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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A Keggin-type polyoxometalate ($Cs_{1.5}H_{1.5}PW_{12}O_{40}$)-supported Pd catalyst is efficient for the direct synthesis of H_2O_2 from H_2 and O_2 in the absence of any acid or halide additives under atmospheric pressure.

Hydrogen peroxide has been widely used for disinfecting, textile and pulp bleaching, wastewater treatment and chemical synthesis *via* green oxidation. In the current chemical industry, H_2O_2 is mainly produced by the multi-step anthraquinone process, which involves the sequential hydrogenation and oxidation of an anthraquinone. This process suffers from several drawbacks such as the consumption of expensive anthraquinone in side reactions, the use of toxic organic solvents and the requirements of energy-intensive separation and purification steps. The direct synthesis of H_2O_2 from H_2 and O_2 would be a more economical and environmentally benign route. Many catalysts or intriguing systems have been reported for the direct synthesis of H_2O_2,[1–4] and supported palladium catalysts show promising performances.[1,2] However, the decomposition and hydrogenation of H_2O_2 can also be catalyzed by the supported palladium catalysts, leading to lower H_2O_2 selectivity and productivity. Acids (*e.g.*, sulfuric acid) and/or halides (typically bromides or chlorides) are generally required to promote H_2O_2 selectivity by retarding the base-catalyzed decomposition of H_2O_2 or poisoning the sites for H_2O_2 conversions.[1,2,5] Special equipment would be required for operations with acid solutions to prevent corrosion, and the acid solution would also cause the dissolution of the active metal.[1b] Furthermore, as compared to the acidic H_2O_2 solution, a neutral and halide-free H_2O_2 solution would be more useful.[6] Therefore, the development of catalysts for the direct synthesis of H_2O_2 in the absence of acid and halide promoters is an important research target.

A few studies showed that the use of acidic supports could enhance the selective formation of H_2O_2 even in the absence of acid promoters. A Pd^{II}-anchored sulfonic acid-functionalized polystyrene resin was reported to be efficient for H_2O_2 synthesis in methanol in the absence of acids at 313 K and 10 MPa.[7]

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A similar sulfonic acid-containing resin was confirmed to be a superior support for H_2O_2 formation at 283 K and 20 bar without promoters, but Pd^0 was proposed to be the active phase.[8] Hutchings and co-workers used CO_2 as a diluent for their supported Au–Pd catalysts, and proposed that the acidic solution formed by CO_2 in water at a high pressure (3.1 MPa) increased H_2O_2 formation activity.[9] The same group also demonstrated that the acid treatment of a carbon support for Au–Pd could significantly increase the selectivity and productivity of H_2O_2.[10] Pd supported on a polyoxometalate was recently reported for H_2O_2 synthesis at high pressure (10 atm), but the advantages of the polyoxometalate support were ambiguous because bromide was still used as a promoter.[11] To the best of our knowledge, there is no report on catalysts with enough efficiency for H_2O_2 synthesis in the absence of any acid or halide promoters under atmospheric pressure, where the reaction can be operated more safely.

Herein, we report our recent finding that Pd nanoparticles supported on a polyoxometalate could catalyze the direct synthesis of H_2O_2 in the absence of any acid or halide promoters under atmospheric pressure. It is known that the protons in Keggin-type tungstophosphoric acid ($H_3PW_{12}O_{40}$) are almost superacidic,[12] but $H_3PW_{12}O_{40}$ is soluble in water and alcohols, and cannot be used as a stable support here. On the other hand, the Cs salts of tungstophosphate are insoluble and the acidity of the Cs salts of heteropoly compounds may be systematically tuned by changing the Cs content.[13] We have prepared Cs salts of tungstophosphate with different Cs contents ($Cs_xH_{3-x}PW_{12}O_{40}$, $x = 0.5$–3.0), and investigated their roles as supports of Pd catalysts for H_2O_2 synthesis.

