

# RuB/Sn-SBA-15 catalysts: Preparation, characterization, and catalytic performance in ethyl lactate hydrogenation

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## Abstract

A series of Sn-containing mesoporous SBA-15 molecular sieves were synthesized and used as supports for RuB catalysts. Effects of Sn doping on the structure of the SBA-15 and on properties and catalytic performance of the RuB/Sn-SBA-15 catalyst in ethyl lactate hydrogenation were studied. The samples were characterized by inductively coupled plasma–atomic emission spectroscopy (ICP–AES), N<sub>2</sub> physisorption, powder X-ray diffraction (XRD), diffuse reflectance UV–vis spectroscopy (DRUVS), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and catalytic tests. The results showed that Sn-containing SBA-15 supports prepared by direct hydrothermal synthesis method maintained the characteristic structure of SBA-15 with Sn species highly dispersed in the support when Si/Sn nominal ratio was above 30. The RuB catalysts supported on the Sn-containing SBA-15 prepared by the direct hydrothermal synthesis method showed higher dispersion and better catalytic performance than corresponding one prepared by the impregnation method. The best catalytic performance was achieved over catalyst with Si/Sn nominal ratio of 30.

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## 1. Introduction

1,2-Propanediol (PDO) has been widely used as a solvent or a reagent in pharmaceutical and chemical industries. It is commercially produced by hydration of propylene oxide that was produced by selective oxidation of propylene. This process involves either hydroperoxidation chemistry or the antiquated chlorhydrin process, which is unfavorable from green-chemistry point of view. Lactic acid, as one of the biomass-based organic acids, can be produced by fermentation of a number of renewable sources such as carbohydrates derived from agricultural crops, and hydrogenation of lactic acid or lactates would lead to the formation of 1,2-PDO. This process

provides an eco-friendly alternative to the petroleum-based process for 1,2-PDO production [1–4].

The hydrogenation of esters is more difficult than that of ketones and aldehydes because of weak polarisability and intrinsic steric hindrance of the C=O bond of the esters [5]. The hydrogenation of esters into the corresponding alcohols is often performed under vigorous reaction conditions, viz. under 20–30 MPa and 473–573 K in the presence of copper chromite- or zinc chromite-based catalysts [6,7]. However, in the cases like lactates or lactic acid that contain a reactive hydroxyl group, high reaction temperature is undesirable because it would lead to side reactions and consequently to a decrease in the selectivity to 1,2-PDO [8,9]. Various efforts have been paid to prepare efficient catalysts that can work under mild reaction conditions for hydrogenation of ester containing reactive functional groups [10–13]. In our previous papers [14,15], RuB/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts prepared by the reductant impregnation method were studied for liquid-phase ethyl lactate hydrogenation. It was found that the RuB/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed good activity for ethyl lactate hydrogenation

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under mild conditions. Addition of a suitable amount of tin significantly increased ethyl lactate conversion and selectivity to 1,2-PDO. A correlation of the reaction results with the characterization data revealed that the improved conversion and selectivity over the tin-promoted catalysts were ascribed to oxidized tin species in the vicinity of RuB particles acting as both a spacer and a Lewis acid site. As a spacer it improved the dispersion and thereby thermal stability of RuB, and as a Lewis acid it activated (or polarized) the C=O bond of ethyl lactate, facilitating the hydrogen transfer from adjacent RuB sites. Consequently, combined effects led to an increase in the conversion of ethyl lactate and the selectivity to 1, 2-PDO [14].

Since the disclosure by Mobil group in 1992 of MCM-41s featuring hexagonal pore-ordered system [16], various micelle-templated silicas (MTS) such as MCM-48 [17], SBA-15 [18,19] and MSU [20] with extremely high surface area, mesopore volume, and narrow pore size distribution have been prepared. These MTS materials have shown great potential in catalysis, among which SBA-15 presented better thermal stability than MCM-41s [21]. Tin-modified MTS materials with different frameworks, such as MFI, MEL, MCM-41, ZSM-48, BTA, and SBA-15 have also been prepared by the “post-synthesis” method such as impregnating or grafting method and by direct hydrothermal synthesis. They have been employed as catalysts for the Baeyer–Villiger (BV) oxidation of ketones, the Meerwein–Ponndorf–Verley reduction of ketones, and the hydroxylation of phenol and phenol ethers with H<sub>2</sub>O<sub>2</sub> [22–29].

