Available hydrogen from formic acid decomposed by rare earth elements promoted Pd-Au/C catalysts at low temperature

Xiaochun Zhou, Yunjie Huang, Changpeng Liu, Jianhui Liao, Tianhong Lu, and Wei Xing* [a]

The usage of hydrogen as a clean, efficient power carrier for stationary and mobile applications is attracting more and more attention.[1] Much effort has been made towards hydrogen application technologies, especially in fuel cells. Nevertheless, the production and storage of hydrogen is the bottleneck of hydrogen economy. In transportable energy applications, hydrogen is generally produced from reforming organic molecules, such as gasoline, methanol, ethanol and so on.[2–4] Hydrogen production suffers from various problems such as low efficiency, high operating temperature, huge volume, weight loading, and excessive formation of CO. On the other hand, hydrogen storage technologies[5–7] are limited by low efficiency and possible danger. Notably, formic acid is a promising hydrogen carrier,[8–21] with advantages of considerable hydrogen content (4.4 wt %), and non-toxic and non-flammable properties. It has been reported that Au-based,[8] Pd-based,[9, 10] Pt-based,[11] and metal (e.g., Ru, Ir, Rh, Fe) complex[12–28] catalysts can be used for the decomposition of formic acid (DCFA). The hydrogen from the DCFA also has been used in proton exchange membrane fuel cell (PEMFC).[20, 21] In our previous study,[10] the Au or Ag additive overcame the deactivation of Pd catalyst. Furthermore, the addition of Ce further improved the activity of the Pd–Au and Pd–Ag catalysts. Then, it is necessary to understand the promotion effect of other rare earth elements (REs) and design new and highly active catalysts. Here, we systematically studied the promotion effect of three REs (Dy, Eu, and Ho) on the Pd–Au/C catalysts in the DCFA reaction. In addition, the application of reforming gas in fuel cell is studied.

Figure 1 a shows the output rates of reforming gas from DCFA catalyzed by Pd–Au/C, Pd–Au–Dy/C, Pd–Au–Eu/C, and Pd–Au–Ho/C. All the R Dy, Eu, Ho) could significantly promote the activity of Pd–Au/C catalyst. The activity order of the four catalysts was Pd–Au–Dy/C > Pd–Au–Eu/C > Pd–Au–Ho/C > Pd–Au/C. All activities increased with the temperature exponentially. In addition, these catalysts were even active at room temperature temporarily and above 325 K steadily. The activation energies for the DCFA reaction on the prepared catalysts were also calculated according to the Arrhenius equation. Figure 1 b and Table 1 show that all the REs-promoted Pd–Au/C catalysts have lower activation energies of DCFA than Pd–Au/C. Among the REs catalysts, Pd–Au–Eu/C had the lowest value of 84.2 ± 7.4 kJ mol⁻¹. However, the most active was Pd–Au–Dy/C, which had a decomposition rate of 1198 mL min⁻¹ g⁻¹ Pd and a turnover frequency (TOF) of 269 ± 202 h⁻¹ at 365 K. This catalytic performance of Pd–Au–Dy/C can provide output power of 106 W g⁻¹ Pd theoretically, which is promising to be used in portable applications.

Generally, promotion effect comes from three aspects, that is, distribution improvement of nanoparticles, electronic effect, and synergistic effect.[24–27] The promotion effect of REs in these three aspects is stated as follows.

Firstly, the particle size distributions of the prepared catalysts were measured by transmission electron microscopy (TEM), as shown in Figure 2A and Figure 2B. The relationships among the average particle size, activity, TOF, and activation energy are shown in Figure 3. The activity of REs promoted Pd–Au/C catalysts increased from 431 to 1198 mL min⁻¹ g⁻¹ Pd with the size decrease from 4.6 ± 1.5 to 2.0 ± 1.5 nm (Figure 3a). The activity of REs-promoted catalysts can be improved by decreasing the particle size, likely due to the increasing surface-to-volume ratio. However, the TOF and activation energy $E_a$ are not clearly dependent on the particle size as shown in Figure 3b and Figure 3c. Interestingly, Figure 3d shows that TOF increased with decreasing activation energy, indicating that the activation energy determines the catalytic activity of the

Table 1. Size, activation energy, and activity of the prepared catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd–Au–Dy/C</th>
<th>Pd–Au–Eu/C</th>
<th>Pd–Au–Ho/C</th>
<th>Pd–Au/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size [nm]</td>
<td>2.0 ± 1.5</td>
<td>4.1 ± 3.0</td>
<td>4.6 ± 1.5</td>
<td>3.5 ± 0.8</td>
</tr>
<tr>
<td>Activity at 365 K [mL min⁻¹ g⁻¹ Pd]</td>
<td>1198</td>
<td>842</td>
<td>431</td>
<td>118</td>
</tr>
<tr>
<td>TOF [h⁻¹]</td>
<td>269 ± 202</td>
<td>387 ± 292</td>
<td>224 ± 73</td>
<td>45 ± 11</td>
</tr>
<tr>
<td>$E_a$ [kJ mol⁻¹]</td>
<td>98.3 ± 4.3</td>
<td>84.2 ± 7.4</td>
<td>102.1 ± 5.3</td>
<td>138.6 ± 6.2</td>
</tr>
</tbody>
</table>

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active sites. Researchers can then judge the activity of a catalyst according to the activation energy. Here, Pd–Au–Eu/C has the highest TOF as well as the lowest activation energy. Therefore, Pd–Au–Eu/C is a promising catalyst if its particle size is decreased. In addition, the results indicate that $E_a$ increases with increasing atomic number of REs, thus it is possible to find more effective elements in lighter REs. It should be pointed out that the particle size is not a key factor for the promotion effect of REs.

