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

Doudou Ding^a, Xingyan Xu^a, Pengfei Tian^a, Xianglin Liu^a, Jing Xu^{a,*}, Yi-Fan Han^{a,b,#}^a State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China^b Research Center of Heterogeneous Catalysis and Engineering Science, School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, Henan, China

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ABSTRACT

TiO₂-supported Pd-Sb bimetallic catalysts were prepared and evaluated for the direct synthesis of H₂O₂ at ambient pressure. The addition of Sb to Pd significantly enhanced catalytic performance, and a Pd₅₀Sb catalyst showed the greatest selectivity of up to 73%. Sb promoted the dispersion of Pd on TiO₂, 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, Sb₂O₃ layers were formed and partially wrapped the surfaces of Pd catalysts, thus suppressing the activation of H₂ and subsequent hydrogenation of H₂O₂. *In situ* diffuse reflection infrared Fourier transform spectroscopy for CO adsorption suggested that Sb homogeneously 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 H₂O₂ formation. As a result, the Sb modified Pd surfaces significantly enhanced the non-dissociative activation of O₂ and H₂O₂ selectivity.

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1. Introduction

Hydrogen peroxide (H₂O₂), 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 H₂O₂ 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 ener-

gy-intensive separation, concentration, and transportation of H₂O₂ [3]. From an economic and environmental point of view, the direct synthesis of H₂O₂ from H₂ and O₂ 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 H₂O₂ 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-

* Corresponding author. Tel: +86-21-64251938; Fax: +86-21-64251928; E-mail: xujing@ecust.edu.cn

Corresponding author. E-mail: yifanhan@ecust.edu.cn

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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, $50 \pm 15 \text{ m}^2/\text{g}$) 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. $\text{Cu-K}\alpha$ 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 $4^\circ/\text{min}$.

XPS analysis was performed on a Thermo ESCALAB 250Xi spectrometer using a monochromatic Al- $K\alpha$ 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 1s peak at 284.8 eV as a reference. The Pd 3d peaks were fitted after Shirley background subtraction; the Pd 3d 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 3d 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 1s transition. Linear background subtraction was used to fit the Sb 3d peaks. It is evident from the shape of the Sb $3d_{5/2}$ transitions that these BEs and those of O 1s 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 3d doublet. The Pd 3d, Sb 3d, and O 1s 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, Hidden 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

atmospheric pressure. The reactor was charged with catalyst (0.05 g) and 60 mL of ethanol and 0.38 mL of concentrated H_2SO_4 as reaction solvent to test the H_2O_2 synthesis. The reagent gases (15 vol% H_2 , 60 vol% O_2 , 25 vol% N_2 , 60 mL/min total flowrate) were introduced to the reactor through a pre-mixer and fine glass frit in sequence with Teflon-rotor magnetic stirring at 1000 r/min. H_2 conversion was analyzed by gas chromatography, and H_2O_2 production was determined by UV/vis spectrophotometry after complexation with a $\text{TiOSO}_4/\text{H}_2\text{SO}_4$ reagent. H_2O_2 selectivity ($S_{\text{H}_2\text{O}_2}$) was determined from the rate of H_2O_2 formation and the rate of H_2 conversion using the equation

$$S_{\text{H}_2\text{O}_2} = \frac{\text{Rate of } \text{H}_2\text{O}_2 \text{ formation (mol/min)}}{\text{Rate of } \text{H}_2 \text{ conversion (mol/min)}} \times 100\% \quad (1)$$

H_2O_2 decomposition and hydrogenation experiments were carried out in a manner similar to the H_2O_2 synthesis, but in the absence of O_2 . The initial H_2O_2 concentration was 0.3 wt%. The reaction was conducted for 1 h with the concentration of H_2O_2 determined every 10 min.

3. Results and discussion

3.1. Catalytic performance

The performance of the Pd-Sb catalysts is summarized in Table 1 and compared with those of typical catalysts reported in the literature (Table S1). The synthesis of H_2O_2 and its hydrogenation/decomposition reactions take place simultaneously. Thus, productivity is the sum of all these processes [28]. A H_2 conversion of 29.5% and a H_2O_2 selectivity of 54% was observed with monometallic Pd. Upon addition of Sb, selectivity increases to 68% for Pd_{80}Sb . A uniquely high H_2O_2 selectivity of 73% corresponding to a H_2O_2 productivity of 1552 mol $\text{H}_2\text{O}_2/\text{kg}_{\text{Pd}}/\text{h}$ was found for Pd_{50}Sb . The activities and selectivities of the catalysts decline at $\text{Pd}/\text{Sb} = 20$, and the catalyst with a Pd/Sb ratio of 2 is inactive.

