



# A Ru-Sn-Co/AlO(OH) as a highly efficient catalyst for hydrogenation of dimethyl adipate to 1,6-hexanediol in aqueous phase

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## ARTICLE INFO

### Article history:

Received 12 July 2012

Received in revised form

13 September 2012

Accepted 14 September 2012

Available online 9 October 2012

### Keywords:

Ruthenium

Tin

Cobalt

Dimethyl adipate

1,6-hexanediol

Hydrogenation

## ABSTRACT

A Ru-Sn-Co/AlO(OH) catalyst was prepared by co-impregnation, calcination, and hydrothermal reduction. The catalyst was well characterized by BET, XRD, SEM-EDX, XPS, H<sub>2</sub>-TPR, and Mössbauer spectroscopy, and then it was applied in the hydrogenation of dimethyl adipate to 1,6-hexanediol in aqueous phase. It was found that the addition of cobalt could stabilize Sn(IV) and the cooperation between tin and cobalt could promote the reduction of ruthenium oxide. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the catalyst Ru-Sn-Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was transformed to AlO(OH) by the hydrothermal reduction. It was suggested that the stabilized Sn(IV) and the interaction between the hydroxyl group on the surface of AlO(OH) and the solvent water played a key role to improve the conversion of dimethyl adipate and the selectivity to 1,6-hexanediol. The conversion of dimethyl adipate and the selectivity to 1,6-hexanediol were up to 98% and 95%, respectively, under 5 MPa of H<sub>2</sub> and 493 K for 10 h.

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## 1. Introduction

Diols are industrially important as they are used as raw materials for a wide variety of fine chemicals, pharmaceuticals and biodegradable polymers. Especially, 1,6-hexanediol is widely applied in the synthesis of polyurethanes, varnishes, adhesives, pharmaceuticals, plasticizers and so on [1]. Currently, the diols are mainly produced by hydrogenating carboxylic acids or their esters. The catalytic hydrogenation in both homogeneous and heterogeneous systems is one of the most significant synthetic methods. In homogeneous systems, ruthenium–phosphine complexes have been widely used as catalysts for ester hydrogenation [2,3]. However, it is a challenging problem to synthesize the organometallic complexes and separate catalysts from products. In addition, it is still difficult to avoid the catalyst being poisoned by carbon monoxide, which is generated by the decarbonylation of the carboxylic acids or esters [4,5]. In heterogeneous system, this reaction is traditionally performed over the copper–chromium or zinc–chromium catalysts under the severe reaction conditions (reaction temperature of 523–623 K and H<sub>2</sub> pressure of 10–20 MPa) [6–8]. The use of Cr is currently discouraged and severe reaction conditions are undesirable, so many noble metallic (Ru, Pd, Pt and Rh) catalysts

have been investigated to carry out the reaction in mild reaction conditions [9–11]. Carvalho and Fraga's group [12–15] has investigated the activity and selectivity about monometallic catalysts of Ru, Pd, Pt and Rh supported on alumina for the hydrogenation of dimethyl adipate (DMA) to 1,6-hexanediol. Among these monometallic catalysts, ruthenium-based catalyst showed a higher activity, reaching about 80% conversion of DMA and 49% selectivity to 1,6-hexanediol at 528 K under 5 MPa of H<sub>2</sub> [12]. Although the hydrogenation conditions were much milder than that over complex oxide catalysts, they gave a low selectivity to alcohol [12,16]. Therefore, a second metal such as Sn, Re, Ge, or Zn had to be introduced to modify the catalytic properties [11,17]. It was found that Ru-Sn catalyst was the most effective for the hydrogenation of DMA [17–19], likewise, ethyl lactate [16], adipic acid [1] and 1,4-cyclohexanedicarboxylic acid [11]. The addition of a second element Sn obviously improved the 1,6-hexanediol selectivity up to 70% over Ru-Sn/TiO<sub>2</sub> with Sn/Ru ratio of 2 [17].

Co, as a non-noble metal, is extensively used for catalytic hydrogenation. For example, Coq et al. had demonstrated that Co had a promising potential for acrolein hydrogenation [20]. It was reported that the superficial structure of Co supported on silica could influence the hydrogenation of C=O bond in crotonaldehyde to crotyl alcohol [21–24]. Similarly, Kouachi et al. reported the hydrogenation of citral in supported cobalt systems [25]. These results also showed that Co particles did favor the hydrogenation of the C=O bond. In our previous works [5,26], it was observed

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