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NOx photocatalytic degradation on gypsum plates modified by TiO_2-N,C photocatalysts

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In presented studies the photocatalytic decomposition of NOx on gypsum plates modified by TiO_2-N,Cphotocatalysts were presented. The gypsum plates were obtained by addition of 10 or 20 wt.% of different types of titanium dioxide, such as: pure TiO_2 and carbon and nitrogen co-modified TiO_2 (TiO_2-N,C) to gypsum. TiO_2-N,C photocatalysts were obtained by heating up the starting TiO_2 (Grupa Azoty Zakłady Chemiczne Police S.A) in the atmosphere of ammonia and carbon at the temperature: 100, 300 i 600°C. Photocatalyst were characterized by FTIR/DRS, UV-Vis/DR, BET and XRD methods. Moreover the compressive strength tests of modified gypsum were also done. Photocatalytic activity of gypsum plates was done during NOx decomposition. The highest photocatalytic activity has gypsum with 20 wt.% addition of TiO_2-N,C obtained at 300°C.

Keywords: photocatalysis, modified gypsum, NOx.

INTRODUCTION

In recent years, a lot of efforts were made to obtain various building materials (cementitious, gypsum, brick materials, etc.) exhibiting self-cleaning, self-sterilizing, bactericidal and anti-fog properties[1]. One of the employed methods involves inducing photocatalytic activity of the building materials by loading them with highly photoactive oxides[2, 3]. Recent findings in nanomaterials development field led to formation of nano size materials, such as titanium dioxide, which possesses a strong oxidizing capability[4]. Moreover, in order to additionally enhance the TiO_2 photoactivity and consequently its effectiveness in removal of larger variety of the pollutants, the titania can be additionally modified with non-metals or metals[3, 4]. The possibility to incorporate titanium dioxide nanoparticles in construction materials (cement, plaster, concrete, etc.) has been recently investigated, leading to the development of commercial products like TioCem[5–7].

Besides direct mixing of TiO_2 powder with the building materials, other techniques, including sputtering, spray coating and sol-gel dip coating[8, 10], have also been used to incorporate the photocatalysts onto the building materials. However, these coatings often have weak adhesion to the substrates, rendering their poor durability[11].

The most popular group of the building materials, exhibiting self-cleaning properties are cements[12–14]. Little attention is given to the other group such as gypsum, which are widely applied interior walls and ceilings coatings[15]. The constantly increasing air quality demands, enforced by the EU[16, 17] gave rise to the investment in the research of new photocatalytic construction and building materials focused on the reduction of pollutant concentration levels, not just in the outdoor atmosphere but also in indoor environments[18]. The atmosphere inside buildings can be gradually contaminated by various chemical species, such as NO_x, SO_x or VOC (volatile organic compounds), deriving from traffic and industry sources[19]. Especially the adverse effects of atmospheric nitrogen oxides (NO_x) on human and environmental health are well-known[20]. The nitrogen oxides are present indoor by the contamination from the exterior air that enters through ventilation systems or windows[21]. The additive of photocatalyst such as TiO_2 to gypsum, which is a natural, environmentally friendly and fireproof material, with good acoustic performance, offers promising potential in elimination of nitrogen oxides, in indoor environments[22].

This paper focusing on the de-polluting effect of gypsum plasters added with titanium dioxide simultaneously modified with carbon and nitrogen, based in the degradation of NO_2. Moreover, the impact of photocatalytic additive to gypsum material on compressive strength was also presented.

EXPERIMENTAL

Sample preparation

The gypsum plate was obtained by addition of 10 and 20 wt.% of unmodified and modified titanium dioxide to gypsum. The unmodified, pure titanium dioxide was mainly anatase TiO_2, supplied by Grupa Azoty Zakłady Chemiczne "Police" S.A., Poland. Modified titanium dioxide was obtained by modification of unmodified titanium dioxide in the carbon and nitrogen atmosphere by method described below.

Firstly, the pure TiO_2 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 TiO_2 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 TiO_2 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 TiO_2 sample was kept in programmed temperature for 1.5 h and 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 1 h 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).

Gypsum plates were obtained by mechanical grinding of gypsum with 10 or 20% wt. of photocatalysts in agate mortar during 20 minutes. Prepared mixtures were blended with distilled water (water to gypsum ratio g/w = 0.8). The obtained pastes were poured into silicone moulds (20 mm x 20 mm x 6 mm) and dried to constant mass at 40°C. The sample codes for modified gypsum plates in Table 1 are presented.

