Two Tungstates Containing Platinum Nanoparticles Prepared by Air-Calcining Keggin-Type Polyoxotungstate-Coordinated Diplatinum(II) Complexes: Effect on Sintering-Resistance and Photocatalysis

Chika Nozaki Kato1,2 · Toshiya Kubota1 · Koki Aono1 · Naoto Ozawa1

Received: 14 September 2021 / Accepted: 25 October 2021 / Published online: 5 November 2021 © The Author(s) 2021

Abstract

Two tungstates containing platinum nanoparticles (Pt Npts) were obtained by air-calcining α-Keggin-type diplatinum(II)-coordinated polyoxotungstates, Cs3[α-PW_{11}O_{39} \{cis-Pt(NH_3)_2\}_2] \cdot 8H_2O (Cs-P-Pt) and Cs_4[α-SiW_{11}O_{39} \{cis-Pt(NH_3)_2\}_2] \cdot 11H_2O (Cs-Si-Pt), at 700–900 °C for 5 h. The polyoxotungstate Cs-P-Pt was transformed to a mixture of Pt Npts and Cs_3PW_{12}O_{40} upon calcination, while the Cs-Si-Pt structures were transformed to Pt Npts and Cs_4W_{11}O_{35}. The Pt Npts generated by air-calcining Cs-P-Pt at 700 °C for 5 h were uniform with an average particle size of 3.6 ± 1.1 nm, which was much smaller than that of the Pt Npts obtained by calcining Cs-Si-Pt (19.9 ± 9.9 nm) under identical conditions. This demonstrated the significant inhibitory effect of Cs-P-Pt on aggregation during high-temperature air-calcination at a high platinum content (10.6 wt.%) and in the absence of a support. During calcination at 700–900 °C, Cs-P-Pt exhibited higher activities than Cs-Si-Pt with respect to hydrogen evolution from aqueous triethanolamine solutions under visible light irradiation in the presence of Eosin Y, α-Keggin-type mono-aluminum-substituted polyoxotungstate, and titanium dioxide. When Cs-P-Pt was calcined at 800 °C for 100 h, no decrease in activity was observed in comparison with that upon calcination for 5 h.
Introduction

Platinum nanoparticle catalysts are extensively used in various industrial processes, including hydrogenation, naphtha reforming, oxidation, automotive exhaust catalysis, and fuel generation (fuel cells) [1, 2]. However, supported platinum nanoparticle catalysts frequently agglomerate into large particles at high reaction temperatures, losing their catalytically active surface areas [3]. For the suppression of such thermally induced deactivation, complex nanostructures, including core–shell nanostructures [4] and well-designed pore structures [5] have been proposed. Although these methods have been successful in maintaining the platinum nanostructures, aggregation still occurs at higher platinum contents and under thermal treatment at higher temperatures.

For the preparation of supported platinum catalysts, various platinum compounds, such as H₂PtCl₆, Pt(NH₃)₄Cl₂, Pt(NH₃)₂(OH)₂, Pt(NH₃)₂(NO₃)₂, H₂Pt(OH)₆, and Pt(C₈H₁₀O₂)₂ are used as precursors [2]. These compounds are heat-treated in the presence of various gases (air, oxygen, hydrogen, H₂O, N₂, and Ar) or under vacuum. In each case, the ligand was eliminated during the heat treatment, and reduction of the oxidized platinum sites (Pt²⁺ and Pt⁴⁺) to Pt⁰ was observed. Further high-temperature treatment induced aggregation.

