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## COMMUNICATION

## Metal-free catalytic hydrogen production from a polymethylhydrosilane-water mixture†

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**Hydrogen gas is the most promising carbon-free energy carrier although its on-demand generation remains a formidable challenge. One of the potential pathways for generating hydrogen is through hydrolytic oxidation of organosilanes. Here, we demonstrate that the hydroxide ion  $\text{OH}^-$  serves as a potent room-temperature metal-free catalyst in the hydrolytic oxidation of polymethylhydrosilane, PMHS to hydrogen gas and the corresponding silanol with turnover number and turnover frequency in excess of 200 and  $8 \text{ min}^{-1}$  respectively. Kinetic studies suggest the hydrogen generation rate is first order with respect to PMHS and  $\text{OH}^-$  but zero order with respect to water. The first step of the reaction, where the Si center of PMHS is attacked by the  $\text{OH}^-$  ion, is believed to be the rate-determining step.**

In light of diminishing fossil fuel resources, hydrogen is viewed as a promising energy carrier. In this regard, one of the most explored storage methods is in the form of energy-rich compounds<sup>1-3</sup>. Organosilanes, which contain the Si-H functional group, undergoes hydrolytic oxidation to produce hydrogen and organosilanols can be considered as half of water splitting. Although the Si-H bond is relatively weak, the oxidation process is kinetically slow<sup>4</sup>, and this has led to the development of homogeneous catalysts based on expensive metals such as rhodium<sup>5</sup>, iridium<sup>6</sup>, rhenium<sup>7</sup>, and ruthenium<sup>8</sup>. Other reported metal catalysts include zinc<sup>9</sup> and iron<sup>10</sup> and although these metals are considered inexpensive, the silane hydrolysis process has to be carried out under oxygen-free conditions. Recently we have also found silver nitrate ( $\text{AgNO}_3$ ) to be very effective in catalysing the hydrolytic oxidation of trialkylsilanes.<sup>11</sup> However, for sustainable and economic-viable applications, the ideal catalyst has to be low-cost and readily available, while exhibiting high catalytic performance in terms of the turnover number (TON) and frequency (TOF). In addition, using a low-cost silane as the reactant in this process would be very desirable for scalability.

Herein, we wish to report the use of the hydroxide ion  $\text{OH}^-$  as a very effective catalyst for the hydrolytic oxidation of polymethylhydrosilane (PMHS) to produce hydrogen gas. PMHS [ $-\text{O}-(\text{CH}_3)\text{Si}(\text{H})-\text{O}]_n$  is a waste product of the silicone industry<sup>12</sup> and

therefore available very cheaply<sup>13</sup>. From the mechanistic point of view, the oxidation process catalysed by  $\text{OH}^-$  is also different, as we have found that it is more effective for silane with electron-withdrawing groups. In contrast, most reported metal complexes catalysed the oxidation of trialkylsilanes much more effectively. We hope that this work could open new frontiers in developing cost-effective and highly efficient hydrogen on-demand generation strategies.

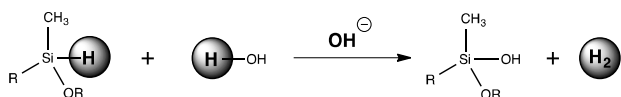
In a typical experiment, a tetrahydrofuran (THF) solution containing PMHS and water in different mole ratios was first prepared (see Table 1). Effervescence was observed when a catalytic amount of sodium hydroxide NaOH was added into the mixture. The strong evolution of gas was also seen as long as any  $\text{OH}^-$  source such as KOH or  $\text{NH}_4\text{OH}$  was used, thus lending strong support to the  $\text{OH}^-$  ion itself as the catalyst. The oxidation can also be carried out in air without any loss of activity. The choice of the solvent, in this case, tetrahydrofuran, is important to enhance miscibility of PMHS, water and the  $\text{OH}^-$  ion. Without the solvent, the catalysis slowed down considerably within the PMHS-water two-phase system.