Secondly, the electronic effect was studied by X-ray photoelectron spectroscopy (XPS). Figure 2 C shows the XPS spectra of Pd/C, Pd–Au/C, Pd–Au–Dy/C, Pd–Au–Eu/C, and Pd–Au–Ho/C. The order of the peak positions can be ranked as Pd/C (335.7 eV), Pd–Au–Eu/C (335.0 eV), Pd–Au–Ho/C (334.9 eV), Pd–Au–Dy/C (334.8 eV), and Pd–Au/C (334.4 eV). The peak shift indicated that the addition of Au, Eu, Ho, and Dy changed the electron binding energy of Pd on the catalyst surface. In our previous study,[10] the negative shift of the electron-binding energy of Pd caused by Au was the reason for anti-poisoning. The XPS results show that Dy, Eu, and Ho decreased the negative shift, which is disadvantageous to the anti-poisoning property of the catalysts. Therefore, the change of electron binding energy of Pd is not the key factor for the promotion effect of REs on Pd–Au/C. On the contrary, REs may have some negative effect on the activity of Pd–Au/C in this aspect.

Thirdly, the synergistic effect of REs on removing poisonous intermediates is discussed. The activities of the catalysts were very high at the beginning of reaction, but decreased dramatically after about 10 min. The deactivation was mainly due to the formation of poisonous intermediates on the active sites.[28, 29] Au or Ag can facilitate the dissociation of the poisonous intermediates, such as CO ad. The dissociation reaction is considered as the rate-determining step, which controls the whole reaction rate. If the poisonous intermediates can be removed easily, the catalysts will show higher activity. XPS results show that there is a strong interaction between Pd and REs. Usually, the addition of REs into catalyst can drastically improve the activity, especially in reverse water–gas shift reactions[30] and auto exhaust-removing reactions.[31, 32] The improvement is mainly because REs can act as oxygen storage materials, stabilizers, and promoters.[33] For the REs-promoted catalysts, it is possible to have similar promotion effects. REs on the Pd surface provide abundant oxygen species, which can react with the poisonous intermediates. For example, CO ad can be removed by a reaction such as water–gas shift reaction:

$$CO_{ad} + H_2O \rightarrow RE_5 + CO_2 + H_2$$

The catalysts can be refreshed by REs besides the direct dissociation. Consequently, more active sites will be free to take part in the reaction. Therefore, the synergistic effect of REs is the promising key factor for the promotion effect.

The hydrogen generation reaction on Pd-based catalysts is a very complex reaction, which mainly includes formic acid decomposition, poisoning, and refreshment process of the catalyst. If these three main reactions are considered, a simple model can be built. The derivation of the model can be found in the Supporting Information. The reaction rate at high temperature is:

$$r = \frac{k_1 k_3 [HCOOH]}{(k_2 + k_3)}$$

where $k_1$, $k_2$, $k_3$ are the rate constants of DCFA, poisoning, and refreshment reactions, respectively.

Loges et al.[12, 20] demonstrated that the hydrogen from DCFA can be used in PEMFC. Here, our reforming gas was also applied directly in the PEMFC. Notably, the CO concentration in

Figure 2. A) TEM images of a) Pd–Au–Dy/C, b) Pd–Au–Eu/C, c) Pd–Au–Ho/C, and d) Pd–Au/C catalysts; B) histograms of catalyst particle size distribution from TEM images; C) XPS spectra for the Pd 3d$_{5/2}$ of Pd/C, Pd–Au–Eu/C, Pd–Au–Ho/C, Pd–Au–Dy/C, and Pd–Au/C.

