Photocatalysis with Ti-pillared clays for the oxofunctionalization of alkylaromatics by O₂

Houria Rezal a, Hussein Khalaf b, Jose Luis Valverdec, Amaya Romeroc, Alessandra Molinarid, Andrea Maldottid, *

a Centre Universitaire, Khemis-Miliana, Algeria
b Laboratoire de Chemical Engineering, University of Blida, P.O. Box 270-09000 Blida, Algeria
c Departamento de Ingeniero Química, Facultad de Químicas, Universidad de Castilla-la Mancha, Campus Universitario s/n, 13004 Ciudad Real, Spain
d Dipartimento di Chimica, Università degli Studi di Ferrara, Via L. Borsari 46, 44100 Ferrara, Italy

1. Introduction

Catalytic oxidation represents a fundamental process for the production of functionalised hydrocarbons and fine chemicals [1–3]. Unfortunately, many of these processes are accompanied by several drawbacks such as low selectivity, poor catalyst stability and the employment of large amounts of pollutant materials. For these reasons, there is a strong demand for the development of robust heterogeneous and/or supported catalysts that can promote selective oxidation by cheap and non-toxic reagents. In this context, the oxygenation of C–H bonds by molecular oxygen under mild temperature and pressure conditions is an ever-expanding area of interest [4].

Among the oxidation catalysts able to fit the above requirements, photoexcited semiconductors such as TiO₂ have attracted much attention in the last two decades [5,6,7]. Combining most of the literature information [5–17] the mechanism for the TiO₂-assisted photooxygenation of C–H bonds of hydrocarbons can be summarized by the following reactions, whose efficiency is influenced by TiO₂ structure [8], nature of dispersing medium [11,12], excitation wavelengths [15,16] and particle size [8,17].

Photochemical excitation of TiO₂ ($\lambda < 380$ nm) leads to charge separation in the semiconductor particle: electrons are promoted to the conduction band ($e^-/C_0$) and holes are left in the valence band ($h^+/C_1$). It is generally accepted that the subsequent oxidation of hydrocarbon (RH₂) to alkyl radicals occurs either through direct electron transfer to the photogenerated positive holes or by hydrogen abstraction by OH$^-$ radicals, which may be formed as a consequence of hole capture by adsorbed OH$^-$ groups.

\[ \text{RH}_2 + h^+ + \text{OH}$\text{surf}^- \rightarrow *\text{RH} + \text{H}^+ + \text{H}_2\text{O} \]  (1)

Scavenging of conduction band electrons by O₂ may lead to the formation of O₂$^-$ and HO₂$^*$ through Eq. (2). The molecule of O₂ can also react with alkyl radicals under a diffusion-controlled rate to give peroxy radicals according to Eq. (3). The photogenerated