To understand the promotional effects of Sb, the H_2O_2 decomposition and hydrogenation side reactions must be taken into account. For H_2O_2 decomposition, H_2O_2 consumption was negligible over all catalysts under N_2 flow. In contrast, H_2O_2 conversion was observed under H_2 flow. We conclude that H_2O_2 hydrogenation is the main pathway for subsequent H_2O_2 con-

version, which lowers the selectivity (Fig. 1). Monometallic Pd showed the greatest H_2O_2 hydrogenation activity with a rate of 2678 mol $\text{H}_2\text{O}_2/\text{kg}_{\text{Pd}}/\text{h}$ (Table 1). The hydrogenation rate declined with increasing Sb concentration. Pd_2Sb exhibited the lowest hydrogenation activity. These results indicate that addition of Sb blocks H_2O_2 hydrogenation. However, Pd_2Sb showed little H_2 conversion activity despite its low H_2O_2 hydrogenation activity. This might result from the absence of active sites on the catalyst surface at large Sb loading. The dependence of catalytic performance on Sb loading suggests that variation of the Pd/Sb atomic ratio finely tunes the electronic and geometric structures of Pd-Sb catalysts. To unveil the mechanism of active sites formation, the catalysts were systematically characterized.

3.2. Catalytic characterization

3.2.1. Catalyst morphology

Fig. 2 displays typical TEM images and particle size distributions of the fresh catalysts. Compared to Pd_{50}Sb , monometallic Pd exhibits a broad particle size distribution and an average size of ca. 3.2 nm (Fig. 2(c)). The lattice fringes with a 0.24-nm spacing corresponding to the $\text{Pd}(111)$ plane are clearly visible in the HRTEM images. The mean particle diameter decreases to ca. 1.8 nm (Fig. 2(d)) for Pd_{50}Sb , suggesting that the addition of Sb significantly promotes dispersion of the Pd particles.

XRD patterns (Fig. 3) show that TiO_2 (Degussa P25) is composed of two phases, anatase and rutile, even after loading Pd. Almost no crystalline Pd was detected, except that a small peak at 40.4° , which was assigned to the $\text{Pd}(111)$ plane, was observed for some catalysts. When the Pd:Sb ratio decreased to 2:1, the 40.4° peak vanished. The results indicate that Pd-Sb catalysts comprise mainly small metal particles (< 4.0 nm), which are beyond the detection limit of XRD. The conclusion is consistent with TEM results [29].

3.2.2. Electronic structure

Fig. 1. H_2O_2 hydrogenation and decomposition over Pd-Sb/ TiO_2 catalysts. (■) H_2O_2 hydrogenation, (▲) H_2O_2 decomposition. Reaction conditions: total gas flow rate = 60 mL/min ($\text{H}_2/\text{N}_2 = 9:51$ (vol/vol) for H_2O_2 hydrogenation and total N_2 for H_2O_2 decomposition), ethanol/ H_2SO_4 solvent, 50 mg catalyst, 283 K, 0.1 MPa, 1 h, stirring rate = 1000 r/min.

Table 1
Performance of Pd-Sb/ TiO_2 catalysts for H_2O_2 synthesis.

Catalyst	H_2 conversion (%)	H_2O_2 selectivity (%)	H_2O_2 productivity (mol $\text{H}_2\text{O}_2/\text{kg}_{\text{Pd}}/\text{h}$)	H_2O_2 hydrogenation rate (mol $\text{H}_2\text{O}_2/\text{kg}_{\text{Pd}}/\text{h}$)
Pd_2Sb	n.d.	n.d.	n.d.	1223
Pd_{20}Sb	13.8	57	1256	2018
Pd_{50}Sb	13.9	73	1552	2158
Pd_{80}Sb	19.3	68	2002	2307
Pd	29.5	54	2541	2678

Reaction conditions: 60 mL solvent (ethanol/ H_2SO_4), total gas flow rate of 60 mL/min ($\text{H}_2/\text{O}_2/\text{N}_2 = 9:36:15$ vol/vol/vol), 50 mg catalyst, 0.1 MPa, 283 K, 1/6 h, stirring rate = 1000 r/min. n.d.: Not detected.

