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RuSn bimetallic catalysts for selective hydrogenation of levulinic acid to γ-valerolactone

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ABSTRACT

Carbon-supported ruthenium catalysts containing different amounts of tin were studied for the hydrogenation of levulinic acid (LA) to gamma-valerolactone (GVL) in a 2-sec-butyl-phenol (SBP) solvent. Results from reaction kinetics measurements (453 K and 35 bar H_2) showed that the Ru/C catalyst was initially more active for hydrogenation of both LA and SBP (i.e., 0.051 s^{-1} for conversion of LA to GVL), followed by continuous deactivation versus time on stream. In contrast, the catalyst containing equal amounts of Ru and Sn had a lower activity for LA to GVL conversion (0.005 s^{-1}), but displayed stable activity versus time on stream and showed 100% selectivity for hydrogenation of LA versus the SBP solvent. Increasing the amount of Sn to a 1 to 4 Ru:Sn atomic ratio creates an additional phase, β-Sn, that is not active for hydrogenation, leaches into the SBP solvent, and sinters under reaction conditions. Results from CO and O_2 chemisorption and electron microscopy measurements indicated that the Ru-based metal particles did not leach or sinter at reaction conditions, and that the surfaces of these particles became progressively enriched with Sn as the Sn-loading increases. In addition, Sn did not significantly leach from the catalysts when present as an intermetallic alloy with Ru, such as Ru_2Sn_3 and Ru_3Sn_7. Using LA produced from corn stover, the $RuSn_4$/C catalyst was stable and demonstrated that it is a promising catalyst to produce valuable chemicals and fuels from real biomass.

1. Introduction

Recent research has focused on the production of lignocellulosic platform molecules that can be converted into a broad range of fuels and chemicals. For example, γ-valerolactone (GVL) has attracted considerable attention [1–6] because high yields can be achieved through hydrogenation of levulinic acid (LA) [1] using heterogeneous catalysts [7,8] for which production methods are available [9,10]. As a pure product, GVL may be used as solvent or blended with conventional gasoline in a capacity similar to ethanol [11]. In addition, GVL can be converted into a variety of chemicals, such as, 1,4 pentanediol [12], α-methylene γ-valerolactone [13], or pentenoate esters [14]. Furthermore, GVL can be used as precursor of gasoline and diesel fuels, such as C_8–C_{16} alkenes [15], C_9–C_{18} alkanes [2], C_9 alkanes [1], valeric esters [16], or butene isomers [17,18].

The production of LA typically employs treatment of cellulose in dilute (0.1–0.5 M) solutions of sulfuric acid (SA) [9]; however, the presence of SA negatively impacts downstream catalytic processes, in particular those involving metal catalysts, such as Ru. The production of LA using solid acid catalysts [19,20] would allow for simple separation of the acid catalyst from the aqueous feed, but LA yields are not competitive with those obtained from reactions catalyzed by SA. Therefore, SA must be either neutralized or removed through combined solvent extraction and distillation [21], with the latter step being preferred in the interest of resource conservation.

We recently described a solvent extraction method using 2-sec-butylphenol (SBP) to recover LA from aqueous solutions of SA [22]. The extracted LA sequentially underwent selective hydrogenation to yield GVL using a RuSn catalyst to minimize the hydrogenation of SBP. In the present paper, we consider the intrinsic activity, selectivity, and stability of various Ru_xSn_y/C catalysts, with particular emphasis on the effect of adding Sn to the Ru/C catalyst. In addition, we report results from characterization studies of fresh and spent catalysts to provide insights into the nature of the active catalyst and possible sources of catalyst deactivation. Importantly, we demonstrate that addition of Sn stabilizes Ru/C, even in the presence of feed streams derived from real biomass, e.g., corn stover.

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2. Experimental

2.1. Catalyst preparation

A 5 wt% Ru/C catalyst (Sigma–Aldrich) was used in this study for LA hydrogenation and for preparation of Ru_xSn_y bimetallic catalysts. The Ru_xSn_y/C samples were prepared by incipient wetness impregnation of 5 wt% Ru/C with an aqueous solution of $SnCl_2{\cdot}2H_2O$, followed by heating in air at 353 K for 2 h. Prior to reactions in fixed bed reactors, catalyst samples were reduced in situ for 3 h at 723 K (1 K min^{-1}). When exposure to air was necessary, catalyst samples were reduced as described above, and subsequently passivated in 2% O_2 in He (50 cm^3 min^{-1}, Airgas) at 298 K for 60 min prior to exposure to ambient conditions. Monometallic Sn/C samples were synthesized by incipient wetness impregnation of Norit SX 1G with an aqueous solution of $SnCl_2{\cdot}2H_2O$, followed by heating in air 2 h at 353 K, and reduction in H_2 (3 h at 723 K).

2.2. X-ray diffraction

X-ray diffraction (XRD) was used to probe interactions between Ru and Sn and to provide information regarding metal particle size. Powder diffraction was carried out using a Rigaku Rapid II with a molybdenum source. Prior to XRD studies, Ru_xSn_y/C catalysts were reduced in flowing H_2, and passivated in flowing 2% O_2 in He. Samples were crushed to a uniform size and loaded into a 0.5 mm borosilicate capillary for analysis.