As a follow-up research of tin promotion, in the present work, tin-modified SBA-15 molecular sieves were synthesized and used as supports for preparing RuB catalysts. The effects of tin loading in SBA-15 and tin incorporation method on the properties and catalytic performance in ethyl lactate hydrogenation were investigated.

## 2. Experimental

### 2.1. Catalyst preparation

The preparation of the RuB/Sn-SBA-15 catalysts consists of two steps: preparation of Sn-modified SBA-15 support and loading of RuB onto the support. Pure siliceous SBA-15 was synthesized according to the well-established method [18,19]. Sn-modified SBA-15 (Sn-SBA-15-*x*, where *x* denotes the nominal Si/Sn molar ratio in the hydrothermal synthesis gel) was synthesized with a similar procedure, except that a desired amount of SnCl<sub>4</sub>·5H<sub>2</sub>O as tin source was added into the TEOS solution before being hydrolyzed. For comparison, a tin-modified SBA-15 (Si/Sn = 10) denoted as Sn-SBA-15-10imp was prepared by an incipient-wetness impregnation method. The supported RuB catalysts were prepared by impregnating the Sn-SBA-15-*x* or Sn-SBA-15-10imp supports with KBH<sub>4</sub> solution and ruthenium chloride solution consecutively, as described in our previous work [14]. The loading amount of Ru was 3.5 wt.%.

### 2.2. Catalyst characterization

The bulk composition of the supports and catalysts were determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES, Thermo Elemental IRIS Intrepid) after dissolution of the samples in HF/HCl solution. The small-angle X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/MAX-RB diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) operated at 60 mA and 40 kV. The wide-angle XRD patterns were recorded on a Bruker D8 advance diffractometer with Cu K $\alpha$  radiation operated at 40 mA and 40 kV. The Brunauer–Emmett–Teller surface area ( $S_{\text{BET}}$ ) and pore volume of the supports and catalysts were determined by N<sub>2</sub> adsorption at 77 K in a Micromeritics TriStar 3000 apparatus. The pore volume was calculated from the amount of N<sub>2</sub> adsorbed at a relative pressure of 0.995. The pore-size distribution curves were calculated from the desorption branches of the isotherms using Barret–Joyner–Halenda (BJH) formula. The pore structure and RuB particle size in the as-prepared catalysts were acquired by transmission electron microscope TEM (JEOL JEM 2011), fitted with an energy-dispersive X-ray emission analyzer (EDX). The amorphous character of the catalysts was verified by selected-area electron diffraction (SAED). The diffuse reflectance UV–vis spectra were collected on a Varian Cary 5 spectrophotometer equipped with a Praying Mantis attachment from Harrick. The sample cell was equipped with a heating unit, a thermocouple, and a gas flow system for in situ measurements. The samples were dehydrated in situ in dry air at 673 K for 30 min. The spectra were recorded upon cooling down to room temperature, with dry air flowing through the sample to avoid rehydration. The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was recorded using a Bruker Vector 22 instrument equipped with a DTGS detector and a KBr beam splitter. All spectra were collected in a nitrogen atmosphere at 473 K. The X-ray photoelectron spectra (XPS, Perkin-Elmer PHI 5000C) were recorded using the Al K $\alpha$  line as the excitation source ( $h\nu = 1486.6$  eV). All the binding energy (BE) values were obtained after removing the surface oxides by Ar ion sputtering and were referenced to the Si 2p line of SiO<sub>2</sub> at 103.3 eV with an uncertainty of  $\pm 0.2$  eV.

### 2.3. Catalytic test

The catalytic test was performed in a 220 ml stainless steel autoclave equipped with a magnetic stirrer. In a typical experiment, 5 ml of ethyl lactate, 30 ml of *n*-heptane as solvent and 1.0 g of catalyst were charged into the reactor. The reactor was purged with hydrogen four times to expel air. After the desired temperature, 423 K, was reached, the H<sub>2</sub> pressure was maintained at 5.5 MPa and the stirrer (1000 rpm) was switched on, and this was taken as the beginning of the reaction. The reaction was allowed to proceed for 10 h with sampling of a small portion of the reaction mixture every one hour. The reaction products were analyzed with a gas chromatograph equipped with a capillary column PEG-20M (50 m  $\times$  0.32 mm) and a flame-ionization detector.

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