

# **CERAMIC PHOTOCATALYSTS OF SILICON OR TITANIUM OXIDE PHOTOSENSITISED WITH RUTHENIUM AND MANGANESE CYCLOPENTADIENYLS**

**C. Gargori, S. Cerro, M. Llusar, N. Fas, G. Monrós**

**Dept. of Inorganic and Organic Chemistry, Universidad Jaume I, Castellón (Spain)**

## **1. INTRODUCTION**

Titanium oxide in its anatase polymorph, thermally unstable in ceramics fired above 900°C, is the reference as a photocatalyst owing to its high activity, relative stability, low cost, and low toxicity. However, there are problems that need to be addressed, such as the low rate of photocatalysis, generation of toxic degradation intermediates, deactivation of the material, and need for UV irradiation as its band gap does not match that of sunlight: the use of ceramic composites can 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 solution and NO<sub>x</sub> dispersed in air (2). This study examines the photocatalytic capability of TiO<sub>2</sub> or SiO<sub>2</sub> composites with transition metals such as Ru, Cu, and Mn sensitised with ruthenium (ruthenocene) or manganese (manganocene) cyclopentadienyls by a sol-gel process with controlled hydrolysis-condensation in an ethanol medium from TEOS and titanium isopropoxide as precursor alkoxides of silicon and titanium oxides, respectively.

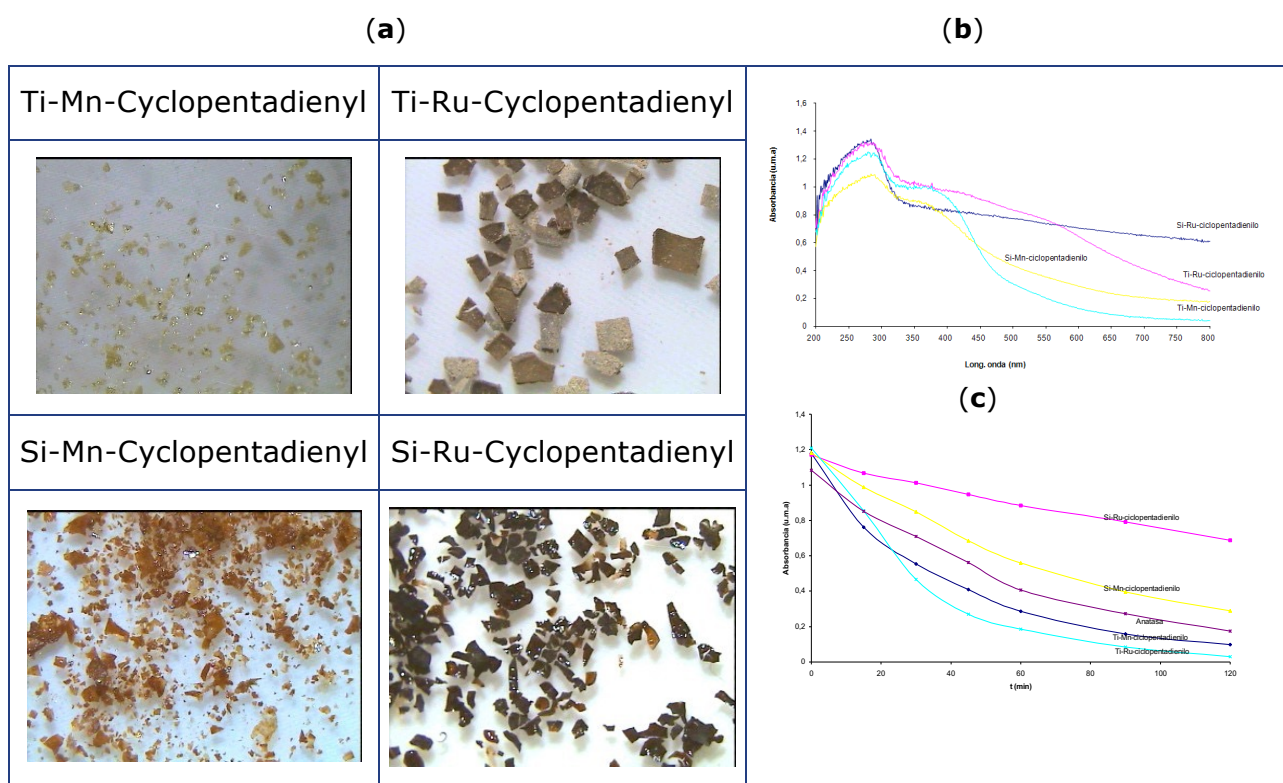
## 2. EXPERIMENTAL AND RESULTS

The dry materials exhibited a glassy appearance in the case of manganocene, with a greenish colour and finer particulate in the case of titanium and orange-brown in the case of silicon. The ruthenocene composites appeared as light brown microtablets in the case of titanium and dark brown with a glassy appearance and smaller particle size in the case of silicon (Figure 1.a).

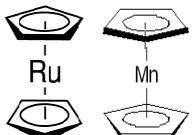
The UV-Vis-NIR spectra with ruthenium displayed a charge transfer band centred at 280 and 290 nm for Si and Ti, respectively, associated with  $M^{4+}-O^{2-}$  transfer as well as high absorption across the Vis-NIR range. In the case of manganese, together with the  $M^{4+}-O^{2-}$  charge transfer band, centred at 290 nm in both silicon and titanium, another band appeared associated with manganese, already in the visible spectrum, at 370 and 390 nm for Si and Ti, respectively (Figure 1.b). The band gap associated with the threshold absorption of the UV band for the ruthenium composites was 3.5 and 3.1 eV for Si and Ti, respectively. The band gap associated with this transfer band in the UV spectrum for manganese composites was 3 eV and those associated with absorption in the visible spectrum were 2.4 and 2.6 eV for Si and Ti, respectively.

## 3. CONCLUSIONS

The results of the photodegradation test with Orange II (Fig. 1.c) followed the Langmuir-Hinshelwood model, the composites exhibiting high photodegradation capabilities, exceeding that of the reference anatase. In the case of silicon, the high relative capability of manganese with average half-life times at the level of anatase may be noted (Table 1).



**Figure 1.** (a) Optical micrograph with binocular magnifying glass (x40) of the composites indicated, (b) UV-Vis-NIR spectroscopy of the cyclopentadienyl composites, (c) Photodegradation curves of Orange II of the cyclopentadienyl composites.

| Ligand                                                                            | Samples      | E <sub>g</sub> (eV)<br>UV | E <sub>g</sub> (eV)<br>Vis | t <sub>1/2</sub> (min) | R <sup>2</sup> |
|-----------------------------------------------------------------------------------|--------------|---------------------------|----------------------------|------------------------|----------------|
| Cyclopentadienyl                                                                  | Si-Ru-Cyclop | 3.5                       | -                          | 153                    | 0.9943         |
|  | Si-Mn-Cyclop | 3.0                       | 2.4                        | 58                     | 0.9981         |
|                                                                                   | Ti-Ru-Cyclop | 3.1                       | -                          | 22                     | 0.9956         |
|                                                                                   | Ti-Mn-Cyclop | 3.0                       | 2.6                        | 32                     | 0.9866         |
|                                                                                   | Anatase      | 3.0                       | -                          | 45                     | 0.9973         |

**Table 1.** Band gap and Langmuir-Hinshelwood parameters of the xerogels.

## ACKNOWLEDGEMENTS

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## REFERENCES

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