

Environmentally friendly Baeyer-Villiger oxidation with H₂O₂ catalyzed by an alumina-aminoporphyrin heterogeneous catalyst.

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Abstract

This work has tested an environmentally benign and selective Baeyer–Villiger oxidation system. The catalyst, an aminoporphyrin supported on alumina, was prepared by the non-hydrolytic sol-gel process. Cyclic ketones were oxidized by hydrogen peroxide with selectivity of 25-41% for the main product. A detailed investigation into how the reaction temperature and the amount of water present in the oxidant influenced the catalytic activity and product selectivity was conducted. The catalyst assessed here is cheap, easy to prepare in large scale, and recyclable.

Introduction

The active site of biological enzymes has inspired the design of stable and selective catalysts. In nature, various enzymes containing heme as the active site, like the Cytochrome P-450, can perform reactions selectively and under mild conditions. This study aims to test the catalytic efficiency of an aminoporphyrin supported on alumina matrix in Baeyer-Villiger (BV) reactions for the oxidation of cyclohexanone by hydrogen peroxide (H₂O₂).

Results and Discussion

The catalyst consisting of the metalloporphyrin mesotetrakis(2,6-dichloro-3-aminophenyl)porphyrin iron (III) (FeTDCNH₂) supported on alumina matrix (Al-FeTDCNH₂) and the blank catalyst (Al-blank) were obtained by the non-hydrolytic sol-gel process, alcohol route. The materials were characterized by infrared (IR) and ultraviolet-visible (UV-VIS) absorption spectroscopy, thermal analysis (TGA/DTG/DTA), X-ray diffraction (XRD), and gas chromatography (GC). The TG/DTG curves revealed an initial weight loss between 25 and 110 °C, attributed to residual molecules of solvent, water, and by-products of the preparation reactions in the material. A second weight loss occurred from 200 to 700 °C, due to pyrolysis and elimination of residual halide groups accompanied by decomposition of FeTDCNH₂. The IR spectra displayed bands at 3412, 2456, 1636, 1390, 1022, and 578 cm⁻¹. The band at 1022 cm⁻¹ in the spectrum of Al-blank shifted to 1108 cm⁻¹ in the spectrum of Al-FeTDCNH₂, possibly because hydrogen bonding emerged

between the aluminol OH-groups and the ironporphyrin, evidencing FeTDCNH₂ immobilization in the alumina matrix. The UV-VIS absorption spectra presented the Soret band characteristic of ironporphyrins at 420 nm, which attested to FeTDCNH₂ immobilization in the solid. The synthesized catalysts were tested in cyclohexane oxidation reactions; cyclohexanol was the sole product. BV cyclohexanone oxidation by hydrogen peroxide (H₂O₂ 70% w/v and anhydrous) in the presence of the catalytic materials was evaluated at 27 and 80 °C. The reaction kinetics was followed; the reaction products were measured at 2, 4, 24, and 48 h. At 27 °C, cyclohexanone conversion to ε-caprolactone in the BV catalytic oxidation with H₂O₂ 70% as oxidant was relatively low (about 4%)—catalyst deactivation took place in the presence of water when aqueous H₂O₂ was the oxidant. Further tests were conducted at 80 °C and using anhydrous H₂O₂ to improve the ε-caprolactone yield. The homogeneous catalyst exhibited higher performance in both tests. In the presence of Al-FeTDCNH₂ and Al-blank, ketone conversion to ε-caprolactone was 41% and 37%, respectively. ε-caprolactone was the only reaction product. The Sheldon test was carried out to determine whether the catalytic activity of Al-FeTDCNH₂ was truly heterogeneous. No product was detected, indicating that the supported solids played an essential role in the reaction.

Conclusions

The catalysts prepared herein act selectively and efficiently during the BV oxidation, to produce the lactone. Hence, the cyclohexanone originating from cyclohexane oxidation can serve as material to obtain the caprolactone. These results are promising. Heterogeneous catalysts are advantageous over homogeneous catalysts because the former is reusable, which makes it economically feasible.

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