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 (Cs\textsubscript{x}H\textsubscript{3−x}PW\textsubscript{12}O\textsubscript{40}, x = 0.5-3.0) were prepared by a reaction between H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} and Cs\textsubscript{2}CO\textsubscript{3}. The precipitates obtained after the addition of the aqueous solution of Cs\textsubscript{2}CO\textsubscript{3} into that of H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} were recovered by filtration, followed by washing with water, drying and calcination at 673 K for 2 h to obtain the Cs\textsubscript{x}H\textsubscript{3−x}PW\textsubscript{12}O\textsubscript{40} samples. The Pd/Cs\textsubscript{x}H\textsubscript{3−x}PW\textsubscript{12}O\textsubscript{40} catalysts were prepared by impregnation of the Cs\textsubscript{x}H\textsubscript{3−x}PW\textsubscript{12}O\textsubscript{40} with PdCl\textsubscript{2} aqueous solution, followed by drying, calcination at 573 K in air, and reduction by H\textsubscript{2} at 573 K.

(2) Catalyst characterization

XRD, N\textsubscript{2} sorption, TEM, XPS and NH\textsubscript{3}-TPD were used to characterize the structures and the physicochemical properties of the Pd/Cs\textsubscript{x}H\textsubscript{3−x}PW\textsubscript{12}O\textsubscript{40} catalysts. XRD patterns were recorded on a Panalytical X’Pert Pro Super X-ray diffractometer equipped with X’Celerator detection system. Cu-K\textsubscript{α} radiation (40 kV and 30 mA) was used as the X-ray source. N\textsubscript{2} 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. NH\textsubscript{3}-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. H\textsubscript{2} and O\textsubscript{2} were added via a glass frit to the stirred slurry containing the solvent (ethanol) and the catalyst. H\textsubscript{2} conversion was analyzed by on-line gas chromatography, and the concentration of H\textsubscript{2}O\textsubscript{2} was measured with colorimetry after complexation with a
TiOSO₄/H₂SO₄ reagent.

2. XRD patterns of the CsₓH₃₋ₓPW₁₂O₄₀ and the Pd/CsₓH₃₋ₓPW₁₂O₄₀ samples

![XRD patterns](image)

Fig. S1 XRD patterns of the CsₓH₃₋ₓPW₁₂O₄₀ and the 1.0 wt% Pd/CsₓH₃₋ₓPW₁₂O₄₀ samples.

3. Surface areas of the CsₓH₃₋ₓPW₁₂O₄₀ samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area /m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs₀.₅H₂.₅PW₁₂O₄₀</td>
<td>2.0</td>
</tr>
<tr>
<td>Cs₁.₀H₂.₀PW₁₂O₄₀</td>
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</tr>
<tr>
<td>Cs₁.₅H₁.₅PW₁₂O₄₀</td>
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</tr>
<tr>
<td>Cs₂.₀H₁.₀PW₁₂O₄₀</td>
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</tr>
<tr>
<td>Cs₂.₅H₀.₅PW₁₂O₄₀</td>
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</tr>
<tr>
<td>Cs₃.₀PW₁₂O₄₀</td>
<td>104</td>
</tr>
</tbody>
</table>

4. NH₃-TPD profiles of the Pd/Cs₁.₅H₁.₅PW₁₂O₄₀ samples with different Pd loadings
Fig. S2 NH$_3$-TPD profiles of the Pd/Cs$_{1.5}$H$_{1.5}$PW$_{12}$O$_{40}$ samples with different Pd loadings. The amount of NH$_3$ 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$_{x}$H$_{3-x}$PW$_{12}$O$_{40}$ samples

Fig. S3 TEM micrographs and particle size distributions for the 1.0 wt% Pd/Cs$_{x}$H$_{3-x}$PW$_{12}$O$_{40}$ samples. (a) $x=0.5$, (b) $x=1.0$, (c) $x=1.5$, (d) $x=2.0$, (e) $x=2.5$, (f) $x=3.0$. 

S3
6. TEM micrograph and particle size distribution for the 2.0 wt% Pd/Cs$_{1.5}$H$_{1.5}$PW$_{12}$O$_{40}$ sample

![TEM micrograph and particle size distribution](image)

**Fig. S4** TEM micrograph and particle size distribution for the 2.0 wt% Pd/Cs$_{1.5}$H$_{1.5}$PW$_{12}$O$_{40}$ sample.