Lacunary polyoxometalates (POMs) can be used as inorganic ligands to form various types of complexes via coordination of metal ions and organometallics to the vacant site(s) [6–9]. Several structurally well-defined Pt²⁺-containing POMs, such as [Pt₂(W₅O₁₈)₂]⁶⁻ [10], [anti-Pt₂(α-PW₁₁O₃₉)₂]¹₀⁻ [11], and [syn-Pt₂(α-PW₁₁O₃₉)₂]¹₀⁻ [11] have been reported. Recently, we have synthesized cesium and tetramethylammonium salts of α-Keggin and α₂-Dawson diplatinum(II)-coordinated polyoxotungstates, including Cs₄[α-PW₁₁O₃₉{cis-Pt(NH₃)₂}₂]·8H₂O, [(CH₃)₄N]₃[α-PW₁₁O₃₉{cis-Pt(NH₃)₂}₂]·10H₂O, [(CH₃)₄N]₄[α-SiW₁₁O₃₉{cis-Pt(NH₃)₂}₂]·13H₂O, [(CH₃)₄N]₄[α-GeW₁₁O₃₉{cis-Pt(NH₃)₂}₂]·11H₂O, [(CH₃)₄N]₄[α-AlW₁₁O₃₉{cis-Pt(NH₃)₂}₂]·11H₂O, [(CH₃)₄N]₄[H(α-AlW₁₁O₃₉{cis-Pt(NH₃)₂}₂)]·10H₂O, [(CH₃)₄N]₄[H(α-BW₁₁O₃₉{cis-Pt(NH₃)₂}₂)]·9H₂O, Cs₄[α-GeW₁₁O₃₉{Pt(bpy)}₂]·10H₂O (bpy = 2,2’-bipyridine), Cs₅H₉[α-GeW₁₁O₃₉{Pt(phen)}₂]·3H₂O (phen = 1,10-phenanthroline), and Cs₅[α₂-P₂W₁₇O₆₁{cis-Pt(NH₃)₂}₂]·13H₂O using a similar approach, and demonstrated a long-term steady production of hydrogen with highly effective utilization of the platinum centers for hydrogen production from aqueous ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) and triethanolamine (TEOA) solutions under visible light irradiation [12–16].
In the process of improving the activities of the platinum sites, it was found that air calcination of a cesium salt of α-Keggin diplatinum(II)-coordinated silicotungstate, \(\text{Cs}_4[\text{Pt(OH)}_2\text{N}_2]\)·11H\(_2\)O, at low temperatures (e.g., 300 °C) led to a hydrophilic colloidal species, \(\text{Cs}_4[\text{Pt(OH)}_2\text{N}_2\text{SiW}_{11}\text{O}_{39}]\)·17H\(_2\)O, at low temperatures, it was found that air calcination of a cesium salt of α-Keggin diplatinum(II)-coordinated silicotungstate, \(\text{Cs}_4[\text{Pt(OH)}_2\text{N}_2\text{SiW}_{11}\text{O}_{39}]\)·17H\(_2\)O, at low temperatures. The evolution of hydrogen, oxygen, carbon monoxide, and methane was analyzed using a gas chromatography (GC) instrument equipped with a thermal conductivity detector (TCD), 5 Å molecular sieves, and stainless-steel columns. The samples were assigned after comparison with standard samples analyzed under identical conditions. The turnover number (TON) was calculated as 2[H\(_2\) evolved (mol)]/[Pt atoms (mol)].

### 3 Results and Discussion

When \(\text{Cs}_4\text{-Pt}\) was calcined at temperatures from 25 °C to 800 °C at a heating rate of 40 °C min\(^{-1}\), followed by maintaining at 800 °C for 5 h in air (without flow), its color changed from yellow to black (the calcined sample was denoted as \(\text{Cs}_4\text{-Pt-800-5}\)), and the obtained powder was insoluble in water.

