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

ORAL/POSTER Ph.D. Student: Y/N Journal: NONE

E.S.Cordeiro¹, L. Burin¹, I.P. Schvartz¹, M.G.A. Vieira², J. F De Souza³. A. De Noni. Jr¹ (1) Federal University of Santa Catarina, Florianópolis, Brazil. (2) State University of campinas, Campinas, Brazil. (3) Instituto Maximiliano Gaidzinski, Cocal do Sul Brazil. <u>eloise.ufpa@hotmail.com</u>



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 ~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°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, ~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, ~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 performance increasead to the level of unglazed tiles $(\sim 58\%)$, which represent at the same time the highest performance in terms of TiO₂ exposure while keeping the surface texture in accordande with the astetic requirements for ceramic tiles. The samples pollished with Nb_2O_5 , 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 successfully obtained with a catalist supported by kaolinite TiO_2 . Under the tested conditions, dopping with Nb_2O_5 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.

Acknowledgments

We would like to thank CAPES, CNPq and INCT MIDAS for financial support and the Federal University of Santa Catarina for the infraestruture.

References

[1] CHEN, X.; MAO, S. S. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. Chemical Reviews, [s. l.], v. 107, n. 7, p. 2891–2959, 2007.

[2] YADAV, S.; JAISWAR, G. Review on Undoped/Doped TiO2 Nanomaterial; Synthesis and Photocatalytic and Antimicrobial Activity. Journal of the Chinese Chemical Society, [s. l.], v. 64, n. 1, p. 103–116, 2017.

[3] KIM, M.; PARK, E.; JUNG, H.; YUN, S.-T.; JURNG, J. Temperature-dependent thermal stability and dispersibility of SiO 2 –TiO2 nanocomposites via a chemical vapor condensation method. Powder Technology, [s. l.], v. 267, p. 153–160, 2014.

[4] HANAOR, D. A. H.; SORRELL, C. C. Review of the anatase to rutile phase transformation. Journal of Materials Science, [s. l.], v. 46, n. 4, p. 855–874, 2011.

[5] BARBOSA, L. V.; MARÇAL, L.; NASSAR, E. J.; CALEFI, P. S.; VICENTE, M. A.; TRUJILLANO, R.; RIVES, V.; GIL, A.; KORILI, S. A.; CIUFFI, K. J.; DE FARIA, E. H. Kaolinite-titanium oxide nanocomposites prepared via sol-gel as heterogeneous photocatalysts for dyes degradation. Catalysis Today, [s. l.], v. 246, p. 133–142, 2015.

[6] YANG, S; HSU, C; CHANG, T. UV illumination control and enhancement of heat transfer during pool boiling process. International Communications in Heat and Mass Transfer, [S. l.], v. 139, p. 106487, 2022. DOI: 10.1016/j.icheatmasstransfer.2022.106487.