



Epoxidation of olefins on photoirradiated TiO₂-pillared clays

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ABSTRACT

The epoxidation of cyclohexene by molecular oxygen was investigated by photoirradiated TiO₂-pillared montmorillonite (Ti-montmorillonite). This reaction selectively produced cyclohexene epoxide as major product. The effects of reaction parameters such as reaction time, pillaring process of the clay mineral, Ti-montmorillonite concentration and solvent nature in the epoxidation of cyclohexene are discussed. Ti-montmorillonite showed higher selectivity for cyclohexene epoxide than TiO₂ (Degussa P25), due to the different specific surface area and hydrophobic nature of the pillared montmorillonite. The maximum yields of cyclohexene epoxide using Ti-montmorillonite and TiO₂ P25 were 45 and 30%, and the maximum selectivities were 45 and 30%, after 8 h reaction time at optimal experimental conditions. Other olefins were also tested, and the activity decreased in the order cyclooctene > cyclohexene > 1-hexene > 1-octene.

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1. Introduction

Catalytic epoxidation of alkenes is both an important industrial reaction and useful synthetic method for the production of a wide variety of fine chemicals, because they are derived directly from alkenes, a primary petrochemical source (Ulmann's encyclopedia, 1998). Epoxides are versatile intermediates in organic synthesis because they can easily undergo ring opening to form mono- or bi-functional compounds (Rao, 1991; Schwesinger and Bauer, 1995; Neumann and Dahan, 1997; Hill, 1999; Jones, 1999; Ishii et al., 2001; Sheldon and van Vliet, 2001). Generally, epoxides can be formed from corresponding alkenes by oxidation on both the laboratory and industrial scales (Grigoropoulou et al., 2003). Many efforts have been made to develop methods of epoxidation (Tabushi and Koga, 1979; Mansuy et al., 1983; Yamada et al., 1992; Mukaiyama and Yamada, 1995; Xi et al., 2001; Wang et al., 2005; Petrovski et al., 2005; Zhang et al., 2006; Farahani et al., 2006; Jhung et al., 2006; Abrantes et al., 2009; Miao et al., 2009a; Quionero et al., 2009; Roldan et al., 2009; Serrano et al., 2009; Wang et al., 2009). Industrially, with the exception of ethylene, which is directly oxidized by oxygen, most alkenes are epoxidized by peroxides or peracids in organic solvents (Li and Chan, 1997). For example, MoO₃/SiO₂ is used as a catalyst in the liquid phase epoxidation of propylene with cumene hydroperoxide (CHP) (Miao et al., 2009b). Another important industrial process commercialized in March 2003 by Sumitomo involves a titanium-based catalyst.

Cyclohexene epoxide is a valuable organic intermediate, used in the synthesis of products such as chiral pharmaceuticals, pesticides, epoxy paints, rubber promoters, dyestuffs, plant-protection agents and stabilizers for chlorinated hydrocarbons (Bhattacharjee and Anderson, 2006; Sreethawong et al., 2006). Epoxidation of cyclohexene has been widely investigated using several metal catalysts under both homogeneous and heterogeneous conditions (Ravikumar et al., 1998; Raja et al., 1999; Fraile et al., 2003; Kotova et al., 2003; Ding et al., 2004; Qi et al., 2005; Rahiman et al., 2006; Castamana et al., 2009; Dinda et al., 2009; Jiang et al., 2009; Lee et al., 2009; Lin et al., 2009; Stamatisa et al., 2009; Tangestaninejad et al., 2009). Prasad et al. (2006) showed that the oxidation of cyclohexene over titanium mesoporous materials yielded cyclohexene epoxide as major product (a conversion of 70.2% and a selectivity of 95.1%). Heterogeneous photocatalysis employing semiconductive photocatalysts, such as TiO₂, can offer an alternative catalytic oxidation technology, because the reaction is promoted under ambient temperature and pressure. Ohno et al. (1998a,b, 2001), reported that olefins, such as 1-decene, 1-hexene and 2-hexene, are converted to the corresponding epoxides by UV-irradiated TiO₂ particles with yields of 68, 79 and 83%. Photo-oxygenation of olefins, especially aromatic olefins, using TiO₂ particles was previously reported by Kanno et al. (1980), Fox and Chen (1981), and Fox (1983). However, in most of their results, the main products were not epoxides, but carbonyl compounds. Although the yields of epoxides in all these studies were low, their generation on photocatalysts using molecular oxygen as the oxidant incited most research on this field. The photogenerated holes on TiO₂ possess high energy, leading to a complete oxidation of most organic compounds. In order to use it as a selective oxidation catalyst for fine chemical production, it is necessary to control its high oxidation power (Shimizu et al., 2002). For improving the selectivity in catalyzed oxidation, the

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