High-quality hydrogen from the catalyzed decomposition of formic acid by Pd–Au/C and Pd–Ag/C†

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Pd–Au/C and Pd–Ag/C were found to have a unique characteristic of evolving high-quality hydrogen dramatically and steadily from the catalyzed decomposition of liquid formic acid at convenient temperature, and further this was improved by the addition of $CeO_2(H_2O)_x$.

Hydrogen is a promising source of energy having profound applications in various fields due to its high energy density and efficiency with low environmental load.[1] Its application in proton exchange membrane fuel cells (PEMFCs) is receiving much attention recently.[2] Generally, there are two ways to supply hydrogen for transportable energy applications, one of which is hydrogen storage technologies,[3–5] while the other is reforming hydrogen from small organic molecules such as methanol and ethanol.[6–8] Though an outstanding progress has been achieved in these routes mentioned above, there are some inherent shortcomings of them,[3–8] such as low efficiency, high operating temperature, huge volume and weight loading, excessive CO content as well as inconvenience, preventing use for applications. On the other hand, the energy densities of small organic molecules is higher than hydrogen but their electrochemical reactivities are much lower than that of hydrogen.[9–11] The application of small organic molecules as fuels is also limited at present. Obviously, it is of high significance to evolve hydrogen from such small organic molecules with convenient methods.[6–8] Noteworthy, it was found that formic acid can decompose to hydrogen and carbon dioxide at convenient temperatures.[12–15] In the literature, the decomposition of formic acid was catalyzed by two types of catalysts, Pd catalysts,[12–14] and those of other metal complexes.[15] The decomposition of formic acid follows two principal pathways,[12]

$$HCOOH \rightarrow CO_2\uparrow + H_2\uparrow: \Delta G = -48.4 \text{ kJ mol}^{-1} \quad (1)$$

$$HCOOH \rightarrow CO\uparrow + H_2O: \Delta G = -28.5 \text{ kJ mol}^{-1} \quad (2)$$

where reaction (1) producing hydrogen is the expected and desired reaction. However, reaction (2) producing carbon monoxide is a side-reaction. Unfortunately, those Pd/C catalysts deactivate quickly due to the poisoning intermediates, resulting in its failing in applications.[12–14] In this paper, we synthesised Pd–Au/C and Pd–Ag/C alloy catalysts, which overcame the poisoning and evolved high-quality hydrogen dramatically and steadily from the decomposition of formic acid at low temperature. The alloy catalysts were also found to be greatly promoted by $CeO_2(H_2O)_x$.

Through a large number of filtrations, elements of the copper group, especially Ag and Au, were found to be dramatically effective in retaining the Pd activity for the decomposition of formic acid‡ in reaction (1), which is shown in Fig. 1 and Fig. S1 (ESI†). The experiment was performed to measure the volume of reforming gas (H_2 + CO_2) during 2 h with 30 mg Pd–Me/C (20 wt% Pd, $n_{Pd} : n_{Me}$ = 3 : 1, Me = Cu, Ag and Au) at 365 K. For the Pd/C catalyst, reforming gas was only evolved for the first few minutes and then the catalytic decomposition reaction stopped. Although the volume of reforming gas of Pd/C is larger than Pd–Cu/C during 2 h, the reaction rate of Pd–Cu/C is not zero but 0.074 mL min^{-1}. However, the volumes of reforming gas from Pd–Au/C and Pd–Ag/C increase sharply at the beginning and then continue to increase linearly with fast rate. Interestingly, Pd–Au/C gives a maximum output of 260 mL reforming gas among the four catalysts during 2 h. The original reaction rate is extremely fast and about 80 mL reforming gas is evolved in the first 5 min, which is 31% of the total reforming gas in 2 h. The volume of reforming gas from Pd–Ag/C is only little smaller than that of Pd–Au/C. The turnover numbers (TON) of Pd–Au/C and Pd–Ag/C after the first 10 min are 27 and 17 h^{-1}, respectively. Table S1 (ESI†) shows detailed data of the four catalysts after the first 10 min. The intercepts in Fig. 1 clearly reflect the original reaction activity of the catalysts, and the slope of the line shows the steady reaction activity after 10 min. Consequently, both the original reaction activity and

