Construction and Building Materials 149 (2017) 257–271

Contents lists available at ScienceDirect

Construction and Building Materials

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

Atmospheric NOx removal: Study of cement mortars with iron- and vanadium-doped TiO_2 as visible light–sensitive photocatalysts

M. Pérez-Nicolás, I. Navarro-Blasco, J.M. Fernández, J.I. Alvarez *

Universidad de Navarra, Facultad de Ciencias, Departamento de Química, MIMED Research Group, Irunlarrea, 1, 31008 Pamplona, Spain

HIGHLIGHTS

- Cements with two doped TiO_2 photocatalysts enhanced NO removal under visible light.
- High NO selectivity with low release of NO_2 was found for air lime and HAC systems.
- The presence in these matrices of $CaCO_3$ synergistically favors the $DeNO_x$ activity.
- V-TiO_2 agglomerates, while most photocatalytically active Fe-TiO_2 is regularly spread.
- Additives conferred increased hydrophilicity to mortars as proved by WCA reduction.

ARTICLE INFO

Article history:
Received 10 April 2017
Received in revised form 12 May 2017
Accepted 14 May 2017

Keywords:
Cement
Calcium aluminate cement
Air lime
Mortar
NO removal
Selectivity
Doped TiO_2
$CaCO_3$

ABSTRACT

Mortars made with Portland cement, two different calcium aluminate cements and air lime were chosen to incorporate photocatalytic additives, because they have large exposed surfaces that boost the photochemical oxidation (PCO) of atmospheric pollutants such as nitrogen oxides. TiO_2 as reference catalyst, and two doped titania, Fe-TiO_2 and V-TiO_2, which were expected to increase the sensitivity of the additives towards the visible light, were studied. Cementing matrices, particularly air lime and high alumina cement mortars, yielded significant amounts of NO removal under the three illumination conditions studied (UV, solar and visible light), with high selectivity response for NO abatement (up to 60–80%) and low NO_2 release. The presence of calcium carbonate has been shown to have a synergistic effect, enhancing the PCO of these mortars under different light sources.

1. Introduction

Atmospheric pollution is one of the most severe problems that scientific community has to face up. Industrial activity is responsible for the presence of toxic gases in the atmosphere. Regarding the chemical composition of these pollutants, nitrogen oxides NO_x ($NO + NO_2$) have been recognised as potential agents causing respiratory diseases and acid rain [1]. In order to remove NO_x from the atmosphere, photochemical oxidation (PCO) has been developed in different systems by means of the use of photocatalysts.

Photocatalysts can be immobilized into cementitious materials with the aim of enhancing their activity and developing applications in new areas. Cement-based materials offer a large ratio of fixation sites for the photocatalysts, as well as extensive exposure surfaces and have been reported as target supports of these photocatalysts [2–7]. These modified materials have been proved to be efficient to depollute the environment by degrading NO_x ($DeNO_x$ effect) [8–10]. Furthermore, photocatalysts can give rise to an increase of the hydrophilicity of the surfaces since they are known to generate photo-induced superhydrophilicity. This point is related to the self-cleaning ability of these surfaces. This ability is based on the synergy of two properties: by one hand, the photo-induced oxidation of the adsorbed organic compounds and, by the other hand, the photo-induced super-hydrophilicity [11]. As main responsible for the stains on the surface of building materials literature has pointed out to composites including organic compounds, such as fatty acids and hydrocarbons, that can trap dust and atmospheric particles [11]. For hydrophilic surfaces water drops spread over the surface and form a film of water (initially water is chemisorbed onto the surface of the photocatalyst; then,

* Corresponding author at: Departamento de Química, Facultad de Ciencias, Universidad de Navarra, C/ Irunlarrea 1, 31008 Pamplona (Navarra), Spain.
E-mail addresses: jalvarez@unav.es, mimed@unav.es (J.I. Alvarez).

http://dx.doi.org/10.1016/j.conbuildmat.2017.05.132
0950-0618/

the thickness of the layer is increased because these water molecules adsorb water by physisorption, either by van der Waals forces or by hydrogen bonds) [12]. This film of water will act as a barrier to prevent the close contact between the surface of the building material and the pollutants. Pollutants close to the surface of the material will be easily removed by this loose water barrier. Therefore, during the process of spreading of water drops, the contaminants on the surface are washed away [13].

For mortars with photocatalysts, water contact angle is expected to decrease making surfaces easily washable by rain water and preventing dirt from accumulation, according to the aforementioned reasons. These building materials would be self-cleaning surfaces [14–17]. This fact reduces the cleaning maintenance costs, obtaining an environmentally friendly material [18,19].

Semiconductor metal oxides are commonly used as photocatalysts in PCO reactions [20]. Semiconductors have an electronic structure characterized by a filled valence band and an empty conduction band. When the energy provided by a photon (light source) matches or exceeds the bad gap, one electron overcomes the energy barrier and is promoted from the valence band to the conduction band, leaving a hole (positively charged) in the valence band [21]. In the presence of air and oxygen, pollutants -that are adsorbed on the semiconductor surface-, may undergo photo-oxidation.

