



Comparison of heterogeneous $B(O^iPr)_3$ -MCM-41 and homogeneous $B(O^iPr)_3$, $B(OEt)_3$ catalysts for chemoselective MPV reductions of unsaturated aldehydes and ketones

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ARTICLE INFO

Article history:

Received 1 February 2012

Received in revised form 31 May 2012

Accepted 3 June 2012

Available online 12 June 2012

Keywords:

Mesoporous MCM-41

Boron tri-isopropoxide

Chemoselectivity

Unsaturated aldehydes and ketones

MPV reduction

ABSTRACT

Boron tri-isopropoxide, $B(O^iPr)_3$, was immobilized on mesoporous material, MCM-41, and denoted as “ $B(O^iPr)_3$ -MCM-41”. The prepared new heterogeneous catalyst, $B(O^iPr)_3$ -MCM-41, was characterized in details by using PXRD, FT-IR-, ^{11}B NMR-, ^{29}Si NMR-, ^{13}C NMR-, TEM, EDX, N_2 adsorption and ICP-OES. The results demonstrated the successful homogenous distribution of the $B(O^iPr)_3$ on the MCM-41 support. Heterogeneous $B(O^iPr)_3$ -MCM-41 catalyst in comparison with the homogeneous $B(O^iPr)_3$ and $B(OEt)_3$ catalysts, display similar catalytic activity in the Meerwein–Ponndorf–Verley (MPV) reduction of unsaturated aldehydes and ketones with alcohols as reductants. Reduced reaction times, higher rate constants and very high selectivities for the unsaturated alcohols were obtained with the heterogeneous catalyst than the homogeneous catalysts. In most cases, there were no side products other than the desired alcohol. The $B(O^iPr)_3$ -MCM-41 catalyst was found to be encouraging as the catalyst is recyclable up to six cycles without any significant loss in its catalytic activity. This work enriches the family of heterogeneous MPV catalysts for chemoselective reductions of unsaturated aldehydes and ketones.

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1. Introduction

Unsaturated alcohols are important and versatile intermediates in the production of pharmaceuticals, agrochemicals and fragrances [1,2]. They may be produced by oxidation of olefins [3], or by alkylation of unsaturated aldehydes [4]; but a more general route is the selective reduction of unsaturated carbonyls to unsaturated alcohols.

In homogeneous catalysis, a major breakthrough was the discovery of the chemoselective reduction with H_2 and a Ru-phosphine-diamine catalyst [5,6]. However, this catalyst requires extra base for its activation; it is not easily recuperated from the reaction mixture and may in the recycling lose its activity. Therefore, considerable effort has been done to develop heterogeneous catalysts for this type of reduction [7]. Especially the combination of group VIII B metals (Pt, Rh, Ru) and some metal additives (Sn, Fe) has been found to be suitable for the selective reduction of unsaturated aldehydes to allylic alcohols [8,9]. However, when applied to the selective reduction of α,β -unsaturated ketones, these catalysts often show high selectivity for the saturated ketone or the alcohol [10]. As an alternative to metal-catalysed

hydrogenations, hydrogen transfer reactions of the Meerwein–Ponndorf–Verley (MPV) type form an attractive approach [11–13].

The reduction of carbonyl compounds by hydrogen transfer from an alcohol is known as the “Meerwein–Ponndorf–Verley reaction” or “MPV reaction” in Organic Chemistry and can be performed under mild conditions using Lewis acids as catalyst [14,15]. The MPV reduction of carbonyl compounds using secondary alcohols as hydrogen donor and the Oppenauer oxidation of alcohols with oxidants are highly selective reactions since only the carbonyl group coordinates with the Lewis acid centre, whilst the double bond remains unreacted [16]. Therefore, the MPV reduction offers a facile access to unsaturated alcohols, many of which are important starting materials for the production of fine chemicals [17]. Traditionally, the MPV reaction has been conducted by using a metal (Al, Zr, Ti) alkoxide as catalyst in a homogeneous process [18,19].

A major advantage of heterogeneously over homogeneously catalyzed MPV reactions is that the catalysts can easily be separated from the liquid reaction mixture [20,21]. So far, a modest number of heterogeneously catalyzed MPV reactions have been reported. Heterogeneous catalysts for the Meerwein–Ponndorf–Verley–Oppenauer (MPVO) reactions include zeolites [22–29], grafted alkoxides [30,31], (modified) metal oxides which exhibit either Lewis acid or basic properties [21,31–35] such as magnesium oxide, zirconia, silica, alumina, etc.

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