The FT–IR spectrum of \(\text{Cs}_4\text{-Pt-800-5}\) contains several bands at 1079 cm\(^{-1}\), 985 cm\(^{-1}\), 888 cm\(^{-1}\), and 804 cm\(^{-1}\), as shown in Fig. 1a. These bands are remarkably different from those of as-prepared \(\text{Cs}_4\text{-Pt}\) (1099 cm\(^{-1}\), 1047 cm\(^{-1}\), 955 cm\(^{-1}\), 915 cm\(^{-1}\), 859 cm\(^{-1}\), 801 cm\(^{-1}\), 757 cm\(^{-1}\), and 721 cm\(^{-1}\)) (Fig. 1b) [13] but almost identical to those of \(\text{Na}_3[\text{Pt(OH)}_2\text{N}_2\text{SiW}_{11}\text{O}_{39}]\)·17H\(_2\)O (1080 cm\(^{-1}\), 984 cm\(^{-1}\), 893 cm\(^{-1}\), and 808 cm\(^{-1}\)) [18] and \(\text{Cs}_4[\text{Pt(OH)}_2\text{N}_2\text{SiW}_{11}\text{O}_{39}]\)·17H\(_2\)O (20 cm\(^{-1}\)) and \(\text{Cs}_4\text{SiW}_{11}\text{O}_{39}\) (20 cm\(^{-1}\)) [19], suggesting that the structure of the α-Keggin-type mono-lacunary polyoxotungstate ligand, \(\text{PW}_{12}\text{O}_{40}\), in \(\text{Cs}_4\text{-Pt}\) transformed to \(\text{PW}_{12}\text{O}_{40}\) under the applied thermal treatment conditions. The band

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Typical photocatalytic reactions were performed at 25 °C. In this work, we report the formation of two types of tungstates containing Pt Npts, via air-calcination of TEOA solutions under visible-light irradiation [17]. The evolution of hydrogen, oxygen, carbon monoxide, and methane was analyzed using a gas chromatography (GC) instrument equipped with a thermal conductivity detector (TCD), 5 Å molecular sieves, and stainless-steel columns. The samples were assigned after comparison with standard samples analyzed under identical conditions. The turnover number (TON) was calculated as 2[H\(_2\) evolved (mol)]/[Pt atoms (mol)].

**2.3 Photocatalytic Reaction Experiments**

Typical photocatalytic reactions were performed at 25 °C. In this work, we report the formation of two types of tungstates containing Pt Npts, via air-calcination of TEOA solutions under visible-light irradiation [17]. The evolution of hydrogen, oxygen, carbon monoxide, and methane was analyzed using a gas chromatography (GC) instrument equipped with a thermal conductivity detector (TCD), 5 Å molecular sieves, and stainless-steel columns. The samples were assigned after comparison with standard samples analyzed under identical conditions. The turnover number (TON) was calculated as 2[H\(_2\) evolved (mol)]/[Pt atoms (mol)].

**2 Experimental**

### 2.1 Materials and Reagents

\(\text{Cs}_4[\text{Pt(OH)}_2\text{N}_2\text{SiW}_{11}\text{O}_{39}]\)·8H\(_2\)O (\(\text{Cs}_4\text{-Pt}\)) [13], \(\text{Cs}_4[\text{Pt(OH)}_2\text{N}_2\text{SiW}_{11}\text{O}_{39}]\)·11H\(_2\)O (\(\text{Cs}_4\text{-Si-Pt}\)) [17], \([\text{CH}_3\text{NH}_3]_4[\text{Pt(OH)}_2\text{N}_2\text{SiW}_{11}\text{O}_{39}]\)·10H\(_2\)O (\(\text{TMA-Pt}\)) [12], \([\text{Pt(NH)}_2\text{N}_2\text{SiW}_{11}\text{O}_{39}]\)_2·4H\(_2\)O (\(\text{Pt-SiW}_{12}\)) [16], \(\text{Na}_3[\text{Pt(OH)}_2\text{N}_2\text{SiW}_{11}\text{O}_{39}]\)·10H\(_2\)O [18], \(\text{K}_3[\text{Pt(NH)}_2\text{SiW}_{12}\text{O}_{40}]\)·17H\(_2\)O [19], \(\text{K}_5\text{SiW}_{11}\text{O}_{39}\)·17H\(_2\)O [20], and \(\text{Cs}_4\text{SiW}_{11}\text{O}_{39}\) were prepared via methods described in the literature. The number of solvated water molecules were determined through TG/DTA measurements. All reagents and solvents were obtained from commercial sources and used as received. Titanium dioxide (anatase:rutile = 80:20) and platinum black (≤ 20 μm; ≥ 99.95% purity) were obtained from Wako Pure Chemical Industries, Ltd. and Sigma-Aldrich Co. LLC., respectively.