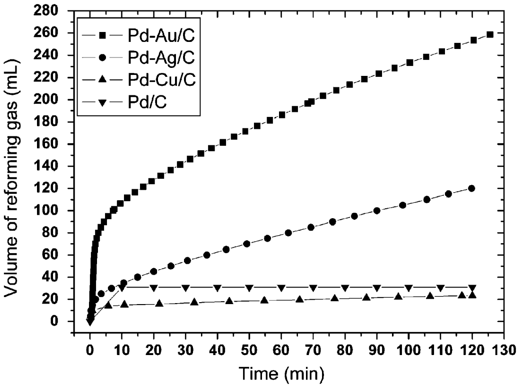

Fig. 1 The output volume of reforming gas (H_2 + CO_2) during 2 h with 30 mg Pd–Me/C (20 wt% Pd, $n_{Pd} : n_{Me}$ = 3 : 1, Me = Cu, Ag and Au), respectively, at 365 K and 5.00 ml 9.94 M formic acid–3.33 M sodium formate solution.

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the steady reaction activity of Pd–Au/C are the highest ones among the four catalysts.

Transmission electron micrographs (TEM) of Pd/C, Pd–Ag/C and Pd–Au/C are shown in Fig. S2 (ESI†), and particle distribution histograms of these catalyst samples were obtained by measuring the metal particles shown in Fig. S3 (ESI†) for the nanoparticles deposited on the carbon support. The average sizes of the three catalysts can be ranked as Pd/C > Pd–Ag/C > Pd–Au/C. The TEM results show that the addition of Ag and Au reduces the size of nanoparticles. Furthermore, the effect of Au is better than Ag, which may be one of the reasons for the better performance of Pd–Au/C compared to Pd–Ag/C.

Considering the moderate reaction rate and experimental convenience, Pd–Ag/C was selected as a model catalyst to study the effects of different factors in detail. First, the atom proportions of Pd : Ag was found to have great influence on the catalyst activity with a saddle shape as shown in Fig. S4 (ESI†). The highest activity appears at 3 : 3 (20 wt% Ag), and the reaction rate is 160 ml min^{-1} g^{-1} (Pd), and TON is 22 h^{-1}. Second, the dependence of the reaction rate on temperature was also studied as shown in Fig. S5 (ESI†). The reaction rate is doubled every 5.0 K and according to the Arrhenius equation (3),

$$\ln k = -(E_a/RT) + B \qquad (3)$$

the activation energy for the decomposition reaction of formic acid is calculated to be $E_a = 115$ kJ mol^{-1} as shown in Fig. S6 (ESI†). This indicates that the working temperature plays an important role in the catalytic decomposition due to the difference in the adsorption and desorption of poisoning intermediates at different temperatures. Third, the effect of proportion of formate/(formic acid and formate) on both reforming rate and concentration of CO in reforming gas was accurately measured using Fourier-transform infrared absorption spectrometry (FTIR). A plot has been constructed between CO content and the corresponding proportions as shown in Fig. 2. The maximum appears at the proportion 0.3. The reaction rate is a saddle shape[14] with the maximum rate 300 ml min^{-1} g^{-1} at the proportion 0.7, where the concentration of carbon monoxide is 80 ppm. Remarkably, the concentration is dramatically lower than that of conventional reforming gas from methanol, ethanol, methane *etc.*,[6–8] and the quality of the hydrogen reaches PEMFC standard with the CO concentration lower than 100 ppm.[16]

