METHODS

A trial water-based suspension containing carbon-doped titanium dioxide (C-TiO_2) (designated KC) was used as a photocatalyst. The KC consists of 40% of solids (mostly C-TiO_2) and has a pH of 7 - 8 (at 20˚C), flash point > 90˚C, a density of 1.35 - 1.55 g/cm^3 (at 20˚C). A water-based colloidal suspension of silica containing 40% of solids was applied. It has a pH of 9.2 - 9.9, a density of 1.3 g/cm^3 (at 25˚C). The carrier, on which the coatings were applied, is wallpaper consisting of a paper substrate coated with a layer of polyvinylchloride.

Two series of coatings were designed, prepared and evaluated:

1. The coatings made with the pure KC suspension (designated **KC**)
2. The coatings containing the KC with 10 mass% of silica (designated **KCs**)

Each formulation was applied on the carrier by a wire-wound coating rod in one, two, or three layers (wet thickness of layer = 8 µm) designated **L1**, **L2**, or **L3**, respectively.

In order to determine the composition of the materials and to analyze the amount of the TiO_2 and SiO_2 particles, an elemental analysis was performed by an energy dispersive X-ray fluorescence (EDXRF) spectrometer / Epsilon 3 range (PANalytical). The morphology of the applied coatings was analyzed by the scanning electron microscope QUANTA FEG (FEI Company) in the backscattered mode, followed by elemental analysis by energy dispersive X-ray spectroscope (EDAX) operated by GENESIS software (EDAX) in order to confirm the distribution of the particles.

The photocatalytic efficiency was assessed by the NO_x (NO and NO_2) removal experiments using a plug-flow experimental set-up (presented in Figure 1) made in accordance with the ISO 22197-1 standard (ISO 22197-1:2007). However, since the experimental conditions specified in ISO standard are far from the real indoor conditions, some of them (inlet pollutant concentration, flow rate, light source) were modified in order to closely simulate the indoor environment. Nitric oxide (NO) was used as a model pollutant and it was mixed with a synthetic air to an inlet concentration of 500 ppb under the flow rate of 1.5 L/min. The applied light source is composed of three fluorescent cool daylight lamps of 25 W each, emitting a visible

light irradiation with the wavelength 400-700 nm, with the intensity of about 10 W/m^2. The experimental conditions, such as the pollutant concentration (500 ppb); flow rate (1.5 L/min); relative humidity (50%); and light intensity (10 W/m^2) were fully controlled. The temperature and the humidity were measured at the inlet of the reactor. The outlet concentration of model pollutant NO and the produced NO_2 was measured and interpreted as NO_x concentration.

