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Heteropoly Acid-Based Materials for Reversible H_2 Storage as Protons and Electrons under Mild Conditions

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S Supporting Information

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Hydrogen (H_2) is one of the most promising energy carriers and offers significant advantages, including reduction of carbon dioxide emissions at the end use and security of the global energy supply.[1] The key to realize hydrogen-based energy systems is a development of reliable materials and procedures for H_2 production, separation (sieving), storage, and sensing. Especially, much attention has been paid to the development of efficient H_2 storage materials and procedures. Among them, solid materials such as adsorbents and hydride-based materials, which can store H_2 physically (as H_2) or chemically (as hydride, H^-), has extensively been studied.[2,3]

Polyoxometallates are a large family of well-defined anionic metal−oxygen clusters of early transition metals and stimulated many current research activities in broad fields of science.[4] Polyoxometallates are thermally and oxidatively stable and have the following interesting redox properties: (i) abilities of reversible stepwise, multielectron redox reactions with retention of their structures and (ii) controllabilities of their redox potentials by choosing constituent elements.[5,6] In addition, heteropoly acids (HPAs, acid forms of polyoxometallates) including fully oxidized as well as reduced forms are intrinsically stable[7] and show excellent proton conductivities.[8] From the above-mentioned unique properties, we came up with an idea that HPAs can reversibly store H_2 as protons (H^+) and electrons (e^-). It is likely that the H_2 storage procedure with HPAs has the following significant advantages: (i) no need for harsh conditions for H_2 storage due to Coulombic interaction between H^+ and heteropolyanions, and (ii) high durability due to the stabilities of HPAs and the smaller ionic radius of H^+, in comparison with H_2, H^-, and the hydrogen atom.

Tungsten oxide (WO_3) reacts with H_2 above 673 K to form tungsten bronze. This reaction readily proceeds, even at room temperature, in the presence of noble-metal catalysts such as Pt and Pd.[9] In this case, H_2 is sorbed in the WO_3 bulk as H^+ and e^-.[10] Recent mechanistic investigations by the groups of Georg[11] and Nakagawa[12] show that a certain amount of H_2 sorbed in WO_3 reacts with the lattice oxygen and/or O_2, resulting in the undesirable formation of H_2O. It has been reported that HPAs reacts with H_2 at temperatures of >520 K. Under such conditions, almost all H^+ formed from H_2 readily react with the lattice oxygen of HPAs to form H_2O.[13] Although it has been reported that molybdate-based HPAs can sorb H_2 (ca. 1.0 mol mol^{-1}) under mild conditions in the presence of Pd/C (Pd on activated carbon), H_2 cannot be released, because of the high stability of reduced heteropolymolybdates (see below).[14] As far as we know, materials that can reversibly store H_2 as H^+ and e^- under mild conditions have never been reported so far.[15]

Herein, we proposed a concept, for the first time, that H_2 is reversibly stored as H^+ and e^-, using very simple heteropoly acid-based materials (in particular, a composite of Pt and $H_4SiW_{12}O_{40}$ (Pt/SiW)).

First, H_2 storage properties of various composites of metal nanoparticles (e.g., Pt, Pd, Ir, Ru, Rh, and Au) and SiW were investigated. Composites with a metal:HPA molar ratio of 1:20 were typically used for H_2 storage experiments (unless otherwise noted). Composites of metal nanoparticles and SiW could store H_2 under ambient conditions (P_{H_2} = 40 kPa, T = 308 K; see the Experimental Section given in the Supporting Information), while no H_2 was stored in the presence of SiW alone under the present conditions. The H_2 storage rates (R) increased in the order of Au/SiW < Ru/SiW < Pd/SiW < Rh/SiW < Ir/SiW < Pt/SiW, in accord with that of dissociative chemisorption energies of H_2 on the corresponding metals.[16] The Pt/SiW composite showed the largest R for H_2 storage. The amounts of H_2 stored (M) in Pt/SiW and Pd/SiW were 0.46 and 0.41 mol mol^{-1}, respectively, and almost the same as each other. In addition, values R (0.079−0.091 mol mol^{-1} min^{-1}) and M (0.41−0.46 mol mol^{-1}) in Pt/SiW were almost independent of the Pt content in the Pt:SiW molar ratio range of 1:10−1:60 (see Figure S1 in the Supporting Information).[17]

