Low temperature activation of benzylic C–H bonds with heterogeneous Fe/MgO catalyst under atmospheric molecular oxygen

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Abstract

The room temperature benzylic oxidation was performed with Fe/MgO catalyst. This Fe/MgO catalyst was prepared by the dissolution-precipitation method. This heterogeneous catalyst, Fe/MgO, activated the C–H bond with atmospheric molecular oxygen even at 10 °C; its catalytic activity was greatly enhanced by the addition of N-hydroxyphthalimide (NHPI) and/or acetaldehyde.

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1. Introduction

The oxidation of C–H bonds with molecular oxygen has been a target for producing oxygenated compounds such as alcohols and ketones, particularly at room temperature [1–4]. For good reactivity and selectivity in an oxidation reaction, the low temperature activity is a crucial part of the catalyst performance. Heterogeneous catalysts, which have advantages of catalyst separation and stability, have poor reactivity and selectivity at low temperatures, and the C–H bond activation with molecular oxygen by heterogeneous catalysts is believed to be very difficult at room temperature. On the other hand, homogeneous catalysts are generally unstable and are easily degraded during an aerobic reaction, and also have intrinsic problems with separation from the reaction mixture. As a typical homogeneous catalyst, Marko et al. reported copper catalyst with a diethylazodicarboxylate ligand for the oxidation of alcohols to form aldehydes and ketones at 70–90 °C in air or O2 [5,6]. Herein, we report the heterogeneous catalyst, Fe/MgO, which activated the benzylic C–H bond with molecular oxygen at room temperature [7].

The oxidation reaction was carried out to give alcohol and ketone even at 10 °C. The catalytic performance was greatly enhanced in the presence of N-hydroxyphthalimide (NHPI) [8–11] and acetaldehyde [12–16], indicating the presence of a radical transformation step.

2. Experimental

An Fe/MgO (1–4 wt % Fe) catalyst was prepared using an incipient wetness impregnation method. Fe(NO3)3 was dissolved in 100 ml of distilled water; then MgO powder was added to this solution followed by constant stirring for 30 min. The slurry mixture was evaporated, dried at 110 °C, and calcined at 460 °C for 16 h. The reactions were carried out in a two-neck flask equipped with a condenser and an oxygen bubbler. Fluorene (0.3 mmol) was dissolved in an acetonitrile solution (60 ml), followed by the addition of NHPI (20 mol%) and acetaldehyde. To the reaction mixture, Fe/MgO powder was added along with bubbling oxygen at two reaction temperatures, 10 and 25 °C, for 20 h. The reaction products were separated and analyzed by the prep-TLC. The Mössbauer spectrum was recorded using a conventional Mössbauer spectrometer with the electromechanical type of a 1.1 × 107 Bq 57 Co source in an Rh matrix.