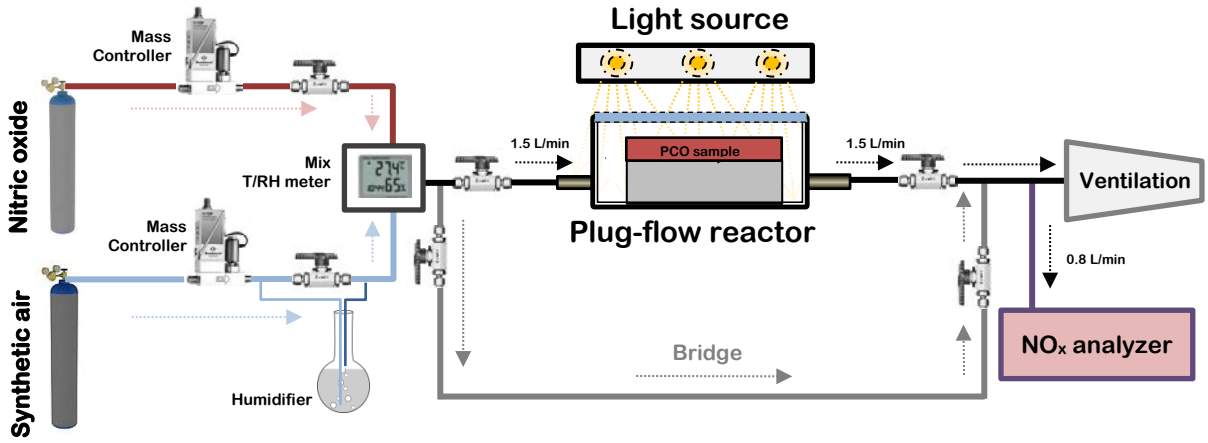

Figure 1: Plug-flow experimental set-up scheme

A previous research (Lorencik et al. 2015) showed that the PCO efficiency could be greatly suppressed due to the coverage of the photocatalyst by, for instance, organic groups present in the coatings. Therefore, a pre-treatment procedure was implemented here to degrade this covering layer, in order to expose the photocatalytic particles to environment and to promote the PCO efficiency of the coatings. The pre-treatment was carried out by irradiating the samples by the ultraviolet (UV) light for a certain period. The applied light source is composed of three fluorescent tubes of 25 W each, emitting UV-A radiation (300-400 nm). The light intensity was set to 10 W/m^2. In order to assess the efficiency of the UV pre-treatment and to establish optimal pre-treatment duration, samples were embedded in the plug-flow reactor and the concentration development of the model pollutant in time was evaluated.

RESULTS

The results of the elemental analysis of KC and KCs are presented in the Table 1. The final amount of the C-TiO_2 is slightly lower in case of KCs (35.7%) compared to the KC (40%), due to the increased amount of silica.

Table 1: SiO_2 and TiO_2 amount and calculated C-TiO_2 and SiO_2 dosages

	Dry state		**-L1** [mg/cm^2]		**-L2** [mg/cm^2]		**-L3** [mg/cm^2]	
	SiO_2 [%]	TiO_2 [%]	C-TiO_2	SiO_2	C-TiO_2	SiO_2	C-TiO_2	SiO_2
KC	0.26	98.13	0.46	0	0.91	0	1.37	0
KCs	10.34	87.66	0.38	0.05	0.77	0.09	1.15	0.14

The scanning electron microscope (SEM) images of the KCL1, KCL3, KCsL1 and KCsL3 are presented in the Figure 2.

