Supporting information

Boosting Hydroformylation Activity of Polyoxometalate-Anchored Rh Single Atom Catalysts in Toluene-Water Media

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Materials

Sodium tungstate (NaWO₄·2H₂O), H₃PW₁₂O₄₀·nH₂O (2880.05 g/mol) and potassium chloride (KCl) were obtained from Shanghai D&B Biological Science and Technology Co., Ltd, rhodium chloride (RhCl₃·nH₂O, Rh content: 39.01wt %) was obtained from Kunming Boren Precious Metals Co., Ltd. Rh(acac)(CO)₂ and HRh(CO)(PPh₃)₃ were obtained from Shanghai Macklin Biochemical Co., Ltd, and all organic solvents and other materials were purchased from Shanghai Titan Scientific Co., Ltd. All deuterium reagent was purchased from Sigma-Aldrich Co., Ltd. High purity H₂ (99.999%) was supplied by Shang Nong Gas Factory. Propene (99.5%) was purchased from by Shanghai Jiajie Gas Factory. CO (99.99%) was purchased from Shanghai Wetry Standard Reference Gas Analytical Technology Co., Ltd. D₂ (99.999%) was supplied by Shanghai Jiajie Gas Factory. HRh(CO)(TPPTS)₃ were prepared according to the literatures. ^[1] SiO₂ (300 m²/g, particle size 7-40 nm) was purchased from Shanghai Macklin Biochemical Co., Ltd. The 1.0 wt % Rh/SiO₂ was prepared by incipient wetness impregnation.^[2]

Characterization

ICP-AES analysis of K, P, W, Rh was performed on a TJA IRIS 1000 instrument. Transmission electron microscopy (TEM) and STEM characterization was performed on a ThermoFisher Talos F200X microscope under 200 kV. High angle annular dark field (HADFF)-STEM images were recorded using a convergence semi angle of 10.5 mrad, and inner- and outer collection angles of 59 and 200 mrad, respectively. Energy dispersive X-ray spectroscopy (EDS) was carried out using 4 in-column Super-X detectors. Powder X-ray diffraction (XRD) patterns were performed in the 2θ range of $5-75^{\circ}$ from Rigaku equipped with a 9 kW rotating anode Cu source at 45 kV and 100 mA. Fourier-transform (FT) IR spectra was recorded from pressed KBr pellets at room temperature on a Nicolet Fourier transform infrared spectrometer (Magna550). A spectrum of dry KBr was also recorded as background. UV-vis spectra were measured using a Varian Cary 500 spectrophotometer. Electrospray ionization time-of-flight mass (ESI-TOF-MS) spectra was recorded in the negative mode on an Agilent 6520 Q-TOF LC/MS mass spectrometer. The sample was dissolved in methanol (CH₃OH) and directly injected into the chamber at 20 µL/min. Typical instrument parameters: capillary voltage, 4000 V; nebulizer, 1.0 bars; dry gas, 6.0 L/min at 120 °C; m/z range, 500-3000. The thermal stability of catalysts was determined by thermogravimetric analysis (TGA; heating rate: 10 °C/min; N2 flow, 100 mL/min) using a PerkinElmerPyris Diamond Analyser. X-ray photoelectron spectroscopy (XPS) was performed using Thermo ESCALAB 250. In-situ X-ray photoelectron spectra (XPS) were determined on a VG ESCALAB MK2 apparatus using Al Ka radiation (1486.6 eV, 12.5 kV, 250 W) to obtain the binding energies and oxidation states of Rh elements. In-situ XPS experiments were performed with the following procedure. For each measurement, the catalyst was pressed to thin sheet and fixed on the sample holder. The sample was heated in 5% CO-H₂ flow (50 mL/min) at a heating rate of 5°C/min. After the inner temperature of the preparation chamber reached 100 °C and maintained for 6 h, the sample was cooled to 30 °C under constant N₂ flow (50 mL/ min). The reduced sample was directly returned to the analyzer chamber without exposure to air. Then XPS data were recorded. Mass spectra were recorded in the negative mode on an Agilent 6520 Q-TOF LC/MS mass spectrometer. The samples were directly injected into the chamber at 20 μ L·min⁻¹. Typical instrument parameters: capillary voltage, 4000 V; nebulizer, 1.0 bars; dry gas, 6.0 L/min at 120 °C; m/z range, 500 – 3000. Mass spectra were recorded in the negative mode on an Agilent 6520 Q-TOF LC/MS mass spectrometer (China). All data were collected and processed using MassHunter (Agilent Technologies Co. Ltd., China) workstation software. In-situ Fourier-transform (FT) IR spectra was collected at 25 °C with a Nicolet iS50 spectrometer equipped with a MCT detector and a high temperature reaction chamber with ZnSe windows. The sample was pressed KBr pellets. The in-situ FT-IR spectra were collected in the range of 4000–650 cm⁻¹ by accumulating 32 scans at a 4 cm⁻¹ resolution. Background spectra were recorded in flowing Ar at the rate of 10 sccm for 0.5 h at 25 °C and subtracted from the sample spectrum for each measurement. Nicolet OMNIC software was used to convert the absorbance data into Kubelka-Munk (KM) format. After that, 1 atm of CO or H₂ were introduced to the sample at 25 °C for 0.5 h and the spectra were collected till the steady state. Afterwards, N₂ was introduced to the sample at 25 °C to remove the physically absorbed CO or H₂. *In-situ* FT-IR spectra of the sample with different gases were then obtained. ²H spectra were recorded on a Bruker Avance NEO 600 MHz NMR spectrometer instrument. The reaction products were analyzed by using gas chromatography (GC) [a Shimadzu GC-2014 gas chromatograph equipped with an RTX-5MS capillary column (30 m × 0.32 mm × 0.50 um)]. The pH value of the aqueous solution was measured by Mettler Toledo FE28 -Standard pH meter using a LE 438 pH electrode.