2.3. Transmission electron microscopy (TEM)

Catalyst samples for TEM measurements were dispersed in ethanol using a mortar and pestle, then mounted on carbon coated Cu grids followed by slow evaporation of the solvent at ambient conditions for examination in a transmission electron microscope (TEM; JEOL 2010F) equipped with an Oxford energy dispersive spectroscopy (EDS) system for elemental analysis. Images were recorded in bright field high resolution (HRTEM) mode as well as in high angle annular dark field (HAADF) mode. A LaB_6 filament at 200 kV was used as the electron beam source. The average particle size was calculated by measuring the diameter of over 1000 particles from multiple TEM images of different grid areas.

2.4. Scanning electron microscopy/electron dispersive spectrometry

A Hitachi S-5200 scanning electron microscope (SEM) equipped with an EDS from Princeton Gamma Tech was operated at 2 kV to image the samples in secondary electron and backscattered modes. For EDS, 15 kV was used for spotlighting and box analysis. For sample preparation, the catalyst was pressed onto carbon double-sided tape that had been attached to an aluminum sample holder.

2.5. Temperature programmed reduction

Temperature programmed reduction (TPR) was performed on dried Ru/C, Sn/C, and Ru_xSn_y/C samples using a residual gas analyzer (RGA) with a quadrupole mass spectrometer (Stanford Instruments, RGA 200). Prior to TPR measurements, the cell volume was purged by flowing helium (50 cm^3 min^{-1}, Airgas, UHP grade) for 30 min at 298 K. The inlet gas feed was then switched to 5% H_2 in N_2 (50 cm^3 min^{-1}, Airgas) and held at 298 K until a stable baseline signal was achieved, before increasing the temperature at a rate of 10 K min^{-1} to 973 K.

2.6. Physisorption

Fresh Ru_xSn_y/C samples were characterized by adsorption–desorption N_2 isotherms, collected using a Micromeritics ASAP 2020 system, to determine catalyst surface area and pore volume. Prior to analysis, catalyst samples were degassed under vacuum at 373 K in He for 12 h. The physisorption was measured at liquid N_2 temperatures. Physisorption measurements on spent samples (i.e., used for reaction kinetics studies) were carried out by first washing the spent catalysts with acetone (to remove residual non-volatile organic species (SBP)), followed by drying. A reduced and passivated sample (fresh) was washed and dried to ensure that the surface area was not affected by the washing procedure. Surface areas were determined using the BET method. Pore volumes were determined from the adsorption branch of the N_2 isotherm at $P/P_0 = 0.97$ single point.

2.7. Chemisorption

Fresh Ru_xSn_y/C samples were characterized by volumetric titration of exposed metal sites with CO and O_2 chemisorption (Micromeritics ASAP 2020). Prior to analysis, catalyst samples were outgassed under vacuum at 303 K and subsequently reduced in flowing H_2 for 4 h at 723 K (80 cm^3(STP) min^{-1} H_2, 1.3 K min^{-1}). The sample was then evacuated at 723 K for 60 min to remove adsorbed H_2 and finally cooled to 303 K. CO chemisorption was measured at 303 K. To limit the extent of bulk Ru oxidation [23] and the potential formation of volatile RuO_4 [24], O_2 chemisorption was determined at 195 K. Chemisorption measurements on samples that had been used for reaction kinetics studies (453 K, 35 bar, 300 h on stream) were carried out by first washing the spent catalysts with acetone (to remove residual non-volatile organic species (SBP)), followed by drying under vacuum and sifting through a sieve to remove residual quartz fibers and granules. Samples were subsequently placed in a quartz chemisorption cell and analyzed according to the above protocol.

2.8. Studies of catalytic activity and stability

The activity and selectivity of each catalyst was measured for the hydrogenation of LA in SBP. Reactions were carried out in a fixed bed reactor in an up-flow configuration as described previously [22]. The catalyst was reduced in situ for 3 h at 723 K (1 K min^{-1}) before use. Feeds for catalytic experiments were prepared by adding commercial LA (Sigma–Aldrich, 98%) to SBP (Alfa-Aesar, >98%). The LA feed from corn stover was prepared as indicated elsewhere [22]. Gas phase products were analyzed using a GC-2014 (Shimadzu) equipped with an FID and a GC-8A (Shimadzu) with a TCD. Liquid samples were analyzed using a GC-2010 (Shimadzu) with an FID and an RTx-5 column. Qualitative identification of products was achieved using GC–MS (Shimadzu GCQP-2010). For the data reported herein, total and individual mass balances for each compound were within 5%.

In this study, both hydrogenation of LA to GVL and hydrogenation of SBP to butyl cyclohexanol/butyl cyclohexanone were observed. The hydrogen consumption selectivity for a given catalyst is thus defined according to Eq. (1):

$$S_i = \frac{\xi_i}{\sum \xi_i} \times 100 \quad (1)$$

where ξ_i represents the percent of hydrogen consumed to hydrogenate the LA and SBP. In general, the LA hydrogenation proceeds to GVL with selectivities >99%, while SBP hydrogenation results in the formation of sec-butyl cyclohexanol and sec-butyl cyclohexanone with selectivities >99%. The hydrogen consumption selectivity