Mass spectroscopy (MS) analysis confirmed that H_2 stored in Pt/SiW could be released as H_2 (not as H_2O) at 308 K when the H_2-stored sample (Pt/SiW−H_2) was simply evacuated or exposed to N_2. The amount of H_2 released was 0.46 ± 0.03 mol mol^{-1} and equal to that of H_2 stored in Pt/SiW (0.46 mol mol^{-1}).[18] This is likely due to the redox potential of the first one-electron reaction of SiW located at ∼0 V (0.041 V vs NHE).[5,7] The H_2 storage−release cycle could be repeated at least six times without an appreciable loss of its performance (see Figure 1a). The XRD patterns of Pt/SiW−H_2 and Pt/SiW−H_2 after H_2 release were almost the same as that of Pt/SiW (see Figure S2a in the Supporting Information), showing that the phase and the lattice constant of Pt/SiW did not change and that large Pt particles were not formed during the cycle.

Next, the effects of HPAs on the H_2 storage−release properties were investigated using composites of Pt and different HPAs

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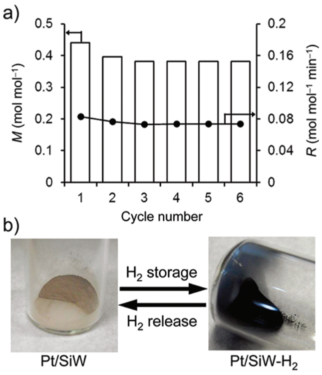

Figure 1. (a) Repeated H_2 storage−release performance of Pt/SiW and (b) pictures of Pt/SiW and H_2 stored Pt/SiW (Pt/SiW−H_2). H_2 storage conditions: Pt/SiW (Pt:SiW molar ratio of 1:20), P_{H_2} = 40 kPa, 308 K. H_2 release conditions: 308 K for 2 h under vacuum. (See the Supporting Information for details.)

(e.g., SiW, $H_3PW_{12}O_{40}$ (PW), $H_4SiMo_{12}O_{40}$ (SiMo), and $H_3PMo_{12}O_{40}$ (PMo)). The M values increased in the order of Pt/SiW (0.46 mol mol^{-1}) < Pt/PW (0.72 mol mol^{-1}) < Pt/SiMo (5.8 mol mol^{-1}) and Pt/PMo (5.8 mol mol^{-1}), in accord with that of the first redox potentials of HPAs in aqueous solutions (0.041 V for SiW, 0.221 V for PW, 0.516 V for SiMo, and 0.558 V for PMo).[5,19] Molybdate-based composites Pt/PMo and Pt/SiMo sorbed large amounts of H_2 (5.8 mol mol^{-1} for both cases) during the reduction of H_2PtCl_6 with H_2 (during the preparation of composites; see the Experimental Section). However, it was confirmed by MS analysis that no H_2 could be released from the H_2-sorbed composite (Pt/PMo−H_2) at 308 K, because of the high stability of reduced heteropolymolybdates.[4] When Pt/PMo−H_2 was heated to 473 K, not only H_2 but also H_2O were released from Pt/PMo−H_2. The amounts of H_2 and H_2O were 1.7 ± 0.1 and 3.8 ± 0.2 mol mol^{-1}, respectively, showing that H_2 sorbed in molybdate-based composites is mainly released as H_2O at elevated temperatures, as has been previously reported.[13,14]