Fig. 2. TEM images and particle size distributions of fresh Pd (a, c) and Pd₅₀Sb (b, d) catalysts.

Fig. 3. XRD patterns of fresh catalysts. (1) Pd, (2) Pd₈₀Sb, (3) Pd₅₀Sb, (4) Pd₂₀Sb, (5) Pd₂Sb.

The chemical nature of the catalyst surface, in particular the Pd²⁺/Pd⁰ ratio, is crucial to H₂O₂ selectivity [11,30]. Thus, XPS analysis was performed to examine the electronic interactions between Pd and Sb and the valence state of Pd surface species. The Pd 3d core-level spectra for all catalysts are displayed in Fig. 4, and results are summarized in Table 2. Peaks with bind-

Fig. 4. Fitted Pd 3d XPS spectra of fresh catalysts. (1) Pd, (2) Pd₈₀Sb, (3) Pd₅₀Sb, (4) Pd₂₀Sb, (5) Pd₂Sb.

ing energies of 334.9 and 340.3 eV are attributed to Pd⁰ 3d_{5/2} and 3d_{3/2}, respectively [31,32], while those at 341.3 and 336.0 eV are assigned to Pd²⁺ 3d_{5/2} and 3d_{3/2} [33,34]. Pd⁰ and Pd²⁺ were detected in all catalysts, and the Pd⁰/Pd²⁺ ratio increased from 58.4/41.6 in Pd to 77.1/22.9 in Pd₂Sb. Thus, addition of Sb inhibited the oxidation of metallic Pd. Our previous study detected only metallic Pd⁰ for Pd/SiO₂ [35], which indicates that formation of Pd²⁺ species might result from interaction between Pd particles and TiO₂ [17,27].

Chemical states in the Sb 3d XPS spectrum (Fig. 5(a)) are difficult to identify by deconvoluting the individual contributions due to overlap of the Sb 3d_{5/2} and O 1s core levels. Because of the low Sb concentration, almost no Sb peaks are observed apart from a distinguishable one at 539.5 eV for Pd₂Sb. The 539.5 and 530.1 eV peaks are attributed to Sb³⁺ 3d_{3/2} and 3d_{5/2} (Fig. 5(b)), respectively. The atomic ratio of Sb/Pd on the surface of Pd₂Sb is 9/10 based on the relative sensitivity factor (RSF) (Pd: 39.787, Sb: 19.353) and their signal intensity, which is markedly greater than the bulk Sb/Pd ratio in the catalyst. This suggests that an Sb₂O₃ layer forms on and covers the Pd surface of Pd-Sb catalysts with a large Sb content [36,37]. Because of the encapsulating Sb₂O₃ layer on the catalyst surface, H₂ and O₂ activation is hindered rendering Pd₂Sb inert in this reaction. A decrease in exposed Pd area also was detected by CO pulse chemisorption (Table S2), which further suggests the encapsulation of Pd particles by Sb. BEs of 531.7, 530.3, and 529.8 eV in the O 1s core-level spectra are attributed, respec-

Table 2

Quantitative XPS data for surface Pd atoms.

Catalyst	Pd 3d _{3/2} (eV)		Pd 3d _{5/2} (eV)		Pd ⁰ (%)	Pd ²⁺ (%)
	Pd ²⁺	Pd ⁰	Pd ²⁺	Pd ⁰		
Pd ₂ Sb	341.6	340.3	336.3	335.0	77.14	22.86
Pd ₂₀ Sb	341.6	340.2	336.3	334.9	67.47	32.53
Pd ₅₀ Sb	341.6	340.2	336.3	334.9	65.58	34.32
Pd ₈₀ Sb	341.6	340.2	336.3	334.9	58.36	41.64
Pd	341.3	340.3	336.0	335.0	54.92	45.08

Fig. 5. (a) Sb 3d and O 1s XPS spectra of fresh catalysts. (1) Pd, (2) Pd₈₀Sb, (3) Pd₅₀Sb, (4) Pd₂₀Sb, (5) Pd₂Sb. (b) Fitted Sb 3d XPS spectra of fresh Pd₂Sb.

tively to the following oxygen species: (1) the oxygen of surface hydroxyl groups or carbonate species formed by exposing the sample to air [38], (2) the lattice oxygen of TiO₂, and (3) oxygen adsorbed on the surface of PdO/SbO_x particles [39].