The catalytic system has been found to be easily scalable. Although PMHS has been restricted to millimole amount for laboratory-scale experiments, the setup can be scaled up considerably to molar quantity without loss of activity. The ease of scalability enables the process to be adapted even for larger scale use at a low cost as no precious metals are involved in the process. Next, we investigated the effect of  $\text{OH}^-$  catalytic loading. Under our experimental conditions, a loading of 0.5% of  $\text{OH}^-$  was still able to generate the full volume of hydrogen gas within a short period, thus leading to a TON of at least 200 and TOF of  $8 \text{ min}^{-1}$ , with respect to  $\text{OH}^-$  concentration. We note that effervescence can still be observed albeit at a slower rate, even with catalytic loading down to 0.1%. Further control experiments have been carried out where the removal of either PMHS or water will shut down hydrogen gas production. The addition of a small quantity of dilute acid such as HCl, which neutralizes the  $\text{OH}^-$ , will also deter the catalysis considerably.

Mass spectrometric analysis of the headspace of the reaction vessel containing PMHS,  $\text{H}_2\text{O}$ , and  $\text{OH}^-$  revealed an intense signal at  $m/z$  2 ( $\text{H}_2$ ). When  $\text{H}_2\text{O}$  was replaced by  $\text{D}_2\text{O}$ , this signal diminished while an equally intense signal at  $m/z$  3 (HD)

was observed. As with previous studies, the mass spectral signals show that hydrogen was formed from both PMHS and water supplying one H atom each.<sup>8,11</sup> An insoluble gel was observed after solvent removal. Upon <sup>1</sup>H NMR analysis, the gel has been determined to be the expected silanol product [ $-\text{O}-(\text{CH}_3)_2\text{Si}(\text{OH})-\text{O}-$ ]<sub>n</sub> with a Si-OH signal at 2.357 ppm while the Si-H signal at 4.714 ppm of PMHS disappeared completely.

**Table 1** Hydrolytic oxidation of PMHS catalyzed by potassium hydroxide.<sup>a</sup>



Entry	Silane	Solvent	Catalytic Loading (%)	Time (min)	H <sub>2</sub> Yield (%) <sup>b</sup>
1	-	THF	1.00	30	0
2	PMHS	-	1.00	30	0
3	PMHS	THF	-	30	0
4	PMHS	THF	2.00	10	>99
5	PMHS	THF	1.00	15	>99
6	PMHS	THF	0.50	25	>99
7	PMHS	THF	0.20	45	42
8	PMHS	THF	0.10	60	27
9	PMHS	Hexane	1.00	30	0
10	PMHS	CHCl <sub>3</sub>	1.00	30	0

<sup>a</sup> Catalytic runs involved 1 mmol of PMHS and 30 mmol of H<sub>2</sub>O at 298 K. <sup>b</sup> Total H<sub>2</sub> yields derived from downward displacement collection of gas.