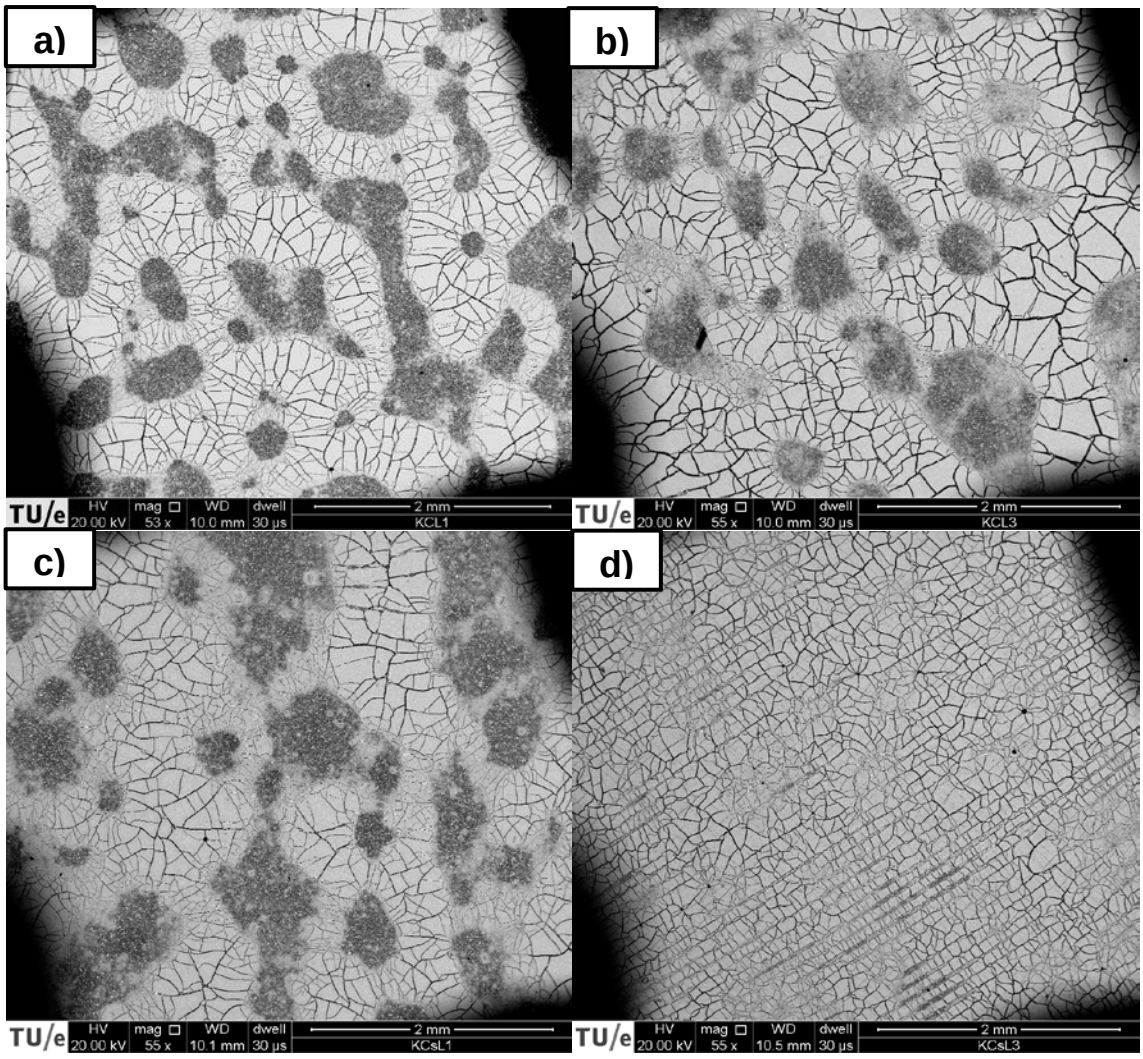

Figure 2: SEM analysis of: a) KCL1; b) KCL3; c) KCsL1; d) KCsL3

The images show that the additional layers have a positive effect on the distribution of the coating on the carrier only in case of the coatings containing nano-silica. Large amount of cracks is present in all coatings. Those could be caused by the curing method as a result of contraction, stress and different thermal expansion coefficients of the top-layer and the carrier as was also observed elsewhere (Rahmani et al. 2011). The EDS analysis (results not shown) confirmed the perfect distribution of Ti in case of KC formulations and perfect distribution of Ti and Si in case of KCs formulation in the whole matrix of the coating.

Figure 3 shows the NO_x degradation efficiency results of the KCL1-3 and KCsL1-3 coatings after 2, 5, 7 and 10 hours of UV irradiation (UV pre-treatment). The results clearly show that the UV pre-treatment duration has an effect on the final PCO efficiency of the coatings. It is also shown that the silica modification or the multi-layer design has a significant effect on the properties of the final product.

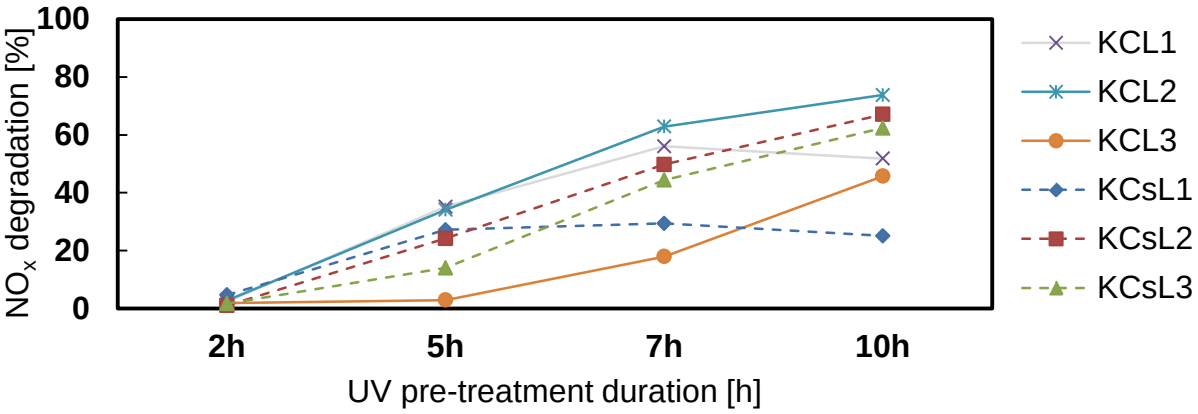

Figure 3: NO_x degradation on KCL1-3 and KCsL1-3 tested under UV irradiation

The most efficient coatings after the 10 hours' UV pre-treatment are the coatings applied in two layers. The NO_x removal efficiency is after 2 hours of irradiation about 1.0% (KCL2) and 2.8% (KCsL2), however, the efficiency rapidly increases in time resulting in high NO_x removal efficiency of 73.8% (KCL2) and 67.1% (KCsL2) after 10 hours of irradiation. The samples made with three layers show high NO_x degradation efficiency of 45.7% (KCL3) and 62.4% (KCsL3). However, those samples require longer pre-treatment in order to reach their maximum potential. The samples coated with only one layer (KCL1 and KCsL1) show their peak PCO performance after about 7 hours' UV irradiation and then their performance declined. The silica modification has a positive effect on the PCO efficiency when increasing the number of layers. The coatings made with three layers (KCsL3) have significantly better PCO efficiency than the unmodified one (KCL3).