### 2.2 Instrumentation and Analytical Procedures

The infrared spectra were recorded on a PerkinElmer Spectrum100 FT-IR spectrometer in KBr discs at approximately 25 °C in air. The services of Eurofins EAG Materials Science (USA) were enlisted for performing XPS analyses. A monochromated Al K\(_\alpha\) radiation (1486.6 eV) was used as the X-ray source. The binding energies are referenced to the C\(_1s\) binding energy at 284.8 eV. Powder X-ray diffraction (PXRD) measurements were performed on an X-ray powder diffractometer (SmartLab, Rigaku, Corp., Japan) using Cu K\(_\alpha\) radiation (K\(_\alpha\) = 1.54 Å). Transmission electron microscopy (TEM) images were recorded using a JEOL-JEM 2100F electron microscope, and the elemental compositions of the samples were studied using energy-dispersive X-ray spectroscopy (EDS, JED-2300 T (JEOL, Japan)).
at 1356 cm\(^{-1}\) corresponding to the four NH\(_3\) groups disappeared, indicating the complete removal of the four ammonia molecules. The same bands as Cs-P-Pt-800-5 were observed for the samples obtained by calcination at 700 °C and 900 °C (these samples are denoted as Cs-P-Pt-700-5 and Cs-P-Pt-900-5, respectively), as shown in Fig. S1. This proved that the α-Keggin structure was maintained at least up to 900 °C. When Cs-Si-Pt was calcined at 800 °C for 5 h (the calcined sample is denoted as Cs-Si-Pt-800-5), its color changed from yellow to gray, and the obtained powder was insoluble in water. The FT-IR spectrum (Fig. 1c) of Cs-Si-Pt-800-5 showed bands at 968 cm\(^{-1}\), 889 cm\(^{-1}\), 861 cm\(^{-1}\), 812 cm\(^{-1}\), 779 cm\(^{-1}\), 730 cm\(^{-1}\), 717 cm\(^{-1}\), and 672 cm\(^{-1}\), which were different from those observed for the as-prepared Cs-Si-Pt (1004 cm\(^{-1}\), 960 cm\(^{-1}\), 944 cm\(^{-1}\), 891 cm\(^{-1}\), 846 cm\(^{-1}\), 789 cm\(^{-1}\), 738 cm\(^{-1}\), and 712 cm\(^{-1}\)) (Fig. 1d) but similar to those of Cs\(_4\)W\(_{11}\)O\(_{35}\) (969 cm\(^{-1}\), 860 cm\(^{-1}\), 816 cm\(^{-1}\), 780 cm\(^{-1}\), 707 cm\(^{-1}\), and 675 cm\(^{-1}\)), which was obtained via a method described in the literature [21]. The same spectral pattern (Fig. S2) was observed when Cs-Si-Pt was calcined at 700 °C and 900 °C (the calcined samples are denoted as Cs-Si-Pt-700-5 and Cs-Si-Pt-900-5). The four NH\(_3\) groups coordinated to the di-platinum site in Cs-Si-Pt were vaporized, as previously reported [17]. A band appeared at 1123 cm\(^{-1}\) which was attributed to the Si-O-Si stretching, suggesting that the internal [SiO\(_4\)] unit in the Keggin structure was transformed to silicon oxide [23].

