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Catalytic hydrogen evolution and semihydrogenation of organic compounds using silicotungstic acid as an electron-coupled-proton buffer in water-organic solvent mixtures



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ABSTRACT

 H_2 and O_2 were produced at separate times from water electrolysis by using silicotungstic acid as an electron-coupled-proton buffer. It was found that the redox property of silicotungstic acid in water could be regulate by the introduction of organic solvents (acetonitrile, DMF and ethanol). The redox wave of silicotungstic acid at ~0.02 V vs. RHE moved in the negative direction, which was good for the production of hydrogen. A high yield of hydrogen (~85%) was obtained in a water-ethanol system (V/V = 1:1), which was higher than that in water (~45%). And the introduction of ethanol didn't affect the rate of hydrogen evolution. Moreover, the semihydrogenation of organic compounds could be achieved in the present system under mild conditions. The conversion of phenylacetylene and acetophenone are 97% and 80% under optimum reaction conditions, while the selectivity of styrene and 1-phenylethanol are 80% and 82%, respectively.

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1. Introduction

Water electrolysis is an important technology for large-scale hydrogen production. Due to large-scale application of hydrogen can solve energy and environment issues at a global level, this technology has received considerable attention in the field of chemistry [1–3]. However, the separation of hydrogen and oxygen is a troublesome problem in this technology, because these gases will diffuse in electrolysis devices and can give rise to hazardous O₂/H₂ mixtures [4–7]. Cronin group has introduced a concept of electron-coupled proton buffer (ECPB) to overcome such gas crossover, which can act to decouple electrolytic H₂ and O₂ production, producing these gases at separate times [8–10]. In the reported systems, silicotungstic acid (H₄SiW₁₂O₄₀) is one attractive material as a candidate of the ECPBs for the electrolysis of water due to its high solubility and reversible redox ability in water [10]. It can accept two electrons to from a 2e-reduced species $(H_6SiW_{12}O_{40})$ in water, while water is oxidized to O₂. Then, its 2e-reduced species can directly reduce H⁺ ions, which come from the oxidation of water $(2H_2O = 4H^+ + O_2)$, into H_2 gas in the present of catalysts (such as Pt/C) without additional inputs. This may not only separate H_2 and O_2 gases, but also let the catalysts freedom from the limitation of the low work surfaces of electrodes.

In theory, one 2e-reduced silicotungstic acid can react with two H⁺ ions to produce one H₂ molecule, because the reduced silicotungstic acid cluster provides two electrons to take part in the hydrogen evolution. However, only 45–60% of the hydrogen is collected in the reported ECPB systems [10,11]. This can be ascribed to the low reducing ability of the 1e-reduced silicotungstic acid (E $(H_5SiW_{12}O_{40}/H_4SiW_{12}O_{40}) = 0.02 V vs.$ RHE, E $(H^+/H_2) = 0 V vs.$ RHE) [10,12,13]. Therefore, improving the H₂ yield *via* regulating the redox property of silicotungstic acid is a significant challenge, which will be conductive to the development of the ECPB systems for the highly efficient hydrogen evolution from water electrolysis. Previous work reported that the redox property of silicotungstic acid is different in water and DMF [14]. The redox potentials of silicotungstic acid in DMF are strikingly more negative than its redox potentials in water. It is believed that introducing organic solvents will regulate the redox property of silicotungstic acid, which can improve the H₂ yield in the ECPB systems.

Aromatic hydrocarbons and β -phenyl alcohols are important components to many industrial chemicals. These compounds can be efficiently obtained by the catalytic semihydrogenation of the corresponding alkynyl and carbonyl compounds under H₂ atmosphere [15–20]. However, this process suffers from the limitations of rigorous reaction conditions, high cost and tedious procedures,



because of the usage of the inflammable and explosive hydrogen gas. Therefore, developing a general, economic and simple route to preparation of these compounds under mild conditions is still of great interest and importance. It is noted that the reduced silicotungstic acid is an excellent ECPB for the water electrolysis and a candidate for the selective hydrogenation of nitroarenes [10,21]. However, it seems that the semihydrogenation of this compounds is not feasible due to their insolubility in water. The introduction of organic solvents can remove this obstacle, because the alkynyl and carbonyl compounds is very soluble in organic mediums. Therefore, the reduced silicotungstic acid may be a suitable hydrogen source for the semihydrogenation of organic compounds in water-organic solvent mixtures.

