Contents lists available at ScienceDirect

Chemical Engineering Research and Design

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

Selectivity engineering in the synthesis of value added chemicals: Oxidation of 1-octanol to 1-octanal over nano-fibrous Ag–OMS-2 catalysts

Ganapati D. Yadav, Rajubhai K. Mewada*

Department of Chemical Engineering, Institute of Chemical Technology Matunga Mumbai 400019 India[1]

ABSTRACT

Oxidation of 1-octanol to 1-octanal is commercially very attractive, since the product is used extensively in the fragrance industry. Among the various methods, selective air oxidation with a suitable heterogeneous catalyst will be green and clean. In this work, novel cryptomelane type octahedral molecular sieve type 2 (Ag–OMS-2) catalysts, with Ag loading from 5 to 15%, w/w, were synthesized and evaluated in air oxidation of 1-octanol in a fixed bed vapour phase reactor. All catalysts were fully characterized to understand the activity and selectivity. The conversion increased with Ag loading but the selectivity was the highest for 10% Ag–OMS-2. A systematic study was conducted to ascertain the effects of various parameters. Use of toluene as a diluant leads to better conversion and selectivity. The optimized conditions are: catalyst mass/molar flow rate of 1-octanol (W/F_{A0})- 20 g h/mol, 523 K, toluene to 1-octanol molar ratio- 4:1, weight hourly space velocity (WHSV)- 16.74 h^{-1}, air flow rate- 6 L/h, air pressure- 101.3 kPa. It follows the Mars-van Krevelen mechanism and is intrinsically kinetically controlled. The activation energy is 14.39 kcal/mol using 10%, w/w Ag–OMS-2. It provides a better green process than those reported so far.

Keywords: Nanocatalysis; Nano-fibrous material; Silver; Octahedral molecular sieve-2(OMS-2); Ag–OMS-2; 1-octanol; Oxidation; 1-Octanal; Mars-van Krevelen mechanism; Selectivity

1. Introduction

Carbonyl compounds have widespread applications in a variety of industries. Oxidation of alcohols is one of the routes which are rampantly used to produce carbonyl compounds. However, selectivity to the desired carbonyl compound is a highly challenging task because it invariably leads to over-oxidation. The selective catalytic oxidation of alcohols using O_2 or H_2O_2 has been proposed as a green methodology to replace the highly polluting processes which employ stoichiometric quantities of inorganic oxidants such as $K_2Cr_2O_7$ and $KMnO_4$ (Sheldon and Kochi, 1981; Mallat and Baiker, 2004).

1-Octanal is used extensively in the fragrance industry and prepared by a variety of synthetic methods. Many patents have appeared on its preparation (Miura et al., 2003; Tanielyan et al., 2004, 2006). Homogeneous catalysts have been used for making 1-octanal and most of the recent literature involves the use of TEMPO ((or 2,2,6,6-tetramethylpiperidin-1-yl)oxyl) based catalysts in liquid phase reactions (Ciriminna and Pagliaro, 2010). Homogeneous catalysts give better conversion and selectivity compared to the heterogeneous catalysts but they suffer from the problem of separation from the reaction mixture and stability under reaction conditions. (Buffin et al., 2005; Che et al., 2006; Coleman et al., 1999; Einhorn et al., 1996; Fritz-Langhals, 2005; Gamez et al., 2003; Gilhespy et al., 2005). Different heterogeneous catalysts have also been used for the synthesis of 1-octanal (Anderson et al., 2003; Bogda and Lukasiewicz, 2000; Ji et al., 2002; Kockritz et al., 2006; Krohn et al., 1996; Noyori et al., 2003; Yamaguchi and Mizuno, 2002). Several reviews have compared various catalysts and their performance in 1-octanal synthesis (Mallat and Baiker, 2004; Muzart, 2003; Zhan and Thompson, 2004). Supported

* Corresponding author. Tel.: +91 22 3361 1001/1111/2222; fax: +91 22 3361 1002/1020.
E-mail addresses: gdyadav@yahoo.com, gd.yadav@ictmumbai.edu.in (G.D. Yadav).
Received 18 March 2011; Received in revised form 17 July 2011; Accepted 3 August 2011
[1] Formerly University of Mumbai Institute of Chemical Technology; now a separate University.
0263-8762/$ – see front matter
doi:10.1016/j.cherd.2011.08.007