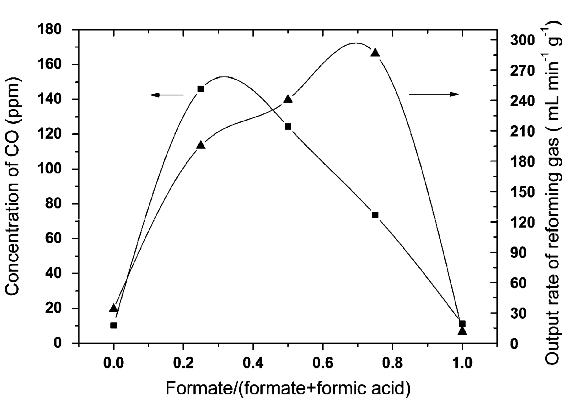

Fig. 2 Effect of proportion of formate to formate and formic acid on the decomposition rate of formic acid and CO concentration in reforming gas with 30 mg Pd–Ag/C (20 wt% Pd, $n_{Pd} : n_{Ag} = 3 : 1$) at 365 K and 5.00 ml solution: (■) concentration of CO, (▲) output rate of reforming gas ($H_2 + CO_2$).

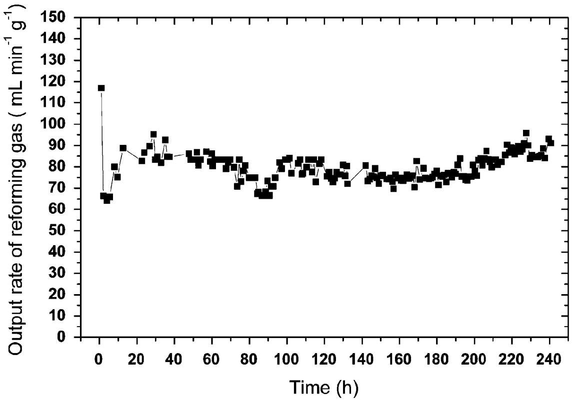

Fig. 3 Lifetime test of 10 mg Pd–Ag/C (20 wt% Pd, $n_{Pd} : n_{Ag} = 3 : 1$) during 240 h at 365 K with 60.0 mL 9.94 M formic acid–3.33 M sodium formate solution.

The lifetime of Pd–Ag/C shown in Fig. 3 had been tested with 10 mg catalyst for 240 h at 365 K. The activity of Pd–Ag/C and the reaction rate indicated high stability during the test. Furthermore, the linear fit for the data shows that the activity of Pd–Ag/C increases slightly with a rate of 1.59×10^{-3} ml min^{-1} g^{-1} h^{-1}. The high stability is due to the fact that the HCOONa solution is basic, while Pd and Ag are stable at relatively higher pH value. The solution containing HCOOH and HCOO$^-$ as reducing agent is important to keep the Pd and Ag in a reduced state, and consequently retains the stability of the alloy catalyst Pd–Ag/C. In addition, we also found that the activities of the catalysts are renewed completely after drying in air at 353 K. At this condition, poisonous intermediates on Pd surface will be oxidized by air.

The characteristics of the elements of copper group, especially Ag and Au, to retain the catalytic activity of Pd for the decomposition of formic acid are discussed primarily herein. It has been reported that the reason for the disappearance of activity of Pd/C is due to the hydrogen adsorption on Pd.[13] Nevertheless, in our experiment, the catalyst activity only decreased slightly after bubbling hydrogen into an aqueous suspension of Pd/C, while it decreased completely after bubbling CO into an aqueous suspension of Pd/C. Obviously, besides the effect of hydrogen adsorption on Pd,[13] poisoning intermediates (such as CO_{ad}) produced by reaction (2) cover the surface of the catalysts and occupy the active sites.[17–19] Additionally, the long lifetime of catalysts Pd–Ag/C and Pd–Au/C in the environment of CO implies that CO cannot steadily adsorb on their surface even at 365 K. According to some previous researches, the adsorption strength of CO on metal surfaces ranks as Pd > Cu > Ag > Au,[18] and Ag and Au do not form stable complexes with CO.[20] When Pd is alloyed with Cu, Ag or Au as shown by XRD experiments in Fig. S7 (ESI†), they effectively inhibit the adsorption of CO on Pd.[16,20–22] The occupied active sites are released due to CO desorbing from the Pd surface,[16,20–22] and consequently reaction (1) is not inhibited. Thus, the concomitant CO poisoning

