

Polyoxometalate-supported Pd nanoparticles as efficient catalysts for the direct synthesis of hydrogen peroxide in the absence of acid or halide promoters

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Electronic Supplementary Information

1. Experimental details

(1) Catalyst preparation

The Cs salts of tungstophosphates with different Cs contents ($\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$, $x = 0.5-3.0$) were prepared by a reaction between $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and Cs_2CO_3 . The precipitates obtained after the addition of the aqueous solution of Cs_2CO_3 into that of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ were recovered by filtration, followed by washing with water, drying and calcination at 673 K for 2 h to obtain the $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ samples. The Pd/ $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ catalysts were prepared by impregnation of the $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ with PdCl₂ aqueous solution, followed by drying, calcination at 573 K in air, and reduction by H₂ at 573 K.

(2) Catalyst characterization

XRD, N₂ sorption, TEM, XPS and NH₃-TPD were used to characterize the structures and the physicochemical properties of the Pd/ $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ catalysts. XRD patterns were recorded on a Panalytical X'Pert Pro Super X-ray diffractometer equipped with X'Celerator detection system. Cu-K_α radiation (40 kV and 30 mA) was used as the X-ray source. N₂ sorption at 77 K was carried out with a Micromeritics Tristar 3000 surface and porosimetry analyzer. TEM measurements were performed on a Tecnai F30 electron microscope (Phillips Analytical) operated at an acceleration voltage of 300 kV. Samples for TEM measurements were suspended in ethanol and dispersed ultrasonically. Drops of the suspensions were applied on a copper grid coated with carbon. NH₃-TPD measurements were performed using a Micromeritics AutoChem II 2920 instrument connected to a ThermoStar GSD 301 T2 mass spectrometer.

(3) Catalytic reaction

Catalytic reactions were performed under atmospheric pressure and at 283 K in a glass reactor. H₂ and O₂ were added via a glass frit to the stirred slurry containing the solvent (ethanol) and the catalyst. H₂ conversion was analyzed by on-line gas chromatography, and the concentration of H₂O₂ was measured with colorimetry after complexation with a

TiOSO₄/H₂SO₄ reagent.

2. XRD patterns of the Cs_xH_{3-x}PW₁₂O₄₀ and the Pd/Cs_xH_{3-x}PW₁₂O₄₀ samples

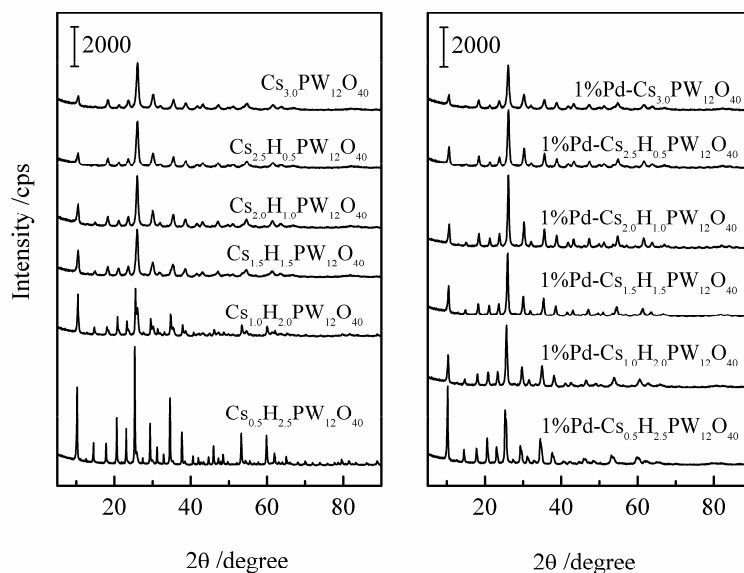


Fig. S1 XRD patterns of the Cs_xH_{3-x}PW₁₂O₄₀ and the 1.0 wt% Pd/Cs_xH_{3-x}PW₁₂O₄₀ samples.

3. Surface areas of the Cs_xH_{3-x}PW₁₂O₄₀ samples

Table S1 BET surface areas of the Cs_xH_{3-x}PW₁₂O₄₀ samples

Sample	Surface area /m ² g ⁻¹
Cs _{0.5} H _{2.5} PW ₁₂ O ₄₀	2.0
Cs _{1.0} H _{2.0} PW ₁₂ O ₄₀	13
Cs _{1.5} H _{1.5} PW ₁₂ O ₄₀	10
Cs _{2.0} H _{1.0} PW ₁₂ O ₄₀	14
Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	106
Cs _{3.0} PW ₁₂ O ₄₀	104

