Supplementary information

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

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Part I. Supplementary Figures

Figure Captions:

Figure S1. The output volume of reforming gas (H_2+CO_2) during 120 minutes with 30 mg Pd-Me/C (20w% Pd, n_{Pd}:n_{Me}=3:1, Me=Pt, Pb, Sn, Ir, Ni or Ag) respectively, at the temperature 365 K and 5.00 ml formic acid solution.

Figure S2. Transmission electron micrographs (TEM) of (a) Pd/C, (b) PdAg/C, (c) PdAu/C catalysts

Figure S3. Histograms of catalyst particle size distribution as measured from TEM micrographs

Figure S4. The effect of the percentage of Ag on the reaction measured at 365 K with 30 mg Pd-Ag/C (20w% Pd, n_{Pd}:n_{Ag}=3:1) and 5.00 ml 9.94 M formic acid/ 3.33

M sodium formate solution, (a) The output volume of reforming gas; (b) the output rate of reforming gas, the rate is expressed by the output gas per minutes and per gram palladium.

Figure S5. The effect of temperature on the reaction measured at 345 K, 350 K, 355 K, 360 K, 365 K and 370 K with 30 mg Pd-Ag/C (20w% Pd, n_{Pd}:n_{Ag}=3:1) and 5.00 ml formic acid solution, (a) The output volume of reforming gas; (b) the output rate of reforming gas, the rate is expressed by the output gas per minutes and per gram palladium.

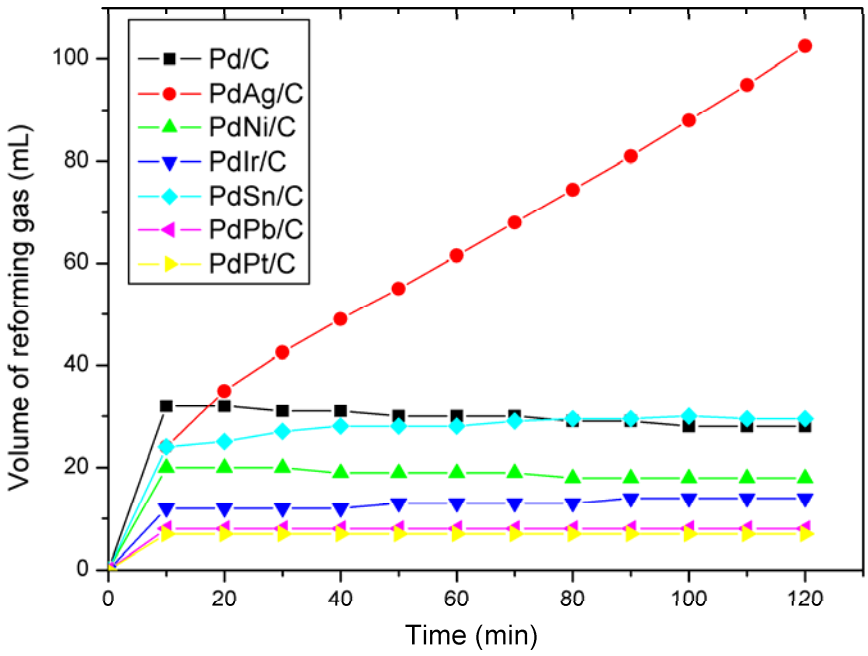
Figure S6. Calculation of the activation energy of the reaction of formic acid decomposition according to the Arrhenius equation.

Figure S7. X-ray diffraction (XRD) patterns of Pd-Me/C (20w% Pd, n_{Pd}:n_{Me}=3:1, Me=Cu, Ag and Au). The red solid and green dash lines refer, respectively, to the standard 2θ values corresponding to the (111) and (200) reflections of Pd metals.

Figure S8. Transmission electron micrographs (TEM) of (a) Pd-Ag/C-CeO_2 , (b) Pd-Au/C-CeO_2 catalysts.

Figure S9. Gas chromatogram of H_2, O_2, N_2, CO, CO_2 and reforming gas (H_2+CO_2).

Figure S10. Effect of catalyst weight on the reaction measured at 365 K with Pd-Ag/C (20w% Pd, n_{Pd}:n_{Ag}=3:1) and 10.00 ml 9.94 M formic acid/ 3.33 M sodium formate solution.



