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Promotional effects of Sb on Pd-based catalysts for the direct synthesis of hydrogen peroxide at ambient pressure

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ABSTRACT

TiO_2-supported Pd-Sb bimetallic catalysts were prepared and evaluated for the direct synthesis of H_2O_2 at ambient pressure. The addition of Sb to Pd significantly enhanced catalytic performance, and a $Pd_{50}Sb$ catalyst showed the greatest selectivity of up to 73%. Sb promoted the dispersion of Pd on TiO_2, as evidenced by transmission electron microscopy and X-ray diffraction. X-ray photoelectron spectroscopy indicated that the oxidation of Pd was suppressed by Sb. In addition, Sb_2O_3 layers were formed and partially wrapped the surfaces of Pd catalysts, thus suppressing the activation of H_2 and subsequent hydrogenation of H_2O_2. *In situ* diffuse reflection infrared Fourier transform spectroscopy for CO adsorption suggested that Sb homogenously located on the surface of Pd-Sb catalysts and isolated contiguous Pd sites, resulting in the rise of the ratio of Pd monomer sites that are favorable for H_2O_2 formation. As a result, the Sb modified Pd surfaces significantly enhanced the non-dissociative activation of O_2 and H_2O_2 selectivity.

1. Introduction

Hydrogen peroxide (H_2O_2), which is an environmental benign oxidant, is widely applied in the textile, pulp/paper bleaching, waste water treatment, and pharmaceutical industries [1]. Currently, over three million metric tons of H_2O_2 are produced annually via the anthraquinone process, which involves sequential hydrogenation and oxidation of anthraquinone [1,2]. However, there are concerns about the carbon efficiency of the process, not least of which is the unselective hydrogenation of anthraquinone that requires replenishment during the cycle. Moreover, the process inherently requires large capital and operating costs, because of the energy-intensive separation, concentration, and transportation of H_2O_2 [3]. From an economic and environmental point of view, the direct synthesis of H_2O_2 from H_2 and O_2 over a Pd-based catalyst is a promising, desirable, and atom-efficient route that provides an alternative to the current process. Direct synthesis avoids the use of expensive anthraquinone, the production of waste, and the complexity of purification. What is more, the coupling of direct, on-line H_2O_2 production with downstream oxidation is highly desirable in that it produces value-added products by shortening the supply chain [4–7].

Although direct synthesis has advantages over the existing process, its industrial implementation has been hindered by the limited selectivity and stability of supported Pd nanoparti-

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cles (NPs), which are the most active known catalysts [8]. It is known that apart from facilitating the selective oxidation of H_2 to H_2O_2, monometallic Pd catalysts also promote the non-selective oxidation of H_2 to water and the hydrogenation of H_2O_2. Several strategies have been employed to overcome this limitation by modifying the structure of Pd NPs: (1) tuning the Pd ensembles with supports [9–13], (2) altering their surface properties with ligands [14], and (3) alloying Pd with a second metal (e.g., Pt, Au, Sn, Zn) [15–19]. Pd-Au and Pd-Sn catalysts are the most selective catalysts operating at high pressure (4.0 MPa) to date. Our previous study of Pd-Au/TiO_2 catalysts showed that Pd monomers surrounded by Au atoms can be primary active sites for H_2O_2 formation [17], in good agreement with theoretical calculations that O–O bond scission is suppressed over Pd-Au sites [20]. Maity et al. [21] demonstrated that bimetallic Ni-Pd catalysts in the presence of halide ions showed three times greater activities than monometallic Pd catalysts. In our recent work, initial H_2O_2 selectivities of more than 90% were obtained over Pd-Te/TiO_2 and Pd/HAp catalysts at 283 K, 0.1 MPa. Even so, the activities and stability of these catalysts do not meet the requirements of commercial production [22,23].

Sb has been shown to improve the performance of Pd catalysts [24] and can be alloyed with Pd [25,26]. We report, herein, the promotional effects of Sb on Pd catalysts for H_2O_2 formation. A series of Pd-Sb/TiO_2 catalysts with different Pd/Sb ratios were prepared and tested for direct H_2O_2 synthesis under ambient conditions. The nature of the active sites was examined thoroughly, and deep insight into the structure-performance behavior of the catalysts was obtained by multiple methods of characterization including transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), *in situ* diffuse reflection infrared Fourier transform spectroscopy for CO adsorption (CO-DRIFTS), and temperature-programmed desorption of H_2 and O_2 (H_2/O_2-TPD).

