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Synthesis of benzaldehyde from toluene by a photocatalytic oxidation using TiO_2-pillared clays

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ABSTRACT

Photo-oxidation of toluene was investigated by using TiO_2-pillared montmorillonite (Ti-montmorillonite). The main intermediates of toluene oxidation were benzaldehyde and *p*-cresol while traces of benzyl alcohol, benzoic acid, pyrogallol and hydroquinone were also found. The solvent effect on the photo-oxidation of toluene on Ti-montmorillonite was significant; the activity was increased by an addition of 10% water in acetonitrile solvent and it was further increased when the reaction was performed in an aqueous environment. In the latter condition, Ti-montmorillonite showed higher activity to benzaldehyde (the desired product) than TiO_2 (Degussa P25), possibly because of the difference value of its surface area and the hydrophobic nature of pillared clay. The maximum yields in benzaldehyde using Ti-montmorillonite and TiO_2 P25 as photocatalysts were 48 and 27%, respectively, after 1 h reaction time in the best experimental conditions.

1. Introduction

The oxidation of aromatics to their corresponding compounds offers an attractive synthesis of higher-value products from relatively inexpensive feedstocks. However, many of the current pathways to produce these products are environmentally hazardous. From the environmental and economical point of view, recent research has focused on the oxidation under mild condition [1–5]. Heterogeneous photocatalysis employing semiconductive photocatalysts, such as TiO_2, can offer an alternative catalytic oxidation technology, because the reaction is promoted under ambient temperature and pressure [6–14]. However, due to the high positive energy of the photogenerated holes on TiO_2, the use of TiO_2 has a potential problem that most organic compounds will undergo complete oxidation. In order to use it as a selective oxidation catalyst for fine chemical production, it is necessary to control its high oxidation power.

In thermally catalyzed oxidation, modification of the catalyst, such as an addition of promoters and formation of mixed oxides, is usually done in order to improve the selectivity. For the photocatalysis by TiO_2, such attempts have not succeeded, because impurities and defects produced by such modifications drastically decrease the activity by increasing the recombination rate of the photo-produced charges [6,8]. On the other hand, it has been reported that there are some effects of solvent on the photo-oxidation of liquid hydrocarbons by TiO_2 [11,15]. For example Almquist and Biswas [15] recently showed that the reaction rate and selectivity to the formation of cyclohexanol and cyclohexanone in the photo-oxidation of cyclohexane on TiO_2 depend on the solvent nature. It is therefore expected that the effectiveness of TiO_2 photocatalysts for the partial oxidation reaction can be improved by controlling reaction environments.

It is well known that TiO_2-pillared clays can provide large surface area and pores volume [16–21], which are beneficial for organic compounds to reach and leave the active sites on the surface. The size of the TiO_2 pillars incorporated between the silicate layers is of nanometer dimension. It has been reported that TiO_2-pillared clay is fairly effective for the photocatalytic degradation of organic substrates [18–20], and it exhibits shape selectivity because of its pore structure [18]. It is also expected that the sorption behavior of photocatalysts can be changed by including TiO_2 particles in the silicate layer of the clays, and hence different property can be obtained for the photocatalytic reaction, depending on the surface properties of the host clays.

Toluene oxidation studies have been previously reported [22–34] Fujihira et al. [22] showed the formation of cresols by means of an oxidative attack to the aromatic ring and benzaldehyde and benzyl alcohol by side-chain oxidation, depending on the pH of the solution. The results reported in [22] were confirmed by Navio et al. [23] as they found benzyl alcohol, benzoic acid and benzaldehyde as products. They reported that benzaldehyde was the main product in all the experimental conditions investigated. Augugliaro et al. [35] have studied the photocatalytic oxidation of gaseous toluene on anatase catalyst and they indicated that

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