Cementitious Plates Containing TiO₂-N,C Photocatalysts for NO_x Degradation

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Abstract:

Studies of photocatalytic decomposition of NO_x on cementitious plates modified by TiO₂-N,C photocatalysts are presented. The cementitious plates were obtained by addition of 10 or 20 wt.% of different types of titanium dioxide, such as commercial P25, pure TiO₂ and carbon and nitrogen modified TiO₂ (TiO₂-N,C) to cement. TiO₂-N,C photocatalysts were obtained by heating up the starting TiO₂ (Grupa Azoty Zakłady Chemiczne Police S.A) in the atmosphere of ammonia and carbon at the temperature 100, 300 i 600 °C. Used photocatalyst were characterized by FTIR/DRS, UV-Vis/DR i XRD methods. Surfaces of modified cementitious plates were studied by optical scanning microscope and the contact angle measurements. Photocatalytic activity of tested materials was done during NO_x decomposition. The highest photocatalytic activity has cementitious plate with 20wt.% addition of TiO₂-N,C obtained at 300°C.

Keywords: photocatalysis, modified cement, NO_x

Introduction

One of the most important development in the construction industry, specifically in the field of pollution migration, is the incorporation of titania photocatalysts into cementitious materials (1-5). Cement materials are widely applied as titania photocatalysts supporting matrix generally due to porous structure of cement- based finished products (6, 7). In recent years, nitrogen oxides, NO_x (NO and NO₂) are classified as serious environmental problem due to photochemical smog formation and contribution of acid rains that have negative impact on forests, crops as well as the wildlife (8). Furthermore, Guerrini (9) discussed the influence of NO_x on human lungs and associated nitrogen oxides with asthma.

Full mechanism of NO_x removal in photocatalytic process was presented in many papers (8, 10-14), generally comprises four steps: adsorption of NO_x, O₂ and H₂O on the surface of the photocatalyst, photocatalyst excitation with UV radiation and photogeneration of e⁻ h⁺ pairs, hydroxyl radicals generation from water molecules adsorbed on the surface of the semiconductor and oxidation of nitrogen oxides (NO and NO₂) to nitrate ions (NO₃⁻).

Cements with addition of TiO₂ nanoparticles are used for photocatalytic abatement of NO_x, which is

known as the most common in urban areas. Depollution activity of cement paste samples, added with 0.0%, 0.5%, 1.0%, 3.0% and 5.0% of titanium dioxide nanoparticles was evaluated through the degradation of nitrogen oxides NO_x pollutants. Different blends of titania phases were considered: 100:0, 85:15 and 50:50 anatase to rutile ratios were used. After 28 days of measurements the best sample was that with a ratio 100:0 and 5.0% of TiO₂ (8). Hassan et al. (15) found that loading of the specimens with 2 wt% of TiO₂ improved NO removal efficiency but 5 wt% additive of TiO₂ to cement resulted in a small decrease in NO decomposition. Hüsken et al. (16) pointed out that the nitrogen oxides removal efficiency carried out on photocatalytic cementitious materials varied significantly, with some products achieving c.a. 40% degradation whereas others showing almost no effect. It was also found that the NO_x degradation efficiency increased with UV-A radiation and decreased with relative humidity. Folli et al. (11) investigated oxidation of NO_x using two commercial titania samples (microsized and nanosized titania) in cement and mortar specimens. It was found that the nitric oxide and nitrogen dioxide were oxidized to nitrites (NO₂⁻) and nitrates (NO₃⁻) in the presence of TiO₂. Primary and secondary particle size of TiO₂, dispersion and agglomerate porosity in cement defined accessible surface area. NO_x molecules easily penetrated into

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Table 1. Short names for cementitious plates modified by titanium dioxide

Sample code	Material composition	Treatment temperature (°C)	TiO ₂ loading (wt %)
c	cement	-	-
c+TiO ₂ -10%	cement/starting TiO ₂	100	10
c+TiO ₂ /N,C-100-10%	cement/TiO ₂ -N,C photocatalysts	100	10
c+TiO ₂ /N,C-300-10%	cement/TiO ₂ -N,C photocatalysts	300	10
c+TiO ₂ /N,C-300-20%	cement/TiO ₂ -N,C photocatalysts	300	20
c+TiO ₂ /N,C-600-10%	cement/TiO ₂ -N,C photocatalysts	600	10

nanosized TiO₂ agglomerate pores. Sugrañez et al. (13) tested the photooxidation of NO_x on six samples of mortars containing 14 wt% cement, 1 wt% TiO₂ and different amount and type of sand. They concluded that the microstructure, more specifically the macroporosity, of photocatalytic mortar cement generally was related to the amount of titania loaded to the mortar. The availability of active sites for the photocatalytic process depended also on the amount of titania at the surface, and played the most important role in photooxidation of NO_x process.