Herein, we used various organic solvents (acetonitrile, DMF and ethanol) to regulate the redox property of silicotungstic acid in water. The hydrogen evolution from water electrolysis were evaluated in water-organic solvent mixtures with silicotungstic acid as an ECPB. Moreover, the semihydrogenation of organic compounds (phenylacetylene and acetophenone) was investigated in the reported system under mild conditions. Our results may allow us to highlight the promising application of polyoxometallates in the highly efficient hydrogen evolution from water electrolysis and semihydrogenation of organic compounds.

2. Experimental

2.1. Electrochemical measurement

Cyclic voltammetry curves of silicotungstic acid (0.083 mol/L, Sinopharm chemical reagent Co. (SCRC)) in water-organic solvent mixtures were taken on a CHI660e workstation (CH Instruments, Inc.). The electrochemical measurements were performed in a typical three electrode cell, using glassy carbon electrode (3 mm in diameter), Pt wire and saturated Ag/AgCl electrode as working electrode, counter electrode and reference electrode, respectively. In all measurements, the saturated Ag/AgCl reference electrode was calibrated with respect to reversible hydrogen electrode (RHE).

2.2. H₂ evolution from water electrolysis

The electrochemical reduction of silicotungstic acid (H₄SiW₁₂- O_{40}) was carried out by a modified method [8–10]: 10 mmol of H₄-SiW₁₂O₄₀ (SCRC) and 60 mL of deionized water were added into one compartment of a two-compartment H-cell, and 0.9 mL H₃PO₄ (13.3 mmol, SCRC) and 60 mL of deionized water were placed into the other compartment. The compartments of the H-cells were separated by a piece of 0.18 mm-thick Nafion N-117 membrane (Alfa Aesar Co.). All electrochemical experiments were performed by using a classical two-electrode configuration (TPR6010S regulated power supply, ATTEN instruments Co.). The H₄SiW₁₂O₄₀ compartment was equipped with a large area carbon felt working electrode $(3 \times 2 \text{ cm}^2)$, and the other compartment of the cell was equipped with a platinum mesh working electrode $(1 \times 1 \text{ cm}^2)$. To fully reduce $H_4 \text{SiW}_{12} O_{40}$ to $H_6 \text{SiW}_{12} O_{40}$ by two electrons, a potential of 8.3 V was set between the working electrodes and 1931 C of charge was passed at this potential (working current: 0.1 A. working time: 5.4 h). The color of the solution changed from colorless to deep blue when the experiment ended. Prior to the experiment, the H₄SiW₁₂O₄₀ solution was bubbled with argon (60 mL/min) for 60 min, stirred vigorously and kept under an argon atmosphere throughout the experiment.

For investigating the effect of the introduction of organic solvents on the H_2 yield in the ECPB system, 10 mg of Pt/C catalyst (5 wt%, Aladdin Co.) and 2 mL of organic solvent (acetonitrile,

dimethyl formamide or ethanol) were mixed in a Schlenk flask (10 mL). After sealed with a rubber stopper, the reaction flask was vacuumed with a mechanical pump and refilled by Ar gas. Then, the deep blue $H_6SiW_{12}O_{40}$ solution (2 mL) was injected slowly into the flask with continuous stirring (600 r/min). The mixture was stirred for 10 min, and the evolving H_2 gas was measured by gas chromatography headspace analysis (GC2014C, Shimazu Co., TCD, molecular sieve 5A column, Ar carrier). The yields of hydrogen were calculated by using the following equation (assuming one mole of hydrogen occupies 24.5 L at room temperature and pressure):