2. Experimental

2.1. Catalyst preparation

Monometallic Pd and bimetallic Pd-Sb catalysts were prepared by an incipient wetness impregnating method as described in a previous study [27]. An aqueous solution of H_2PdCl_4 (Sigma-Aldrich) and $SbCl_3$ (Aladdin, 99.9%) were used as the precursor. TiO_2 (Degussa P25, 50 ± 15 m^2/g) was adopted as the support. Pd-Sb catalysts with Sb/Pd atomic ratios of 0, 1/80, 1/50, 1/20, and 1/2 were prepared. Each catalyst had a 3 wt% Pd loading. Prior to reaction, all catalysts were calcined in static air at 773 K for 2 h and then reduced at 573 K in a 1:2 H_2:N_2 flow at 75 mL/min for 2 h at a ramp rate of 5 K/min. The resulting catalysts are denoted as Pd_xSb, where x is the molar ratio of Pd to Sb.

2.2. Catalyst characterization

TEM measurements were performed on a JEOL JEM 2010F electron microscope at an operating voltage of 200 kV. The catalysts were ultrasonically suspended in ethanol. One drop of this slurry was deposited on a carbon-coated copper grid. The liquid phase was evaporated before loading the grid into the microscope. The size distribution of each sample was derived from the analysis of over 300 particles.

XRD powder patterns at ambient conditions were recorded using a Rigaku D/max 2550 diffractometer with an accelerator voltage of 40 kV and a detector current of 100 mA. Cu-K_α radiation was used for continuous scanning with a step-size of 0.02° over a 2θ range of 10°–80° with a scan speed of 4°/min.

XPS analysis was performed on a Thermo ESCALAB 250Xi spectrometer using a monochromatic Al- K_α radiation source (1486.6 eV, pass energy 20.0 eV). The base pressure of the instrument was about 1×10^{-9} Torr. Binding energies (BEs) were calibrated using the C 1*s* peak at 284.8 eV as a reference. The Pd 3*d* peaks were fitted after Shirley background subtraction; the Pd 3*d* orbitals were described by two features in each state. A branching ratio of 1.5 for $3d_{5/2}$:$3d_{3/2}$ and the full width at half maximum (FWHM) of the Pd 3*d* peaks were held constant. The $3d_{3/2}$ and $3d_{5/2}$ peaks of Sb also were measured with the latter being overlapped by the O 1*s* transition. Linear background subtraction was used to fit the Sb 3*d* peaks. It is evident from the shape of the Sb $3d_{5/2}$ transitions that these BEs and those of O 1*s* are very close making deconvolution of the individual contributions difficult. Thus, we chose to constrain only the peak position based on the energy difference (9.35 eV) of the Sb 3*d* doublet. The Pd 3*d*, Sb 3*d*, and O 1*s* spectral features were fitted using a sum of Gaussian-Lorentzian distributions (SGL (20)).

In situ CO-DRIFTS was recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer equipped with a reaction cell (modified Harricks Model HV-DR2) that allowed gas to flow continuously through the catalyst bed (ca. 0.1 g) during spectra acquisition. Before adsorption, the sample was reduced *in situ* and then cooled to 283 K in pure Ar. CO gas was introduced into the system for 30 min. The spectra were collected at 4 cm^{-1} resolution. The bridge- to linear-bound ratios reported here do not take into account the differences in extinction coefficient between adsorption sites. Therefore, the bridge- to linear-bound ratio does not represent quantitative coverages, but rather the qualitative differences between catalysts.

H_2/O_2-TPD experiments were performed using a U-tube connected to a GC-QMS (HPR-20, Hiden Analytical Ltd.), where masses of m/e = 2 (H_2), 18 (H_2O), 32 (O_2), and 40 (Ar) were monitored. Prior to the adsorption, the catalysts were pretreated in static air at 773 K for 2 h, in H_2/Ar at 573 K for 2 h, and then cooled in ultrapure Ar. H_2/O_2 adsorbate (20 mL/min, 30 min) was introduced into the system at 283 K. The system was purged with Ar (40 mL/min) until the H_2/O_2 signal reached a constant value. The temperature was ramped from 283 to 1073 K at a rate of 20 K/min in Ar (40 mL/min).

2.3. Catalyst testing

H_2O_2 synthesis and degradation activity were evaluated using a modified micro-triphase-semi-batch reactor at 283 K and