In this study the photocatalytic removal of NO_x in the presence of N,C co- modified TiO₂ prepared in one- step process and loaded to the cementitious building materials are presented. Gaseous ammonia and n- hexane were used as a source of nitrogen and carbon, respectively. The TiO₂-N,C photocatalyst was used as an additive to cement powder due to the enhanced photocatalytic performance in comparison to N- or C- doped TiO₂.

Experimental

Sample Preparation

The cementitious plates were prepared using Portland cement CEM I 32.5R (Izolbet, Poland). The mortar for plate preparation was obtained by addition of 10 and 20 wt.% of unmodified and modified titanium dioxide. The unmodified, pure titanium dioxide (mainly anatase, supplied by Grupa Azoty Zakłady Chemiczne "Police" S.A., Poland) was applied in the preparation process of the co-modified TiO₂-N,C photocatalysts.

Firstly, the pure TiO₂ was rinsed with 240 mL of ammonia water (2.5 wt%) and then distilled water until pH value reached 6.8. Acquired suspension was filtered and then obtained TiO₂ slurry was pre-dried for 24 hours at 105 °C to remove ammonium residues and water molecules adsorbed on the surface of titanium dioxide powder. Secondly the carbon and nitrogen modification of titanium dioxide was performed, the quartz crucible with 15 g of pre-dried TiO₂ was placed in a central part of tubular furnace and heated up to 100, 300 and 600 °C (5 °C/min) in

argon gas flow (100 mL/min, gas grade purity of 99.9995% (Messer, Poland)). In the point of maximal calcination temperature argon flow was closed. The TiO₂ sample was kept in programmed temperature for 1.5 hand gaseous ammonia with a flow of 200 mL/min was passed through a glass scrubber with n-hexane. After that time the furnace was firstly cooled down for 1h in argon flow (100 mL/min) and then automatically to room temperature without argon flow. Prepared samples were micronized using analytical grinder IKA A11 basic (IKA, Germany).

Commercial AEROXIDE TiO₂ P25 (Evonik Industries, Germany) was used as a reference materials.

10 g of TiO₂-cement and suitable TiO₂ was mixed with 5 mL of water. Hydrated cement paste was put in a 3 silicone moulds (2 cm x 2 cm x 0.6 cm). In the case of cement-P25 composites, additive of that type of TiO₂ photocatalyst led to significant increase of cement paste density and due to this fact it was necessary to add 8 mL of water to 10 g in order to avoid too rapid setting time of these materials.

The sample names for modified cementitious plates in Table 1 are presented.

Sample Characterization

The characteristic of obtained carbon and nitrogen modified photocatalysts (TiO₂-N,C-100, TiO₂-N,C-300, TiO₂-N,C-600) was precisely presented in our earlier publication. UV-Vis/DR, FTIR/DRS, XRD analysis were done. Moreover the BET specific surface were calculated and carbon and nitrogen content in the photocatalysts were also measured (17). The most important data in Table 2 are presented.

Characterization of the surface of the cementitious materials was performed by laser scanning microscope.

NO_x Decomposition Tests

The NO_x decomposition test were done in the reactor which scheme in Figure 1 is presented. A cylindrical Pyrex glass vessel ($\phi \times H$, 5 cm x 32 cm) was used as the photoreactor for the degradation of NO_x and a four gypsum plates (each at dimensions 20 mm x 20 mm x 6 mm, each) were located inside the

Figure 1. Scheme of photoreactor for NO_x decomposition

Table 2. Characteristic of carbon and nitrogen modified TiO₂

Photocatalyst	S _{BET} (m ² /g)	Nitrogen content (wt%)	Carbon content (wt%)
TiO ₂	312	0	0
TiO ₂ -N,C-100	219	1.27	0.12
TiO ₂ -N,C-300	206	0.97	0.05
TiO ₂ -N,C-600	24	0.22	0.14

vessel. Reactor was surrounded by UV lamp 4 x 22 W (Philips) and placed inside thermostatic chamber. NO_x degradation was carried out at 25°C using an air stream containing 25 ppm NO₂ as feedstock with flow 500 ml/min. The NO₂ was passed through the washer with water. The water was necessary for OH radicals production using during photocatalytic decomposition of NO₂. The flow of gases was controlled by mass flow meters. An on-line chemiluminescent NO_x analyzer (T200, Teledyne) continuously monitored NO and NO₂ concentrations for gas analysis in the outlet.

