# Effect of promoters on the structures and properties of the RuB/γ-Al₂O₃ catalyst

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## Abstract

Effect of promoters (Co, Fe, Sn, Zn) on structures, properties and catalytic performance of RuB/γ-Al₂O₃ catalyst was studied using in situ XRD, TEM, $H_2$-TPD, XPS and liquid-phase hydrogenation of ethyl lactate to 1,2-propanediol (PDO). It was found that incorporation of Sn or Fe improved the dispersion and thermal stability of RuB. The electron density of Ru and the strength and capacity of $H_2$ adsorption on the RuB catalyst were also enhanced by the incorporation of Sn or Fe. The incorporation of Co or Zn led to a significant decrease in $H_2$ adsorption capacity of the RuB catalyst. Both ethyl lactate conversion and selectivity to 1,2-PDO increased with the incorporation of Sn or Fe. The ethyl lactate conversion decreased sharply with the incorporation of Zn or Co accompanied by an increase in selectivity to 1,2-PDO and lactic acid. The effect of promoters on reaction behavior was discussed on the basis of the characterizations.
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## 1. Introduction

1,2-Propanediol (PDO), a material that has been widely used in pharmaceutical and chemical industries is commercially produced by the hydration of propylene oxide that is produced via the oxidation of propylene. This process involves either hydroperoxidation chemistry or the antiquated chlorhydrin process [1]. Development of alternative green processes for the synthesis of 1,2-PDO has attracted great attentions. It is reported that 1,2-PDO is formed by the transesterification of propylene carbonate with methanol using solid base catalysts, in which equimolar amount of dimethyl carbonate is co-generated [2]. The co-generation of two compounds makes the transesterification process very complicated and economically uncompetitive. Zhang et al. [3] and Cortright et al. [4] reported that 1,2-PDO can be synthe-

sized via direct hydrogenation of lactic acid using Ru/C and Cu/SiO₂ catalysts; lactic acid can be produced through the fermentation of a number of renewable resources such as carbohydrates derived from agricultural crops and biomass streams [5,6]. This process provides a clean and economic approach to the synthesis of 1,2-PDO from renewable carbohydrate feedstock instead of from non-renewable petroleum.

Hydrogenation of free carboxylic acids to the corresponding alcohols is more difficult than the hydrogenation of corresponding esters and aldehydes, not only because reactivity of the carbonyl group of the acids is lower than that of the corresponding esters and aldehydes but also acids are reactive with the alcohol product, leading to the formation of esters. Therefore, it is advisable to convert acids to esters before hydrogenation. Hydrogenations of carboxylic acids and esters to the corresponding alcohols are often carried out under vigorous reaction conditions due to weak polarisability and intrinsic steric hindrance of the C=O bond [7]. However, for lactic acid and lactates that contain a reactive hydroxyl group, high reaction temperature is undesirable because it may

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lead to side reactions such as polymerization, dehydration, transesterification, and consequently to a decrease in selectivity to 1,2-PDO [3,4]. Therefore, development of active catalysts capable of hydrogenating lactic acid or lactates to 1,2-PDO under mild conditions is of great importance.

Ru-based catalysts, due to its good intrinsic hydrogenation activity for carbonyl compounds, have received great attention in the hydrogenation of a wide range of carboxylic acids and esters. Ru-based catalysts with different supports or different preparation methods have been studied extensively by a number of researchers [8–18]. Promoting effect of tin on the ruthenium has also been studied intensively by several research groups [17–24]. It is found that addition of tin significantly enhanced the selectivity to the corresponding alcohol. Addition of platinum to Ru–Sn catalyst can further improve the catalytic performance in the hydrogenation of carboxylic acids [25]. A widely accepted explanation for the promoting effect of tin is that the active species of tin in ionic form plays a role of activating the carbonyl group by adsorption of carbonyl oxygen, facilitating the attack of carbonyl carbon by the hydrogen atom on adjacent ruthenium site. To our knowledge, effect of promoters other than tin on Ru-based catalysts for hydrogenation of carboxylic acids has not been reported.

In the present work, RuB/$\gamma$-Al$_2$O$_3$ has been prepared by a novel chemical reduction method. Effect of promoters (Fe, Sn, Co and Zn) on composition, structure and properties as well as catalytic performance in the hydrogenation of ethyl lactate of RuB/$\gamma$-Al$_2$O$_3$ catalyst has been investigated.