4. NH₃-TPD profiles of the Pd/Cs_{1.5}H_{1.5}PW₁₂O₄₀ samples with different Pd loadings

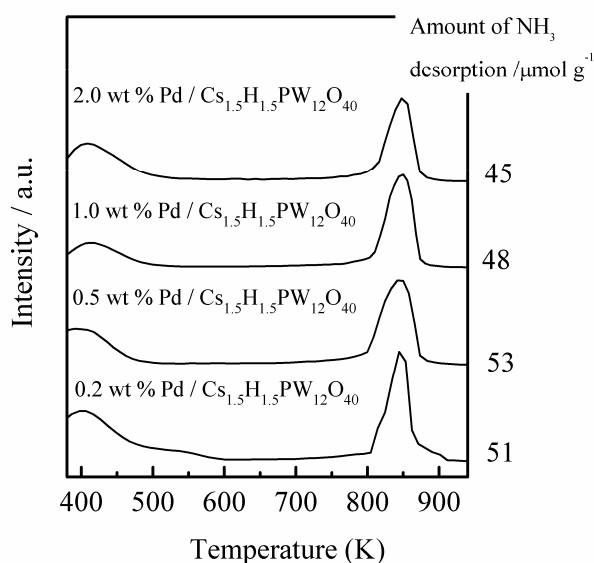


Fig. S2 NH₃-TPD profiles of the Pd/Cs_{1.5}H_{1.5}PW₁₂O₄₀ samples with different Pd loadings. The amount of NH₃ desorption for the main peak at 800-900 K was listed in the figure.

5. TEM micrographs and particle size distributions for the 1.0 wt% Pd/Cs_xH_{3-x}PW₁₂O₄₀ samples

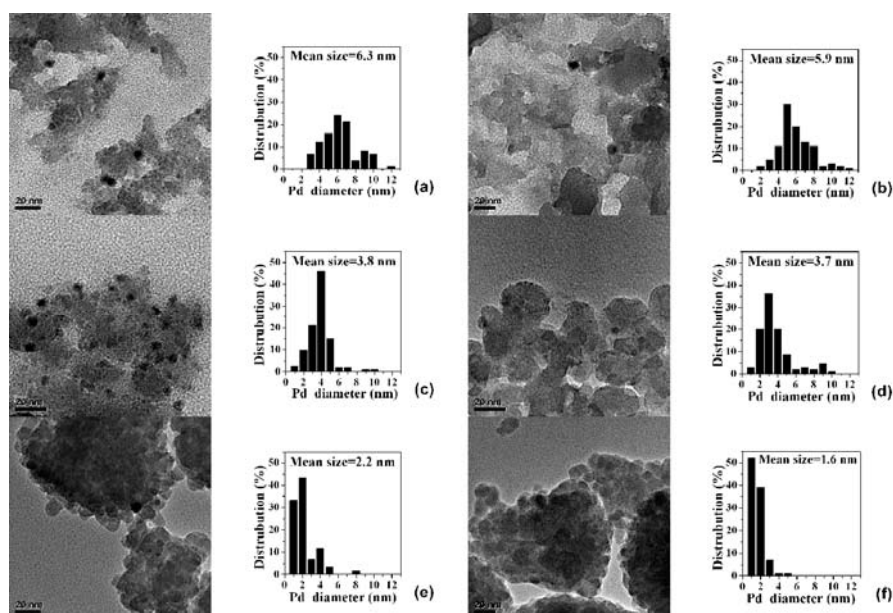


Fig. S3 TEM micrographs and particle size distributions for the 1.0 wt% Pd/Cs_xH_{3-x}PW₁₂O₄₀ samples. (a) $x = 0.5$, (b) $x = 1.0$, (c) $x = 1.5$, (d) $x = 2.0$, (e) $x = 2.5$, (f) $x = 3.0$.

6. TEM micrograph and particle size distribution for the 2.0 wt% Pd/ Cs_{1.5}H_{1.5}PW₁₂O₄₀ sample

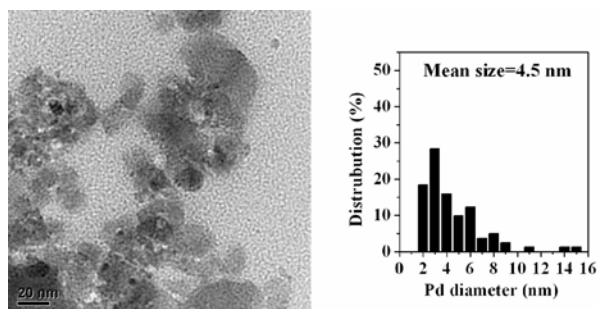


Fig. S4 TEM micrograph and particle size distribution for the 2.0 wt% Pd/Cs_{1.5}H_{1.5}PW₁₂O₄₀ sample.