Applied Catalysis A: General 419–420 (2012) 203–209

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Liquid phase oxidation of benzyl alcohol with molecular oxygen catalyzed by metal chromites

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ARTICLE INFO

Article history:
Received 8 September 2011
Received in revised form 23 January 2012
Accepted 24 January 2012
Available online 1 February 2012

Keywords:
Spinel
Metal chromites
Selective oxidation
Benzyl alcohol

ABSTRACT

The spinel type chromites MCr_2O_4 (M = Co, Ni and Cu) were synthesized by the co-precipitation method and have been characterized by a number of analytical tools. The efficacy of the synthesized system as catalysts for the oxidation of benzyl alcohol by molecular oxygen has been studied wherein it has been observed that benzaldehyde is formed with 100% selectivity. The catalytic activity of the chromites follows the order Co > Ni > Cu. The effect of the reaction parameters like the amount of the catalyst and reaction time was studied and it has been observed that the surface area and chemical hardness of the catalysts play a significant role.

1. Introduction

Oxidation of alcohols to carbonyl compounds is a fundamental transformation for the production of a large variety of versatile intermediates in synthetic organic chemistry [1]. The catalytic conversion of benzyl alcohol to benzaldehyde is one of the important processes in the perfumery and pharmaceutical industries [2]. Stoichiometric oxidants, such as permanganate and dichromate were frequently used for this purpose, but these reagents are toxic and produce large amount of hazardous wastes causing serious environmental problems [3–5]. Several studies have been reported on the oxidation of benzyl alcohol to benzaldehyde with different catalysts and oxidants under solvent free conditions [6–9]. Öztürk et al. [10] reported the oxidation of benzyl alcohol over $CrBO_3$ catalyst yielding around 40% conversion and 50% selectivity. Ji et al. [11] studied the benzyl alcohol oxidation over various catalysts among which Ru–Mn–Fe–Cu–O system showed better selectivity and conversion. Noble metals such as palladium and gold supported on metal oxides have also been reported to have promising catalytic activity [12–14] but they are not cost-effective. Recently there has been considerable interest in the use of perovskite and spinel-type metal oxides. These catalysts are thermodynamically stable at high temperatures and can be employed for a wide range of temperatures in various reactions such as oxidation [15–19], combustion [20,21] and reduction [22–24] of hydrocarbons and oxygenated compounds.

In most of the studies of mixed metal oxides, the reactivity (in terms of parameters like activity, TOF, temperature for a particular percentage conversion, activation energy) has been correlated with M—O bond length or metal—oxygen bond energy with a view to formulate methodology for catalyst selection. These structure–activity correlations not only facilitated the formulation of new catalyst systems but also provided clues on the course of surface reactions like whether the lattice oxygen or adsorbed oxygen is involved in the oxidation reaction. This information is essential possibly to devise effective partial oxidation catalysts. Another aspect in the case of mixed metal oxides is that they expose multiple active sites. For example in the case of spinels, either A and B cations can be in tetrahedral or octahedral coordination depending on the lattice either normal or inverse [25,26]. The A—O—B bonds that are possible in addition to B—O—B and A—O—A bond change the binding of oxygen and can thus be modulated to preferentially promote partial oxidation reactions.

With growing environmental concerns, much attention has been driven towards the eco-friendly heterogeneous oxidation by clean oxidants such as molecular oxygen [27–31], air [32], hydrogen peroxide [33], etc., for the oxidation of alcohols in gas and liquid phase [34,35]. Literature reports reveal that studies on the oxidation of benzyl alcohol with metal chromites have not been probed in much so far. Hence, we have synthesized metal chromites of the type MCr_2O_4 (M = Co, Ni, Cu) by co-precipitation method and

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doi:10.1016/j.apcata.2012.01.028