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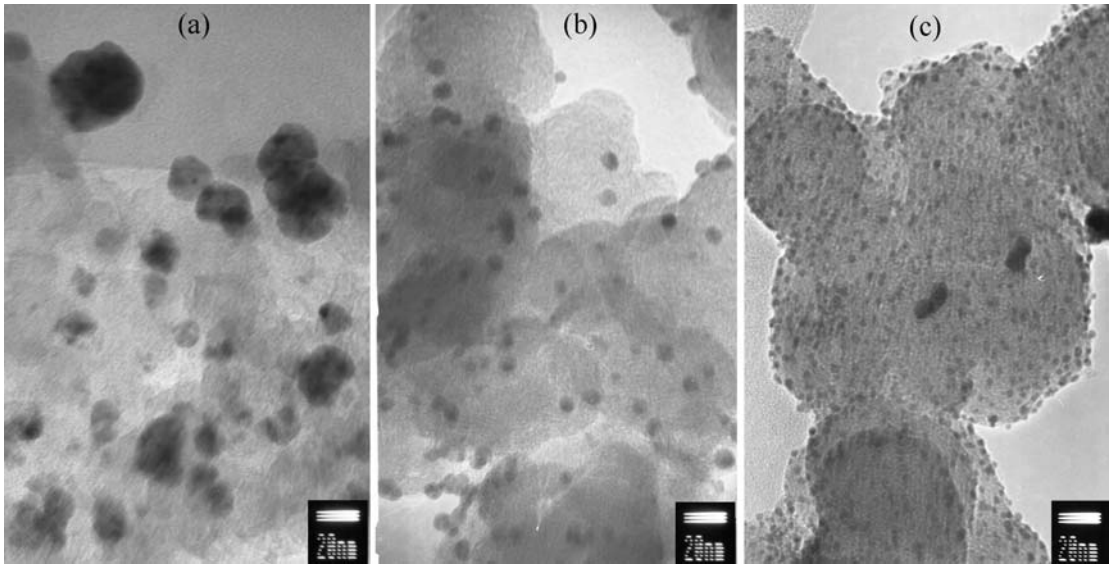

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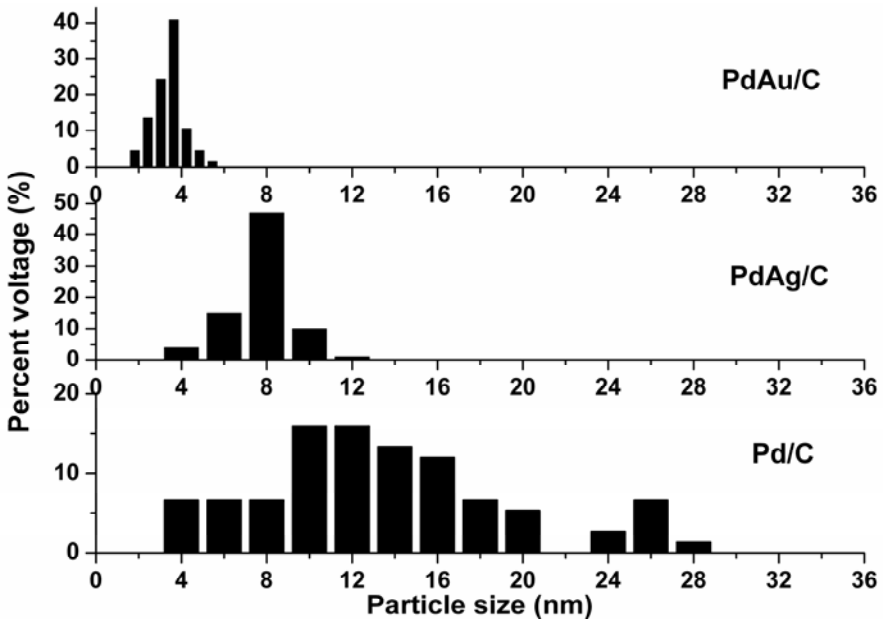
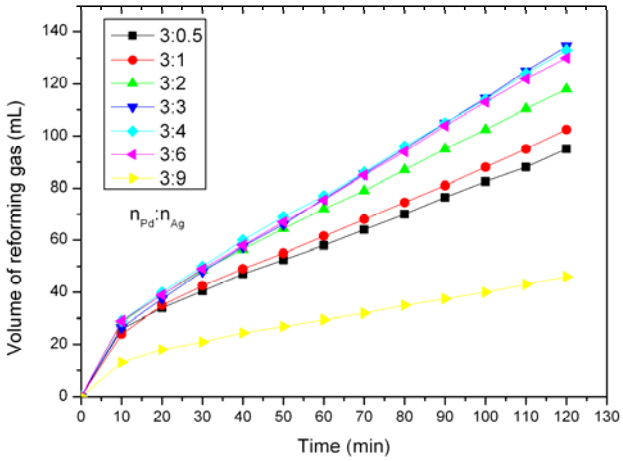
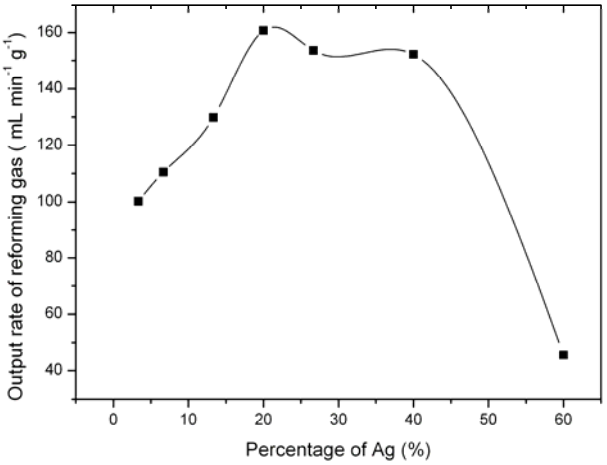