The PXRD pattern of Cs-P-Pt-800-5 (Fig. 2a) showed the same peaks as that of Cs\(_3\)PW\(_{12}\)O\(_{40}\) (ICDD: 00-050-1857), and similar peaks were observed for Cs-P-Pt-700-5 and Cs-P-Pt-900-5, as shown in Fig. S3. These results prove that the {PW\(_{11}\)O\(_{39}\)} unit in Cs-P-Pt was transformed to {PW\(_{12}\)O\(_{40}\)} under the reported thermal treatment conditions. This was validated by the FT-IR spectra. In contrast, the PXRD pattern of Cs-Si-Pt-800-5 (Fig. 2b) exhibited the same peaks as that of Cs\(_4\)W\(_{11}\)O\(_{35}\) (ICDD: 00-051-1891). A similar structural transformation of the {SiW\(_{11}\)O\(_{39}\)} unit to {W\(_{11}\)O\(_{35}\)} was observed for Cs-Si-Pt-700-5 and Cs-Si-Pt-900-5, as shown in Fig. S4. As previously reported, the {SiW\(_{11}\)O\(_{39}\)} unit in Cs-Si-Pt was transformed to {SiW\(_{12}\)O\(_{40}\)} by air calcination in the lower temperature range of 250–500 °C [17]. However, at higher temperatures in the range of 700 °C to 900 °C, the Keggin structure was transformed to {W\(_{11}\)O\(_{35}\)}.

A broad peak corresponding to Pt(111) (2θ(°) = 40, ICDD: 00-04-0802) was observed. This indicates that the di-platinum(II) sites in Cs-P-Pt and Cs-Si-Pt were reduced to crystalline Pt(0) by the applied thermal treatment. As shown in Figs. 2, S3 and S4, the peak intensity increased as the calcination temperature was increased. These results suggest that the crystallite size of platinum increases with the calcination temperature.

The Pt(4f) XPS spectra of Cs-P-Pt-800-5 and Cs-Si-Pt-800-5 are shown in Fig. 3. In both the spectra, the platinum sites were primarily composed of Pt\(^0\), with low levels of Pt\(^{2+}\) and Pt\(^{4+}\). The occurrence of Pt\(^{3+}\) needs to be

![Fig. 1 FT-IR spectra of a Cs-P-Pt-800-5, b Cs-P-Pt, c Cs-Si-Pt-800-5, and d Cs-Si-Pt](image-url)
interpreted with caution because of the high levels of signal overlap with Cs(4d). The W(4f) XPS spectra (Figs. S5a and S6a) of Cs-P-Pt-800-5 and Cs-Si-Pt-800-5 showed that the tungsten sites were composed of W⁶⁺. The Cs(3d) XPS spectra of Cs-P-Pt-800-5 and Cs-Si-Pt-800-5 indicated that the existence of cesium in the monovalent form, as shown in Figs. S5b and S6b.

Figure 4a and b show TEM images of Cs-P-Pt-700-5 and -800-5. The corresponding size distributions are shown in Figs. 4c and 4d. Homogeneously dispersed Pt Npts can be observed as small black grains in the tungstate matrix. The average sizes of the Pt Npts in the calcined samples are summarized in Table 1. Surprisingly, Cs-P-Pt-700-5 and Cs-P-Pt-800-5 exhibited average particle sizes of 3.6 ± 1.1 nm and 5.3 ± 2 nm, respectively, at a high platinum content (10.6 wt.%), in the absence of a support. The average particle size of Cs-P-Pt-900-5 was 9.3 ± 2.8 nm, which was approximately twice that of Cs-P-Pt-800-5, indicating slight aggregation at 900 °C (Fig. S7). However, the average particle size reached upon calcination at 800 °C for 100 h was 5.4 ± 1.9 nm, and negligible aggregation of Pt Npts was observed after long-term heat treatment, as shown in Fig. S8.

In contrast, the average sizes of the Pt Npts in Cs-Si-Pt-700-5, -800-5, and -900-5 were 19.9 ± 9.9 nm, 42.8 ± 21.2 nm, and 100.8 ± 70.7 nm, respectively, and the particle sizes increased remarkably with the calcination temperature, as shown in Figs. 5, S9a, and S10. The black grains were confirmed to be platinum particles via tungsten and platinum EDS mapping (Figs. S9b and S9c).