3.2.3. CO-DRIFTS

The spectra of adsorbed CO (Fig. 6) show absorption bands of CO ($\nu(\text{CO})$) at 2078, 1982, and 1923 cm⁻¹ for the monometallic Pd catalyst [40,41]. The peak at 2078 cm⁻¹ represents linearly bonded CO (Pd-CO) at the small population of Pd atoms that are located at corner or edge positions on Pd particles. The bands at 1700–2010 cm⁻¹ are assigned to bridging and multiply bonded CO on Pd ensembles comprising two or three contiguous Pd atoms [42,43]. With the incorporation of Sb, the ratio of bridging and multiply bonded CO to linearly bonded CO increases gradually (Table 3). This suggests that the concentration of small Pd clusters increase with increasing Sb content leading to an increase in the number of low-coordinated Pd sites at the corners and edges. For Pd₂Sb, only linearly bonded CO is observed indicating that only highly dispersed clusters or

isolated Pd atoms are formed. The results indicate that the proportion of contiguous Pd surface sites decreases and the number of single Pd sites increases due to the dilution effect of Sb. This change is responsible for the geometric effect produced by changing the relative Pd and Sb contents. A red shift of bridging CO bands from 1982 to 1969 cm⁻¹ is observed in the presence of Sb. It is attributed to enhancement of the *d*-orbital electron density of Pd by charge-transfer from Sb to Pd, which produces strong electron back-donation to the 2π* molecular orbitals of CO [44]. A similar phenomenon has been observed for Pd-Au/TiO₂ (SiO₂) catalysts [17,35].

Since the catalysts were under an O₂-rich circumstance in the reaction, herein the effect of O₂ on Pd surface was investigated by pretreating the samples with O₂ for 30 min following the reduction process. Compared to the samples without O₂ pretreatment (Fig. 6), the relative intensities of peaks for O₂ pretreated catalysts changed remarkably, and a new peak at 2123 cm⁻¹ was observed for Pd₅₀Sb and Pd₂₀Sb (Fig. 7). The changes in the peak positions and intensities probably stem from the geometric and electronic modification of Pd atoms with the adsorption of O₂. The new peak at 2123 cm⁻¹ can be attributed to the vibration mode of CO bonded on Pd^{σ+}, which represents partially oxidized Pd formed via the pre-adsorption of O₂ [45,46]. Interestingly, the peak at 2123 cm⁻¹ was not observed for pure Pd. It has been demonstrated that CO could not be adsorbed on bulk PdO at room temperature [47,48]. In comparison with the samples without pretreatment, the O₂-pretreated Pd₅₀Sb and Pd₂₀Sb catalysts showed a reduction in the intensities of the linearly bonded CO; thus, we deduce

Fig. 6. *In situ* DRIFTS for CO adsorption over different catalysts at 283 K in stream of Ar (50 mL/min). (1) Sb, (2) Pd, (3) Pd₈₀Sb, (4) Pd₅₀Sb, (5) Pd₂₀Sb, (6) Pd₂Sb.

Table 3

Correlation of the intensities of CO-Pd in DRIFT spectra.

Catalyst	Calculation results of peak area from DRIFT spectra		
	Peak 1 (2010–2115 cm ⁻¹)	Peak 2 (2010–1700 cm ⁻¹)	Peak 2 / Peak 1
Pd ₂ Sb	1.91	1.46	0.76
Pd ₂₀ Sb	12.13	43.71	3.60
Pd ₅₀ Sb	13.72	57.70	4.21
Pd ₈₀ Sb	8.09	54.01	6.68
Pd	3.77	44.13	11.72

Fig. 7. *In situ* DRIFTS spectra for CO adsorption over catalysts pre-treated with O₂. (1) Pd, (2) Pd₅₀Sb, (3) Pd₂₀Sb.

that O₂ prefers to adsorb at the corner or edge sites of Pd. Moreover, from the change in the vibration mode of CO on contiguous ensembles, it can be inferred that O₂ also existed on the plane sites of Pd particles. Thus, in comparison with the Pd-alone catalyst, the highly reactive sites for O₂ dissociation at the corner or edge of Pd-Sb catalysts were significantly deactivated by pre-adsorbed O₂, and the interaction between molecular O₂ and Pd-Sb catalysts weakened remarkably. Therefore, the addition of Sb is beneficial for the selective activation of O₂ and subsequent H₂O₂ synthesis.