Sample characterization

The characteristic of obtained carbon and nitrogen modified photocatalysts (TiO_2-N,C-100, TiO_2-N,C-300, TiO_2-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[23]. The most important data in Table 2 are presented.

The compressive strength tests of modified gypsum were done on the several series of cylinder specimens. Similarly to gypsum plasters, prepared mixtures were blended with distilled water, with water-gypsum ratio (w/g) 0.8. Successor, received pastes were poured into cylindrical silicone moulds (16 mm x ø 15 mm). Acquire samples were removed from the molds and dried at 40°C, during for 72 hours. Dried specimens were placed into exsiccator for 24 hours, before being tested for compressive strength.

NOx decompostion tests

The NOx decomposition test were done in the reactor which scheme in Figure 1 is presented. A cylindrical Pyrex glass vessel (φ *x H,* 5 cm x 32 cm) was used as the photoreactor for the degradation of NOx and a four gypsum plates (each at dimensions 20 mm x 20 mm x 6 mm, each) were located inside the vessel. Rector was surrounding by UV lamp 4 x 22W (Philips) and placed inside thermostatic chamber. The emission spectrum of the lamp in Figure 2 is presented. The irradiation

Table 1. Sample codes for gypsum plates modified by titanium dioxide

Sample code	Material composition	Treatment temperature [°C]	TiO_2 loading [wt %]
g	gypsum	–	–
g+TiO_2-10%	gypsum/starting TiO_2	100	10
g+TiO_2/N,C-100-10%	gypsum/TiO_2-N,C photocatalysts	100	10
g+TiO_2/N,C-300-10%	gypsum/TiO_2-N,C photocatalysts	300	10
g+TiO_2/N,C-300-20%	gypsum/TiO_2-N,C photocatalysts	300	20
g+TiO_2/N,C-600-10%	gypsum/TiO_2-N,C photocatalysts	600	10

Table 2. Characteristic of carbon and nitrogen modified TiO_2

Photocatalyst	S_{BET} [m^2/g]	Anatase crystallite size [nm]	Nitrogen content [wt%]	Carbon content [wt%]
TiO_2-N,C-100	219	6.7	1.27	0.12
TiO_2-N,C-300	206	7.7	0.97	0.05
TiO_2-N,C-600	24	50.0	0.22	0.14