The most common photocatalyst used in building materials is TiO_2. The PCO chain reaction of the NO_x removal by TiO_2 has been generally accepted as follows [7]:

$$TiO_2 + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$H_2O + h^+ \rightarrow H^+ + OH^{\cdot} \quad (2)$$

$$O_2 + e^- \rightarrow O_2^{\cdot -} \quad (3)$$

$$NO + O_2^{\cdot -} \rightarrow NO_3^- \quad (4)$$

$$NO + OH^{\cdot -} \rightarrow HNO_2 \quad (5)$$

$$HNO_2 + OH^{\cdot} \rightarrow NO_2 + H_2O \quad (6)$$

$$NO_2 + OH^{\cdot} \rightarrow NO_3^- + H^+ \quad (7)$$

Titania is an excellent photocatalyst under UV light. Nevertheless, outdoor radiation only presents a minor 4–5% of UV photons [22]. Different attempts to improve the sensitivity of titania towards photons of the visible light spectrum have been carried out [23–25]. Among these strategies, the doping of TiO_2 with transition metals (Fe, V, Cr...) has shown to be useful [25–27] and will be employed in this work.

Although usually ordinary Portland Cement, PC, has been studied as the main building material acting as support of TiO_2, previous studies have also shown the potential usefulness of cementing matrices based on calcium aluminate cement (CAC) to support bare TiO_2. Different behavior was found for high alumina cements, HAC (iron-lean calcium aluminate cements) and cements with a high amount of ferrite phase (iron-rich calcium aluminate cements, so called low alumina cements, LAC), the first ones being the most effective in the NO_x removal. This efficiency was related to a good ability for NO_2 sorption: the incidence of UV illumination gave rise to the formation of holes on calcium aluminates (Lewis acid sites) that preferentially interacted with the Lewis base NO_2 [28]. However, the effect of other photocatalysts with expanded sensitivity towards visible light on the atmospheric NO_x removal has not yet been tackled in these calcium aluminate cements.

On the other hand, lime-based materials for construction purposes have shown a growing development over the last years [29–31]. Lime mortars, in monolayer as well as in renders, could also be an interesting supporting binder for these active agents, but this topic remains almost unexplored in the literature [32].

Chemical composition, heterogeneity and pore structure of the supporting materials can have a strong influence on the PCO activity [7,20]. Synergistic effects improving the atmospheric NO_x removal efficiency have been reported in different systems leading, for example, to a precise separation between active sites which reduces the electron-hole recombination rates [32–35].

The present work aims to explore the use of photocatalytic additives with expanded sensitivity towards visible light radiation in four different binding materials (PC, two calcium aluminate cements, HAC and LAC, and air lime-based mortars) to remove atmospheric NO_x gases. The outcome of this research could be useful to apply new depolluting building materials that would be active under different illumination conditions, particularly in exposed areas with low sunlight illumination (where the scarce UV component is further restrained). Three nanostructured photocatalytic additives were used for the obtaining of the active mortars: bare TiO_2, which was used for comparative purposes, and two different doped TiO_2, Fe-TiO_2 and V-TiO_2. DeNO_x activity of these mortars was assayed under three distinct radiation types, namely UV, solar and visible radiation, in order to investigate the real effect of the doped additives in these binding matrices. Attention will be also focused on the release of harmful NO_2 as intermediate product of the PCO of the NO: for depolluting building materials, a complete NO photo-oxidation until nitrates (which can be rain-washed) would be desirable in order to effectively reduce the atmospheric pollution. The efficiency of these new photocatalytic cementing matrices in terms of NO_x (considering NO removal and NO_2 release) vs. NO degradation will be assessed. Finally, the hydrophilicity of the mortars is also monitored by the static water contact angle, as an indicator of the potential self-cleaning ability of these mortars.

2. Experimental section

2.1. Materials

Four different binders were used to prepare the mortars:

a) Portland Cement (PC) (type CEM II32.5 N, Portland),
b) High alumina cement (HAC) (Ternal White, Kerneos)
c) Low alumina cement (LAC) (EN 14647 CAC, Ciments Molins Industrial)
d) Dry slaked lime (class CL 90-S according to European standard [36], CALINSA, Spain).

Chemical and mineralogical compositions, obtained by X-ray fluorescence (XRF) and X-ray diffraction (XRD), of the binders are summarized in Table 1. A siliceous aggregate was also used: its mineralogical composition and grading has been reported elsewhere [37].

Three photocatalysts were used: bare TiO_2 (Aeroxide P25, Evonik) and Fe-TiO_2 and V-TiO_2 (synthesized by flame spray pyrolysis, FSP [27], and supplied by Centro Tecnológico L'Urederra, Spain). According to the data provided by the supplier, Fe-TiO_2 was obtained by a solution of Fe^{3+} ion as precursor, whereas V-TiO_2 was obtained from a V_2O_5-TiO_2 mixture.

2.2. Characterization of the photocatalytic additives

Specific surface area was determined in samples by the BET method (ASAP 2020 equipment, Micromeritics) studying N_2 adsorption at 77 K. XRD and XRF were used to study the mineralogical and chemical composition of the additives. Table 2 summarizes the experimental specific surface values obtained for bare titania and doped additives. Particle size of the crystallites was determined according to the Scherrer equation from the XRD results (Table 2) [38]. Anatase and rutile appeared as the only crystalline compounds in all samples (Fig. 1a).

The surface chemical composition of the powders was investigated by quantitative studied of X-ray photoelectron Spectroscopy (XPS) (Equipment ESACALAB 200-X with ECLIPSE data-system (VG Scientific) and MgK-alpha excitation). Survey spectra