3.2.4. H₂/O₂-TPD

Sb has been proved to be inert for the activation of H₂ [36]. Therefore, the presence of Sb was expected to suppress H₂ adsorption. Accordingly, H₂-TPD was conducted for all Pd-Sb/TiO₂ and Pd-alone catalysts (Fig. 8). For the Pd-alone sample, two peaks at 741 and 794 K were observed at room temperature. The peak at 794 K can be assigned to H₂ from the

Fig. 8. H₂-TPD profiles of Pd-Sb/TiO₂ catalysts with different Pd/Sb ratios. (1) Blank, (2) Pd₂Sb, (3) Pd₅₀Sb, (4) Pd₈₀Sb, (5) Pd.

recombination and desorption of sub-surface hydrogen species upon heating, and the one at 741 K can be attributed to the surface hydrogen species weakly bonded to the surface in the presence of sub-surface hydrogen species. Due to their small sizes in contrast to Pd crystals, hydrogen atoms can deeply migrate into the bulk far away from the surface, and thus, the sub-surface hydrogen species are available for the reaction. Upon heating the samples, surface hydrogen species were repopulated by the migration of hydrogen atoms from the sub-surface region [49–51]. With the increase in Sb loading, the peak shifted from 794 to 682 K gradually, and it disappeared completely for Pd₂Sb, indicating that the dilution of the surface Pd atoms with Sb suppressed the H₂ adsorption and dissociation. It explains the great suppression effect of Sb on the hydrogenation of H₂O₂.

The dissociative activation of O₂ is generally accepted to lead to the side reactions over Pd-based catalysts. O₂-TPD profiles (Fig. S1) showed that the activation of O₂ weakened in the presence of Sb. No obvious O₂ desorption was observed below 800 K. The peak at 930 K can be attributed to atomic oxygen resulting from the decomposition of PdO_x [52–54]. With the increasing ratio of Sb/Pd, the atomic oxygen peak became weaker, owing to the weakness of O₂ activation, suggesting that Sb species on the surface may inhibit the dissociative activation of O₂ and oxidation of Pd. It agreed with the XPS results.

3.3. Structure-performance relationship

H₂O₂ is produced by the hydrogenation of molecular O₂ on the Pd surface, whereas the sequential hydrogenation of H₂O₂ and the O–O bond rupture of surface species would lead to the formation of H₂O [55]. Tian et al. [56] has reported that the higher binding energy of O–O-containing surface species are not favorable for H₂O₂ synthesis because the higher BE results in lower dissociation barriers. The selectivity toward H₂O₂ is therefore mainly determined by the competition between O–H bond formation and O–O bond cleavage reactions of species containing O–O bonds. Density-functional theory (DFT) calculations demonstrated that low-coordinated Pd monomers embedded in Au sites were energetically unfavorable for the dissociation of O₂ with a relative lower desorption (< 0.48 eV) and higher dissociation barrier (> 1.17 eV) than that of contiguous Pd ensembles [57]. Potentially, the isolated Pd sites, on which the O–O bonds are more difficult to rupture, match the requirement of H₂O₂ formation better. In this work, Pd upon alloying with Sb can significantly enhance the H₂O₂ selectivity. To better understand the effect of the Sb promoter, the characterization results were thoroughly analyzed and a plausible mechanism was proposed.

As measured by TEM and XRD, Pd-Sb catalysts showed smaller particle sizes and higher Pd dispersion than the monometallic Pd samples. Hutchings et al. [58] reported that reducing the size of the Pd NPs led to more exposed Pd atoms and enhanced the activation of H₂ and O₂. However, Pd-Sb catalysts in this work exhibited lower activity than monometallic Pd, and the catalysts with higher Sb/Pd ratios (> 0.5) were inert for the formation of H₂O₂. It can be inferred that the incorporation of

Sb remarkably changed the surface state of the Pd NPs. XPS results have proved that the surfaces of Pd-Sb catalysts were partially covered by Sb_2O_3 layers. In this case, few contiguous Pd ensembles are exposed to H_2 and O_2 , retarding the activation of H_2 and O_2 and suppressing the catalyst activity. The BEs of the Pd 3d core levels had a blue-shift of ca. 0.1–0.3 eV, indicating weak electronic interaction between Sb and Pd. A similar shift was also reported in the Pt-Sb systems [59]. In addition, the ratio of $\text{Pd}^0/\text{Pd}^{2+}$ on the particle surface increased with an increase in the Sb concentration. Sb might inhibit the oxidation of Pd and weaken the metal-support interaction.