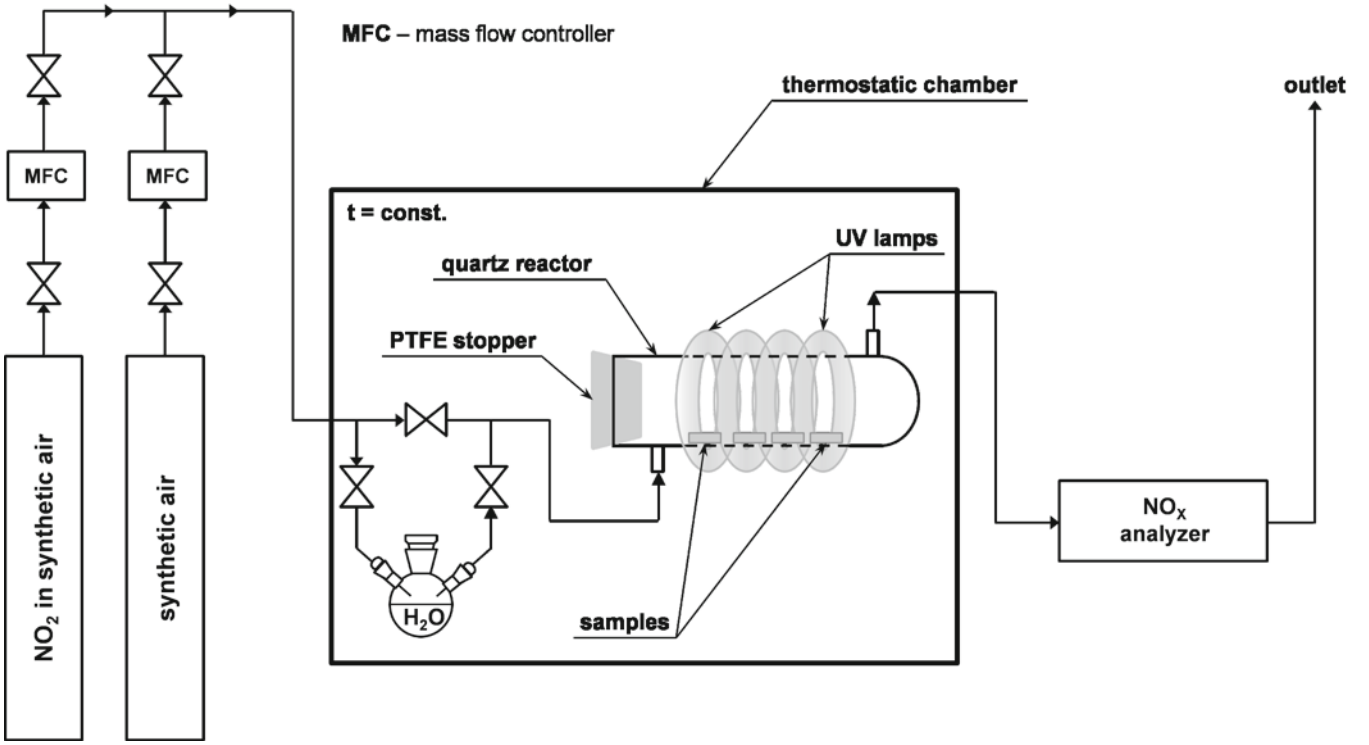

Figure 1. Scheme of photoreactor for NOx decomposition

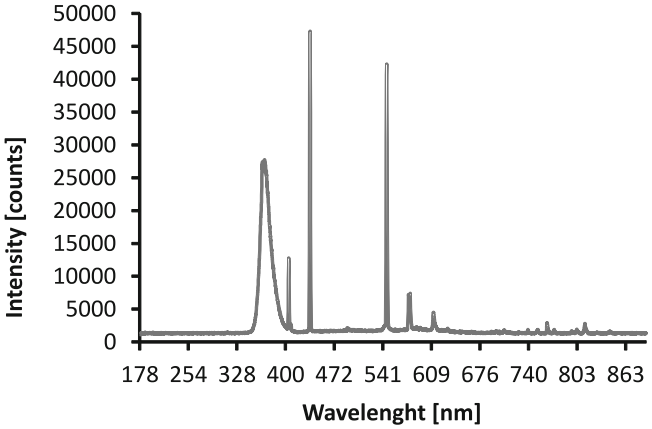

Figure 2. Emission spectrum of UV lamps

intensity amounted 100 W/m^2 of UVA and 4 W/m^2 of visible light. NOx degradation was carried out at 25°C using an air stream containing 25 ppm NO_2 as feedstock with flow 500 ml/min. The flow of gases was control by mass flow meters. An on-line chemiluminescent NOx analyzer (T200, Teledyne) continuously monitored NO and NO_2 concentrations for gas analysis in the outlet.

RESULTS AND DISCUSSIONS

NOx decomposition

Photocatalytic activity of obtained modified gypsum plates was tested during NOx decomposition. In the reactor four gypsum plates with dimensions 20 mm x 20 mm x 6 mm were placed. Then the gas containing 25 ppm of NO_2 was continuously pass through the reactor for 1 hour to obtained equilibrium state. After that time UV lamps were switch on and 1 hour irradiation starts. In Figure 3 the absolute concentration of NO_2, NO and NOx is presented. In Figure 3a) the photolysis effect can be observed. In Figure 3b) degradation of NOx in presence of gypsum plate modified by addition of 20 wt% of TiO_2-N,C modified at 300°C is presented. As it can be seen in Figure 3 a) when the light was on the concentration of NO_2 decrease while concentration of NO increased, but the concentration of NOx stayed on the same level. Its mean that photolysis occur. But when gypsum plates modified by TiO_2 was placed inside the reactor and the light was switch on the concentration of NO_2 decrease while concentration of NO increased but not so much like during photolysis and moreover the concentration of NOx also decreased. Its mean that TiO_2-N,C modified gypsum decomposed NO_x.