Figure 3. Relationship between a) size and activity at 365 K, b) size and TOF, c) size and $E_a$, and d) $E_a$ and TOF. Number in the bracket is the atomic number. Dy, Eu, and Ho represent Pd–Au–Dy/C, Pd–Au–Eu/C, and Pd–Au–Ho/C, respectively. The dotted lines show the change in trend.
our reforming gas was much lower (see the Supporting Information) than that of conventional reforming gas from methanol, ethanol, methane, and so on.\textsuperscript{2-41} The high quality of the hydrogen reached tolerance standard of PEMFC, which is <100 ppm CO.\textsuperscript{\textit{a}}\textsuperscript{44} Thus, the reforming gas here could be applied directly. In addition, the Pd–Au–REs/C catalysts are heterogeneous catalysts, which can be easily applied in transportable applications.\textsuperscript{\textit{35, 36}}

As shown in Figure 4, the reforming gas was applied into PEMFC, and compared with pure hydrogen gas and direct formic acid. The power density of fuel cell using pure hydrogen was 150 mW cm\textsuperscript{-2} and is the highest. The power densities of fuel cells using reforming gas with filtering and without filtering were 150 mW cm\textsuperscript{-2} and 75 mW cm\textsuperscript{-2}, respectively, which are much higher than the direct formic acid fuel cell with a power density of only 10 mW cm\textsuperscript{-2}. Furthermore, the open circuit potential (OCP) for the reforming gas was almost the same as that for hydrogen, and also much higher than that for formic acid. Generally, high OCP is very advantageous in fuel cell applications.

In summary, REs (Dy, Eu, and Ho) were found to be very effective in promoting the Pd–Au/C catalysts for DCFA. High-quality hydrogen was produced conveniently, rapidly, and economically at low temperature. It was found that REs can effectively in promoting the Pd–Au/C catalysts for DCFA. High-quality hydrogen was produced conveniently, rapidly, and economically at low temperature. It was found that REs can reduce the activation energy of the DCFA reaction. The activities for REs-promoted Pd–Au/C catalysts increased with decreasing size. However, the TOF increased with decreasing activation energy or decreasing atomic number of REs. The promotion effect was mainly due to the ability of REs to provide abundant oxygen species, which can react with the poisonous intermediates and then refresh the catalyst. In addition, a PEMFC using the reforming gas as fuel was demonstrated to have a performance of 105 mW cm\textsuperscript{-2}. The activity of Pd–Au catalysts can be further improved by trying more REs and synthesizing methods. These catalysts are also very promising in the application of portable fuel cells.

**Experimental Section**

The catalysts were prepared by dispersing carbon black (Vulcan XC-72, from Cabot Co.) into 400 mL ethanol and water (V\textsubscript{ethanol} / V\textsubscript{water} = 1:1). Then PdCl\textsubscript{2} (9.96 mg mL\textsuperscript{-1} Pd) and HAuCl\textsubscript{4} (4.60 mg mL\textsuperscript{-1} Au) solutions were added into the above suspension. Two hours later, REs elements (Dy(NO\textsubscript{3})\textsubscript{3}, Eu(NO\textsubscript{3})\textsubscript{3}, Ho(NO\textsubscript{3})\textsubscript{3}) were added. The total quantity of active carbon, Pd, and RE\textsubscript{2}O\textsubscript{3} was 0.5 g. The suspension was reduced by 0.4 g NaBH\textsubscript{4}, diluted with 100 mL water. After reaction of 4 h, the resulted product was filtered, washed, and dried at 80 °C. The weight percentage of Pd in Pd/C and Pd–Au/C was 20% and the mole ratio n\textsubscript{Pd}/n\textsubscript{Au} was 1:1. The weight percentages of Pd and RE\textsubscript{2}O\textsubscript{3} in Pd–Au–REs/C (REs = Dy, Eu, Ho) were 10% and 50%, respectively.

Thirty milligrams of Pd–Au/C catalyst (or 60.0 mg Pd–Au–REs/C) and 5 mL formic acid solution were mixed to generate the reforming gas. The formic acid solution was composed of 9.94 mL formic acid and 3.33 mL sodium formate. The temperature was controlled by an ultra-precise thermostat bath (Shanghai Instrument, China), which could maintain the temperature within ±0.1 °C. The reforming gas was collected with a 100 mL injector, which was recorded by a PC camera. The TOF here is defined as: (number of hydrogen molecules in reforming gas)/(reaction time × number of Pd atoms on surface).

X-ray photoelectron spectroscopy measurements were performed in the spectroscopy chamber using a standard Mg anode X-ray source (and the Mg K\textsubscript{a} X-rays at 1253.6 eV) and a 150 mm hemispherical electron energy analyzer by an ESCALAB MKII photoelectron spectrometer (VG Scientific).

To obtain information about the particle size and shape of the catalysts, transmission electron microscope analysis was performed with a JEOL JEM-2010 microscope operating at 200 kV with nominal resolution. The samples were dispersed well in ethanol ultrasonically. A drop of the dispersion solution was deposited onto a carbon film with 400 mesh Cu grid covered with a holey film. The single-cell test was performed without back pressure at a cell temperature of 85 °C and atmospheric pressure. Anode: Pt loading (1 mg cm\textsuperscript{-2}), hydrogen flow rate (17 cm\textsuperscript{3} min\textsuperscript{-1}) or formic acid flow rate (2.0 mL min\textsuperscript{-1}); cathode: Pt loading (1.0 mg cm\textsuperscript{-2}), dry oxygen (18 cm\textsuperscript{3} min\textsuperscript{-1}); cell potentials were not compensated by series resistance.

CAUTION: formic acid is harmful to skin and eyes. It is very important to prevent the leakage of formic acid during the experiments and applications.

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