Figure S3. Histograms of catalyst particle size distribution as measured from TEM micrographs

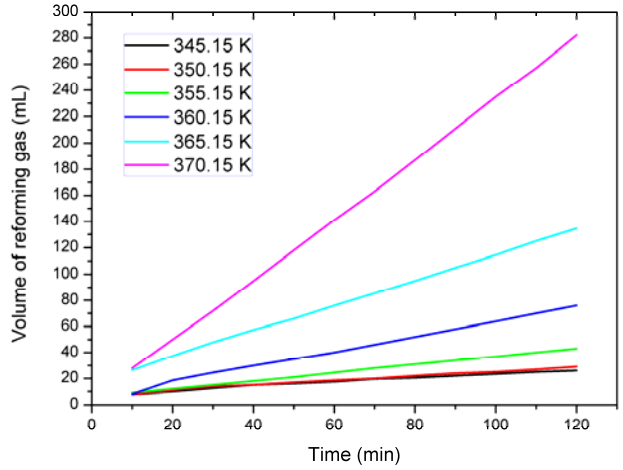


a



b

Figure S4. The effect of the percentage of Ag on the decomposition reaction measured at 365 K with 30 mg Pd-Ag/C (20w% Pd) and 5.00 ml 9.94 M formic acid/ 3.33 M sodium formate solution, (a) The output volume of reforming gas during two hours; (b) the output rate of reforming gas, the rate is expressed by the gas output per minutes and per gram palladium.



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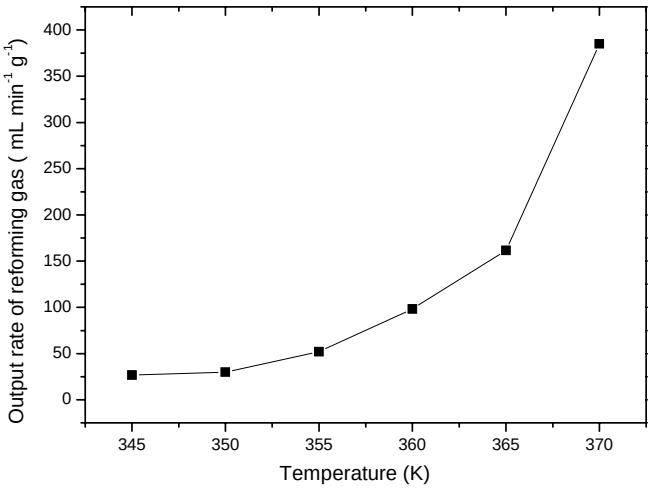