In Figure 4 the conversion of NO_2 is presented. The amount of produced NO and oxidized NO_2 is shown. During photocatalytic decomposition of NO_2 several reaction may occur. The efficiency and selectivity of NO_2 reaction were calculated as following[24]:

$$NO_2 conversion = (1 - \frac{NO_{2,out}}{NO_{2,in}}) \times 100\%$$

Undesirable NO during decomposition of NO_2 occurred due to photolysis of NO_2 under the influence of UV irradiance:

$$NO_2 + hv(\lambda < \sim 430nm) \rightarrow NO + O$$

Moreover NO_2 can react with the water vapor producing NO, as follows[25]:

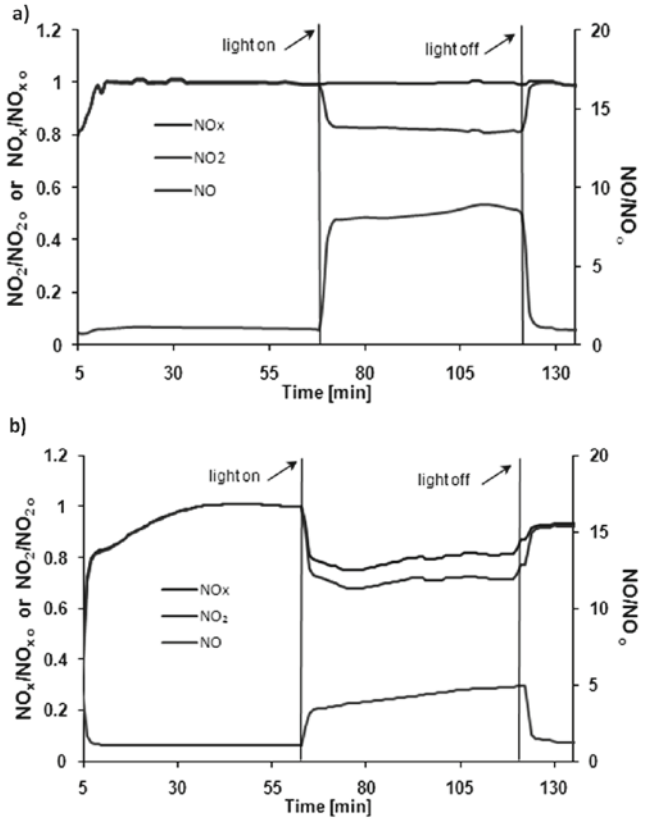

Figure 3. Time-course of the changes in concentration of NO, NO_2 and NOx: a) as a results of photolysis and b) in the presence of g+TiO_2-N,C-300-20%; inlet concentration of NO_2: 25 ppm, inlet flow rate: 500 ml/min, reaction temperature: 25°C where [NO]x = [NO] + [NO_2]

$$3NO_2 + H_2O \rightarrow NO + 2HNO_3$$

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

$$NOproduced = \frac{NO_{out} - NO_{in}}{NO_{2,in} - NO_{2,out}} \times 100\%$$

NO_2 may be also partially converse to oxidative forms (NO_3^-)

$$NO_2 oxidized = NO_2 conversion - NOproduced$$

As it can be seen in the case of pure gypsum and with the case of plates containing less active photocatalyst such as TiO_2-N,C modified at 100 and 600°C under UV light irradiation NO_2 pass to NO, probably because of photolysis process. In the case of plates containing 10 wt% and 20 wt% of TiO_2-N,C-300 the photocatalysis occur, because it can be observed the decreasing of NO_2

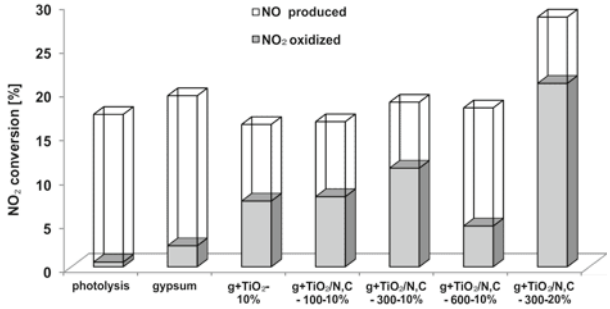

Figure 4. NO_2 conversion on various modified gypsum plates under UV light irradiation

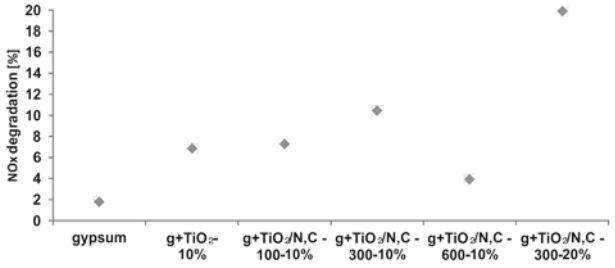

Figure 5. Degradation of NOx on modified gypsum under UV light irradiation

concentration and also the amount of produced NO is not so high and even tree times less than in the case of photolysis. NO_2 is probably oxidize to NO_3^- which is adsorbed on modified gypsum surface.

