



Research in Advanced Oxidation Processes

Effect of Calcination Temperature on Sulfurdoped TiO₂/SiO₂ Regarding Photocatalytic Activity under Simulated Sunlight



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INTRODUCTION

RESULTS AND DISCUSSION

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Among the emerging technologies for the catalytic

Table 1 shows that the TiO₂ crystal size increased





oxidation of VOCs is heterogeneous photocatalysis, with TiO₂ being the most used for this purpose. Despite having several advantages, TiO₂ has a high charge recombination rate and limitations in the absorption of visible light [1]. Although there are some works that have already studied the use of non-metal doped TiO₂ [1,2], there are no works that discuss the effect of calcination temperature on non-metallic doped TiO_2 supported on silica gel. Thus, the objective of this work is to study the effect of calcination temperature on sulfur-doped TiO_2/SiO_2 materials and their application in a LED- irradiated gas-solid reactor for the photocatalytic degradation of VOCs under sunlight.

MATERIALS AND METHODS

with increasing calcination temperature due to grain sintering and nucleation. Regarding crystal microstrain, sulfur-doped TiO₂/SiO₂ showed greater microstrain than TiO_2/SiO_2 due to the cationic substitution of Ti⁴⁺ by S⁶⁺, generating a charge imbalance with consequent crystal distortion. However, there was a reduction in crystal microstrain with increasing calcination temperature due to the diffusion of sulfur out of the crystal lattice.

Figure 1 shows the comparison between the diffractograms of S-TiO₂/SiO₂ and TiO₂/SiO₂ calcined at 1000 °C. It is clear that sulfur doping delayed the transformation from the anatase to the rutile phase. Regarding the photocatalytic tests, first the efficiency of the doped and undoped material was compared, and the doped material showed 61% degradation of *n*-hexane under sunlight, while the second one showed only 34%. XPS, EPR, photoluminescence, UV-VIS and XRD analyses showed that the sulfur atoms diffused into the TiO_2 crystal lattice, creating energy sublevels above the valence band, allowing light absorption at higher wavelengths [4]. In addition, the analyses showed that there was a reduction in the rate of recombination of photogenerated charges due to the self-doping of Ti³⁺, which starts to act as an electron trap. The catalyst calcined at 1000 °C did not show photocatalytic activity under sunlight, due to the presence of the rutile phase. In addition, the catalyst could not fluidize due to its high density.



Fig. 2 XRD analyses of materials synthesized at 1000 °C.



The synthesis of $S-TiO_2/SiO_2$ materials was based on the procedure originally described by Gusmão (2022) for the synthesis of $S-TiO_2/SiO_2$, varying the calcination temperature from 150 °C to 1000 °C. The tests were carried out in a continuous gas-solid photoreactor irradiated by a high-power metal halide lamp (400 W HPI-T, Phillips Co.). The reactor was placed 18 cm from the lamp so that the UV irradiance on its surface was equivalent to the ASTM AM 1.5G Standard for solar irradiation at sea level (4.6 mW cm⁻²). The photocatalytic efficiency of the materials was evaluated by comparing their steady-state degradation. The model pollutant chosen to perform the tests was *n*-hexane.





Fig. 4 Photocatalytic activity of the synthesized materials.

Table 1 Properties of synthesized materials.

Catalyst	Band gap energy (eV)	Crystal size (nm)	Crystal microstrain (ε)
TiO_2/SiO_2_450C	3.20	4.3	0.054
$S-TiO_2/SiO_2_150C$	3.44	2.4	1.9
S-TiO ₂ /SiO ₂ _450C	3.13	4.4	0.38
S-TiO ₂ /SiO ₂ _600C	3.14	7.1	0.208
S-TiO ₂ /SiO ₂ _750C	3.12	7.0	0.178
$S-TiO_{2}/SiO_{2}_{1000C}$	2.95	29.1	0.012

CONCLUSIONS

Fig. 1 Scheme of the experimental unit.

It was concluded that S-doped TiO₂/SiO₂ increased the steady-state degradation of *n*-hexane from 34% to 61.7%. Crystal size and band gap energy increased with increasing calcination temperature. The transformation of anatase to rutile was retarded up to 1000 °C by sulfur doping. On the other hand, S_{BFT} decreased due to sintering and grain nucleation. The increase in the calcination temperature led to an increase in the efficiency of the photocatalysts up to an optimal value at 450 °C.



REFERENCES

[1] C.A. Gusmão, P.H. Palharim, B. Ramos, A.C.S.C. Teixeira, *Environ. Sci. Pollut. Res.* 26 (2021). [2] M. Xu, Y. Wang, J. Geng, D. Jing, *Chem. Eng. J.* 307 (2017) 181–188. [3] O. Carp, C.L. Huisman, A. Reller, *Prog. Solid. State Ch.* 32 (2004) 33-177. [4] M.R. Khan, T.W. Chuan, A. Yousuf, M.N.K Chowdhury, C.K. Cheng. Catal. Sci. Technol. 5 (2015) 2522.