Table 1 compares the catalytic performances of Pd catalysts loaded on various supports. Pd/graphite and Pd/XC-72 were efficient catalysts for H_2O_2 synthesis under similar conditions except for in the presence of HCl.[2c,d] However, without acid promoters, all of the catalysts in Table 1 except for $Pd/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ showed very low H_2O_2 productivity and selectivity. The use of sulfated TiO_2 or ZrO_2 as a support was also ineffective for H_2O_2 formation. $Pd/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ exhibited outstanding H_2O_2 productivity and selectivity. The concentration of H_2O_2 formed in 4 h was almost one order of magnitude higher than those obtained over other catalysts. The selectivity for H_2O_2 was 67%, comparable to those attained over superior catalysts in the presence of acid promoters at atmospheric pressure.[1a,d,2c,d]

We found that the Cs content in the polyoxometalate was crucial for H_2O_2 formation. With increasing Cs content from $x = 0.5$ to $x = 1.5$ in $Cs_xH_{3-x}PW_{12}O_{40}$ H_2 conversion decreased but H_2O_2 selectivity and productivity increased

Table 1 Catalytic performances of Pd catalysts loaded on various supports for H_2O_2 synthesis in the absence of promoters[a]

Catalyst	H_2 conversion/%	H_2O_2 concentration/wt%	H_2O_2 selectivity/%
Pd/SiO_2	16	0.07	5.9
Pd/TiO_2	15	0.11	9.4
Pd/ZrO_2	13	0.04	3.9
Pd/sulfated TiO_2	15	0.08	7.4
Pd/sulfated ZrO_2	24	0.07	4.0
Pd/SBA-15	21	0.11	6.5
Pd/HZSM-5	11	0.06	7.2
Pd/Hβ	18	0.13	9.7
Pd/SAPO-34	8.4	0.06	9.9
Pd/AC	16	0.05	3.5
Pd/XC-72	22	0.09	6.3
Pd/graphite	21	0.13	9.1
$Pd/Cs_{1.5}H_{1.5}PW_{12}O_{40}$	21	1.1	67

[a] Reaction conditions: catalyst (Pd loading, 1.0 wt%), 0.050 g; T = 283 K; $H_2 : O_2 : N_2$ = 1 : 4 : 1; gas flow rate, 60 cm^3 min^{-1}; solvent, ethanol 60 cm^3; time, 4 h.

Table 2 Catalytic performances of Pd catalysts loaded on $Cs_xH_{3-x}PW_{12}O_{40}$ with different Cs contents for H_2O_2 synthesis in the absence of promoters[a]

Catalyst	H_2 conversion/%	H_2O_2 concentration/wt%	H_2O_2 selectivity/%
$Pd/H_3PW_{12}O_{40}$	—	—	—
$Pd/Cs_{0.5}H_{2.5}PW_{12}O_{40}$	31	0.22	9.3
$Pd/Cs_{1.0}H_{2.0}PW_{12}O_{40}$	24	0.49	27
$Pd/Cs_{1.5}H_{1.5}PW_{12}O_{40}$	21	1.1	67
$Pd/Cs_{2.0}H_{1.0}PW_{12}O_{40}$	22	0.38	22
$Pd/Cs_{2.5}H_{0.5}PW_{12}O_{40}$	28	0.10	4.7
$Pd/Cs_{3.0}PW_{12}O_{40}$	24	0.03	1.6

[a] Reaction conditions: catalyst (Pd loading, 1.0 wt%), 0.050 g; T = 283 K; $H_2 : O_2 : N_2$ = 1 : 4 : 1; gas flow rate, 60 cm^3 min^{-1}; solvent, ethanol 60 cm^3; time, 4 h.

significantly (Table 2). However, a further increase in Cs content (x > 1.5) again decreased H_2O_2 selectivity and productivity markedly. Thus, the $Pd/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ catalyst affords the highest H_2O_2 selectivity and productivity.

Table 3 Catalytic performances of the $Pd/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ catalysts with different Pd loadings for H_2O_2 synthesis in the absence of promoters[a]

Catalyst	H_2 conversion/%	H_2O_2 concentration/wt%	H_2O_2 selectivity/%
$Cs_{1.5}H_{1.5}PW_{12}O_{40}$	2.4	0.05	25
1.0 wt% PdO/ $Cs_{1.5}H_{1.5}PW_{12}O_{40}$[b]	36	0.40	15
0.20 wt% Pd/ $Cs_{1.5}H_{1.5}PW_{12}O_{40}$	9.9	0.11	14
0.50 wt% Pd/ $Cs_{1.5}H_{1.5}PW_{12}O_{40}$	23	0.44	25
0.75 wt% Pd/ $Cs_{1.5}H_{1.5}PW_{12}O_{40}$	23	0.56	31
1.0 wt% Pd/ $Cs_{1.5}H_{1.5}PW_{12}O_{40}$	21	1.1	67
1.5 wt% Pd/ $Cs_{1.5}H_{1.5}PW_{12}O_{40}$	21	0.84	52
2.0 wt% Pd/ $Cs_{1.5}H_{1.5}PW_{12}O_{40}$	29	0.71	33

[a] Reaction conditions: catalyst, 0.050 g; T = 283 K; $H_2 : O_2 : N_2$ = 1 : 4 : 1; gas flow rate, 60 cm^3 min^{-1}; solvent, ethanol 60 cm^3; time, 4 h. [b] Without reduction.