 $\label{eq:Yield of hydrogen} \begin{array}{l} \mbox{(\%)} = & \frac{Production \mbox{ of } H_2(mL)}{24.5*Mole \mbox{ number of } H_4SiW_{12}O_{40}(mmol)} \\ & *100\% \end{array}$

2.3. Semihydrogenation of phenylacetylene and acetophenone

For the semihydrogenation of phenylacetylene and acetophenone, 10 mg of the catalyst (Pt/C or Pd/C, 5 wt%, Aladdin Co.), 2 mL of ethanol and a certain amount of phenylacetylene (or acetophenone, Aladdin Co.) were mixed in a Schlenk flask (10 mL). After sealed with a rubber stopper, the reaction flask was vacuumed with a mechanical pump and refilled by Ar gas. Then, the deep blue $H_6SiW_{12}O_{40}$ solution (2 mL) was injected slowly into the flask with continuous stirring (600 r/min). The mixture was



Fig. 1. (a) Cyclic voltammetry curves of silicotungstic acid and (b) H_2 yield in water-organic solvent mixtures (V/V = 1:1).

stirred for 10 min, and the products were detected by GC technique (6820, Agilent Co., FID, HP-5 capillary column, N₂ carrier). Prior to GC analysis, 4 mL of dichloromethane (A.R., SCRC) was added into the reaction solution. After shaking for 5 min and standing for 5 min, the organic phase was moved to a sample vial (10 mL), and was dehydrated by adding a certain amount of Na₂SO₄ (A.R., SCRC). Then, 2 μ L of the sample was injected for GC analysis.

3. Results and discussion

The redox property of silicotungstic acid in water-organic solvent mixtures (V/V = 1:1) has been investigated by cyclic voltammetry. As shown in Fig. 1a, the introduction of organic solvents (acetonitrile, DMF and ethanol) can regulate the redox property of silicotungstic acid in water. The redox wave of silicotungstic acid (H₅SiW₁₂O₄₀/H₄SiW₁₂O₄₀) at ~0.02 V vs. RHE moves in the negative direction, which will be good for the reaction between the reduced silicotungstic acid and H⁺ ions to produce hydrogen in the presence of the catalyst. Fig. 1b shows the H₂ yield in various water-organic solvent systems in the present of the Pt/C catalyst and H₆SiW₁₂O₄₀. It is found that the introduction of organic solvents can improve the H₂ yield in present systems may be attributed to their own dielectric constants [14]. A high yield of hydrogen (6.95 mL, ~ 85%) can be obtained in a water-ethanol sys-



Fig. 2. (a) H₂ yield and (b) cyclic voltammetry curves of silicotungstic acid in the water-ethanol system with different volume ratios.

tem, corresponding a Faradaic efficiency of 85% for the hydrogen evolution, which is higher than the yield of hydrogen in water (3.62 mL, ~ 45%). Because of the equilibrium between hydrogen gas and H₄SiW₁₂O₄₀ [10], the yield of hydrogen is less than 100% in the present system. Control experiments further indicate that the production of H₂ is negligible in the absence of the Pt/C catalyst or H₆SiW₁₂O₄₀. These results confirm the catalyst and reduced silicotungstic acid are indispensable for the hydrogen evolution in water-organic solvent systems.

Moreover, the effect of the contents of the organic solvents on the H₂ yield has been investigated in this work. The H₂ yield in the water-ethanol system with different volume ratios are shown in Fig. 2a. The results reveal that the H₂ yield increases with the increase of the content of ethanol in the present system. When the content of ethanol over 50%, the H₂ yield has no significant increase, indicating the optimal content of ethanol is 50%. The voltammetry curves of silicotungstic acid in the water-ethanol system with different volume ratios have also been obtained (see Fig. 2b). It is found that the redox wave of silicotungstic acid moves in the negative direction with the increase of the content of ethanol. The results reveal that silicotungstic acid possess strong reducing ability at a high ethanol content. This may explain the high H₂ yield in the water-ethanol system (V/V = 1:1) in the present of the Pt/C catalyst and H₆SiW₁₂O₄₀.



