Applied Catalysis A: General 421–422 (2012) 154–160

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Catalytic oxidation of ethylene at low temperatures using porous copper manganese oxides

Eric C. Njagi, Homer C. Genuino, Cecil K. King'ondu, Saminda Dharmarathna, Steven L. Suib*

Department of Chemistry, University of Connecticut, 55 North Eagleville Road, U-3060 Storrs, CT 06269, USA

ARTICLE INFO

Article history:
Received 20 July 2011
Received in revised form 27 January 2012
Accepted 9 February 2012
Available online 17 February 2012

Keywords:
Catalytic oxidation
Copper manganese oxide
Ethylene
Volatile organic compounds (VOCs)

ABSTRACT

Amorphous manganese oxide and binary copper manganese oxides were synthesized using the redox method, characterized, and tested in the catalytic oxidation of ethylene. The catalytic activity of the synthesized catalysts toward ethylene oxidation was high (100% conversion of 1.0% C_2H_4 at 200 °C with space velocity of 35, 000 mL h^{-1} g_{cat}^{-1}) and compared favorably with that of a commercial Hopcalite catalyst. The high catalytic activity was attributed a combination of factors including the poor crystallinity, the high surface areas (≥163 m^2 g^{-1}), porosity, presence of Mn^{4+} species, and compositional homogeneity of the synthesized copper manganese oxides. Incorporation of copper into the amorphous manganese oxide matrix significantly enhanced the catalytic activity of the resultant bimetallic oxides by increasing the reducibility and ease of removal of lattice oxygen species. The synthesized materials were characterized using FE-SEM, HR-TEM, BET, FAAS, XPS, and TPD methods.

1. Introduction

The removal of volatile organic compounds (VOCs) from air is crucial for reduction of air pollution, photochemical smog, and tropospheric ozone. VOCs are also known to cause adverse health effects and thus, their removal is important for environmental health [1,2]. Among the air pollutants, ethylene is unique as a plant hormone that enhances ripening, inhibits growth, causes leaf abscission, and senescence [3,4]. Thus, it is important to reduce ethylene emissions into the atmosphere and to remove C_2H_4 from fruit storage facilities. In addition, carbon dioxide obtained as a byproduct during the synthesis of ethylene oxide contains trace amounts of ethylene, which should be removed before use for various industrial purposes. This is especially important if such CO_2 is to be used as a food additive since ethylene is a known growth hormone [3].

Several approaches have been used to remove ethylene from industrial gases, gaseous effluents, and horticultural storage facilities including adsorption, absorption, biological filtration, incineration, and catalytic combustion [4,5]. Catalytic combustion is the most promising cost-effective method of removing low concentrations (~1.0%) of VOCs from gaseous streams [6]. Catalytic combustion occurs at significantly lower temperatures (350–500 °F) than thermal incineration (800–1100 °F) leading to lower energy requirements and avoiding the formation of noxious nitrogen oxides [7]. Additionally, unlike condensation and adsorption technologies, catalytic combustion does not transfer pollutants to another phase but oxidizes them completely to CO_2 and water.

Supported noble metals [8–10], metal oxides [11–13], and mixed metal oxides [3,14–17] have been widely employed for the catalytic oxidation of VOCs. Transition metal oxides, although generally less active than noble metals, are cheaper, more environmentally friendly, and more resistant to deactivation by poisoning than these other materials [7,18]. Mixed copper manganese oxides, commonly referred to as Hopcalite, have been used in the catalytic combustion of acetone [19], ethanol [7,20], propane [21], ethylene [3], and toluene [6].

In our previous studies, we prepared copper manganese oxides using a redox method and found them to have excellent catalytic activity for CO oxidation under diverse experimental conditions [22,23]. Herein, we investigate the catalytic oxidation of ethylene using amorphous manganese oxide and copper manganese oxides prepared using the afore-mentioned method. The structural, morphological, and catalytic properties of catalysts prepared using the redox method are compared to those of Carulite 500®, a commercial Hopcalite catalyst being utilized for complete oxidation of ethylene oxide. The effect of copper loading on catalytic performance and stability is also investigated.

2. Experimental

2.1. Preparation of the catalysts

Amorphous manganese oxide (AMO) and copper manganese oxides were synthesized using a redox method described previously [22]. Briefly, AMO was prepared by the dropwise addi-

* Corresponding author. Tel.: +1 860 486 2797; fax: +1 860 486 2981.
E-mail address: Steven.Suib@uconn.edu (S.L. Suib).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2012.02.011