



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

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ABSTRACT

Ti-pillared montmorillonite clays (Ti-PILCs) have been investigated as photocatalysts for the selective oxygenation of the following liquid alkylaromatics: toluene, para-xylene and ortho-xylene. The photocatalytic processes occur using O₂ as oxidizing species, upon near UV light, in mild pressure and temperature conditions and with good stability of the catalytic materials. Accumulation of valuable carboxylic derivatives is possible since their over-oxidation to carbon dioxide is negligible. In particular, proper reaction conditions are found for obtaining carboxylic compounds with about 90% selectivity, which is significantly higher than that obtained when the same experiments are carried out with commercial TiO₂ Degussa P25. Detailed results on the chemical–physical characterization of these materials are also presented. In this regard, particular attention is devoted to the effects of surface interaction with substrates and reaction intermediates on efficiency and selectivity of the photocatalytic processes. In particular, the hydrophobic nature of the Ti-PILCs as well as adsorption phenomena are beneficial for alkylaromatics to reach the photoactive sites. The results obtained in mixed alkylaromatics/cyclohexane reaction media show that the Ti-PILCs are also able to discriminate among the substrates in favour of the aromatic compounds.

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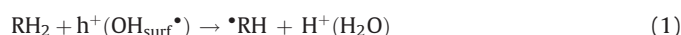
1. Introduction

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^-) and holes are left in the valence band (h^+). 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.



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

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