b

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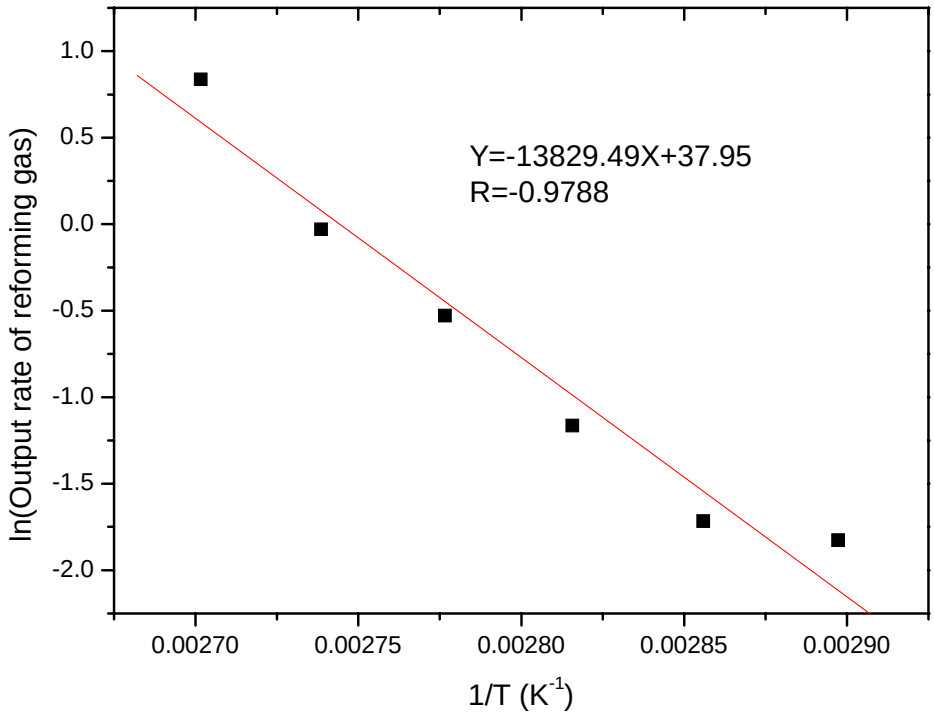
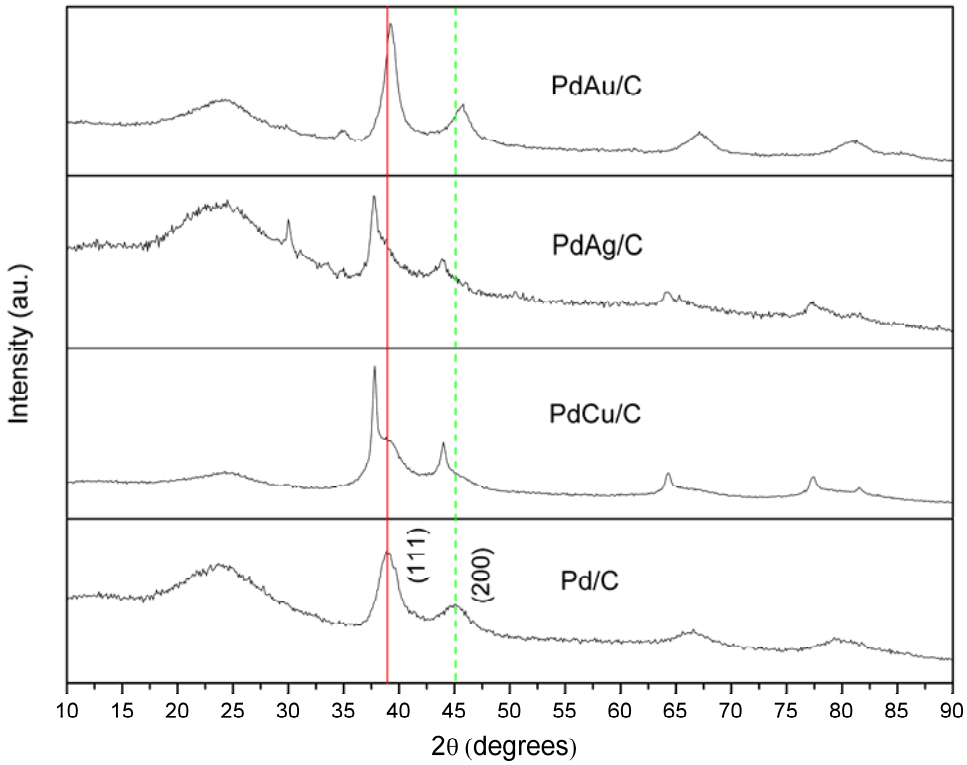


Figure S6. Calculation of the activation energy of the decomposition reaction of formic acid according to the Arrhenius Equation,

$$\ln k = -\frac{E_a}{RT} + B \qquad (1)$$

The activation energy was calculated to be 115 kJ mol^{-1}.



