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Restructuring of supported PtSn bimetallic catalysts during aqueous phase oxidation of 1,6-hexanediol

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ABSTRACT

A series of carbon-supported bimetallic PtSn catalysts having various Pt/Sn molar ratios was prepared and tested in the oxidation of 1,6-hexanediol with 1 MPa dioxygen at 343 K in aqueous solvent. The PtSn/C catalysts, which were initially reduced with sodium borohydride, did not produce Pt–Sn alloy particles. Instead, the catalysts were composed of SnO_x moieties that were well-dispersed on the surfaces of the carbon support and the Pt nanoparticles. Subsequent treatment in H_2 at 673 K induced Pt–Sn alloy formation. Whereas addition of SnO_x to the Pt nanoparticles promoted the initial 1,6-hexanediol oxidation rate by 39%, the formation of Pt–Sn alloy particles decreased the initial rate. Under 1,6-hexanediol oxidation conditions, however, the Pt–Sn alloy phase separated, leading to the recovery of the catalytic activity. No significant change of product distribution was observed on bimetallic PtSn catalysts, regardless of the composition and structure.

1. Introduction

Bimetallic catalysts consisting of Pt and Sn have been studied extensively in hydrogenation [1–6], hydrocarbon reforming [7–11], CO oxidation [12,13] and alcohol electro-oxidation [14–32] because they have demonstrated enhanced activity, selectivity and/or stability, compared to monometallic Pt catalysts. The addition of Sn to Pt presumably leads to the formation of unique active sites, specifically those associated with Pt–Sn alloys and Pt–SnO_x interfaces. When Pt and Sn are in close proximity, an electronic interaction between the components and modification of Pt ensembles can alter the catalytic performance. A large body of work has reported on the promotional effects of Sn, which are attributed mainly to a change in the adsorption energy of certain molecules [6,12,14,20,25,27,28,33,34], a modified rate of C—C bond cleavage reactions [1,20,27,30], the efficient removal of strongly adsorbed poisons [17,25,30] and the introduction of acid sites [8,10,11] and/or an O_2 adsorption site [12]. For example, in the hydrogenation of α,β-unsaturated aldehyde, the dilution of the Pt ensembles by SnO_x hindered the adsorption of C=C groups relative to C=O groups, thus favoring preferential hydrogenation of the aldehyde to produce an unsaturated alcohol with high selectivity [2–6]. The added SnO_x can also act as a Lewis acid site in hydrocarbon reforming reactions, which leads to a significant increase in activity [8,11]. In the oxidation of CO, Michalak et al. attributed the promoted activity over a PtSn bimetallic catalyst to the Pt–SnO_x interface [12]. The SnO_x provides an active site for O_2 adsorption while Pt is covered with strongly adsorbed CO.

In the electro-oxidation of alcohols, supported bimetallic PtSn electro-catalysts exhibited higher activity and stability compared to monometallic Pt electro-catalysts [15,19,26,32]. Although the addition of Sn often increases the activity of Pt by a factor of 2–10 [18,19,21,24,27], Biallozor et al. reported a steady-state current density with a poly(3,4-dioxyethylenethiophene)-supported PtSn catalyst that was 2 orders of magnitude greater than that of Pt during the electro-oxidation of methanol [15]. Ishikawa et al. studied the oxidation of methanol on Pt–Sn alloy using density-functional theory (DFT) and suggested that the adsorption of both methanol and CO was weaker on the Pt–Sn alloy surface [14], which may account for the faster rate and greater stability of the alloy. A lower adsorption energy of methanol and ethanol on the surface of Pt–Sn alloy was also observed in a temperature-programmed desorption (TPD) study [35], which is consistent with DFT results. In addition to Pt–Sn alloy formation, the presence of SnO_x adjacent to Pt ensembles is also thought to play an important role in the electro-oxidation of alcohols. Castro Luna et al. report that catalysts containing the largest amount of SnO_x exhibited the best performance in ethanol oxidation [31]. The superior activity of a SnO_x-promoted catalyst was attributed to an enhancement

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in the dissociative adsorption of alcohol in the low potential region [20,25]. Furthermore, Pergato et al. and Rato et al. proposed that SnO_x might promote the removal of adsorbed CO and other strongly-adsorbed remnants from C—C bond cleavage reaction [28,29].

One potential complication with bimetallic catalysts is that their structure may change during the reaction. Whereas many studies correlate the catalytic performance of bimetallic particles with the structure of the as-prepared catalysts, changes in the structure of PtSn catalysts have been reported under both hydrogenation and oxidation conditions [12,15,25,36]. To understand the promotional effect of Sn on Pt catalysts, it is therefore important to examine the influence of the reaction environment on catalyst structure.

The present work explores the influence of added Sn on Pt catalysts for the selective oxidation of 1,6-hexanediol (HDO). Oxidation of HDO can produce adipic acid (DA), which is one of the top ten commodity chemicals by volume [37] and is widely used in the synthesis of nylon-6,6, for carpet fibers, tire reinforcements, upholstery and apparel [38]. Adipic acid is currently produced from a mixture of cyclohexanol and cyclohexanone via nitric acid oxidation, which emits a considerable amount of nitrous oxide [39,40]. One promising environmentally-friendly route to produce adipic acid begins with hexose (glucose and fructose), derived from biomass. A high yield of 5-hydroxymethylfurfural (HMF) can be obtained from the dehydration of hexose, which can then be efficiently converted to HDO [41,42] and subsequently oxidized to adipic acid. Among supported metal catalysts, Au has demonstrated the highest activity for polyol oxidation under basic conditions [43]. The use of base, however, is not attractive because of the cost involved in neutralizing the product stream to recover the free acid. Oxidation of alcohol over Pt does not require high concentration of base for the diacid production [44,45]. Unfortunately, severe deactivation can be observed during the oxidation of HDO over Pt catalysts, which was tentatively attributed to strongly adsorbed species generated from C—C bond cleavage [46]. Since the addition of Sn to Pt may enhance the removal of strongly adsorbed species on the surface, PtSn bimetallic catalysts are promising candidates for the selective oxidation of HDO.