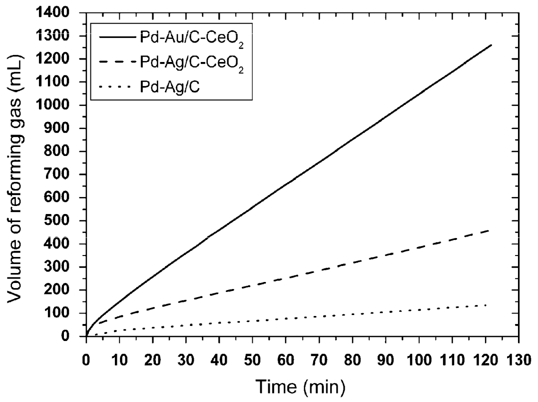

Fig. 4 The output volume of reforming gas at 365 K with 5.00 ml 9.94 M formic acid–3.33 M sodium formate solution. (Solid line) 60 mg PdAu/C–CeO_2 10 wt% Pd, 50% CeO_2, $n_{Pd} : n_{Au} = 1 : 1$; (dashed line) 60 mg PdAg/C–CeO_2 10 wt% Pd, 50% CeO_2, $n_{Pd} : n_{Ag} = 1 : 1$; (dotted line) 30 mg PdAg/C 20 wt% Pd, $n_{Pd} : n_{Ag} = 1 : 1$.

process during decomposition of small organic molecules has been removed effectively by the Pd alloyed catalysts with Au or Ag.

In addition, the activities of Pd–Au/C and Pd–Ag/C here can be enhanced enormously by co-deposition with CeO_2-$(H_2O)_x$ (simply written as CeO_2) as shown in Fig. 4. It can be seen that the activities of 60 mg Pd–Me/C–CeO_2 (10 wt% Pd, 50 wt% CeO_2, Me = Au and Ag, $n_{Pd} : n_{Me} = 3 : 3$) reach 1640 and 548 ml min^{-1} g^{-1}, or 10.3 and 3.4 times that of 30 mg Pd–Ag/C (20 wt% Pd, $n_{Pd} : n_{Ag} = 3 : 3$), respectively. The TONs of Pd–Au/C–CeO_2 and Pd–Ag/C–CeO_2 are 227 and 76 h^{-1}, respectively. With increasing the working temperature by 10 degrees, the reaction rate for Pd–Au/C–CeO_2 became extremely fast (>6000 ml min^{-1} g^{-1}, TON up to 832 h^{-1}), which shows high potential in transportable application. Fig. S8 (ESI†) shows the TEM of Pd–Ag/C–CeO_2 and Pd–Au/C–CeO_2 catalysts. Looking at Fig. S2, the dispersion of nanoparticles of Pd–Ag is improved by adding CeO_2, while it becomes poor for Pd–Au. This result implies that a higher dispersion is not the key fact for the improvement of activity. The promotion of CeO_2 on the activity of Pd-based catalysts is probably due to that the CeO_2 produces cationic palladium species, which show high activity in CO oxidation[23] and methanol decomposition.[24] Another reason is due to that $CeO_2(H_2O)_x$ on the Pd surface can induce the decomposition of formic acid by a more efficient route, in which fewer poisoning intermediates will be produced. Because of the lowest adsorption strength of CO on Au surfaces, Au is most effective to reduce the adsorption of CO on Pd surface.[18] This effect is further strengthened by the addition of CeO_2. Pd–Au/C–CeO_2 thereby become much more active than Pd–Ag/C–CeO_2.

The yield of 1640 ml min^{-1} g^{-1} reforming gas indicates a theoretical power density of 135 W g^{-1} for PEMFC, which can being further improved by increasing activity and decreasing the working temperature by optimising the catalyst composition and working conditions. The main contribution of the work is to inhibit the CO poisoning, and consequently provide a new route to rapidly and conveniently evolve high quality hydrogen at low temperature, which is of high potential for transportable, especially portable, hydrogen sources. The breakthrough of the advanced catalysts in preventing CO poisoning is a valuable contribution for advancement of oxidation and between CO content and the corresponding proportion of electro-oxidation of small organic molecules.[16]

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Notes and references

‡ **CAUTION**: formic acid is harmful to skin or eyes and thus it is important to prevent the leakage of formic acid during the experiments and applications.

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