The oxidation state and loading amount of Pd also significantly affected the H_2O_2 formation activity. Without loading Pd, only very low H_2 conversion was observed over $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ (Table 3), confirming that Pd was the active phase. As compared to $Pd/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ after H_2 reduction at 573 K, $PdO/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ without reduction (but after calcination at 573 K) exhibited higher H_2 conversion but lower H_2O_2 selectivity and productivity (Table 3). XPS measurements clarified that the binding energy of Pd $3d_{5/2}$ in $Pd/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ after H_2 reduction was ∼335.0 eV, confirming that the state of palladium in this sample was Pd^0. These demonstrate that, in our system, the metallic Pd is more selective toward H_2O_2 formation than the oxidized Pd species. For the $Pd/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ series of catalysts, H_2 conversion went up as the Pd loading rose from 0 to 0.5 wt%, and then did not undergo remarkable changes in a Pd loading range of 0.50–1.5 wt%. On the other hand, H_2O_2 selectivity and productivity increased significantly as Pd loading increased from 0.2 to 1.0 wt%, and then decreased gradually. Thus, $Pd/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ with a Pd loading of 1.0 wt% demonstrated the best catalytic performance for H_2O_2 formation.

To gain insight into the structure–performance relations for the present polyoxometalate-supported Pd catalytic system, we have characterized the catalysts with different Cs contents. XRD patterns of $Cs_xH_{3-x}PW_{12}O_{40}$ and 1.0 wt% $Pd/Cs_xH_{3-x}PW_{12}O_{40}$ with different Cs contents were quite similar (see Fig. S1, ESI†), and could be ascribed to a cubic lattice of Keggin structure, typically associated with the pure alkaline heteropoly salts.[14] The BET surface areas of the 1.0 wt% $Pd/Cs_xH_{3-x}PW_{12}O_{40}$ samples increased gradually as x changed from 0.5 to 2.0. When x further rose to 2.5, a marked increase in BET surface area was observed (Table 4). This trend is similar to those observed for the $Cs_xH_{3-x}PW_{12}O_{40}$ alone (see Table S1, ESI†) and the $Cs_xH_{3-x}PMo_{12}O_{40}$ reported previously,[13] and can be explained by the fact that the introduction of larger countercations (i.e., Cs^+) to replace the smaller H^+ in a heteropoly compound can cause the formation of micropores and mesopores. Comparison of the trends in Tables 2 and 4 indicates that there is no relationship between catalytic performance and the BET surface area.

The acidity of the support is expected to play a key role in determining the catalytic performance. NH_3 temperature-programmed desorption (NH_3-TPD) studies demonstrate that 1.0 wt% $Pd/Cs_{0.5}H_{2.5}PW_{12}O_{40}$ exhibits a main NH_3 desorption peak at 854 K (Fig. 1), which corresponds to the NH_3 molecules adsorbed on Brønsted acid sites of the polyoxometalates.[13] The

Table 4 Physicochemical properties of the 1.0 wt% $Pd/Cs_xH_{3-x}PW_{12}O_{40}$ samples with different Cs contents

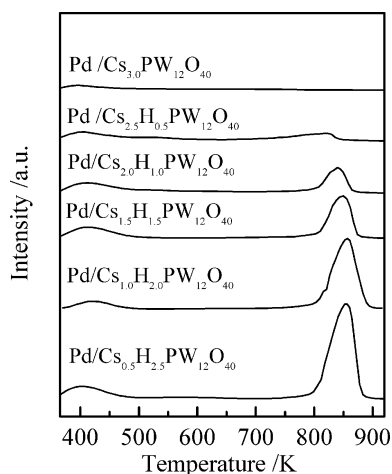| Sample[a]	Surface area/m^2 g^{-1}	Amount of NH_3 desorption/μmol g^{-1}	Mean size of Pd/nm
$Pd/Cs_{0.5}H_{2.5}PW_{12}O_{40}$	7.4	114	6.3
$Pd/Cs_{1.0}H_{2.0}PW_{12}O_{40}$	15	80	5.9
$Pd/Cs_{1.5}H_{1.5}PW_{12}O_{40}$	17	48	3.8
$Pd/Cs_{2.0}H_{1.0}PW_{12}O_{40}$	29	26	3.7
$Pd/Cs_{2.5}H_{0.5}PW_{12}O_{40}$	88	14	2.2
$Pd/Cs_{3.0}PW_{12}O_{40}$	86	Trace	1.6

[a] Pd loading was 1.0 wt%.