K₇PW₁₁O₃₉·9 H₂O (K-PW₁₁)

K-PW₁₁ was synthesized according to the previous literature.^[3] 20 g (6.94 mmol) of H₃PW₁₂O₄₀·nH₂O (2880.05 g/mol) were dissolved in 100 ml of distilled water. 1 g KCl was added and a white precipitate to form. The pH was adjusted to 5.0 with 1M KHCO₃ 30 mL and the reaction mixture was stirred for 10 min. A light white precipitate was centrifuged off and the clear solution was concentrated to half its solvent volume at 70 °C. After the solution was stored in the refrigerator for 24 h, the white crystals of K₇PW₁₁O₃₉·9 H₂O were formed and collected by filtration, followed by washing with cool water (10 ml) and drying under vacuum for 12 h at 60 °C. Yield of K₇PW₁₁O₃₉·9 H₂O: 13.5 g (67.5% based on H₃PW₁₂O₄₀·nH₂O). IR: 1083 and 1037 cm⁻¹ (v_{as} P–O_a), 956 cm⁻¹ (v_{as} W=O_d), 892 cm⁻¹ (v_{as} W–O_b–W), 808 and 730 cm⁻¹ (v_{as} W–O_c–W), 1621 and 3452 cm⁻¹ (vO-H).

K₁₀P₂W₁₇O₆₁·15H₂O (K-P₂W₁₇)

K-P₂W₁₇ was synthesized according to the previous literature.^[4] 100 g Na₂WO₄·2 H₂O was dissolved in 350 mL of distilled water and heat to 100 °C. Then 150 mL 85 % H₃PO₄ was slowly added to the boiling solution, reflux to obtain a yellow-green solution for 8 h. 100 g KCl were added after the solution has cooled. The light green precipitate is collected, redissolved in 20 mL H₂O (90 °C), and crystallized overnight at 5 °C. After a few hours of vacuum drying at 80 °C, the white crystals were formed and collected. Yield of K₆P₂W₁₈O₆₂·14 H₂O: 70.1 g. (74.2% based on Na₂WO₄·2 H₂O).