## 2. Experimental

### 2.1. Catalyst preparation

The monometallic ruthenium catalyst RuB/$\gamma$-Al$_2$O$_3$ (labeled as RuB) was prepared by a novel reductant impregnation method described below. A weighed amount of $\gamma$-Al$_2$O$_3$ was immersed into a 3.0 M potassium borohydride solution at 298 K for 15 min. The excessive solution was decanted and an aqueous solution of RuCl$_3$ was poured into a flask containing the impregnated $\gamma$-Al$_2$O$_3$ to start the reduction. The molar ratio of KBH$_4$ to Ru is 6:1. The mixture was kept undisturbed at 298 K until bubble generation ceased. The resulting black solids were washed with distilled water to neutrality and then with absolute alcohol three times to replace water. The solids were then kept in absolute alcohol for characterizations and activity test.

The bimetallic catalysts RuMB/$\gamma$-Al$_2$O$_3$ (labeled as RuMB, M = Zn, Co, Fe or Sn) were prepared in a similar procedure to that for the RuB catalyst except that the mixed solutions containing desired concentrations of RuCl$_3$ and the corresponding metal chlorides of the promoter were used. The molar ratio of KBH$_4$ to (Ru + M) is 6:1. The precursors for promoters Zn, Co, Fe and Sn were ZnCl$_2$, CoCl$_2$·6H$_2$O, FeCl$_3$·6H$_2$O, and SnCl$_2$·2H$_2$O of analytical purity, respectively.

### 2.2. Characterizations

The bulk compositions of the catalysts were analyzed by inductively coupled plasma (ICP, IRIS Intrepid).

The Brunauer–Emmett–Teller surface areas ($S_{BET}$) of the as-prepared catalysts were determined by N$_2$ adsorption at 77 K in a Micromeritics TriStar 3000 apparatus. Samples with the storage liquid were transferred to the adsorption glass tube and treated at 383 K under ultrahigh purity nitrogen flow for 2 h before measurement. The samples were weighed by the difference in the adsorption tube on completion of the experiment.

The in situ powder X-ray diffraction (XRD) patterns were acquired on a Bruker AXS D8 Advance X-ray diffractometer using Ni-filtered Cu K$\alpha$ radiation ($\lambda = 0.15418$ nm). The tube voltage and current were 40 kV and 40 mA, respectively. The sample with solvent was loaded in the in situ cell, with argon flow (99.9995%) purging the sample throughout the detection to avoid oxidation.

The temperature-programmed desorption of hydrogen (H$_2$-TPD) experiment was performed in a flow system using a thermal conductivity detector (TCD) to monitor H$_2$ desorption. Prior to H$_2$ adsorption, the sample was treated at 423 K for 2 h under argon flow (99.9995%, deoxygenated by an Alltech Oxy-trap filter), then cooled down to room temperature. The saturation chemisorption of hydrogen was performed by pulse injection until the eluded peak area leveled off. The sample was purged with argon again and was heated at a rate of 20 K min$^{-1}$, when a steady level of baseline was achieved. An additional H$_2$-TPD experiment for RuSnB/$\gamma$-Al$_2$O$_3$ was also performed, in which the conditions for catalyst pretreatment and TPD were the same as those mentioned above except that a Stanford Research Systems QMS Series Gas Analyzer instead of a TCD was used to monitor hydrogen. The TPD profile obtained using the gas analyzer including the shape and peak temperature was almost the same as that observed by TCD.

The X-ray photoelectron spectroscopy (XPS) experiment was carried out on a Perkin-Elmer PHI 5000C ESCA using Al K$\alpha$ line as the excitation source ($hv = 1486.6$ eV). The sample was pressed into a self-supported disc before being mounted on the sample plate. Then it was degassed in the pretreatment chamber at 383 K for 2 h in vacuum before being transferred into the analyzing chamber, where the background pressure was lower than $2 \times 10^{-9}$ Torr. All the binding energy (BE) values were obtained after removing the surface oxides by Ar$^+$ sputtering and were referenced to the Al 2p line of the $\gamma$-Al$_2$O$_3$ support at 74.4 eV with an uncertainty of $\pm 0.2$ eV. The XPS peaks were decomposed into subcomponents using a Gaussian–Lorentzian curve-fitting program.

Transmission electron microscopy (TEM) images were recorded on a JEOL JEM 2011 electron microscope operating at 200 kV. The catalyst specimens for electron microscopic analysis were prepared by gently grinding the powder samples in an agate mortar, suspending and sonicating the powder in alcohol, and placing a drop of the suspension on