In situ DRIFT spectra revealed that the CO vibration mode over the fresh catalysts experienced an obvious change with the addition of Sb. The fraction of the linear CO bands increased with the higher Sb loadings, indicating that Sb can generate more isolated Pd sites and reduce the contiguous Pd ensembles on the surface. Therefore, the non-dissociative activation of molecularly adsorbed O_2 is pivotal for this reaction. Previous results have confirmed that isolated Pd sites surrounded by less active metal atoms showed lower activity for the dissociation of O–O bonds, and they were more favorable for H_2O_2 formation than contiguous Pd ensembles [60]. Therefore, the higher H_2O_2 selectivity over Pd-Sb bimetallic catalysts could be attributed to the isolation effect of active Pd atoms by Sb. In contrast, the reason why the isolated Pd sites are unfavorable for the O–O bond rupture is not yet clear for the reaction. Accordingly, *in situ* CO-DRIFTS over the Pd-Sb/ TiO_2 pretreated with O_2 was performed to simulate the O_2 -rich environment in the reaction. Tian et al. [56] demonstrated that the addition of Te led to an increase in the low-coordinated active sites at the corner and edge sites, which are much more active for the undesired production of H_2O . The appearance of surface $\text{Pd}^{\sigma+}$ species and the reduction of linearly bonded CO with the addition of Sb suggest that these low-coordinated active sites were partially oxidized by the O_2 pretreatment, and their activities for O–O bond scission reactions were suppressed. As a result, the H_2O_2 selectivities for the Pd-Sb catalysts were enhanced.

As evidenced by TPD results, the addition of Sb suppressed the adsorption and dissociation of H_2 and O_2 over Pd catalysts, resulting in lower H_2 conversions and higher H_2O_2 selectivities. Obviously, Sb hindered the hydrogenation and decomposition of H_2O_2 primarily by weakening the activation of H_2 on Pd. The weak adsorption of O_2 at the Pd-Sb/ TiO_2 interface is proposed to enhance the selectivity of H_2O_2 .

In summary, the catalyst structures were characterized using multiple techniques to identify the origin of active sites responsible for the observed high selectivity. The role of Sb on the active sites of Pd catalysts was investigated by: (1) isolating contiguous Pd sites via the formation of Pd-Sb bimetallic sites, (2) coating Pd surface via the formation of Sb_2O_3 layer, and (3) promoting the formation of $\text{Pd}^{\sigma+}$ species located on the surface during the reaction. Therefore, an optimum Pd/Sb ratio should be finely tuned to obtain the best performance. A plausible mechanism for H_2O_2 synthesis was proposed as illustrated in Scheme 1. With the addition of Sb, Pd-Sb bimetallic sites were formed and Pd NPs were diluted, leading to the reduction of the Pd particle size. The isolated Pd sites surrounding by Sb are

Scheme 1. Proposed mechanism for the direct synthesis of H_2O_2 over Pd-Sb/ TiO_2 catalysts.

responsible for the non-dissociative activation of O_2 and selective synthesis of H_2O_2 . In contrast, the contiguous Pd ensembles are more favorable for H_2O formation because of their high activity for the O–O rupture reactions. Sb, which is supposed to be concentrated on the catalyst surfaces, inhibited H_2 adsorption and decreased the activity of H_2O_2 hydrogenation. However, due to the limitations of *in situ* characterizations in the tri-phase liquid system, the dynamic structures of Pd catalysts during the reaction and the mechanism of the effects of $\text{Pd}^{\sigma+}$ species on the catalytic performance should be further investigated.

4. Conclusions

In this work, direct H_2O_2 synthesis from H_2 and O_2 has been studied using a series of bimetallic Pd-Sb/ TiO_2 catalysts with different Pd/Sb ratios, among which the Pd_{50}Sb catalyst exhibited the best performance with the H_2O_2 selectivity of 73%. H_2O_2 hydrogenation rates decreased rapidly with the increase in the Sb/Pd ratios. Multiple characterization results indicated that the electronic and geometric structures of Pd-Sb catalysts were finely tuned with the Sb concentrations. *In situ* CO-DRIFT, XPS, and H_2 -TPD results proved that the increase in Sb concentration led to an increase in the ratio of isolated Pd sites that are assumed to be less active for side reactions and more favorable for H_2O_2 formation. In the meantime, the amount of contiguous Pd ensemble sites that are highly reactive for H_2O_2 hydrogenation were reduced, thus improving the selectivity. In summary, through adding a second nonprecious metal Sb to Pd, the highly selective Pd-based bimetallic catalysts were obtained for H_2O_2 synthesis. Deep insight into the effect of Sb on Pd particles will have more implications for the understanding of the mechanism and rational design of Pd catalysts for H_2O_2 synthesis.