IR: 1093 and 1047 cm⁻¹ (ν_{as} P–O_a), 985 cm⁻¹ (ν_{as} W=O_d), 879 cm⁻¹ (ν_{as} W–O_b–W), 792 and 740 cm⁻¹ (ν_{as} W–O_c–W), 1620 and 3450 cm⁻¹ (ν O-H).

A sample of 8 g K₆P₂W₁₈O₆₂·14 H₂O was then dissolved in 20 mL of distilled water. 2 g (0.2 mol) potassium bicarbonate solution was added to the solution and and the reaction mixture was stirred for 1 h. After the reaction was completed, the white solid product was collected by filtration, washed with 10 mL KCl solution (1 M) and redissolved with 50 mL H₂O (90 °C). The snow-like crystals that appear after cooling to ambient temperature. After filtration and vacuum drying at 70 °C, the white crystals were collected as $K_{10}P_2W_{17}O_{61}$ ·15 H₂O. Yield: 5.8 g (72.5% based on $K_6P_2W_{18}O_{61}$ ·14 H₂O). IR: 1093 and 1047 cm⁻¹ (v_{as} P–O_a), 985 cm⁻¹ (v_{as} W=O_d), 879 cm⁻¹ (v_{as} W–O_b–W), 792 and 740 cm⁻¹ (v_{as} W–O_c–W), 1620 and 3450 cm⁻¹ (vO-H).

$K_4PW_{11}O_{39}Rh \cdot 9 H_2O (K-PW_{11}Rh)$

K-PW₁₁Rh was synthesized using a procedure described in the previous reports.^[3] RhCl₃ solution was introduced dropwise and mixed with solution of K-PW₁₁ by vigorous stirring at 90 °C for 2 h. 4 equivalent methanol was added to the solution after cooling the solution. The orange solid was obtained by filtration, followed by washing with methanol (10 mL) and drying under vacuum for 12 h at 80 °C. Yield: 0.92g (66.2% based on W). IR: 1083 and 1037 cm⁻¹ (v_{as} P–O_a), 956 cm⁻¹ (v_{as} W=O_d), 896 cm⁻¹ (v_{as} W–O_b–W), 808 and 730 cm⁻¹ (v_{as} W–O_c–W), 1621 and 3452 cm⁻¹ (vO-H). Anal. calcd for K₄PW₁₁O₃₉Rh·9 H₂O: K, 5.0; P, 1.0; W, 65.2; Rh, 3.3. Found: K, 5.3; P, 0.98; W, 65.2; Rh, 3.2.

$K_7P_2W_{17}O_{61}Rh \cdot 15H_2O(K-P_2W_{17}Rh)$

K-P₂W₁₇Rh was synthesized using a procedure described in the previous reports. RhCl₃ solution was introduced dropwise and mixed with solution of K-P₂W₁₇ by vigorous stirring at 90 °C for 2 h. 4 equivalent methanol was added to the solution after cooling the solution. The orange solid was obtained by filtration, followed by washing with methanol (10 mL) and drying under vacuum for 12 h at 80 °C to afford K-P₂W₁₇Rh as a brown powder. Yield: 0.88g (64.3% based on W). 1093 and 1048 cm⁻¹ (ν_{as} P–O_a), 986 cm⁻¹ (*v*_{as} W=O_d), 885 cm⁻¹ (*v*_{as} W–O_b–W), IR: 781 and 741 cm⁻¹ (*v*_{as} W–O_c–W), 1620 and 3450 cm⁻¹ (*v* O-H). Anal. calcd for K₇P₂W₁₇O₆₁Rh·15H₂O: K, 8.8; P, 2.0; W, 100.8; Rh, 3.3. Found: K, 9.2; P, 1.94; W, 100.8; Rh, 3.1.