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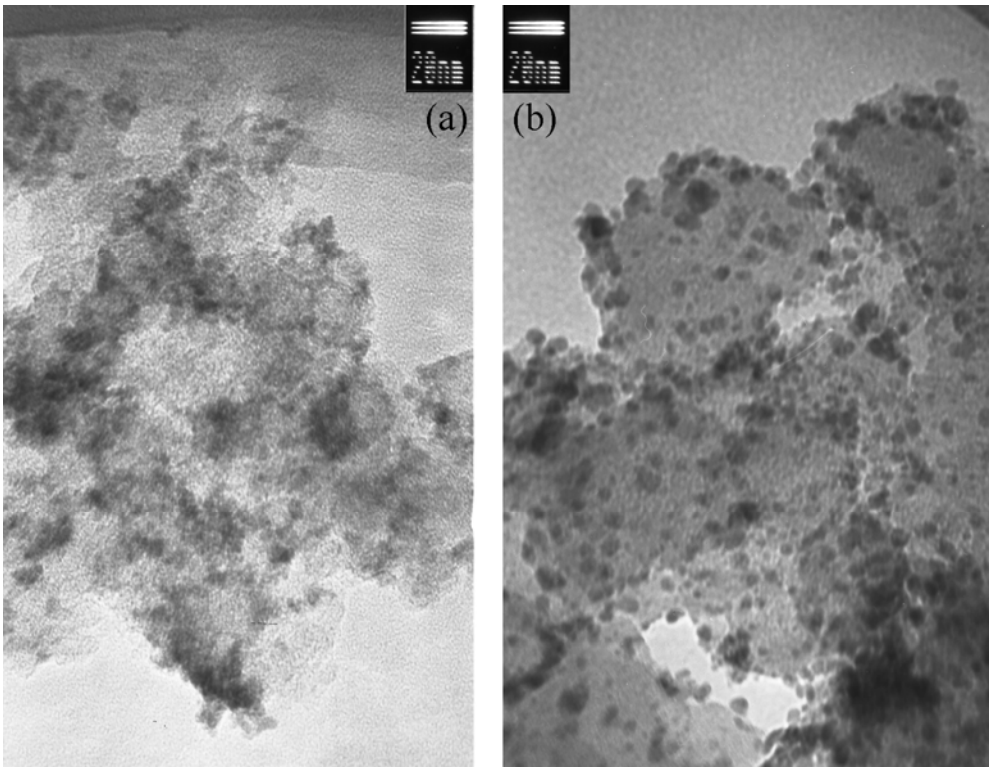

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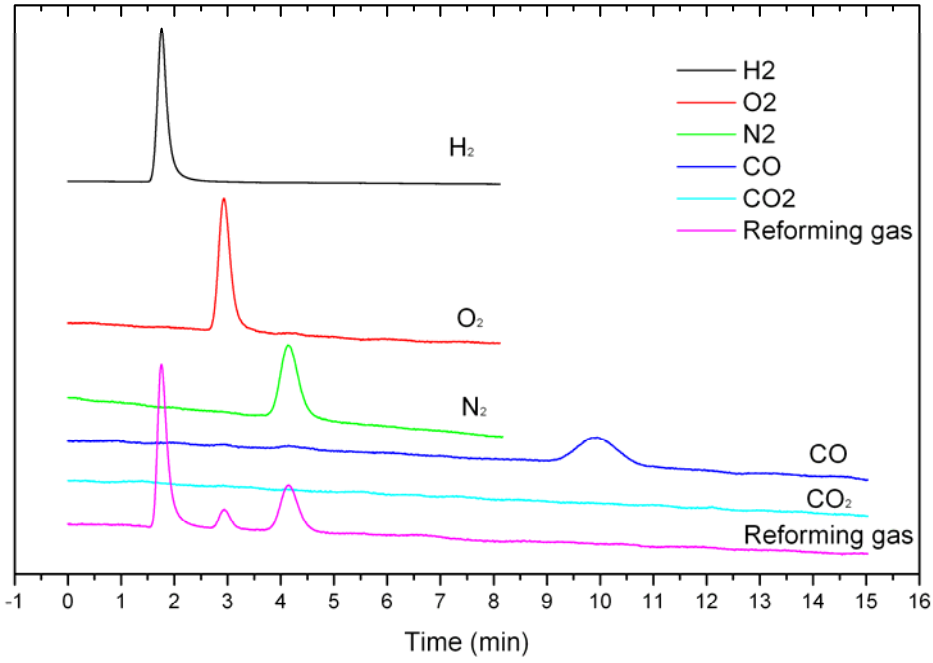

Figure S9. Gas chromatogram of H_2, O_2, N_2, CO, CO_2 and reforming gas (H_2+CO_2).