Fig. 3. (a) A typical apparatus configuration for determining volumes of H_2 and (b) the production of H_2 as a function of the reaction time. The inset is the color of the solution after the reaction.

Note that the reaction rate, as the yield, is an important factor in the large-scale hydrogen production from water electrolysis. In order to measure the rate of hydrogen evolution in the waterethanol system, 50 mg of the Pt/C catalyst was dispersed in 10 mL of deionized water (or ethanol) in a 50 mL three-necked, round-bottomed flask. After thoroughly flushed with argon, 10 mL of the freshly produced $H_6SiW_{12}O_{40}$ was added to the sample aqueous dispersion under Ar atmosphere and stirred vigorously *via* a pressure-equalizing dropping funnel. The evolving H₂ gas was captured in a 50 mL measuring cylinder filled with water (see Fig. 3a). Fig. 3b shows the production of H_2 as a function of the reaction time. The initial rate of the H_2 evolution is $\sim 0.8 \text{ mL s}^{-1}$, giving a rate of 47 mmol of H₂ per hour per mg of Pt catalyst, which confirms the highly efficient hydrogen evolution from water electrolysis in the present ECPB system. It is found that there is no obvious change for the rate of hydrogen evolution in the waterethanol system. Furthermore, as shown in the inset in Fig. 3b. the color of the solution is deep blue after the reaction in the water system. But the color of the solution can change into light brown by introducing ethanol, indicating more reduced silicotungstic acid take part in the hydrogen evolution. These results reveal that the introduction of ethanol can enhance the reduce ability of silicotungstic acid to improve the production of H₂, but do not affect the rate of hydrogen evolution in the present system.

Due to the low boiling point for ethanol, the Pt/C catalyst and silicotungstic acid can be easily recycled by centrifugation and drying. Fig. 4a and b shows FT-IR spectra and X-ray diffraction (XRD) patterns of silicotungstic acid before and after the reaction. It is found that the crystal structure of silicotungstic acid is intact after the hydrogen evolution. Transmission electron microscope (TEM) images indicate that the morphology of the Pt/C catalyst has no significant change. And the Pt⁴⁺ concentrations measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) are 4.0 and 4.1 ppm before and after the reaction, respectively. Furthermore, the yield of hydrogen remains above 80% in the 3th cycle of testing by using recycled $H_4SiW_{12}O_{40}$ and Pt/C catalyst. These suggest that the ECPB ($H_4SiW_{12}O_{40}$) and catalyst (Pt/C) exhibit high stability for the hydrogen evolution in the waterethanol system.

As mentioned above, the semihydrogenation of organic compounds is usually achieved under H₂ atmosphere [15–20]. However, this process suffers from the limitation of rigorous reaction conditions, because of the usage of the inflammable and explosive hydrogen gas. In this work, the semihydrogenation of organic compounds (phenylacetylene and acetophenone) has been evaluated under mild conditions, which the reduced silicotungstic acid is used as a hydrogen source. As shown in Table 1, phenylacetylene can be efficiently hydrogenated to styrene in the presence of the reduced silicotungstic acid and Pt/C as the hydrogen source and catalyst, respectively. Satisfying selectivity of styrene can be obtained at high levels of phenylacetylene. It is found that the selectivity of styrene is \sim 80% at a high conversion (\sim 97%) for the semihydrogenation of phenylacetylene (see Table 1, entry 2). Furthermore, acetophenone can be reduce to 1-phenylethanol, while the reduced silicotungstic acid and Pd/C as the hydrogen source and catalyst, respectively. The conversion of acetophenone and



Fig. 4. (a) FT-IR spectra, (b) XRD patterns of silicotungstic acid and (c, d) TEM images of the Pt/C catalyst before and after the reaction.