For compsarsion, The reference monometallic Rh/SiO₂ catalyst was also prepared by incipient-wetness impregnation with anaqueous solution of rhodium chloride(III).^[2]

Typical procedure for catalytic hydroformylation of propylene

The hydroformylation reaction was conducted in a 50 mL stainless-steel autoclave. Typically, 1 µmol catalyst of K-PW₁₁ or K-P₂W₁₇ (with a molar ratio of propene/Rh = 14,200), 3 mL of toluene, and 3 mL of water were added to the reactor. The autoclave was pressurized with 14.2 mmol propene (0.6 g, weighed by electronic balance) and a 1:1 molar ratio of a CO and H₂ mixture(4 MPa). The reaction mixture was heated to the desired temperature under continuous stirring. After cooling the reaction vessel in an ice-water bath, the gas was depressurized. The products were analyzed using gas chromatography (GC), and yields were determined by GC analysis with dodecane as an internal standard. The conversion of substrates and product yields were calculated as following eqs. (1) and (2):

$$Conversion (\%) = \frac{amount \, of \, substrates \, converted \, (mole)}{total \, amount \, of \, substrates \, (mole)} \times 100\%$$
(1)

$$Yield (\%) = \frac{amount of a product (mole)}{total amount of substrates (mole)} \times 100\%$$
(2)

The turnover frequency (TOF, h^{-1}) values were calculated based on the total number of Rh atoms. The TOF (h^{-1}) was determined using the following equation (Eq 3):

TOF $(h^{-1}) = [(reacted mol substrate)]/[(total mol metal) \times (reaction Time)]$ (3)

The recyclability of the catalyst was evaluated by hydroformylation of propylene. For recycling, after the reaction, the upper toluene phase containing the product was removed for GC analysis, while the catalyst was still reserved in lower water phase and can be directly used for the next cycle once propylene was charged with toluene phase.



Fig. S1. TG curves of Rh-substituted POM catalysts.



Fig. S2. (a) ³¹P NMR(85% H₃PO₄, reference) of K-PW₁₁O₃₉ and K-PW₁₁O₃₉Rh, (b) ³¹P NMR(85% H₃PO₄, reference) of K-P₂W₁₇O₆₁ and K-P₂W₁₇O₆₁Rh. (c) Raman spectroscopic data of K-PW₁₁Rh and K-P₂W₁₇Rh in aqueous solution.



Fig. S3. Negative mode ESI-MS spectra of Rh substituted POM salts. (a) K-PW₁₁Rh, (b) K-P₂W₁₇Rh.

| Table S1. I | ESI-MS data | collected | for K- | -PW ₁₁ Rh |
|-------------|-------------|-----------|--------|----------------------|
|-------------|-------------|-----------|--------|----------------------|

| POM anions | Calculated m/z | Measured m/z |
|------------|----------------|--------------|
| | | |

| [KPW ₁₁ O ₃₉ Rh] ³⁻ | 939.7325 | 939.3745 |
|--|-----------|-----------|
| $[K(PW_{11}O_{39}Rh)(H_2O)]^{3-}$ | 945.7375 | 945.8928 |
| $[K(PW_{11}O_{39})(H_2O)_2]^{3-1}$ | 951.7426 | 951.4826 |
| $[K_4(PW_{11}O_{39})(H_2O)_{17}]^{3-2}$ | 1046.6155 | 1046.7569 |
| $[K_4(PW_{11}O_{39})(H_2O)_{19}]^{3-2}$ | 1058.6257 | 1058.7725 |
| $[H_2(PW_{11}O_{39}Rh)(H_2O)_2]^{2-}$ | 1409.0728 | 1409.8456 |
| $[H_2(PW_{11}O_{39}Rh)(H_2O)_3]^{2-}$ | 1418.0804 | 1418.0975 |
| $[H_2(PW_{11}O_{39}Rh)(H_2O)_4]^{2-}$ | 1427.0880 | 1427.0831 |
| | | |

Table S2. ESI-MS data collected for $K-P_2W_{17}Rh$

| POM anions | Calculated m/z | Measured m/z |
|--|----------------|--------------|
| $[H_2P_2W_{17}O_{61}Rh]^{5\text{-}}$ | 853.6237 | 853.5797 |
| $[K_2P_2W_{17}O_{61}Rh]^{5-1}$ | 868.8599 | 868.5997 |
| $[H_6(P_2W_{17}O_{61})(H_2O)_3]^{4-}$ | 1055.8227 | 1055.7158 |
| $[H_3(P_2W_{17}O_{61}Rh)]^{4-}$ | 1067.2816 | 1067.4192 |
| $[H_3(P_2W_{17}O_{61}Rh)(H_2O)]^{4-}$ | 1071.7855 | 1071.6510 |
| $[K_4(P_2W_{17}O_{61}Rh)]^{3-1}$ | 1474.1653 | 1474.3519 |
| $[K_4(P_2W_{17}O_{61}Rh)(H_2O)]^{3-1}$ | 1480.1704 | 1480.1864 |