In Figure 5 the degradation of NO_x is presented. In the case of gypsum plates containing TiO_2-N,C modified at 100 and 600°C NO_2 cross in NO and concentration of NOx keeps on the same level. In the case plates containing 10 wt% and 20 wt% of TiO_2-N,C-300, NO_2 cross in NO_3^- which is adsorbed on plates surface and concentration of NO_2 decrease.

As it can be seen that there is no NOx degradation on pure gypsum. The highest degradation of NOx is when plates contain 10 wt% and 20 wt% of TiO_2-N,C modified at 300°C. The explanation may be the fact that this photocatalyst has high surface area, amounted 206 m^2/g and content of 0.97 wt% of nitrogen, mainly these are ammonia groups $–NH_4^+$ presents on the surface of photocatalyst and only 0.05 wt% of carbon groups, FTIR/DRS spectra in Figure 6 is presented. Presence of ammonia on the surface of photocatalysts caused alkalinity of the surface and acidic NO_2 is easier adsorbed.

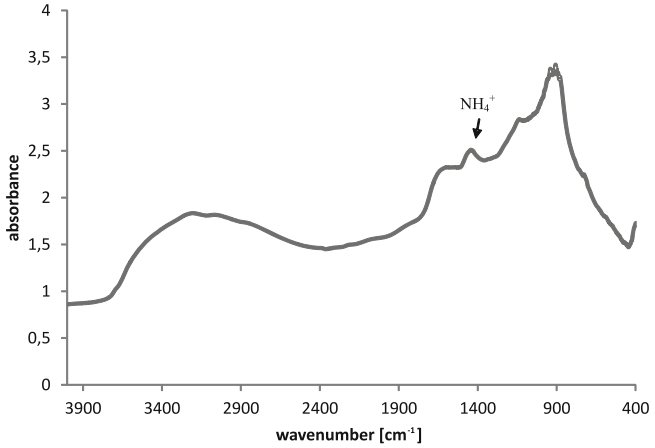

Figure 6. FTIR/DRS spectra of TiO_2-N,C photocatalyst modified at 300°C

The compressive strength analysis

The values of compressive strengths of gypsum modified by 10 wt% addition of TiO_2-N,C in Table 3 are presented. Additionally, a distinctly growing tendency in compressive strength of gypsum cylinder specimens can be observed with the treatment temperature of prepared co–modified photocatalysts. According to the XRD analysis anatase crystallite size was appointed. The anatase crystallite size of carbon and nitrogen modified TiO_2 in Table 2 are presented. It can be seen that there is dependence between the crystallite size of photocatalyst and the compressive strength of gypsum cylinders specimens modified by these photocatalysts. In general, tested results indicated that the compressive strengths gradually increased with the size of TiO_2 particles. Consequently, sample designed as g+TiO_2/N,C-600-10%, which contained the largest sized of TiO_2 particles (50 nm) revealed the highest values of compressive strength (6.64 MPa). Similar observation was reported by Haruehansapong et al.[26], for cement mortars containing nanosilica with various sizes. They confirmed that medium particle size of nanosilica (40 nm) improvement the compressive strength of cement mortars.

CONCLUSION

The addition of TiO_2-N,C to gypsum has influence on photoactivity and the compressive strength of these new materials. The higher activity during NOx degradation has gypsum modified by addition of 20 wt% of TiO_2/N,C modified at 300°C. The explanation may be the fact that this photocatalyst has high surface area, amounted 206 m^2/g and content of 0.97 wt% of nitrogen, mainly these are ammonia groups $–NH_3^+$ presents on the surface of photocatalyst and only 0.05 wt% of carbon groups. Presence of ammonia on the surface of photocatalysts caused alkalinity of the surface and acidic NO_2 is easier adsorbed. On the other hand the highest value of the compressive strength (6.64 MPa) has sample designed as g+TiO_2/N,C-600-10%, which contained the largest sized of TiO_2 particles (50 nm).

Table 3. Compressive Strength of modified gypsum

Sample code	Compressive Strength [MPa]
g	5.84
g+TiO_2/N,C-100-10%	3.66
g+TiO_2/N,C-300-10%	4.52
g+TiO_2/N,C-600-10%	6.64

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