Fig. 1 NH$_3$-TPD profiles for 1.0 wt% Pd/Cs$_x$H$_{3-x}$PW$_{12}$O$_{40}$.

increase in Cs content shifted the peak position to lower temperatures. For example, the peak temperature shifted from 854 to 840 K as x increased from 0.5 to 2.0, suggesting that the acidity became gradually weaker. The peak shifted more significantly to 824 K as x rose to 2.5 and almost disappeared at $x = 3.0$. The amount of NH$_3$ desorption also declined markedly with increasing x value (Table 4). On the other hand, the influence of Pd loading on the acidity of the Cs$_{1.5}$H$_{1.5}$PW$_{12}$O$_{40}$-supported Pd samples was less significant, and only slight decreases in the amount of NH$_3$ desorption were observed when the Pd loading increased to >0.5 wt% (see Fig. S2, ESI†).

The size of the Pd nanoparticles may also affect catalytic performance. Lunsford and co-workers proposed that Pd nanoparticles with sizes of ∼3.6 nm have a preponderance of Pd atoms in the (110) plane, which is desirable for H$_2$O$_2$ formation.[2c] We found that the mean size of the supported Pd nanoparticles was dependent on the Cs content. A typical TEM image and the corresponding Pd particle size distribution for 1.0 wt% Pd/Cs$_{1.5}$H$_{1.5}$PW$_{12}$O$_{40}$ are shown in Fig. 2. The mean sizes of Pd nanoparticles in other 1.0 wt% Pd/Cs$_x$H$_{3-x}$PW$_{12}$O$_{40}$ samples evaluated from TEM images are listed in Table 4 (see Fig. S3 for details, ESI†). The increase in Cs content decreased the mean size of the Pd nanoparticles. We tentatively speculate that the smaller Pd nanoparticles in the catalysts with larger Cs contents may stem from the higher surface areas of the porous structures created by the replacement of the smaller H$^+$ by the bigger Cs$^+$. TEM also clarified that, over the Cs$_{1.5}$H$_{1.5}$PW$_{12}$O$_{40}$ support, the mean size of Pd
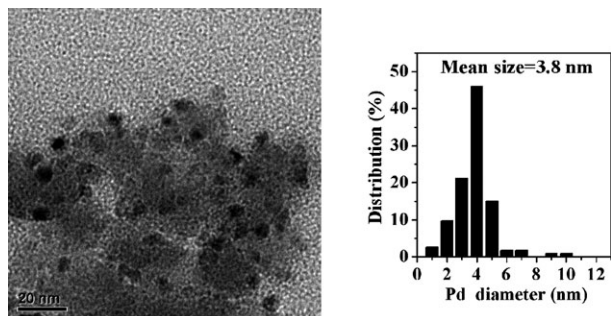

Fig. 2 TEM micrograph and Pd particle size distribution for 1.0 wt% Pd/Cs$_{1.5}$H$_{1.5}$PW$_{12}$O$_{40}$.

increased from 3.8 to 4.5 nm when the Pd loading increased from 1.0 to 2.0 wt% (see Fig. S4, ESI†).

The combination of the characterizations and the catalytic reactions suggest that the acidity of polyoxometalate and the mean size of Pd nanoparticles may both determine the catalytic behaviour of our catalyst for the direct synthesis of H$_2$O$_2$. The samples with either lower acidity (higher Cs contents) or bigger Pd nanoparticles (lower Cs contents or higher Pd loadings) are unfavorable for the formation of H$_2$O$_2$. Furthermore, we have observed a decrease in activity on prolonging the reaction time, and such a deactivation is more serious for the catalysts with lower Cs contents. Thus, the 1.0 wt% Pd/Cs$_{1.5}$H$_{1.5}$PW$_{12}$O$_{40}$ catalyst with an optimum mean size of Pd (3.8 nm), a proper acidity and stability affords the best performance for H$_2$O$_2$ formation.

In summary, we have demonstrated that a polyoxometalate (Cs$_{1.5}$H$_{1.5}$PW$_{12}$O$_{40}$)-supported Pd catalyst can work efficiently for the direct synthesis of H$_2$O$_2$ in the absence of any acid or halide promoters under atmospheric pressure. The H$_2$O$_2$ selectivity and productivity depend significantly on Cs content, Pd oxidation state and Pd loading. The acidity of polyoxometalates and the size of Pd^0 nanoparticles are proposed to control the catalytic performance.

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