Results and Discussions

Cementitious Plates Characterization

In Figure 2 images obtained from laser scanning microscope of cementitious plates with addition of 10wt% of TiO₂-N,C are presented. The presence of 10wt% of TiO₂-N,C changed the surface morphology of plates. Presence of TiO₂-N,C photocatalysts smoothed the surface of cementitious plates. Moreover the influence of modification temperature of TiO₂-N,C on surface can be also observed, with the

increasing of modification temperature the smoothing of surface of cementitious plates also increasing.

NO_x Decomposition

Photocatalytic activity of obtained modified cementitious plates was tested during NO_x decomposition. In the reactor were placed four cementitious plates with dimensions 20 mm x 20 mm x 6 mm, each. Then the gas containing 25 ppm of NO₂ was continuously converted through the reactor for 1 hour to obtain equilibrium state. After that time UV lamps were turned on and 1 hour irradiation starts. In Figure 3 the absolute concentration of NO₂, NO and NO_x is presented. Concentration of NO_x is total of NO₂ and NO concentration. When NO₂ was passed through the reactor, photolysis occurred and also NO was produced. In Figure 3a) the photolysis effect can be observed. Without irradiation, the level of NO is almost zero and ratio of NO₂ input the reactor and NO₂ outlet the reactor amounted 1. The same situation is in the case of NO_x, the ratio of NO_x input and outlet the reactor is 1. When the light was turned on undesirable NO production during decomposition of NO₂ occurred due to photolysis of NO₂.

NO₂ is transferred to NO but the concentration of NO_x stayed on the same level.

In Figure 3b) degradation of NO_x in presence of cementitious plate modified by addition of 20wt% of TiO₂-N,C modified at 300°C is presented. As it can be seen without irradiation the modified cementitious

Figure 2. Images from scanning electron microscope of: a) pure cementitious plate, b) cementitious plate with 10wt% addition of $\text{TiO}_2\text{-N,C}$ modified at 100°C , c) cementitious plate with 10wt% addition of $\text{TiO}_2\text{-N,C}$ modified at 300°C , d) cementitious plate with 10wt% addition of $\text{TiO}_2\text{-N,C}$ modified at 600°C .

plates have the same characteristic like unmodified one. It is possible to observe that after the light was turned on, photocatalytic decomposition of NO and NO_2 occurred because concentration of NO_x decreased.

In Figure 4 the conversion of NO_2 on different kind cement is presented. The amount of produced NO and

oxidized NO_2 is shown. During photocatalytic decomposition of NO_2 several reactions may occur.

The proposed photocatalytic oxidation mechanism of NO_x was presented (18).

Figure 3. Time-course of the changes in concentration of NO, NO₂ and NO_x: a) as a results of photolysis and b) in the presence of c+TiO₂-N,C-300-20%; inlet concentration of NO₂: 25 ppm, inlet flow rate: 500 ml/min, reaction temperature: 25°C where (NO)_x= (NO)+(NO₂).

The efficiency and selectivity of NO₂ reaction were calculated as following (19):

$$\text{NO}_2\text{ conversion} = \left(1 - \frac{\text{NO}_{2,t}}{\text{NO}_{2,0}}\right) \times 100\%$$

Moreover NO₂ can react with the water vapor producing NO, as follows:

The amount of produced NO was calculated by using the following equation:

$$\text{NO produced} = \frac{\text{NO}_t - \text{NO}_0}{\text{NO}_{2,0} - \text{NO}_{2,t}} \times 100\%$$

As seen in the case of pure cement and unmodified TiO₂ under UV light irradiation NO₂ converted to NO because of photolysis process. In the case of plates containing 10wt% and 20wt% of TiO₂-N,C the photocatalysis occurs, because it can be observed the decreasing of NO₂ concentration and also the amount

of produced NO is not so high and two times less than in the case of photolysis. NO₂ is probably oxidized to NO₃⁻ which is adsorbed on modified gypsum surface.

In Figure 5 the degradation of total NO_x is presented. NO_x degradation was calculated from below equation:

$$\frac{(\text{NO} + \text{NO}_2)_0 - (\text{NO} + \text{NO}_2)_t}{(\text{NO} + \text{NO}_2)_0} \times 100\%$$

In the case of pure cement plate and cementitious plate containing unmodified TiO₂, NO₂ cross in NO and concentration of NO_x keeps on the same level. In the case of plates containing 10wt% and 20wt% of TiO₂-N,C, two times higher degradation of NO_x can be observed.

Conclusion

TiO₂ modified by carbon and nitrogen may be add photocatalyst activity to cement. Modified building material may be used for NO₂ decomposition. Increasing of modification temperature of photocatalysts from 100 to 600 °C insignificantly increased its photocatalytic activity.

Figure 4. NO₂ conversion on various modified cementitious plates under UV light irradiation.

Figure 5. Degradation of NO_x on modified gypsum under UV light irradiation.

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