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Highly Selective Palladium-based Bimetallic Catalysts for the Direct Synthesis of Hydrogen Peroxide

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Highlights

- Direct H_2O_2 synthesis over Pd-M (M=Te, Sn, Bi) catalysts were thoroughly studied.
- Near-100% H_2O_2 selectivity was acquired over a Pd-Te catalyst.
- Te remarkably suppressed the dissociative activation of O_2 over Pd.
- Te promoted the dispersion of Pd particles on the support.

1. Introduction

Hydrogen peroxide (H_2O_2), an effective and environmentally benign oxidant, is used as an indispensable chemical in a wide range of applications within the textile, waste water treatment, pulp/paper bleaching, and pharmaceutical industries.[1] The organic autoxidation processes dominantly used in current industrial production of H_2O_2 generally generates remarkable amount of pollutants and requires high capital cost. The direct synthesis of H_2O_2 from H_2 and O_2 is a promising alternative to the industrial process. Pd-based catalysts have proved to be most effective for this reaction.[2-6] However, the direct process has not been used in industrial production of H_2O_2 because of the low selectivity. In this work, density functional theory (DFT) calculation and experimental methods were combined to probe and design high-selectivity Pd-based bimetallic catalysts for direct H_2O_2 synthesis. The promotional effects of Te, Sn, and Bi and the structure-performance relationship of Pd-based catalysts were thoroughly studied (Fig. 1). Moreover, preparation methods and Pd concentrations in the bimetallic catalysts were finely tuned to achieve the optimized performance.
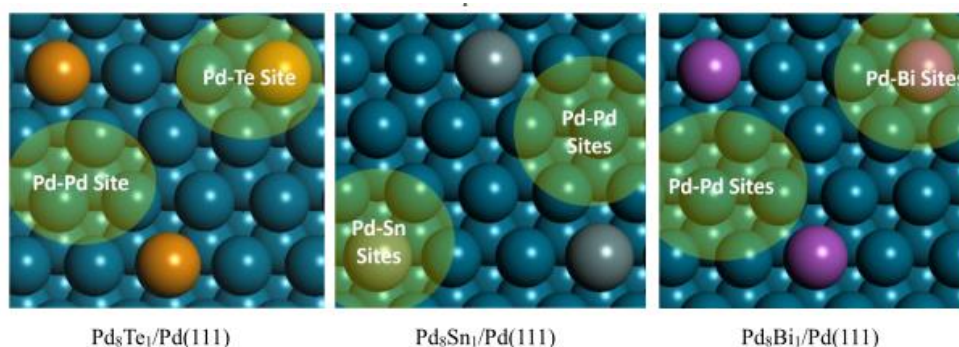
2. Methods

Figure 1. Models of $Pd_8Te_1/Pd(111)$, $Pd_8Sn_1/Pd(111)$ and $Pd_8Bi_1/Pd(111)$ surfaces. Blue, brown, blackish green, and purple spheres are palladium, tellurium, tin, and tellurium atoms, respectively.

DFT calculations were performed using the Vienna ab-initio simulation package (VASP). The models used for calculations are shown in Figure 1. Catalysts were prepared by incipient wetness impregnation using an aqueous solution of H_2PdCl_4 and $TeCl_4$. A Pd loading of 3 wt % was used for each catalyst. All reactions were carried out in a modified micro triphase semi-batch reactor at 283 K and atmospheric pressure using 50 mg of catalyst; the reagent gases (15 vol% H_2; 60 vol% O_2; 25 vol% N_2; 60 mL/min) were introduced into

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the reactor via a premixer and a fine glass frit in sequence; H_2 conversion and H_2O_2 selectivity were analyzed with a gas chromatograph and a UV–Vis spectrophotometer, respectively.

3. Results and discussion

Compared to Pd-Sn and Pd-Bi catalysts, Pd-Te catalysts showed the highest selectivity for H_2O_2 synthesis at the low coverage of reactants. Interestingly, a near-100% H_2 selectivity towards H_2O_2 was acquired by finely tuning the Pd/Te atomic ratio (Figure 2). Te is inert to the adsorption and activation of surface species containing O-O bonds, and it thus has a dilute effect on continuous Pd sites. Meanwhile, the addition of Te can also alter the electronic structure of active sites remarkably. DFT calculations indicates that Pd-Te sites and Pd-Pd sites adjacent to Te atoms have lower capacity for adsorption and dissociative activation of O_2, and they thus are highly selective active sites for direct H_2O_2 synthesis. The low-coordinated terrace and corner sites of Pd-Te clusters showed low selectivities. Therefore, the particle size should be deliberately controlled in application. Excessive amounts of Te would lead to the deactivation of catalysts, due to the low ability of Te in the adsorption and dissociative activation of H_2.
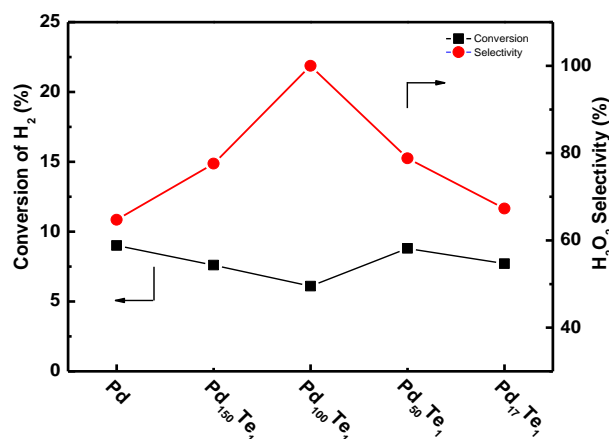

Figure 2. Performance of Pd-Te catalysts with different Te concentrations.

4. Conclusions

With the combination of experimental and theoretical methods, for the first time a Pd-Te catalyst with a near-100% selectivity toward H_2O_2 was rationally designed and obtained. The formation of Pd-Te bimetallic particles is the origin of active sites for the high-selectivity production of H_2O_2. By suppressing the dissociative activation of O_2 on Pd, Te plays a critical role in enhancing the catalytic performance. This work makes great advance on adding second nonprecious metal to Pd to acquire catalysts with high efficiency for H_2O_2 synthesis. Meanwhile, it would benefit the rational design of catalysts for both the H_2O_2 direct synthesis and other relations involving hydrogenation and oxidation, such as oxygen reduction reactions (ORR).

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