As a control experiment, Pt Npt-supported TiO₂ (Pt content: 11 wt.%) was prepared as follows: cis-diamminedichloroplatinum(II) (cisplatin) (0.169 g; 0.56 mmol) was dissolved in 50 mL water. TiO₂ (0.83 g) was added to the solution, and the mixture was stirred for 2 h at approximately 25 °C. After evaporation to dryness at 100 °C, the obtained solid was calcined at 700 °C for 5 h in air. The calcined product was denoted as cisplatin/TiO₂-700-5. The average particle size of cisplatin/TiO₂-700-5 was 31.4 ± 19.7 nm, which was larger than that of Cs-P-Pt-700-5 and Cs-Si-Pt-700-5, as shown in Fig. S11. When the platinum salt of α-Keggin silicotungstate [Pt(NH₃)₄]²⁺[α-SiW₁₂O₄₀]·4H₂O (platinum content: 11.2 wt.%) was calcined at 800 °C for 5 h in air (the calcined product was denoted as Pt-SiW₁₂-800-5), particles with non-uniform sizes were formed with some particles growing above 50 nm.
Fig. 3  Pt(4f) XPS spectra in the range 66.5–84 eV of a Cs-P-Pt-800-5 and b Cs-Si-Pt-800-5
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1.3

It can be seen from the FT–IR spectrum of Pt-SiW12-800-5 (Fig. S12b) that the Keggin-type structure was decomposed and {W11O35} unit was not formed. A platinum salt of phosphotungstate retaining the structure of PW12 O403– could not be obtained using the same method as that used to obtain SiW12 O404−. It was confirmed from the FT-IR spectrum (Fig. S13b) that the Keggin structure was decomposed when TMA-P-Pt (platinum content: 11 wt.%) was calcined at 800 °C for 5 h in air (the obtained sample was denoted as TMA-P-Pt-800-5). The particle size was non-uniform, and some particles grew to several tens of nanometers, as shown in Fig. S13a.

According to these results, Cs-P-Pt, which retained the α-Keggin polyoxotungstate and Cs3PW12 O40 after calcination, exhibited an excellent aggregation inhibitory effect at high platinum content and in the absence of a support. Such inhibition of platinum aggregation is not observed in platinum compounds from which the ligands disappear upon calcination [2]. It is critical to coordinate the platinum species to the mono-vacant sites in α-Keggin-type mono-lacunary phosphotungstates and isolate them as cesium salts for the expression of such an effect.

The activities of the Pt Npts in the calcined samples as co-catalysts were studied by using Cs-P-Pt-800-5 and Cs-Si-Pt-800-5 to catalyze the evolution of hydrogen from aqueous TEOA solutions under light irradiation (λ ≥ 440 nm) in the presence of Eosin Y (EY), K5[α-SiW11{Al(OH2)}O39]·7H2O (denoted as K-Si-Al), and titanium dioxide.

Table 1 Average size of Pt Npts in the calcined samples

| calcined sample         | Pt content (wt.%) | average Pt Npts size (nm) |
|-------------------------|-------------------|----------------------------|
| Cs-P-Pt-700-5           | 10.6a             | 3.6 ± 1.1                  |
| Cs-P-Pt-800-5           | 5.3 ± 2           | 9.3 ± 2.8                  |
| Cs-P-Pt-900-5           | 5.4 ± 1.9         | 19.9 ± 9.9                 |
| Cs-Si-Pt-700-5          | 10.1a             | 42.8 ± 21.2                |
| Cs-Si-Pt-800-5          | 100.8 ± 70.7      | 100.8 ± 70.7               |
| cisplatin/TiO2-700-5    | 11.0              | 31.4 ± 19.7                |

*a*The platinum contents were calculated based on the composition formulae of Cs-P-Pt and Cs-Si-Pt.

