

The catalytic photocatalytic degradation of 2,4,6-trichlorophenol over M^{x+}/ZrO_2 photocatalysts

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Introduction

The degradation of organic pollutants into less-toxic products through the use of heterogeneous photocatalytic processes represents an alternative approach to traditional water treatment methods. The irradiation of semiconductor dispersions²⁻³ can, in most cases, lead to complete mineralization of the harmful organic species. The crucial role played by oxidizing radicals formed during the reaction of holes with water is to attack and destroy pollutant molecules⁴. Due to the nature of the degradation process, the assessment of pollutant disappearance is not sufficient to ensure the absence of dangerous products and careful analytical control during photocatalytic treatments is a necessary step.

In this study, the photocatalytic oxidation of 2,4,6-trichlorophenol (2,4,6-T) was performed over ZrO_2 and M^{x+}/ZrO_2 photocatalysts, where $M = Mn, Fe, Co, Ni$ and Cu . The photocatalysts were prepared by the sol-gel method and were annealed at 400°C. X-ray diffraction, DTA, TGA and FTIR spectroscopy were carried out to characterize the samples.

Materials and Methods

The synthesis was performed in the following manner: 6 mL of deionized water was mixed with 61 mL of ter-butyl alcohol (Sigma-Aldrich, 99.7%) under continual stirring for 10 min. Concentrated HNO_3 was added until a pH of 3 was obtained. The solution was heated at 70°C and was maintained at that temperature for a period of 10 min. It was later decreased to 60°C while the dropwise addition of 39 mL of zirconium n-butoxide was performed (Sigma Aldrich 80%). Following the addition, the alkoxide mixture was maintained in reflux at 70°C for 24 hours under constant stirring. For the case of M^{x+} where $M = Mn, Fe, Co, Ni, Cu$, a quantity of nitrate corresponding to that of the ionized metal (Sigma-Aldrich, 99% purity) was dissolved in deionized water such that the concentration of the resulting solution was 1% mole cogelled during the hydrolysis reaction of sol-gel zirconium oxide. The obtained nanomaterials were

ground and calcined in air at 200°C, 400°C, 500°C, 600°C and 800°C for 12 hours. A temperature increase rate of 2°C/min was used.

Results and Discussion

In all of the samples, an endothermic peak was observed at 150°C. This peak corresponds to approximately 18 to 25% of weight loss in the samples due to the sorption of residual water and solvent. At 300°C a partial dehydroxylation process takes place and between 400 to 500°C further dehydroxylation occurs, as well as the exothermic crystalline transformation of zirconia, from amorphous to tetragonal and monoclinic. These results are in agreement with the XRD patterns as shown in Figure 1.

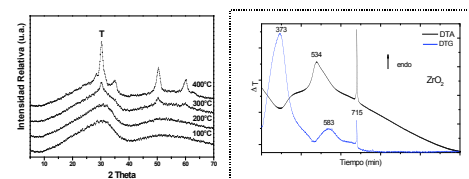


Figure 1. (a) XRD diffraction pattern of Mn/ZrO_2 sample on function of the annealed treatment. (b) DTA-TGA thermogram of Mn/ZrO_2 sample.

The degradation of the 2,4,6-T was using UV-Vis spectroscopy. A calibration curve using Lambert-Beer law was made, in order to obtain the concentration of 2,4,6-T during the photodecomposition reaction. The E_g values vary from 3.6 up to 4.5 eV and the solution test was irradiated using a UV lamp with an energy higher than the photocatalyst band-gap. The disappearance of the organic toxic molecule in the solution follows approximately pseudo-first order kinetics.

Significance

Organic pesticides are a continual threat to the environment. Their removal by water treatment methods are a considerable drain on the economics of water purification. Novel, more efficient methods of pollutant removal could be important to water purification economics.

References

1. O. Legrini, E. Oliveros and M. Braun. *Chem. Rev.* **93** (1993), p. 671
2. N. Serpone, E. Pelizzetti (Eds.), *Photocatalysis. Fundamental and Applications*, Wiley, New York, 1989.
3. P. Pichat, C. Gulliard, C. Maillard, L. Amalric, J.C. D'Oliveira, in: D.F. Ollis, H. Al-Ekabi (Eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993, p. 207.
4. D. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat, N. Serpone, in: G.R. Helz, R.G. Zepp, D.G. Crosby (Eds.), *Aquatic and Surface Photochemistry*, Lewis, Boca Raton, FL, 1994, p. 261.
5. *Environ. Sci. Technol.* **23** (1989), p. 1380.
6. M. Zamora, T. Lopez, R. Gomez, M. Asomoza, R. Melendrez. *Catalysis Today* **107** (2005) 289–293.