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Partial oxidation of allylic and primary alcohols with O_2 by photoexcited TiO_2†

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Proper reaction conditions have been found for the conversion of geraniol, citronellol, *trans*-2-penten-1-ol and 1-pentanol to the corresponding aldehydes with good chemo-selectivity (>70%) by photochemical excitation of suspensions of P25-TiO_2. It is demonstrated that adsorption of the alcohol on the surface as an alcoholate is necessary for its oxidation. ESR-spin trapping experiments point out that oxidation of alcohols starts with the formation of alkoxide radicals. Water content in the dispersing medium strongly inhibits alcohol adsorption and subsequent oxidation. In fact, water increases the polarity of the dispersing medium favouring the affinity between the polar alcohol and the CH_3CN–H_2O mixture itself; moreover, water competitive adsorption with the alcohol causes the removal of the latter from the photocatalytic surface with consequent difficult oxidation, as evidenced by ESR-spin trapping investigation. The reactivity of the alcohol on the surface of photoexcited P25-TiO_2 is also affected by the nature of its hydrophobic aliphatic chain: geraniol and citronellol are more susceptible to the water content than their short analogues *trans*-2-penten-1-ol and 1-pentanol. Moreover, in anhydrous CH_3CN, specific interaction between the surface and the OH group enhances the reactivity of the primary aliphatic alcohols towards their partial oxidation to aldehyde, which can be accumulated in the reaction environment.

Introduction

The partial oxidation of alcohols for the production of fine and specialty chemicals is a demanding chemical transformation. Moreover, stringent ecological standards increase the need to develop environmentally friendly methods, with the employment of clean oxidants and of heterogeneous catalysts that are easy to handle, recover and recycle. The results obtained by using solid catalysts for the selective oxidation of alcoholic groups to carbonyl compounds using molecular oxygen as the only oxidant have been recently reviewed in detail by Mallat *et al.*;[1] the authors point out that, despite the efforts produced, some catalysts do not represent a real alternative to conventional methods because of their very low activity and that the selective and fast oxidation of aliphatic primary alcohols remains an unsolved problem.

In this framework heterogeneous photocatalysis can provide a new synthetic method since it requires milder conditions with respect to thermal activation and allows shorter reaction