Upon exposure of Pt/SiW to H_2 (P_{H_2} = 40 kPa, T = 308 K), the color of Pt/SiW changed from light gray to dark blue (see Figure 1b), and the absorption band assignable to the intervalence charge transfer between W^{5+} and W^{6+} appeared (see Figure S2b in the Supporting Information). Upon exposure of the sample (Pt/SiW−H_2) to N_2, the dark blue color of Pt/SiW−H_2 changed to the original light gray color of Pt/SiW, with the release of H_2, and the intervalence charge transfer band disappeared (see Figure S2b). In addition, the UV/vis spectrum of Pt/SiW−H_2 was quite similar to that of the one-electron reduced SiW ($H_5SiW_{12}O_{40}$). The infrared (IR) spectrum of Pt/SiW−H_2 showed that the Keggin-type structure was retained after the H_2 storage, and that the intensities of the band at 3106 cm^{-1}, assignable to the stretching vibration of the hydrogen bond $O\cdots H^+\cdots O$ between the neighboring Keggin units,[20] was increased (see Figure S2c in the Supporting Information). The integrated area of the band increased from 1.0 to 1.2, and the increase corresponds to that estimated from the H_2 storage experiments (from 1.0 to 1.2). The bands at ~1500−1700 cm^{-1}, assignable to the bending vibrations of H_2O and protonated clusters such as H_3O^+ and $H_5O_2^+$, were not observed for Pt/SiW−H_2. In addition, the IR spectrum of Pt/SiW−H_2 was quite similar to that of $H_5SiW_{12}O_{40}$. All these results suggest that all of the H_2 is stored as H^+ and e^- in the SiW bulk without the formation of H_2O.

It is likely that H_2 storage in Pt/SiW proceeds through the following two steps: (i) dissociation of H_2 on Pt and (ii) diffusion of H^+ and e^- in the SiW bulk. As previously mentioned, the rate of H_2 storage in Pt/SiW (R) was independent of Pt contents (see Figure S1), suggesting that the dissociation of H_2 on Pt is not the rate-determining step.[17] Therefore, the H_2 storage profiles can be adequately reproduced by the Fickian diffusion equation (eq 1):[21]

$$\partial C/\partial t = D\left(\left(\partial^2 C/\partial r^2\right) + (2/r)(\partial C/\partial r)\right) \tag{1}$$

where C, r, and D are the concentration of H^+ and/or e^- in the bulk, the radial coordinate, and the diffusion coefficient of H^+ and/or e^-, respectively. Supposing that the surface concentration of H^+ and/or e^- is constant, the solution for eq 1 is given by eq 2:

$$\frac{M_t}{M_{\mathrm{rev}}} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left[\left(-\frac{Dn^2\pi^2}{a^2}\right)t\right] \tag{2}$$

where M_t is the amount of H_2 stored in SiW at time t, M_{rev} the maximum amount of H_2 reversibly stored (at 308 K), and a the average particle radius of SiW. The average particle radius was estimated from the surface area calculated using N_2 adsorption data (4.0 m^2 g^{-1}) and the density of the particle (5.5 g cm^{-3}) to be 1.4 × 10^{-5} cm. The best fits for the experimental profile for H_2 storage was obtained using D = 2.9 × 10^{-13} cm^2 s^{-1} (see Figure S3 in the Supporting Information). This value of D was 1 order of magnitude larger than that of the sorption of polar molecules such as methanol, ethanol, and 1,4-dioxane into the solid bulk of nonporous PW (10^{-14} cm^2 s^{-1}).[22] Time courses of the relative amounts of H_2 stored (M_t/M_{rev}) in Pt/SiW were independent of P_{H_2} (in the range of 10−80 kPa) (see Figure S4 in the Supporting Information), suggesting that diffusion of H^+ and/or e^- in the bulk is the rate-determining step. It has been reported by Klemperer and co-workers that (i) the redox behavior of SiW in the solid state is analogous to that in aqueous solutions, where reversible redox reactions of SiW (single crystals of $H_4SiW_{12}O_{40}\cdot 31H_2O$) in the solid form can take place (e.g., stepwise two one-electron redox reactions at −0.030 and −0.18 V vs NHE) and (ii) the potentials were almost the same as those for aqueous SiW solutions (at 0.041 and −0.16 V vs NHE).[7] Therefore, it is possible that SiW in the solid state undergoes two reversible one-electron reductions as in the solution state. Thus, the present H_2 storage reaction in Pt/SiW is expressed by eqs 3−6:

$$H_2 \rightleftharpoons 2H \tag{3}$$

$$H \rightleftharpoons H^+ + e^- \tag{4}$$

$$\mathrm{SiW} + H^+ + e^- \rightleftharpoons \mathrm{HSiW} \tag{5}$$

$$\mathrm{HSiW} + H^+ + e^- \rightleftharpoons \mathrm{H_2SiW} \tag{6}$$

where HSiW and H_2SiW are one- ($H_5SiW_{12}O_{40}$) and two-electron ($H_6SiW_{12}O_{40}$) reduced silicotungstates, respectively. The Langmuir isotherm for dissociative adsorption is given by eq 7,

$$C_{\mathrm{H}} = C_{\mathrm{H,sat}}\left(K_1 P_{\mathrm{H_2}}\right)^{1/2}\Big/\left[1 + \left(K_1 P_{\mathrm{H_2}}\right)^{1/2}\right] \tag{7}$$

where C_{H} is the concentration of the surface hydrogen atom on Pt, $C_{\mathrm{H,sat}}$ the saturated concentration of the surface hydrogen atom on Pt,

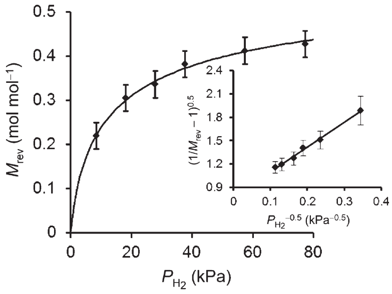

Figure 2. Dependence of the maximum amount of H_2 reversibly stored in Pt/SiW (M_{rev}) on P_{H_2}. Symbols and solid lines indicate the experimental and calculated data, respectively. The calculation was carried out with $K_1 = 0.059$ kPa^{-1} and $K_2{}^2K_3K_4C_{H,sat}{}^2 = 1.7$ cm^6 mol^{-2}. Inset shows plots of $(1/M_{rev} - 1)^{0.5}$ vs $P_{H_2}{}^{-0.5}$.

and K_1 the equilibrium constant for dissociative adsorption. From eqs 3−7, M_{rev} can be expressed by eq 8:[23]

$$M_{rev} = \frac{K_1K_2{}^2K_3K_4C_{H,\,sat}{}^2P_{H_2}}{(1 + \sqrt{K_1P_{H_2}})^2 + K_1K_2{}^2K_3K_4C_{H,\,sat}{}^2P_{H_2}} \tag{8}$$

where K_2, K_3, and K_4 are the equilibrium constants for eqs 4, 5, and 6, respectively. Experimental data for the dependence of M_{rev} on P_{H_2} could be well-reproduced with eq 8 (see Figure 2). From the plots of $(1/M_{rev} - 1)^{0.5}$ vs $P_{H_2}{}^{-0.5}$, K_1 and $(K_2{}^2K_3K_4C_{H,sat}{}^2)$ were estimated to be 0.059 kPa^{-1} and 1.7 cm^6 mol^{-2}, respectively (see Figure 2, inset).

The experimental profiles for H_2 storage at different P_{H_2} values (in the range of 10−80 kPa) could be well-reproduced using eqs 2 and 8 (see Figure S5 in the Supporting Information), supporting the above-mentioned mechanism that the H_2 storage proceeds through the dissociation of H_2, followed by the diffusion of H^+ and e^- in the SiW bulk.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) When the H_2 storage experiment was carried out using Pt/SiW with the Pt:SiW molar ratio of 1:100, the values R (0.060 mol mol^{-1} min^{-1}) and M (0.37 mol mol^{-1}) decreased.

(18) The mass of H_2 (wt %) stored in Pt/SiW was compared with those of typical H_2 storage materials (or procedures) (see Table S1 in the Supporting Information). Although the mass of H_2 stored in Pt/SiW is small and should be increased for practical utilization, the concept and the present findings will be applied to the development of not only storage materials but also separation and sensing materials in the future.

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