

Unraveling the Role of CuO in Cu_xO/TiO₂ Photocatalyst for the Direct Propylene Epoxidation With O₂ in a Fluidized Bed Reactor

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Propylene epoxidation in mild conditions using molecular O₂ is a highly desirable reaction that represents a significant challenge in the field of heterogeneous catalysis for the synthesis of oxygenated organic compounds of industrial interest. In this work, Cu_xO/TiO₂ composites with different nominal CuO loadings (in the range of 0.5–8.4 wt %) were used to promote the photocatalytic epoxidation of propylene with molecular oxygen under UV-A irradiation in a fluidized bed system. The photocatalysts were prepared by a straightforward method consisting of thermal annealing of physical mixtures between copper acetate and sol-gel-derived TiO₂. Different characterization techniques were employed to assess the influence of Cu_xO content on the physical-chemical properties of the Cu_xO/TiO₂ composites. The best combination in terms of

propylene conversion and selectivity towards propylene oxide (18.1 % and 72 %, respectively) was obtained with Cu_xO/TiO₂ at 1.1 wt % CuO, as shown by photocatalytic tests. The high propylene oxide selectivity is due to the ability of CuO in the Cu_xO/TiO₂ composite to transform molecular O₂ into hydrogen peroxide that, in turn, is able to directly oxidize propylene to propylene oxide. By using a UV-A light intensity of 297.2 mW cm⁻², the propylene conversion and the epoxide yield were 31.5 and 22.2 %, respectively, significantly higher than that reported in the literature. Moreover, the energy consumption of the reaction system employed in this paper was significantly lower than that of photocatalytic systems studied in the literature dealing with selective propylene epoxidation.

1. Introduction

Propylene oxide, also known as propene oxide, methyloxirane or 1,2-epoxypropane, is an important raw material used in the chemical industry for the synthesis of several compounds, such as polyols, propylene glycol, glycol ethers, and non-ionic surfactants.^[1] In particular, propylene oxide appears to be the third propylene derivative most synthesized by the process industry, following polypropylene and acetonitrile.^[2–3] For this reason, the global propylene oxide market is expected to experience significant growth in the next years.

Nowadays, the synthesis of propylene oxide (PO) by industrial chemical plants occurs through five different conventional processes (Figure S1): i) Chlorohydrin Process (CL), ii) Tert-

butyl alcohol co-product process (PO/TBA), iii) Styrene co-product process (PO/SM), iv) Hydrogen Peroxide Process (HPPPO), and v) Cumene Process (POC).^[6]

The predominant method for producing PO is the chlorohydrin procedure (CHPO), constituting 37 % of global production.^[6] However, to eliminate the use of chlorine in synthesis, alternative processes have been developed employing organic hydroperoxides for olefin epoxidation. Specifically, organic intermediates such as Ethylbenzene (PO/SM), isobutene (PO/TBA), or cumene (CHP) are utilized. These methods involve initial peroxidation of the intermediate molecule followed by propylene epoxidation through olefin interaction with the generated peroxide. The cumene process (CHP) offers the advantage that the coproduct, dimethylphenylmethanol, can be recycled by hydrogenation and dehydration back into cumene. On the other hand, the direct epoxidization of propylene using H₂O₂ and TS-1 catalyst,^[9] with over 90 % PO selectivity, commercialized by Evonik (formerly Degussa) in 2008, generates only water as a byproduct. However, the relatively high cost of H₂O₂ in 2019 (around 500 USD/t) compared to propylene oxide (PO) (approximately 1500 USD/t) poses a significant economic challenge for this process.^[10] Consequently, while the preference is for oxidation using abundant and inexpensive oxygen, a catalytic process capable of selectively epoxidizing propylene remains a challenge. Indeed, the main limitation of such processes is that they do not allow direct oxidation of the olefin by molecular oxygen. This peculiarity implies the following disadvantages: i) low atom economy, ii) harsh reaction conditions (high T and P, low pH),

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