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Full Length Article

Insight on mechanism of Sn modification in alumina supported RhSn catalysts for acetic acid hydrogenation to fuel-grade ethanol

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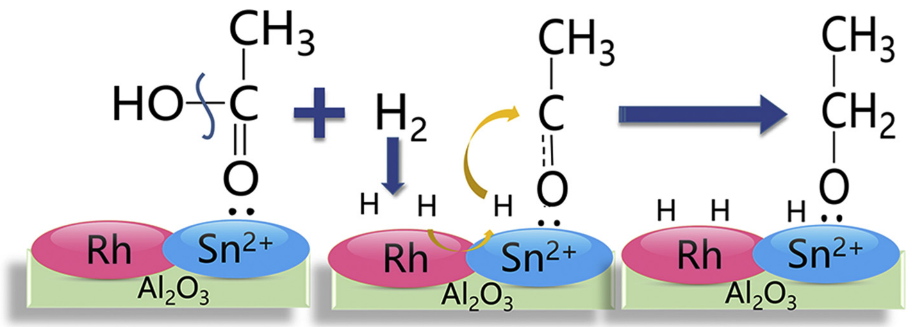
HIGHLIGHTS

- $RhSn/Al_2O_3$ with high Sn/Rh ratio was suitable for acetic acid hydrogenation.
- Coexistence of metallic Rh and Sn oxides enhanced hydrogen spillover.
- Tin(II) species can stabilize top adsorption of acetyl species.

GRAPHICAL ABSTRACT



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ABSTRACT

Acetic acid hydrogenation has been carried out over Rh/Al_2O_3 and $RhSn/Al_2O_3$ with various Sn/Rh ratios and different loadings. Metallic Rh, Rh oxides and Sn oxides were detected after reduction of $RhSn/Al_2O_3$ at 623 K. Spillover of hydrogen was observed in H_2 desorption process due to the coexistence of metallic Rh and Sn oxides. The addition of Sn improved dissociation of C—OH bond and stabilized top adsorption of acetyl species during the adsorption of acetic acid at 548 K. With the introduction of hydrogen, high Sn/Rh ratio suppressed methane production and generated more ethoxy species. High loadings of Sn and Rh can also improve catalytic performance of acetic acid hydrogenation to ethanol. In our experiments, $3Rh5Sn/Al_2O_3$ achieved the selectivity to ethanol of 74% with the corresponding conversion value of about 98%.

1. Introduction

With increasing discrepancy between great energy demand of global industrialization and poor energy supply from limited petroleum resources, a technology for alternative transportation fuels needs to be identified, developed and commercialized [1]. Ethanol is a high valued renewable fuel with less negative environmental issues [2]. Currently, fuel ethanol is mostly produced on large scale by fermentation of biomass such as corn grain and sugar cane [3–5], which may have competition with food supply. Since 1950s, methanol carbonylation has been applied to manufacture acetic acid massively[6]. Considering theoretical feasibility and cheap raw materials from acetic acid to ethanol, hydrogenation of acetic acid to ethanol could be an appropriate technology to ease energy issue in efficient and sustainable ways.

Several patent literatures [7–9] presented acetic acid can be hydrogenated over Group VIII or IB metal catalysts supported on Group III or IV element oxide. Rhodium as a Group VIII metal has remarkable activity for hydrogenation. Hoogers et al. [10] studied

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adsorption and decomposition of acetic acid on Rh(111) through temperature programed desorption and laser induced desorption. Upon saturation exposure of acetic acid at room temperature, a crowed acetate ad-layer was formed and decomposition of acetate species over Rh (111) belonged to autocatalytic process. Hence, monometallic Rh catalysts are not appropriate for acetic acid hydrogenation to ethanol.

In bimetallic catalysts, the addition of promoter brings about bimetallic nature. Sn modified Rh catalysts may have distinct catalytic behavior towards acetic acid hydrogenation compared to Rh catalysts. Coupé et al. [11] revealed that the presence of Sn on Rh-based catalysts can improve selectivity to unsaturated alcohol in hydrogenation of corresponding aldehydes. The selectivity of product depended on various RhSn ensembles under different Sn/Rh ratios. Candy et al. [12] conducted a series of researches on ethyl acetate hydrogenation over RhSn/SiO_2 to figure out that low Sn/Rh ratio decreased selectivity for hydrogenolysis to CO and CH_4 and high Sn/Rh ratio improved both the activity and the selectivity for ethanol formation.

Alumina supported RhSn catalysts for acetic acid hydrogenation to ethanol has been rarely investigated. This work is focused on the effect of Sn addition on catalytic performance of acetic acid hydrogenation over RhSn/Al_2O_3. The catalysts with different RhSn loadings and Sn/Rh ratios were prepared and mainly characterized by temperature programmed reduction, temperature programmed desorption of hydrogen, diffuse reflectance infrared Fourier transform spectroscopy and X-ray photoelectron spectroscopy.

