Thermal stability of TiO² supported on kaolinite for application in ceramic tiles

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This study presents an innovative approach involving the incorporation of titanium dioxide $(TiO₂)$ into ceramic coatings to reduce pollution caused by organic compounds under exposure to ultraviolet radiation (UVA). The research specifically investigates the challenges associated with the transformation of titania, focusing on the use of kaolinite and $Nb₂O₅$ at elevated temperatures. The main results were achieved with a concentration of 12% TiO₂ for maximum photocatalytic activity with \sim 30% activity, increasing to $~60\%$ after polishing, outperforming other photocatalysts, thermal stability after firing at 1185°C, making titania supported on kaolinite viable in ceramic coatings. This work highlights promising strategies for photocatalitic coatings, proving a relevant future for cheaper applications in ceramic tiles.

Introduction

When exposed to UV radiation, $TiO₂$ produces free radicals that oxidize organic and inorganic compounds adsorbed on its surface¹. However, the use of $TiO₂$ in ceramic tiles presents issues due to the heat treatment required for this manufacturing process, which ranges between 1150 and 1200°C2. Titania undergoes a transition from anatase to rutile (TAR) at high temperatures, particularly >800°C, resulting in a substantial loss in photocatalytic activity³. Commercial TiO2-functionalized ceramic tiles require a second firing at 850 \degree C to adhere the TiO₂ particles to the glazed surface, greatly raising production costs. In powder form, kaolinite-supported TiO² nanoparticles and niobium-dopped $TiO₂$ particles have been shown to delay TAR. Therefore, the goal of this work is to apply these strategies to delay TAR and its ability to be applied in a single-fire ceramic tile regular process that occurs at temperatures ranging from 1150°C to 1200°C4.

Material and Methods

The photocatalysts syntesis followed the procedure described by Barbosa et al. (2015)5, using the sol-gel hydrolytic technique, with 12% photocatalyst applied to glazed ceramics coating, with approximately 1.36 g/m² per ceramic piece. All materials were submited to the firing process at 1185°C, a heating rate of 20°C/min plus 5 min of holding time at the maximum firing temperature. The photocatalytic efficiency was evaluated through the degradation of methylene blue (MB) dye solution (concentration: 3.7mg/L) capacity 200 mL, under exposure to UVA light power 9W (model DULUX S BL UVA 9W/78, Osram) with the distance between sample surface and solution of 50mm.

Results and Discussion

Figure 1 shows the effetct of $TiO₂$ concentrations ranging from 0% to 12% on kaolinite-supported TiO₂. First, it is important to notice the P25 reference activity under the same reaction conditions. When P25 is applied to an unglazed tile and fired at 800°C, the active surface can degrated $~64\%$ of the inicial concentration of MB. The same material fired at 1185°C drops its performance to \sim 18%, close to the photolysis level, \sim 14%, as does kaolinite without TiO₂, \sim 17%. This results once again proves the loss of photoactivity when anatases are exposed to temperatures over 800°C due to TAR. Over the tested interval the photocatalytic efficiency increased as the amount of $TiO₂$ increased. The best result was reachead using 12% KaTiO₂, with ~40% of MB degradation.

Figure 2 shows the MB photodegradation over time for different conditions of 12% TiO₂ kaolinite-supported photocatalyst fired at 1185°C. The photolysis and P25 results are also ploted, which showed basically the same performance, with 15.4 and 18.6% as the highest degradation after 390 min of UV-light exposure. Among the different funcionalized tiles, K-T12-sfv, representing the unglazed product, degrades ~55% of MB. The glazed version of this condition showed a drop in degradation performance, \sim 30%, representing the glass encapsulation effect. $Nb₂O₅$ dopping with $TiO₂$, K-12T5Nfv, presented basically the same result \sim 29% showing that Nb₂O₅ was not an effective strategy in this case. When the tiles were submited to a surface polishing to minimally remove the glass layer on the $TiO₂$ particles, the degradation perfornance increasead to the level of unglazed tiles (~58%), which represent at the same time the highest perfornance in terms of $TiO₂$ exposure while keeping the surface texture in accordande with the astetic requirements for ceramic tiles. The samples pollished with $Nb₂O₅$, K-12T5N-2C, showed a performance level comparable to the photolysis results, problably due to excessive polishing that removed the funcionalized layer.

The PE and P25 samples exhibited contact angles of 72.3° and 49.6°, respectively, on their ceramic surfaces, indicating that the surfaces are hydrophilic, resulting in an irregular distribution of water. Photoinduced testability is higher in coatings without a vitreous phase, possibly due to surface porosity6. These differences in contact angles may be attributed to the

Figure 1. Effect of the amount of TiO₂ in the kaolinite-suported TiO² photocatalist in the methilene blue dye degradation, for unglazed ceramic tiles.

characteristics of the photocatalyst, which likely impart greater hydrophobicity to the surface. These results are in agreement with the MB degradation performance shown in Figure 2. testability is higher in coatings without a vitreous phase, possibly due to surface porosity⁶. These differences in contact angles may be attributed to the characteristics of the photocatalyst, which likely impart greater hydrophobicity to the surface. These results are in agreement with the MB degradation performance show in Figure 2.

Figure 2. AM degradation (%) compared to the enameled standard and the commercial photocatalyst.

Conclusions

Photoactive ceramic tiles produced by single firing route were sucessfully obtained with a catalist supported by kaolinite TiO₂. Under the tested conditions, dopping with Nb₂O₅ yielded no noteworthy results. After surface polishing, the best performance was measured. Compared to currently available technologies, the authors believe this is the easiest and cheapest technique to mafacture photoactive ceramic tile. However, there are significant bottlenecks to overcome before moving to a commercial application.

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