CERAMIC PHOTOCATALYSTS OF SILICA PHOTOSENSITISED WITH METALS

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1. INTRODUCTION

Advanced oxidation processes (AOPs) use the hydroxyl radical in sufficient concentrations to oxidise organic pollutants, either dissolved in water or dispersed in air, which are resistant to biological degradation, to mineral forms or at least to harmless organic compounds. Titanium oxide is at present the reference as photocatalyst material, given its high activity, relative stability, low cost and low toxicity. However, problems relating to titanium oxide still need solving, such as the low rate of photocatalysis, generation of toxic degradation intermediates, deactivation of the material, and the need for UV irradiation as its band gap does not match sunlight. The use of ceramic composites could improve these aspects (1). Cerro et al. have applied ceramic glazes and ceramic composites as photocatalysts, with interesting results in the photodegradation of substrates such as Orange II in dissolution and NO_x dispersed in the air (2). In addition, Badr et al. (3) studied the photodegradation of organic colorants by means of silica nanoparticles doped with metals. They conclude that doping with Au^{3+} ions is more efficient than with Ag^{+}.

2. EXPERIMENTAL AND RESULTS

In this study, the metals used as sensibilisers were those of the first transition series Mn and Fe. With a view to fixing the working conditions, in principle acetates were chosen as precursor metal salts in order to avoid the interference of inorganic anions in the synthesis with alkoxides. Since manganese acetate is insoluble, preliminary studies were performed to select the manganese metal salt, as well as the quantity of water in the alkoxide hydrolysis–condensation process. Manganese nitrate and acid catalysis were chosen, which optimise the photodegradation and cyclability of the powder. Moreover, as the photocatalytic capability stabilises with an addition of 2.5 mole water/formula weight, this addition was used as a base water concentration. Having fixed the conditions, studies were conducted with different drying methods: (a) slow: in a glass closed with a polystyrene film with needle holes and drying at room temperature, (b) fast drying: under an infrared lamp. The xerogels were characterised by different techniques, such as X-ray diffraction, indicating only the amorphous halo of silica (Fig. 1.a), differential thermal and thermogravimetric analysis (DTA-TG) (Fig. 2c and d), UV-Vis-NIR spectroscopy, measurement of the BET specific surface area (Table 1), scanning electron microscopy with linked energy-dispersive analysis (SEM-EDS) (Fig. 2a and b), as well as by the Orange II photodegradation test (Fig.1.b) (2).

3. CONCLUSIONS

The results of the Orange II photodegradation test indicate good performance, in which the manganese–slow drying composite, with a lower half-life time ($t_{1/2}$ in Table 1) than the reference anatase, stood out. The samples with fast drying exhibited slightly higher values than anatase, while the slow iron sample exhibited higher ones. The silica sample (non-doped SiO_2) displayed a linear degradation curve, indicating absence of photocatalytic capability. The data in Table 1 do not allow the photoactivity of the samples to be associated with the specific surface area measurement. All the samples displayed a monolithic appearance with specific surface area always below 8 m^2/g (the best $t_{1/2}$ of the Si-Mn slow drying sample only reached 3.8 m^2/g); however the worst results (Si-Fe slow drying) were indeed associated with a low specific surface area (0.75 m^2/g). The size of the particles (SEM in Fig. 2) was similar in both cases (10–30 μm). In addition, the EDS composition map of the particles (not included) in both cases indicates a homogeneous distribution of manganese.

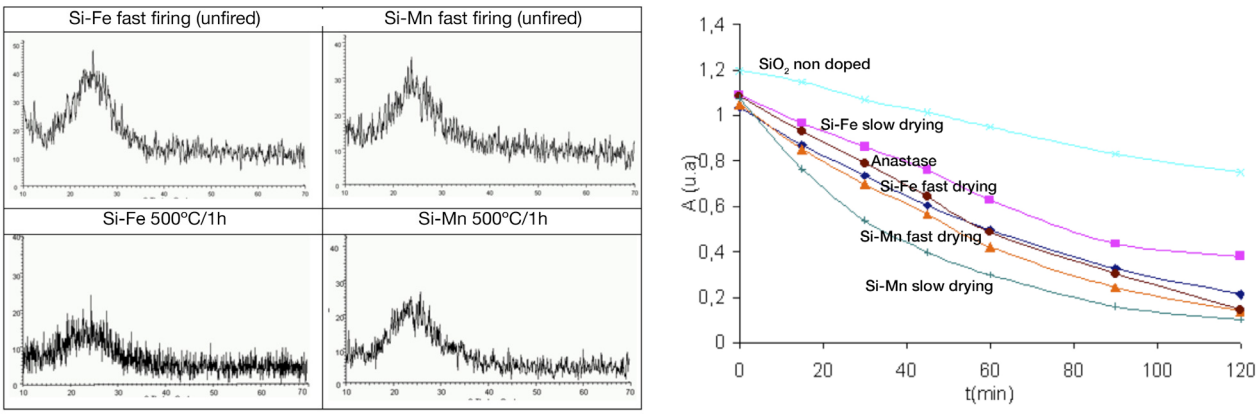

Figure 1. (a) X-ray diffraction, (b) Photodegradation curves of Orange II of the indicated unfired samples.