Table 1

Entry

2

3

4

5 6

Catalytic hydrogenation of phenylacetylene in water-ethanol mixture^a.

0.270

0 0 9 0

0.090

	$\frac{H_{6}SiW_{12}O_{40}}{EtOH/H_{2}O},$	Ar, RT + B	c
Catalyst	Reactant (A, mmol)	Conversion (A, %)	Selectivity (B, %)
Pt/C	0.090	100	28
Pt/C	0.135	97	82
Pt/C	0.180	81	85

^a Conditions: 2e-reduced silicotungstic acid (H₆SiW₁₂O₄₀), 0.33 mmol; catalyst, 10 mg; water-ethanol mixture (V_{water}: V_{ethanol} = 1:1), 4 mL; reaction time, 10 min. ^b Water 4 mL

58

0

0

Table 2

Catalytic hydrogenation of acetophenone in water-ethanol mixture^c.

Pt/C

Pt/C



Entry	Catalyst	Reactant (D, mmol)	Conversion (D, %)	Selectivity (E, %)	Selectivity (F, %)
1	Pd/C	0.085	92	54	46
2	Pd/C	0.170	80	82	18
3	Pd/C	0.255	57	90	10
4	Pd/C	0.340	42	93	7
5	Pt/C	0.170	0	-	_
6	-	0.170	0	-	
7	Pd/C ^d	0.170	0	-	-

^c Conditions: 2e-reduced silicotungstic acid (H₆SiW₁₂O₄₀), 0.33 mmol; catalyst, 10 mg; water-ethanol mixture (V_{water}: V_{ethanol} = 1:1), 4 mL; reaction time, 10 min. ^d Water, 4 mL.

selectivity of 1-phenylethanol are 80% and 82% under optimum reaction conditions. Together the amounts of hydrogen (\sim 2.4 mL) evolved from these systems, the Faradaic efficiencies for these semihydrogenation reactions are \sim 80%. Note that the conversions of phenylacetylene and acetophenone are negligible in water (see Table 1, entry 6 and Table 2, entry 7), even if the reduced silicotungstic acid and catalyst (Pt/C or Pd/C) are used as the hydrogen source and catalyst, respectively. These results indicate that, the introduction of organic solvents not only can improve the H₂ yield in present system, but also can help to develop the promising application of polyoxometallates in the semihydrogenation of organic compounds under mild conditions.

4. Conclusions

The introduction of organic solvents (acetonitrile, DMF and ethanol) can regulate the redox property of silicotungstic acid in water. The redox wave of silicotungstic acid at ~0.02 V vs. RHE moves in the negative direction. This change is good for the reaction between the reduced silicotungstic acid and H⁺ ions to produce hydrogen in the presence of the Pt/C catalyst. A high yield of hydrogen (~85%) is obtained in a water-ethanol system (V/ V = 1:1), which is higher than the yield of hydrogen in water (~45%). Further experiments reveal that the introduction of ethanol can enhance the reduce ability of silicotungstic acid to improve the production of H₂, but do not affect the rate of hydrogen evolu-

tion. And the catalyst (Pt/C) and ECPB (H₄SiW₁₂O₄₀) exhibit high stability for the hydrogen evolution in the present system. Moreover, the semihydrogenation of organic compounds can be achieved in the water-organic solvent system under mild conditions in the presence of the reduced silicotungstic acid as a hydrogen source. The conversion of phenylacetylene and acetophenone are 97% and 80% under optimum reaction conditions, while the selectivity of styrene and 1-phenylethanol are 80% and 82%, respectively. Our results may allow us to highlight the promising application of polyoxometallates in the highly efficient hydrogen evolution from water electrolysis and semihydrogenation of organic compounds.

87

Selectivity (C, %)

72

18

15

13

Declaration of Competing Interest

None.

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