Figure 4 presents the results of the NO_x removal assessment on the pre-treated samples, tested for 1 hour under the visible light irradiation.

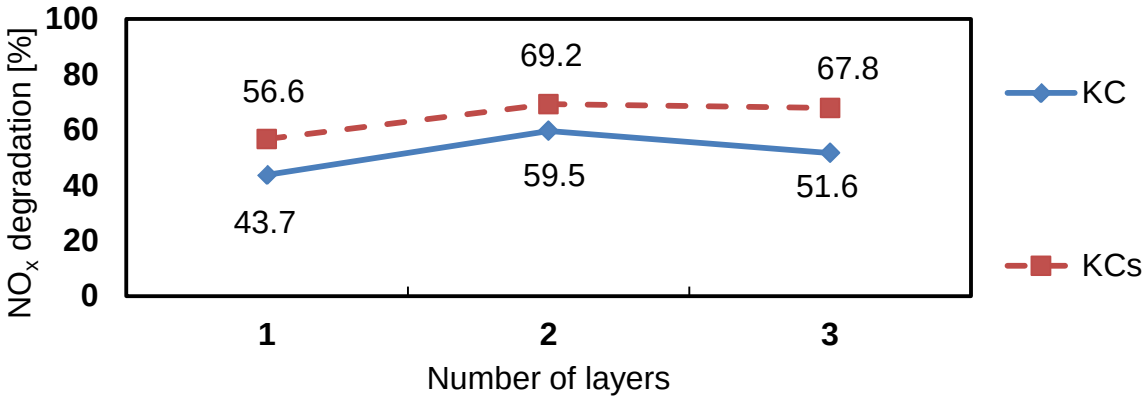

Figure 4: NO_x degradation on KCL1-3 and KCsL1-3 tested under VIS irradiation

The results show that the KC coatings exhibit very good degradation efficiencies. The silica modification clearly promotes the PCO efficiency. The multiple layers have a profound effect on the PCO efficiency, which was also reported by other researchers (Chen & Dionysiou 2006; Krýsa et al. 2014; Wu et al. 2013). The highest NO_x degradation is reached by the two-layered coatings, 59.5% by KCL2 and 69.2% KCsL2, respectively.

DISCUSSION

The C-TiO_2 suspension (KC) or the silica-modified KC (KCs) is applied on wallpaper carriers in one, two or three layers.
The elemental analysis shows that the silica particles are indeed incorporated in the coating, which is beneficial in terms of absorption ability and durability. The UV-pretreatment is found to be an efficient pre-treatment method in order to promote the PCO efficiency of the developed coatings. The results of the pre-treatment showed that the optimal duration is dependent on the number of layers. The best performing coatings, which show the maximal efficiency after the 10 hours of pre-treatment, are the ones coated with two layers in both formulations.
The NO_x removal assessments of the samples tested under indoor air conditions show very high NO_x removal efficiencies up to 69%. The silica modification has a good enhancement effect on the PCO efficiency, e.g. leading to the average (KCsL1-3) NO_x removal efficiency of 64% compared to the 52% in case of the unmodified (KCL1-3) coatings. These results are in line with other studies that showed beneficial effect of silica modification, where the focus was mainly paid to water treatment/self-cleaning effect (Zhang et al. 2014; Yao et al. 2013; Pinho & Mosquera 2013; Bellardita et al. 2010; Zhou et al. 2006). In these studies, 40% methylene blue degradation increase (Zhang et al. 2014), 62% organic dye degradation increase (Yao et al. 2013), or 37.5% more effective self-cleaning effect, was observed in case of silica-modified TiO_2 compared to the pure TiO_2. The beneficial effect is attributed to the better adsorption and improved dispersion of the photocatalytic particles, resulting in a higher number of active sites, or better utilization of light.

CONCLUSIONS

This article addresses the effect of the silica modification and the effect of multi layers of the photocatalytic coating on the photocatalytic efficiency, for the application in indoor environment. The following conclusions can be drawn:

- The silica incorporation improves the uniformity of the applied coatings;
- The silica incorporation (10% by TiO_2 mass) enhances the PCO efficiency under indoor conditions in average by 25%;
- The increasing number of layers have a positive effect on the PCO efficiency with two-layer design showing the best performance
- Highest measured NO_x removal efficiencies are 59% (KCL2) and 69% (KCsL2).

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