Sample	E_g(eV) UV	E_g(eV) Vis	Kinetics Langmuir-Hinshelwood		BET (m^2/g)
			$t_{1/2}$(min)	R^2	
Si-Fe fast drying	3.5	2.1	53.9	0.9967	3.91(3)
Si-Fe slow drying	3.5	2.0	75.8	0.9839	0.75(3)
Si-Mn fast drying	3.8	-	42.1	0.9914	7.9(2)
Si-Mn slow drying	3.6	-	33.3	0.9937	3.8(3)
SiO_2 without doping	3.9	-	-	-	-
Anatase	3.0	-	42.0	0.9910	9.17(3)

Table 1. Band gap, Langmuir-Hinshelwood parameters, and BET specific surface area of the xerogels.

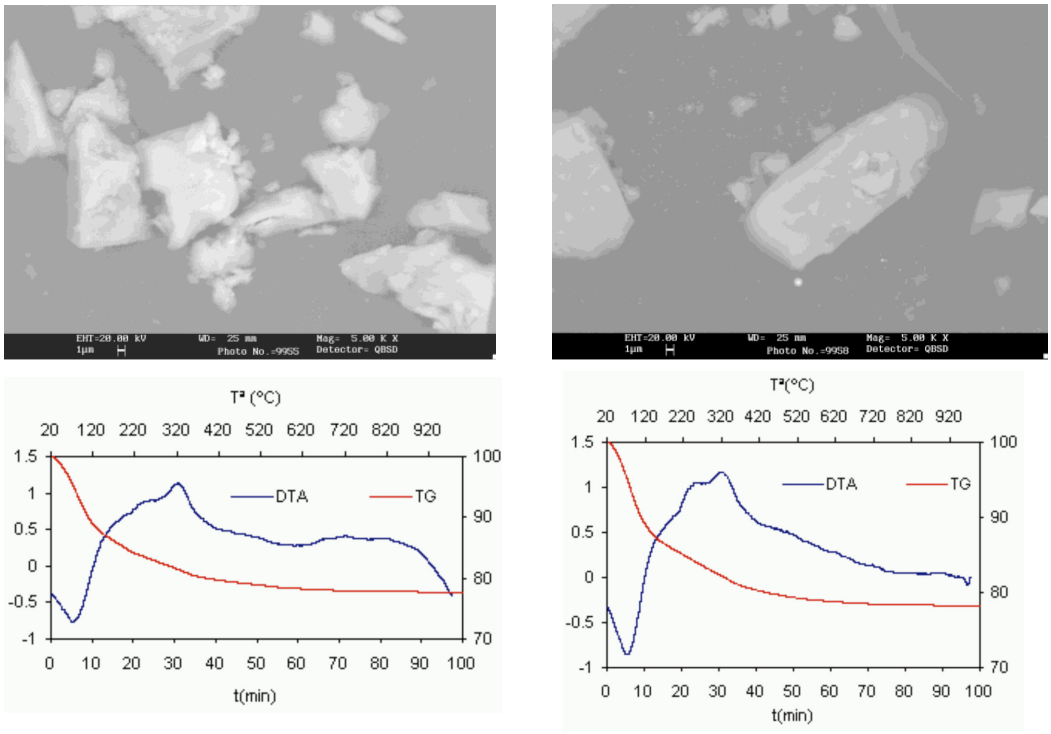

Figure 2. (a) SEM of xerogel Mn-slow drying (b) SEM of xerogel Mn-fast drying, (c) DTA-TG of xerogel slow drying, (d) DTA-TG of xerogel fast drying.

REFERENCES

[1] C. Gargori, R. Galindo, M. Llusar, M.A. Tena, G. Monrós, J. A. Badenes, Photocatalytic degradation of Orange II by titania addition to sol-gel glasses, J. of Sol-Gel Sci. and Tech., 50(2009)314-320.

[2] S. Cerro, R. Galindo, A. García, A. Monrós, J. Badenes, C. Gargori, G. Monrós, Fotocatalizadores de y en cerámica, Proceedings Qualicer 2012.

[3] Y. Badr, M.G. Abd El-Wahed, M.A. Mahmoud, Photocatalytic degradation of Methyl red dye by silica nanoparticles, Hazard. Mater 154(2008)245–253.

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