(Fig. S12a). It can be seen from the FT–IR spectrum of Pt-SiW12-800-5 (Fig. S12b) that the Keggin-type structure was decomposed and {W11O35} unit was not formed. A platinum salt of phosphotungstate retaining the structure of PW12 O403− could not be obtained using the same method as that used to obtain SiW12 O404−. It was confirmed from...
(anatase:rutile = 80:20), as shown in Figs. 6a and b [14, 17, 24, 25]. The precursors, Cs-P-Pt and Cs-Si-Pt were weighted while ensuring that the amount of platinum was 0.2 μmol (the contents of Pt in the catalysts containing TiO₂ and the platinum samples were 0.084 wt.% and 0.080 wt.%, respectively). Subsequently, they were calcined at 800 °C for 5 h in air. TEOA was used as the sacrificial reagent. EY and K-Si-Al were used as the photosensitizer and EY stabilizer, respectively. Although TiO₂ was used to promote charge separation, the tungstates containing Pt Npts were not supported on the surface of TiO₂. In order to compare the activities with the samples before calcination, TiO₂ was simply dispersed in the solutions. Hydrogen was formed with 100% selectivity, and oxygen, carbon dioxide, carbon monoxide, and methane were not detected under these reaction conditions. It has already been confirmed that no reaction was observed in the absence of platinum catalysts or Eosin Y under the reported conditions.

After 6 h of light irradiation, the amounts of hydrogen evolved in presence of Cs-P-Pt-800-5 and Cs-Si-Pt-800-5 were 180 μmol and 156 μmol, respectively. These values were higher than those of Cs-P-Pt and Cs-Si-Pt (TONs observed after 6 h were 703 and 409, respectively. These results suggest that the photocatalytic activities of Cs-P-Pt and Cs-Si-Pt were improved upon calcination. The turnover frequencies (TOF = TON/reaction time (h)) of Cs-P-Pt-800-5 and Cs-Si-Pt-800-5 after 1 h were 685 and 336 h⁻¹, respectively. These values are higher than those of similar photocatalytic systems containing platinum co-catalysts prepared via the photo-reduction of H₂PtCl₆, EY, and TiO₂. For example, the TOFs of Pt/EY/nitrogen-doped TiO₂ [26], Pt/EY/modified TiO₂ with phosphate [27], Pt/EY/Fe³⁺/TiO₂ [28], and Pt/EY/SiW₁₁O₃₉⁸⁻/TiO₂ [25] are less than 150 h⁻¹ with respect to hydrogen evolution from aqueous TEOA solutions under visible-light irradiation. When platinum black (3.0 μmol Pt) was used as a co-catalyst, the TOF after 1 h was 11.7 h⁻¹, which was significantly lower than those of Cs-P-Pt-800-5 and Cs-Si-Pt-800-5. It is difficult to discuss the differences in activities based on the sizes of the Pt Npts alone because of the influences of Cs₃PW₁₂O₄₀ and Cs₄W₁₁O₃₅ contained in Cs-P-Pt-800-5 and Cs-Si-Pt-800-5, respectively. However, upon calcination at 700–900 °C, Cs-P-Pt showed higher activities than Cs-Si-Pt, as shown in Fig. 7.
using Cs-P-Pt-800-100, 192 μmol hydrogen was generated after 6 h (TON: 1919), and there was no reduction in catalytic activity upon extending the calcination time from 5 h to 100 h.

In the cases of Cs-P-Pt-800-5 and Cs-Si-Pt-800-5, the amount of hydrogen generated gradually decreased with time, as shown in Figs. 6a and b. For the hydrophilic platinum-polyoxotungstate colloidal particles obtained by air-calcining Cs-Si-Pt at 300 °C for 5 h, the TON after 3 h exceeded 4600 under similar reaction conditions. However, rapid decomposition of the platinum sites was observed and the activity did not improve upon re-addition of EY [17]. To confirm that Cs-P-Pt-800-5 was not decomposed, we performed the following experiment: The aforementioned photocatalytic reaction was performed in the presence of Cs-P-Pt-800-5 (0.2 μmol Pt) under light irradiation for 20 h. The residual solid was collected using a membrane filter (JG 0.2 μm) and washed with water and ethanol. Thereafter, the solid containing Cs-P-Pt-800-5 and TiO₂ was dispersed again in an aqueous TEOA solution containing EY and K-Si-Al. After 6 h of light irradiation, approximately 200 μmol of hydrogen was generated. It was also confirmed that the photocatalytic activity of Cs-Si-Pt-800-5 was restored by the re-addition of EY (Fig. S14). These results demonstrate that Cs-P-Pt-800-5 and Cs-Si-Pt-800-5 did not decompose under the applied reaction conditions and were recyclable.

