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β-pinene oxidation by hydrogen peroxide catalyzed by modified niobium-MCM

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ABSTRACT

Although solid niobium has a high surface area, its high Lewis and Brønsted acidity is a drawback that always compromises its catalytic performance in oxidation reactions. In this work, treating the niobium catalyst with hydrogen peroxide circumvents this disadvantage and results in a significant increase in the selectivity of the oxidation of β-pinene. In addition, the efficiency of the niobium catalysts supported on MCM was investigated. Nb-MCM//H_2O_2 and Nb-MCM were the most active catalysts. Good selectivity of up to 85% at a 93–97% substrate conversion has been achieved. The catalyst can easily be recovered and reused several times without loss in activity.

1. Introduction

The oxidation of monoterpenes is an attractive route for the valorization of these inexpensive and renewable natural olefins [1]. Oxygenated terpenes serve as raw materials for pharmaceutical industries [2], fragrances [3] and fine chemistry and are used in organic synthesis as chiral building blocks [4]. However, in olefins, oxidation reactions generally use toxic and expensive metallic oxidants required in stoichiometric quantities [5]. Thus, the development of processes based on a clean oxidant such as hydrogen peroxide is environmentally and economically welcomed [6–8]. Heterogeneous catalysts with a high surface area can be an attractive option. Mesoporous materials, such as MCM-41, are inorganic solid materials that have uniform pores ranging from 20–500 Å. They are synthesized in the presence of a surfactant, such as cetyltrimethylammonium halide, that arranges itself into cylindrical micelles with the polar groups pointing out towards the surface of the cylindrical arrangement [9]. The main problems in using MCM-41 for catalysis are its poor acidity and low thermal stability. However, silicon substitution for metal could make the material a very active catalyst for some reactions [10]. Niobium compounds are important catalysts for various reactions. Niobium oxides significantly enhance the catalytic activity and prolong the catalyst life when small amounts are added to known catalysts. Mixed oxides containing niobium and niobium oxide supported on other oxides also show this effect. Nb-zeolite, mesoporous Nb-MCM-41 and Nb-layer compounds have redox properties, acidic properties and/or photosensitivities that give them interesting catalytic behaviors [11–13]. Over the past several years, increasing interest has been shown with regard to niobium-containing mesoporous molecular sieves. Niobosilicate mesoporous molecular sieves were first synthesized in 1997 [14–16]. The niobium species in this material can play various functions in heterogeneous catalysis and can exhibit a very high activity in the oxidation of organic compounds with hydrogen peroxide [13,14]. Our group proposed a modification in the Nb-MCM material by H_2O_2-treatment as a means to increase the number of oxidizer groups on the surface through the formation of the peroxo species [12,17].

Following up on our previous study, we report in this paper, for the first time, the results obtained for the oxidation of β-pinene by H_2O_2 in CH_3CN solutions catalyzed by niobium-containing MCM-41. After treatment with hydrogen peroxide, we assessed the catalytic performance of niobium oxide alone and niobium oxide supported by MCM in β-pinene oxidation reactions.

2. Experimental

2.1. Chemicals

All chemicals were purchased from commercial sources. β-pinene (99% w/w) was purchased from Sigma–Aldrich. The ammonium niobium oxalate $NH_4[NbO(C_2O_4)_2(H_2O)](H_2O)_3$ was

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