In this study, a series of carbon-supported PtSn bimetallic catalysts was prepared and evaluated in the oxidation of HDO in liquid water by O_2 without the addition of base. Extensive characterization of the catalysts before and after reaction was performed to enable correlation of performance to catalyst structure and composition.

2. Materials and methods

2.1. Catalyst preparation

All carbon-supported Pt and PtSn bimetallic catalysts were synthesized using a $NaBH_4$ reduction method. The loading of Pt was always 3 wt% while the amount of Sn was varied. The Pt and Sn precursors used were H_2PtCl_4 and Na_2SnO_3 (Sigma–Aldrich), respectively, and activated carbon (Norit, Ultra SX) was used as the support. Activated carbon (2 g) was dispersed ultrasonically in 150 cm^3 of a 1 mM NaOH solution (Aldrich) for 1 h. The desired amount of Na_2SnO_3 and 0.3 mmol of the H_2PtCl_4 were dissolved separately in 25 cm^3 of 1 mM NaOH and added to the carbon slurry with vigorous stirring. The Pt and Sn precursors were reduced by the rapid addition of 10 cm^3 of a freshly prepared 0.3 M $NaBH_4$ solution (Aldrich). The slurry was left under vigorous stirring for 2 h. Finally, the slurry was filtered, washed thoroughly with distilled, deionized water and dried in air at room temperature. These catalysts are denoted as *x*Pt*y*Sn/C, where *x*:*y* is the nominal molar ratio of Pt to Sn.

The *x*Pt*y*Sn/C catalysts were then heated to 673 K at 1 K min^{-1} under 100 cm^3 min^{-1} of flowing dihydrogen (GTS Welco 99.999%) and reduced for 2 h. These catalysts are denoted as *x*Pt*y*Sn/C–H. To study the potential structural and compositional changes of *x*Pt*y*Sn/C–H, catalysts were recovered after HDO oxidation, washed with distilled and deionized water and dried at room temperature. The used catalyst after reaction was denoted as *x*Pt*y*Sn/C–H–R. In addition, the 3Pt3Sn/C catalyst was also heated to 473 K at 1 K min^{-1} under 100 cm^3 min^{-1} of flowing dihydrogen and treated for 4 h, giving a sample denoted as 3Pt3Sn/C-473H.

2.2. Catalyst characterization

The fraction of available Pt on the surface of a catalyst was estimated by H_2 chemisorption using a Micromeritics ASAP 2020 automated adsorption analyzer. The catalysts were heated to 473 K at 4 K min^{-1} under flowing H_2 (GTS Welco 99.999%) and reduced for 2 h. The samples were then evacuated for 2 h at 473 K before being cooled to 308 K for analysis in the pressure range of 1.33–59.9 kPa. The amount of exposed Pt was evaluated by the total amount of H_2 adsorbed, extrapolated to zero pressure, assuming a stoichiometry (H/Pt_{surf}) equal to unity.

The X-ray diffraction (XRD) patterns were recorded using a PANalytical X'Pert Pro MPD (Multi-Purpose Diffractometer) instrument with Cu Kα radiation (45 kV, 40 mA) and scanning of 2θ from 20° to 80° with a step size of 0.0025° at a rate of 0.125° min^{-1}.

Transmission electron microscopy (TEM) was performed on a JEOL 2000 operating at 200 kV to obtain the metal particle size distribution of the catalysts. The high-resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (STEM) were performed on an FEI Titan 80-300 operating at 300 kV that is equipped with a Gatan 794 Multi-scan Camera (EFTEM) and an energy dispersive spectrometer for elemental X-ray analysis. To prepare a sample, ~1 mg of catalyst was suspended in 10 cm^3 of ethanol by agitating the mixture for 30 min in a sonication bath. A copper grid with a holey carbon film was dipped into the solution to capture the particles and the ethanol was thoroughly evaporated before microscopy.

The X-ray photoelectron spectroscopy (XPS) was carried out at the Nanomaterials Core Characterization Facility of the Virginia Commonwealth University (Richmond, VA), utilizing a Thermo Scientific ESCALAB 250 spectrometer equipped with a focused monochromatic Al Kα X-ray radiation source (1486.6 eV) and a hemispherical analyzer with a 6-element multichannel detector. The incident X-ray beam was 45° off normal to the sample while the X-ray photoelectron detector was normal to the sample. A large area magnetic lens with a 500 μm spot size in constant analyzer energy mode was utilized with a pass energy of 20 eV for region scans. Charge compensation was employed during data collection with an internal electron flood gun (2 eV) and a low energy external Ar ion flood gun. All spectra were deconvoluted with a curve fitting routine in CasaXPS software. The background was corrected using the linear method and the binding energy of the C 1s peak assigned at 284.5 eV, which is attributed to the support, was used to reference the peak positions [19]. The integral of each peak was calculated after subtracting the background and fitting with a combination of Lorentzian asymmetric curves of variable proportions. The Pt:Sn surface atomic ratios were calculated from peak areas normalized by atomic subshell photoionization cross sections of the corresponding element [47]. The detailed XPS curve fitting parameters are listed in Table S1.

Elemental analysis was used to determine some of the Pt and Sn weight loadings on the supported PtSn bimetallic catalysts and the concentration of leached Pt and Sn in the reaction solution after 4 h