Fig. S4. (a) FT-IR spectrum of the spent K- $P_2W_{17}Rh$ catalyst. (b) HADFF-STEM image of the spent K- $P_2W_{17}Rh$ catalyst.



Fig. S5. Visual observations of the toluene-water biphasic system for hydroformylation reaction. Viewing the cell volume with a working volume of 60 mL, 1 μ mol of the catalyst, 0.6 g propene, 3 mL toluene, 3 mL H₂O, 100 °C. (a1) stirred for 0 min. (a2) 20 min. (a3) 40 min. (a4) 60 min. (a5) 80 min. b1-b5 and c1-c5 denoted the second and third cycle, respectively.^[5]



Fig. S6. (a) Rh 3d (b) W 4f and (c) O 1s XPS spectra of the K-PW₁₁Rh catalyst, (d) Rh 3d (e) W 4f and (f) O 1s XPS spectra of the K-PW₁₁Rh after treating with 4.0 MPa total pressure $(CO_2/H_2=1)$ at 100 °C for 4 h.



Fig. S7. Room-temperature solid-state ESR curves of the fresh $PW_{11}Rh$ and $P_2W_{17}Rh$ and the reduced POM with H₂. Reduced conditions: catalyst 20 mg, 2 h, 100 °C in 5% H₂ atmosphere.^[6]



Fig. S8. Photographs of WO₃ with or without catalysts at different H₂ treatment time at 25 °C. In the experimental, only a small amount of the catalysts (10mg) was mixed with *ca*. 1.0 g WO₃.



Fig. S9. D NMR of propene hydroformylation reaction. Reaction condition: 14.2 mmol propene, K-P₂W₁₇Rh 1 μ mol, 3 mL toluene and 3 mL D₂O, 2 MPa CO, 2 MPa H₂, 100 °C, 2h.



Scheme S1. Graphical representation of product distribution observed during hydroformylation of propene. Reaction condition: 14.2 mmol propene, K-P₂W₁₇Rh 1 μ mol, 3 mL toluene and 3 mL D₂O, 2 MPa CO, 2 MPa H₂, 100 °C, 2h.



Scheme S2. Proposed reaction mechanism for the hydroformylation of propene over Rh substituted POMs.



Fig. S10. GC-MS of propene hydroformylation. Reaction condition: 14.2 mmol propene, K-P₂W₁₇Rh 1 μ mol, 3 mL toluene and 3 mL H₂O, 2 MPa CO, 2 MPa H₂, 100 °C, 2h.



Fig. S11. GC-MS of propene hydroformylation. Reaction condition: 14.2 mmol propene, K-P₂W₁₇Rh 1 μ mol, 3 mL toluene and 3 mL D₂O, 2 MPa CO, 2 MPa H₂, 100 °C, 2h.



Fig. S12. ¹H NMR spectra of H_2 adsorbed in D_2O :THF = (1:9).



Fig. S13. ¹H NMR spectra of H_2 adsorbed in D_2O :THF = (2:8).



Fig. S14. ¹H NMR spectra of H_2 adsorbed in D_2O :THF = (3:7).



Fig. S15. ¹H NMR spectra of H_2 adsorbed in D_2O :THF = (4:6).



Fig. S16. GC analysis. Reaction condition: 5 mmol propene, $K-P_2W_{17}Rh$ 1 µmol, 3 mL toluene and 3 mL H₂O, 2 MPa CO, 2 MPa H₂, 100 °C, 2h.



Fig. S17. GC analysis. Reaction condition: 5 mmol 1-hexene, K-P₂W₁₇Rh 1 µmol, 3 mL toluene and 3 mL H₂O, 2 MPa CO, 2 MPa H₂, 100 °C, 4h.