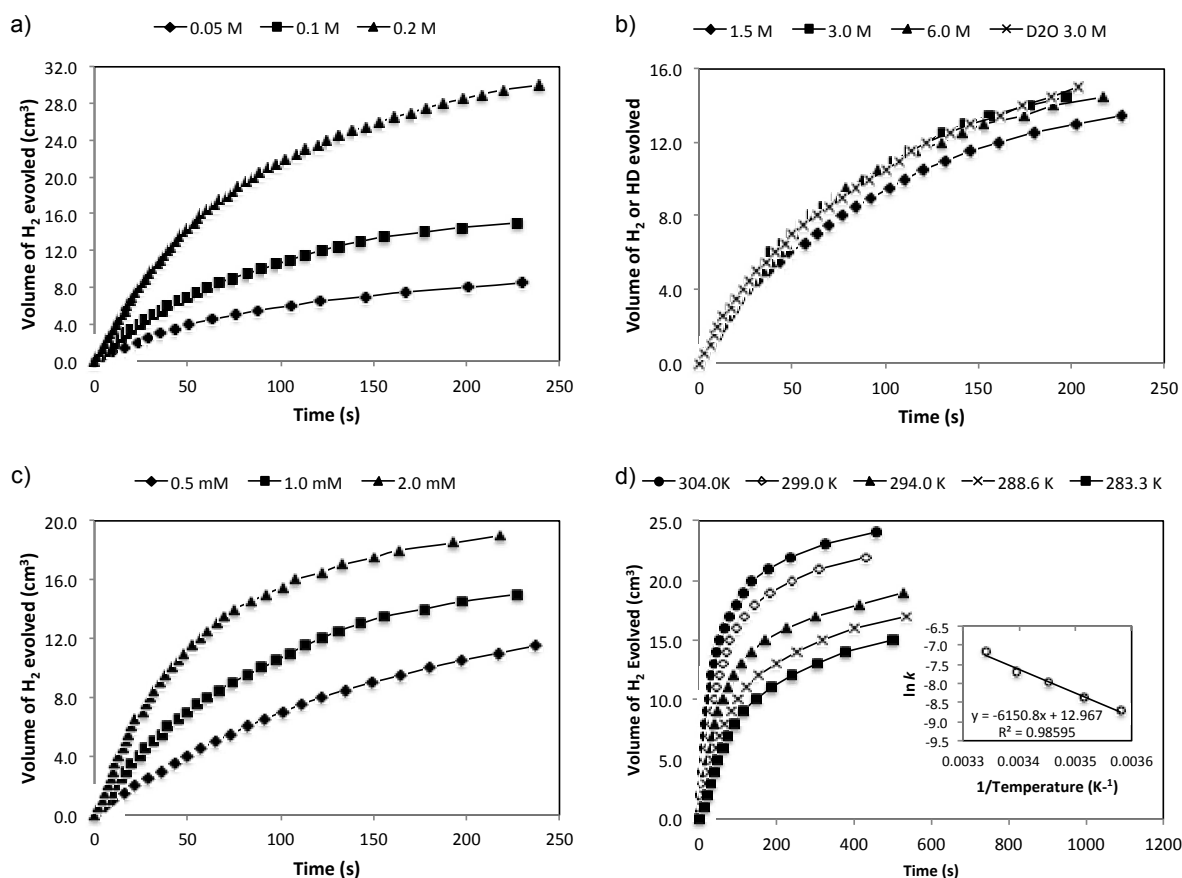
The scope of the catalysis was investigated by varying the silane and catalyst (see Table 2). Contrary to previous studies using metal-centered catalysts, trialkylsilanes reacted sluggishly while phenylsilanes showed better conversion to the silanol counterparts in the presence of OH<sup>-</sup>. PMHS remains the most effective silane with its hydrogen generation rate even higher than that of diphenylsilane. The presence of electron-donating alkyl groups on the silanes appears to be detrimental to the catalytic efficiency, while having electron-withdrawing phenyl or the O-Si group on PMHS promotes the catalysis. In particular, as tabulated in Table 2, the use of dimethylphenylsilane (entry 4) rather than triethylsilane (entry 3) as the substrate altered the catalytic efficiency significantly. However triphenylsilane (entry 5) is a poorer substrate compare to diphenylsilane (entry 6) which suggests that steric effects also play a role in this catalytic process. It comes as a surprise that the PMHS oligomer serves as an excellent substrate despite its size; presumably the effect of the O-Si group must have exerted a large influence on the reaction kinetics.

**Table 2** Product details for the hydrolysis of PMHS and various organosilanes catalyzed by potassium hydroxide ion.<sup>a</sup>

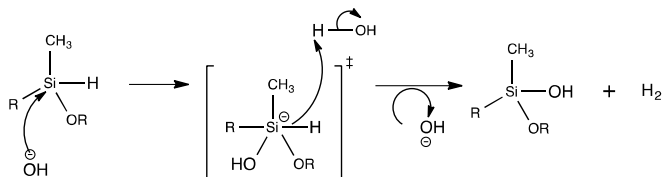
Entry	Silane	Time (min)	H <sub>2</sub> Yield (%) <sup>b</sup>
1	PMHS	15	>99
2	<i>i</i> -Pr <sub>3</sub> SiH	30	0
3	Et <sub>3</sub> SiH	30	0
4	PhMe <sub>2</sub> SiH	30	20
5	Ph <sub>3</sub> SiH	30	42
6	Ph <sub>2</sub> SiH <sub>2</sub>	30	75

<sup>a</sup> Catalytic runs involved 1 mmol of organosilanes and 30 mmol of deionized H<sub>2</sub>O with 5.0% catalytic loading at 298K. <sup>b</sup> Total H<sub>2</sub> yields derived from downward displacement collection of gas.

