Photocatalytic oxidation of chlorinated hydrocarbons with TiO_2 on magnesium silicate monoliths

Benigno Sánchez[1], Roberto Candal[3], Ana Cardona[1], Pedro Ávila[2], Moisés Rebollar[2].
[1] CIEMAT Av. Complutense 22; 28040 Madrid, Spain, benigno.sanchez@ciemat.es
[2] Instituto de Catálisis y Petroleoquímica, Cantoblanco,- 28049 Madrid, Spain
[3] Univ. de Buenos Aires, C. Universitaria, Pabellón 2, 1428 Buenos Aires, Argentina

1. Introduction

Chlorinated hydrocarbons, like trichloroethylene (TCE), perchloroethylene (PCE) and chloroform are used as industrial solvents, polluting water and air. These organics have been tested for photocatalytic oxidation, showing different sensibilities to this process [1-4]. In this paper, we compare the efficiency of the photocatalytic destruction of TCE with a sepiolite-based monolith on which the active phase, TiO_2, was incorporated in different ways: i) incorporation of commercial TiO_2 powder into the silicate matrix; ii) sol-gel dip-coating of magnesium silicate monolith and iii) impregnation of the same supports with a commercial TiO_2 aqueous suspension.

2. Experimental System

The preparation of magnesium silicate monolith supports, without TiO_2, has been previously described [5]. The square-cell monoliths, after drying at 110ºC and treating at 500ºC for 4 hours in air, had a 3.1cm pitch, wall thickness of 0.11 cm and geometric surface of 832 m^2m^{-3}. The synthesis of the TiO_2-and magnesium silicate monolith has been described before [5]. This photocatalyst was labeled the "massic monolith". The Sol-gel monolith was prepared by dip-coating the monolith support with a TiO_2 sol precursor. The TiO_2 sol was prepared by hydrolysis of titanium isopropoxide (Aldrich) in excess of water acidulated with nitric acid (Merck), followed by peptization at 80ºC for 16 hours [6]. The "impregnated monolith" was coated by immersion in a basic aqueous suspension of TiO_2-G5 Rhöne Poulenc for 20 seconds at a rate of 20 cm/s. The process was repeated three times and in all the cases the impregnated monolith was dried at room temperature (c.a. 22 ºC).

Trichloroethylene (TCE) was used to study the photocatalytic performance of the three different photocatalysts. Continuous-flow-mode tests lasting several hours were conducted to evaluate conversion efficiencies. The photoreactor is stainless steel and has an effective aperture diameter of 4 cm enclosed by a Pyrex window. A Xenon lamp illuminates the front window and the catalyst monoliths. The gas carrier (CO_2-free air) containing the contaminants flowed through the illuminated catalyst, and was then analyzed by direct on-line sampling using a GC-HP 6890 with FID. At different time intervals, samples of outlet gases from manually opened valves were adsorbed through Tenax, 2,6-diphenyl-*p*-phenylene oxide, for further GC/MS identification of generated by-products. The experimental set-up, methodologies and diagrams of the monolithic photoreactor and experimental apparatus have been previously described [2-3]. Samples of monolithic catalysts before and after use in the reaction were studied with: mercury intrusion porosimetry (MIP), BET, X-rays diffraction (XRD), the TiO_2 content and overall composition of the monoliths was determined by inductively coupled plasma (ICP) optical emission spectroscopy.

3. Results and discussion

The massic monolith has the greatest BET surface area and porosity. This phenomenon is a consequence of the interpenetration of the TiO_2 particles among the magnesium silicate fibers. The sol-gel and the impregnated monoliths have a smaller surface area because pores are clogged by the TiO_2 particles deposited on the monolith surface. X-ray diffraction analysis of the catalysts showed that the main phase of TiO_2 in the monolith was anatase. In the case of the impregnated monolith, a fraction of rutile was determined. The surface of the sol-gel monolith contains only anatase with a crystallite size of 5 nm, as determined by the Scherrer equation.

Under the conditions studied, the best photocatalytic performance was observed for the massic monolith, followed by the sol-gel coated and the impregnated monolith. By comparing the TiO_2 content of each catalyst with the above results, it is clear that the larger the amount of the TiO_2 catalyst and the higher the BET area and porosity of this catalyst, the better the photocatalytic activity of the massic monolith. However, it is also noticeable that, in spite of the small amount of TiO_2 supported on the other catalysts, they showed activity comparable to the massic monolith. This observation confirms that in the case of the massic monolith, the TiO_2 that remains in the bulk of the magnesium silicate support does not show significant catalytic activity. The higher activity of the sol-gel monolith in comparison to the impregnated monolith may be a consequence of both the larger amount and the smaller particle size of the TiO_2 present in these catalysts.

4. Conclusions

Taking into account the different amounts of TiO_2 in the two catalysts with the best results, massic monolith and sol-gel monolith, it may be said that the sol-gel catalyst yields greater net activity due to the fact that a large percentage of the TiO_2 in the massic monolith is inside the walls and, therefore, ineffective for reaction. However, the massic catalyst has better total performance and its fabrication is simpler than the sol-gel catalyst. On the other hand, the results demonstrate that by coating monolith supports with TiO_2 it is possible to obtain photocatalysts with acceptable efficiency. Since with the sol-gel process it is simple to incorporate doping agents that change the properties of the original catalyst, the combination of sepiolite supports coated with metal oxide sols is a promising method for the preparation of novel photocatalysts.

References

1. Jacoby, W.A., Blake, D.M., Noble, R.D., & Koval, C.A. J Cat, *157,* (1995), 87-96.
2. Sánchez, B., Cardona, A.I., Romero, M., Avila, P., Bahamonde, A. Cat Tod, 54*,* (1999), 369-377.
3. Cardona, A.I., Sánchez, B., Romero, M., Blanco, J., Avila, Phys.IV France, 9, (1999), Pr3-271-Pr3-276.
4.Ku, Y., Ma, C.-M., Shen, Y.-S.. App Cat B34, (2001)181-190.
5.Avila, P., Blanco, J., Sánchez, B., Cardona, A.I., Romero, M. App Cat B.17, (1998), 75-88.
6. B. L. Bischoff and M. A. Anderson, Chem. Mater., 7, (1995), 1772-1778.