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Graphical Abstract

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

Doudou Ding, Xingyan Xu, Pengfei Tian, Xianglin Liu, Jing Xu *, Yi-fan Han *

East China University of Science and Technology; Zhengzhou University

Highly selective Pd-Sb/TiO₂ bimetallic catalysts for the direct synthesis of H₂O₂ were obtained, and the addition of Sb increased the isolated Pd sites, which are favorable for H₂O₂ formation.

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Sb 对 Pd 基催化剂用于常压直接合成 H_2O_2 的促进效应

丁豆豆^a, 徐兴妍^a, 田鹏飞^a, 刘向林^a, 徐晶^{a,*}, 韩一帆^{a,b,#}

^a华东理工大学化学工程联合国家重点实验室, 上海200237

^b郑州大学化工与能源学院多相催化工程科学研究中心, 河南郑州450001

摘要: H_2O_2 作为一种高效绿色氧化剂, 广泛应用于造纸、纺织、水处理等工业领域。目前蒽醌法是工业上生产 H_2O_2 的主要方法, 相比之下, 利用 H_2 和 O_2 直接合成 H_2O_2 , 能耗低, 污染小, 适合与下游工艺技术进行耦合。而缺乏高性能催化剂是制约直接法合成 H_2O_2 工业化的主要原因。本文通过浸渍法制备了一系列负载型 Pd-Sb/TiO₂ 双金属催化剂, 并用于常压下 H_2O_2 直接催化合成反应。利用透射电子显微镜 (TEM), X 射线光电子能谱 (XPS), H_2/O_2 程序升温脱附 (H_2/O_2 -TPD), X 射线衍射 (XRD), 原位 CO 吸附的傅里叶变换漫反射红外光谱 (CO-DRIFTS) 等手段对催化剂的电子和几何结构进行解析, 深入研究了助剂 Sb 对该体系的促进作用。

结果显示, 与单金属 Pd 催化剂相比, 适量金属 Sb 的加入有效提高了催化性能, 抑制了副反应的发生。当 Pd/Sb 摩尔比为 50/1(Pd₅₀Sb) 时, H_2O_2 的选择性高达 73%; 但是当 Pd/Sb 为 2 时, 催化剂对生成 H_2O_2 几乎没有活性。TEM 和 XRD 证明, Sb 的加入显著促进了 Pd 颗粒在载体 TiO₂ 上的分散。XPS 和 H_2 -TPD 实验, 发现, Sb 改变了催化剂表面 Pd²⁺/Pd⁰ 的比例, 抑制了金属 Pd 的氧化; 同时, Sb 主要以氧化态存在, 在催化剂表面形成 Sb₂O₃ 氧化层, 覆盖表面的 Pd 活性位, 从而抑制了反应中 H_2 在催化剂表面的活化以及 H_2O_2 加氢副反应的发生。O₂-TPD 结果表明, 随着 Sb 的加入, O₂ 的脱附峰明显减弱, 表明 Pd-Sb/TiO₂ 不利于 O₂ 的解离吸附。此外, 原位 CO-DRIFTS 实验结果表明, Sb 均匀分布在 Pd-Sb 催化剂表面, 致使有利于生成 H_2O 的连续 Pd 活性位明显减少, 而有利于合成 H_2O_2 的单个 Pd 原子活性位明显增加。

总的来说, Sb 对 Pd 表面起到了显著的修饰作用, 提高了催化剂表面 O₂ 的非解离活化, 从而促进了 H_2O_2 的高选择性合成。但是过量 Sb 的加入会抑制催化剂对 H_2 的活化作用, 致使催化剂活性下降, 因此优选 Pd/Sb 的比例对于提高催化剂性能具有重要作用。

关键词: 双金属催化剂; 过氧化氢; 钯; 锑; 直接合成

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*通讯联系人. 电话: (021)64251938; 传真: (021)64251928; 电子信箱: xujing@ecust.edu.cn

#通讯联系人. 电子信箱: yifanhan@ecust.edu.cn

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