Fig. S18. GC analysis. Reaction condition: 5 mmol 1-octene, K-P₂W₁₇Rh 1 μ mol, 3 mL toluene and 3 mL H₂O, 2 MPa CO, 2 MPa H₂, 120 °C, 6h.



Fig. S19. GC analysis. Reaction condition: 5 mmol styrene, K-P₂W₁₇Rh 1 μ mol, 3 mL toluene and 3 mL H₂O, 2 MPa CO, 2 MPa H₂, 100 °C, 2h.



Fig. S20. GC analysis. Reaction condition: 5 mmol 4-methylstyrene, $K-P_2W_{17}Rh$ 1 μ mol, 3 mL toluene and 3 mL H₂O, 2 MPa CO, 2 MPa H₂, 100 °C, 2h.



Fig. S21. GC analysis. Reaction condition: 5 mmol 3-methylstyrene, $K-P_2W_{17}Rh$ 1 μ mol, 3 mL toluene and 3 mL H₂O, 2 MPa CO, 2 MPa H₂, 100 °C, 2h.



Fig. S22. GC analysis. Reaction condition: 5 mmol 2-methylstyrene, $K-P_2W_{17}Rh$ 1 μ mol, 3 mL toluene and 3 mL H₂O, 2 MPa CO, 2 MPa H₂, 100 °C, 2h.



Fig. S23. GC analysis. Reaction condition: 5 mmol cyclohexene, K-P₂W₁₇Rh 1 µmol, 3 mL toluene and 3 mL H₂O, 2 MPa CO, 2 MPa H₂, 120 °C, 4h.



Fig. S24. GC-MS of Deuteration experiment. Reaction condition: 5 mmol n-butanal, K-P₂W₁₇Rh 1 μ mol, 3 mL toluene and 3 mL H₂O/D₂O, 2 MPa CO, 2 MPa H₂, 120 °C, 2h.



Fig. S25. GC-MS of 1-octene hydroformylation. Reaction condition: 5 mmol 1-octene, $K-P_2W_{17}Rh \ 1 \ \mu mol$, 3 mL toluene and 3 mL H_2O , 2 MPa CO, 2 MPa H_2 , 120 °C, 2h.



Fig. S26. GC-MS of 2-octene hydroformylation. Reaction condition: 5 mmol 2-octene, $K-P_2W_{17}Rh \ 1 \ \mu mol$, 3 mL toluene and 3 mL H_2O , 2 MPa CO, 2 MPa H_2 , 120 °C, 2h.



Fig. S27. GC-MS of styrene hydroformylation. Reaction condition: 5 mmol styrene, K- $P_2W_{17}Rh \ 1 \ \mu mol$, 3 mL toluene and 3 mL H_2O , 2 MPa CO, 2 MPa H_2 , 100 °C, 2h.



Fig. S28. GC-MS of 2-Methylstyrene hydroformylation. Reaction condition: 5 mmol 2-Methylstyrene, K-P₂W₁₇Rh 1 μ mol, 3 mL toluene and 3 mL H₂O, 2 MPa CO, 2 MPa H₂, 100 °C, 2h.



Fig. S29. GC-MS of 3-Methylstyrene hydroformylation. Reaction condition: 5 mmol 3-Methylstyrene, K-P₂W₁₇Rh 1 μ mol, 3 mL toluene and 3 mL H₂O, 2 MPa CO, 2 MPa H₂, 100 °C, 2h.



Fig. S30. GC-MS of 4-Methylstyrene hydroformylation. Reaction condition: 5 mmol 4-Methylstyrene, K-P₂W₁₇Rh 1 μ mol, 3 mL toluene and 3 mL H₂O, 2 MPa CO, 2 MPa H₂, 100 °C, 2h.

Fig. S31. GC-MS of cyclohexene hydroformylation. Reaction condition: 5 mmol cyclohexene, $K-P_2W_{17}Rh$ 1 µmol, 3 mL toluene and 3 mL H₂O, 2 MPa CO, 2 MPa H₂,

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