Finally, the following experiment was conducted to investigate the sizes of the Pt Npts after light irradiation: Cs-P-Pt-800-5 (37.6 mg) was dispersed in aqueous TEOA containing dissolved EY, and subjected to light irradiation for 6 h. The residual solid was collected through a membrane filter (JG 0.2 μm) and washed with water and ethanol. The TEM images and the corresponding size distributions of the obtained samples are shown in Figs. 8a and b. After light irradiation, homogeneously dispersed Pt Npts were observed in the tungstate matrix. The average particle size was 5.1 ± 2.5 nm, which was nearly the same as that prior to light irradiation. Although it has been reported that the sizes of Pt Npts increase during hydrogen evolution under light irradiation [29], no aggregation of the Pt Npts comprising Cs-P-Pt-800-5 was observed under the applied reaction conditions.
This reaction mechanism is similar to that of a reported Pt co-catalyst/EY/K-Al-Si/TiO₂ system [14]. However, since the water-insoluble calcined samples were used without being supported on the surface of titanium oxide, it is possible that the efficiency of electron transfer between titanium oxide and the platinum and/or tungstate sites was reduced. Sintering at high temperatures may also induce three-dimensional microstructural changes and inhibit proton transfer to the platinum sites. In order to overcome these problems, we are investigating methods to support the calcined samples on the surfaces of some semiconducting photocatalytic materials. The results will be reported in due course.

4 Conclusion

Two tungstates containing platinum nanoparticles were obtained by air-calcining Cs₃[α-PW₁₁O₃₉\{cis-Pt(NH₃)₂\}_2]⋅8H₂O (Cs-P-Pt) and Cs₄[α-SiW₁₁O₃₉\{cis-Pt(NH₃)₂\}_2]⋅11H₂O (Cs-Si-Pt), at 700–900 °C for 5 h. When Cs-P-Pt was calcined, its {PW₁₁O₃₉} unit transformed to {PW₁₂O₄₀}. In contrast, Cs-Si-Pt exhibited a structural transformation of the {SiW₁₁O₃₉} unit to {W₁₁O₃₅} under identical calcination conditions. The di-platinum(II) sites in Cs-P-Pt and Cs-Si-Pt transformed to Pt Npts. The average particle size of Pt Npts generated via air-calcination of Cs-P-Pt was much smaller than that observed when Cs-Si-Pt was calcined. Thus, Cs-P-Pt exhibited an excellent aggregation inhibitory effect at high platinum content and in the absence of a support.

The calcined samples were applied as co-catalysts for hydrogen evolution from aqueous TEOA solutions under visible light irradiation (λ ≥ 440 nm) in the presence of Eosin Y, K₅[α-SiW₁₁{Al(OH₂)}O₃₉]⋅7H₂O, and titanium dioxide. Upon calcination at 700–900 °C, Cs-P-Pt exhibited higher activities than Cs-Si-Pt. The activity of Cs-P-Pt did not diminish after calcination at 800 °C for 100 h, in comparison with its activity after 5 h of calcination. It was also confirmed that the Cs-P-Pt sample calcined at 800 °C for 5 h exhibited no change in the sizes of the Pt Npts when subjected to light irradiation. Platinum aggregation was thus suppressed under the applied photocatalytic reaction conditions.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10562-021-03843-x.

Acknowledgements This work was supported by JSPS KAKENHI Grant Number JP19H02489, and the Research Institute of Green Science and Technology Fund for Research Project Support (2021-RIGST-21E03) at National University Corporation, Shizuoka University. We acknowledge Mr. Ryota Kasai (Shizuoka University) for supporting several experiments on the photocatalytic reactions.

Declarations

Conflict of interest The authors of this work declare that a potential competing interest does not exist. There is not any financial or personal interest or belief that could affect this research work.

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