2. Experimental

2.1. Catalyst preparation

Supported monometallic and bimetallic catalysts were prepared by impregnation and co-impregnation, respectively. The γ-alumina as support was calcined in air at 823 K for 4 h before impregnation. Then, calcined support was impregnated by an aqueous solution of rhodium (III) nitrate hydrate (denoted as xRh/Al_2O_3). xRhySn/Al_2O_3 catalysts were obtained by the co-impregnation of Al_2O_3 with mixed aqueous solution of rhodium (III) nitrate hydrate and tin (IV) chloride ($SnCl_4 \cdot 5H_2O$). After impregnation, the catalysts were dried at 383 K for 12 h, followed by calcination in air at 823 K for 6 h. The loadings of both Rh and Sn were varied from 1 wt% to 5 wt% (x, y = 1, 2, 3, 4, 5). Textural properties and chemisorption capacities of various catalysts and support are shown in Table S1.

2.2. Catalyst characterization

The specific surface areas, pore volumes and pore sizes of catalysts were calculated from adsorption isotherms of nitrogen at 77 K using a Micromeritics ASAP 2020M automated system. Temperature-programmed reduction (TPR), hydrogen temperature-programmed desorption (H_2-TPD) and CO pulse chemisorption were studied by using Micromeritics Autochem II 2020 chemisorption apparatus. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) for CO adsorption, acetic acid adsorption and acetic acid hydrogenation was carried out using Nicolet 6700 spectrometer. The details of these characterizations have been demonstrated in Supplementary materials.

2.3. Catalytic performance

The catalytic hydrogenation reaction was performed in 10-mm-inner-diameter tubular stainless steel fixed bed reactor loading with 2.8 g catalysts of 180 meshes. Prior to hydrogenation reaction, the catalysts were reduced in situ at 623 K in 120 ml/min of flow H_2 for 2 h, followed by cooling to 548 K in H_2 atmosphere. The hydrogen gas flow was controlled and metered by an electronic mass flow controller. During reaction, acetic acid was pumped and preheated to vapor phase with liquid weight hourly space velocity of 0.9 h^{-1}. H_2 was introduced into reactor with H_2: AcOH mole ratio of 10:1. The reaction pressure was controlled at 2 MPa by back pressure regular and the reaction temperature was maintained at 548 K. The liquid products separated by condenser and off-gas were detected by GC Agilent 7890A. Particularly, acetic acid left in liquid was determined by titration of 1 mol/L solution of NaOH.

3. Results and discussion

3.1. H_2-TPR

Fig. 1 shows TPR profiles of Rh-based catalysts with different Rh/Sn ratios and loadings. For 3Rh/Al_2O_3 catalyst, a broad peak with a maximum at 390 K was attributed to the reduction of Rh_2O_3 [13]. However, TPR profiles of 3RhySn/Al_2O_3 catalysts from Fig. 1 (b)–(d) showed higher temperatures and intensities of first reduction peaks because part of Sn oxides were also reduced below 450 K. A shoulder at 450–800 K corresponding to the reduction of Sn oxides was also observed after the addition of Sn [14]. In higher Sn/Rh ratio, the shoulder at 450–650 K turned to an obvious peak and even another shoulder at 700–800 K corresponding to the reduction of Sn(II) can be visible at 3Rh5Sn/Al_2O_3 catalyst, which was attributed to the formation of isolated Sn oxides far from Rh species [15]. The TPR profiles of xRhySn/Al_2O_3 (x = y) catalysts displayed lower reduction temperature and higher intensity of first peak at more loadings of rhodium and tin corresponding to reduction of rhodium oxides adjacent to tin species. Difficult reduction of rhodium at low loadings may be caused by interaction between these metal species and Al_2O_3 support due to high dispersions of Rh and Sn on low loaded xRhySn/Al_2O_3 (x = y) catalysts, which have been obtained from CO-pulse chemisorption in Table S1.

3.2. H_2-TPD

Fig. 2 shows H_2-TPD profiles of Rh-based catalysts. In 3Rh/Al_2O_3 catalyst, the peak of H_2 desorption at 350 K–500 K belonged to hydrogen on metallic Rh [16], which was also displayed at

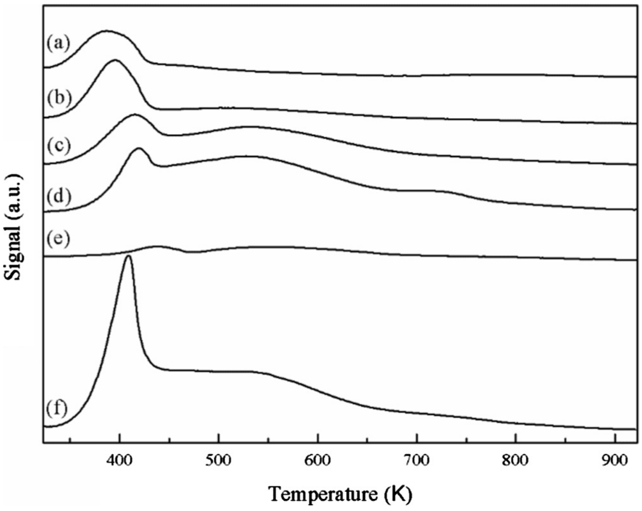

Fig. 1. TPR profiles of different catalysts: (a) 3Rh/Al_2O_3, (b) 3Rh1Sn/Al_2O_3, (c) 3Rh3Sn/Al_2O_3, (d) 3Rh5Sn/Al_2O_3, (e) 1Rh1Sn/Al_2O_3, (f)5Rh5Sn/Al_2O_3.