Applied Catalysis A: General 435–436 (2012) 141–147

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Effect of the tungsten precursor on the high activity of the WO_3/ZrO_2 catalyst in the oxidative lactonization of 1,2-benzenedimethanol

Quanjing Zhu, Xiaofeng Chu, Zhaoyan Zhang, Wei-Lin Dai*, Kangnian Fan

Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, PR China

ARTICLE INFO

Article history:
Received 21 February 2012
Received in revised form 7 May 2012
Accepted 27 May 2012
Available online 5 June 2012

Keywords:
WO_3/ZrO_2 catalysts
Tungsten precursor
Oxidative lactionzation
H_2O_2

ABSTRACT

A series of tungsten oxide supported on commercial ZrO_2 was synthesized via a traditional impregnation method using ammonium tungstate, phosphotungstic acid hydrate and tungstic acid–oxalic acid complex as the tungsten precursors. The supported catalysts were characterized by XRD, UV–vis DRS, Raman and XPS. It was found that the tungsten precursor and the calcination temperature were crucial to the dispersion and the nature of the tungsten species on ZrO_2. The catalytic performances of the catalysts were investigated in the oxidative lactonization of 1,2-benzenedimethanol to phthalide with H_2O_2. The excellent catalytic performance of the catalyst prepared by calcination at 823 K after using tungstic acid-oxalic acid complex as the tungsten precursor was attributed to the presence of polymeric WO_6 units.

1. Introduction

Zirconia-supported tungsten oxide catalysts have been extensively studied in recent years because of their ability to catalyze a wide range of reactions such as selective reduction of NO_x to N_2 [1,2], oligomerization of $<C_{20}$ alkanes to gasoline, diesel and lubricants (C_{30+}) [3], and isomerization of alkanes [4,5]. In addition, many research groups have attempted to combine WO_x/ZrO_2 catalysts with additives such as Pt or Rh to remove sulfur- and nitrogen-containing impurities from hydrocarbon streams or to oxidize ethylene to acetic acid [6,7]. There have been many studies about the influence of the preparation method [4], tungsten oxide loading [5] and calcinations temperature [8] on the activity of the WO_x/ZrO_2 catalysts. Most of these investigations have revealed that the strong solid acidity of the WO_x/ZrO_2 catalysts played a crucial role in the catalytic reactions, but the oxidation properties of the zirconia-supported tungsten oxides has been rarely reported.

Lactones and their derivatives are an important family of organic compounds in nature and industry because many substances containing the lactone ring show interesting biological activity [9,10]. Lactones can also be used in the production of various kinds of polymers [11–13]. Although oxidation of alcohols has been widely used for the synthesis of lots of chemicals, the oxidation of diols to lactones usually requires fierce reaction conditions and specific oxidants. The reaction can be carried out under mild conditions in the presence of organic co-oxidants which are not green oxidants, such as α,β-unsaturated ketones [14,15], PhBr [16], *N*-methylmorpholine *N*-oxide, or acetone. Among the diol oxidations to lactones, the oxidative lactonization of 1,2-benzenedimethanol to phthalide can be taken into account as a probe reaction, since phthalide and its derivatives are commonly used in the manufacturing of dyes, pharmaceuticals [17,18], bactericides and other useful products. The oxidation of 1,2-benzenedimethanol with aqueous H_2O_2 can be called as a green process for the synthesis of phthalide, owing to the avoidance of waste or pollutant.

In our previous work, tungstic acid was proved to be an efficient homogeneous catalyst for the synthesis of phthalide from 1,2-benzenedimethanol using H_2O_2 as the oxidant [19]. However, the difficulties of separating the catalysts from the product mixture during the homogeneous process made such catalysts impractical for large-scale industrial production processes. One of the most promising approaches is to synthesize a supported tungsten oxide catalyst. In recent years, WO_x species have been dispersed on sorts of meso-porous silica to catalyze oxidation of cyclopentene [20], 1,5-COD [21,22], dehydration reactions of 2-butanol and methanol [23], hydroxylation of cyclohexene [24]. Koo et al. have reported that WO_3 nanoparticles supported on MCM-48 work as a highly efficient and selective heterogeneous catalyst for the oxidation of olefins, sulfides and cyclic ketones with a broad substrate scope [25]. However, the supports cannot be easily synthesized due to the usage of the expensive organic templates. Metal oxides have also been reported as good supports for tungsten species in such catalytic processes as dehydration of 2-butanol [26] and alkene

* Corresponding author. Tel.: +86 21 55664678; fax: +86 21 55665701.
E-mail address: wldai@fudan.edu.cn (W.-L. Dai).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2012.05.045