To obtain more insight into the reaction pathway for the hydrolytic oxidation of PMHS, kinetic studies have been performed by determining the initial rate of hydrogen evolution through the displacement of water from an inverted measuring cylinder. The rate of hydrogen generation was found to be first order with respect to the PMHS concentration. The successive doubling of the PMHS concentration increases the initial rates from  $0.08 \pm 0.002 \text{ cm}^3 \text{ s}^{-1}$  to  $0.17 \pm 0.003 \text{ cm}^3 \text{ s}^{-1}$  and  $0.34 \pm 0.01 \text{ cm}^3 \text{ s}^{-1}$  respectively (Figure 1a), while keeping the water and catalyst concentrations constant. Similarly, doubling the OH<sup>-</sup> concentration also doubled the initial reaction rate which suggests that the reaction rate is also first order with respect to the OH<sup>-</sup> concentration. In contrast, changes in the concentration of water produce very little change in the initial rate and hence the reaction rate appears to be independent of water. A similar conclusion was drawn when the substitution of H<sub>2</sub>O with D<sub>2</sub>O as the reactant also did not alter the reaction rate; primary kinetic isotope effect was not observable under our experimental conditions. We have also investigated how the rate changes with respect to temperature so that the activation parameters could be obtained. By conducting the catalysis over a temperature range of 283–305 K, these thermodynamic activation parameters,  $\Delta H^\ddagger = 54 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -165 \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $\Delta G^\ddagger (298 \text{ K}) = 103 \text{ kJ mol}^{-1}$  have been determined using the Eyring equations for the catalytic hydrolytic oxidation of PMHS.



**Figure 1** The effect of (a) PMHS, (b) water, (c) catalyst, and (d) temperature, on the rate of hydrogen gas evolution through hydrolysis of PMHS catalysed by potassium hydroxide. Conditions: (a)  $c(\text{H}_2\text{O}) = 3.0 \text{ M}$  and  $c(\text{KOH}) = 1.0 \text{ mM}$ ; (b)  $c(\text{PMHS}) = 0.1 \text{ M}$  and  $c(\text{KOH}) = 1.0 \text{ mM}$ ; (c)  $c(\text{PMHS}) = 0.1 \text{ M}$  and  $c(\text{H}_2\text{O}) = 3 \text{ M}$ ; (d)  $c(\text{PMHS}) = 0.25 \text{ M}$ ,  $c(\text{H}_2\text{O}) = 7.5 \text{ M}$ , and  $c(\text{catalyst}) = 2.5 \text{ mM}$ .



**Figure 2** Proposed pathway for the  $\text{OH}^-$ -catalysed generation of  $\text{H}_2$  from PMHS and  $\text{H}_2\text{O}$ .

A reaction pathway consistent with the experimental results is proposed in Figure 2. The first step involves the hydroxide ion attack on the silicon atom of PMHS to form a penta-coordinate silane intermediate or transition state. Penta-coordinated silanes<sup>14</sup> are well known as some of their X-ray crystal structures have been obtained before. Alternatively, this step could be a simple  $\text{S}_{\text{N}}2$  exothermic process where the hydride ion is displaced by the  $\text{OH}^-$  ion whose driving force is the formation of a much stronger Si-O bond compared to the Si-H bond. The second step of the process would consist of the coordinated or free hydride ion abstraction of the proton from water to form hydrogen gas and regenerates the  $\text{OH}^-$  ion. The hydroxide ion is indeed the ideal catalyst as it is constantly replenished by the dissociation of water molecules. The experimental data strongly support the first step as the rate-determining step as it shows the first-order rate dependences on PMHS and  $\text{OH}^-$ . The measured  $\Delta\text{H}^\ddagger$  and  $\Delta\text{S}^\ddagger$  values indicate a low

activation barrier as well as a loss of entropy which is consistent with the combination of two reactants molecules to form a single transition state or reactive intermediate. The large negative entropy value also favours the formation of the pentacoordinate silicon intermediate rather than a direct displacement of  $\text{H}^-$  by  $\text{OH}^-$ .

As the water molecule is only featured in the second and much faster step, its rate dependence or kinetic isotopic effect will be absent, which agrees with the experimental observation. In addition, if the first step was rate-determining, it would explain why trialkylsilanes are poor reactants as the electron-donating alkyl groups are unable to stabilise the anionic intermediate or transition state compared to the electron-withdrawing phenyl or O-Si functional groups.

## Conclusions

We have demonstrated a simple and cost-effective metal-free  $\text{OH}^-$ -catalysed hydrolytic oxidation of the silicone industry waste product, PMHS, and water into hydrogen gas. This process is readily scalable while retaining its high activity and excellent stability. The turnover number and turnover frequency have been determined to be in excess of 200 and  $8 \text{ min}^{-1}$ . The kinetics and activation parameters were studied and a mechanism, consistent with all aspects of our experiments, has been proposed.

## Notes and references

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Graphical abstract

Silane = polymethylhydrosilane

