

Effect of peripheral substituents in the catalytic activity of iron phthalocyanines for the allylic oxidation of α -pinene and limonene

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Introduction

Over the last 40 years, metallophthalocyanines (MePc) have attracted considerable interest in oxidation reactions because of their structural similarity to the active center of natural metalloenzymes, such as Cytochrome P-450 [1]. The catalytic system iron sulfophthalocyanine (FePcS-SiO₂)/tert-butyl hydroperoxide (TBHP) is active for cyclohexene oxidation to the allylic ketone (43% yield); however, catalyst deactivation was detected in the reaction [2]. Control of chemical and physical properties, as well as activation and stabilization of MePc catalysts may be attained by ring substitution [3]. In this contribution, we evaluate the effect of electron withdrawing and electron donating peripheral substituents of iron phthalocyanines on the allylic oxidation of limonene and α -pinene.

Materials and Methods

Complexes with electron withdrawing groups (EWG): FePc(SO₂)₄ and FePc(NO₂)₄, and electron donating group (EDG), FePc(CH₂Cl)₄, were synthesized and immobilized on silica following previously reported methods [4]. Catalysts were characterized by elemental analysis and diffuse reflectance UV-VIS spectroscopy. Oxidation reactions were carried out by adding an amount of iron phthalocyanine (FePc) catalyst sample to obtain 0.5 % mol Fe in the mixture and the oxidant (dried TBHP) to a solution of the substrate (0.125 M) in acetone; then, the reaction mixture was stirred at 40°C for 7 h. Products were identified by GC-MS and quantified by GC with commercial samples and decane as internal standard.

Results and Discussion

Chemical analysis and the presence of UV-Vis bands between 640 – 680 nm of fresh and used catalysts (table 1) confirmed the presence of iron phthalocyanine complexes anchoring on silica.

Table 1. Iron content and UV-Vis bands of iron phthalocyanine immobilized catalysts.

Catalyst	FePc(SO ₂) ₄	FePc(NO ₂) ₄	FePc(CH ₂ Cl) ₄
Iron content ($\mu\text{mol Fe/g cat}$)	37	95	100
UV-Vis bands (nm)	Fresh	640	686
	Used	640, 683	626, 686

* UV-VIS spectrum exhibited no phthalocyanine bands.

Catalytic activity of iron phthalocyanine (FePc) catalysts is shown in figure 1. α -pinene was more reactive than limonene for oxidation over tested catalysts. Similar results were previously reported [5]. Ketone yield did not show any dependence on the catalyst peripheral substituents with both substrates. Notwithstanding, higher yields of verbenone than carvone are

obtained. The lower carvone yield has been related to the presence of several possible oxidized sites in limonene structure [6], which decreases ketone selectivity.

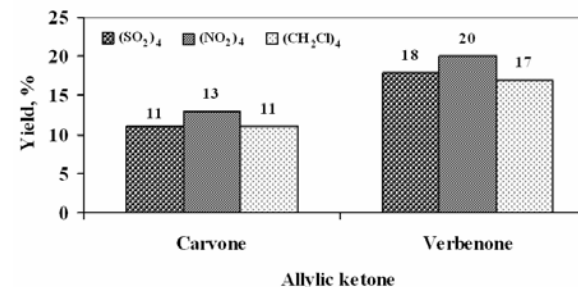


Figure 1. Carvone and verbenone yield over iron phthalocyanine/SiO₂/TBHP system.

In spite of their similar activity, catalyst stability depended on the peripheral substituent group. As can be observed in table 1, UV-Vis results suggest that the complex was completely destroyed when the donating group was the peripheral substituent, FePc(CH₂Cl)₄. The presence of new bands in the other two catalysts can be related to the modification of some of the initial species in the catalysts during the reaction. In the case of the FePc(SO₂)₄-SiO₂ catalyst, the new band can be associated with the presence of monomeric and/or N-oxide species [4], whereas in the case of the FePc(NO₂)₄-SiO₂ formation of dimeric species is expected [4].

Significance

This study shows that immobilized iron phthalocyanines are more active catalysts for α -pinene than for limonene allylic oxidation. Their activity does not depend on the peripheral substituents but on substrate reactivity. Low stability of iron phthalocyanine substituted with an EDG was observed.

Acknowledgments

The authors acknowledge financial support from Colciencias through CENIVAM Center of Excellence RC No.432 and from CNRS (France). L.M.G. acknowledges a doctoral fellowship from Colciencias.

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