



## Highly dispersed supported ruthenium oxide as an aerobic catalyst for acetic acid synthesis

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### ARTICLE INFO

#### Article history:

Received 13 December 2011

Received in revised form 17 May 2012

Accepted 19 May 2012

Available online 29 May 2012

#### Keywords:

Heterogeneous catalysis

Ruthenium oxide

Aerobic ethanol oxidation

RuO<sub>4</sub>

Support effects

High-loading catalysts

Ru(VI) oxide

### ABSTRACT

The increasing need for shifting to renewable feedstocks in the chemical industry has driven research toward using green aerobic, selective oxidation reactions to produce bulk chemicals. Here, we report the use of a ruthenium mixed oxide/hydroxide (RuO<sub>x</sub>) on different support materials for the selective aerobic oxidation of ethanol to acetic acid. The RuO<sub>x</sub> was deposited onto different oxide supports using a new gas-phase reaction, which in all cases resulted in homogeneous nanoparticulate films. The RuO<sub>x</sub> particle size ranged from 0.3 to 1.5 nm. The catalytic activity was evaluated on TiO<sub>2</sub>, Mg<sub>6</sub>Al<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>16</sub>·4(H<sub>2</sub>O), MgAl<sub>2</sub>O<sub>4</sub>, Na<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> nanotubes, ZnO, γ-Al<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, CeO<sub>2</sub>, and Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> supports. The CeO<sub>2</sub> supported RuO<sub>x</sub> had the highest activity, and selectivity toward acetic acid, of all the materials when normalized with respect to Ru-loading. This high activity was independent of the surface area of the support and the loading of RuO<sub>x</sub> under the tested conditions. This was attributed to the highly uniform size of the RuO<sub>x</sub> deposits, demonstrating that the deposition is suitable for producing small nanoparticles at high loadings. To elucidate the reason for the promotional effect of CeO<sub>2</sub>, Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> was investigated as a high oxygen storage capacity support, however, this did not result in higher catalytic activity. The high activity of CeO<sub>2</sub> supports compared to the low activity ZnO appear correlated to the presence of high valence Ru(VI) species analogous to that observed in literature.

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### 1. Introduction

The need for synthesizing bulk chemicals from non-fossil alternative feedstock rather than fossil resources increases as the latter becomes more scarce. This production of bulk chemicals should be as benign as possible for the environment, or “green” [1]. One such bulk chemical is acetic acid, which is produced on the millions of tonnes scale worldwide from syngas, butane, and naphtha [2]. The production of biomass-derived ethanol or “bio-ethanol” has increased dramatically since the late 1990s [3]. This bio-ethanol could find use as a versatile, sustainable chemical feedstock for the green production of “bio-acetic acid” [4].

Selective partial oxidation of organic molecules has attracted increasing attention over the past decade, especially using molecular oxygen, i.e. aerobic oxidation [5–14]. Aerobic oxidation is considered to be a “green” process because the only by-product

is water, unlike the use of classic metal oxide oxidants, which generate stoichiometric amounts of metal waste [15,16]. Furthermore, aerobic oxidation is also attractive due to the low cost of ubiquitous oxygen.

RuO<sub>2</sub> is perhaps most well known as the archetypical electrocatalyst for the oxygen evolution reaction (OER) [17]. Several reactions are also reported in literature to be catalyzed by ruthenium-based catalysts, e.g. ammonia synthesis/decomposition [18], metathesis reactions [19], dehydrogenation of ethane [20], and oxidation reactions [21]. The number of reports on heterogeneous ruthenium-based aerobic oxidation catalysts are limited, and primarily focused on the oxidation of alcohols to oxo compounds in organic solvents [5,22–25], and in aqueous solution [26–28]. In this work we focus on the green selective aerobic oxidation of ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) to acetic acid (CH<sub>3</sub>COOH) in aqueous solution.

Recently, we reported a new procedure for the conformal coating of metal oxide supports with a high coverage of ruthenium oxide (RuO<sub>x</sub>) nanoparticles [29]. The RuO<sub>x</sub> deposited on TiO<sub>2</sub> and WO<sub>3</sub>, according to this procedure, showed good results as OER catalysts for electrocatalytic and photoelectrocatalytic water splitting, respectively. It was demonstrated that the nanoparticles covered

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