It can be seen that H_2 can be detected, and CO cannot be. The existence of oxygen and nitrogen is due to the interfusion of air.

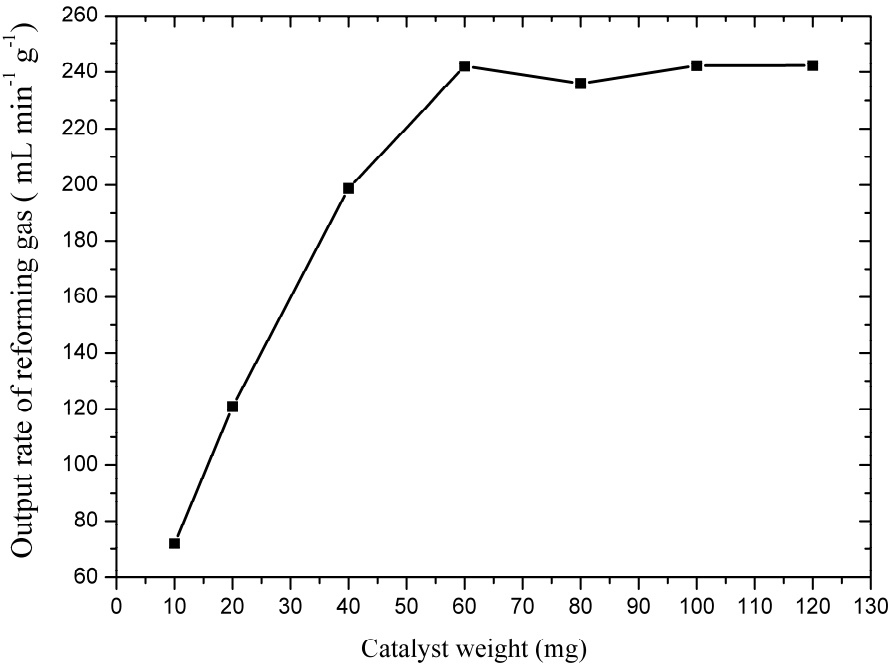

Figure S10. Effect of catalyst weight on the decomposition reaction measured at 365K with Pd-Ag/C (20w% Pd, n_{Pd}:n_{Ag}=3:1) and 10.00 ml 9.94 M formic acid/3.33 M sodium formate solution.

Part II. Supplementary Tables

Table S1. The detail data of the four catalysts in figure 1 after the first 10 minutes

	Pd/C	Pd-Au/C	Pd-Ag/C	Pd-Cu/C
slope / mL min^{-1}	0.000	1.227	0.741	0.076
intercept/ mL	31.00	110.14	32.60	14.45

Part III. Supplementary Methods

Catalyst preparation. Specific VC-72R active carbon was dispersed into 300 mL ethanol and water (Vethanol : Vwater = 1:1). Then 10.04 mL 9.9604 mg mL^{-1} Pd ($PdCl_2$) was added into the suspension. Two hours later, specific atom proportion of other elements was added. The total quality of active carbon, Pd and other elements was kept 0.5 g. After two hours stirring, the suspension was reduced by 0.4 g $NaBH_4$ diluted with 100 mL water. The result production was filtered, washed and dried at 80 ℃, after 4 hour stirring. At last, the catalyst was triturated to be ready to use. During synthesizing Pd-Me/C-CeO_2, $Ce(NO_3)_3 \cdot H_2O$ was added to carbon suspension following the addition of $PdCl_2$ and other metal elements.

Generation and measurement of reforming gas. In reforming gas generation, 30 mg catalyst and 5 mL formic acid solution was used. The formic acid solution is composed with 9.94 M formic acid and 3.33 M sodium formate, generally. In the experiment about the effect of formate:(formate and formic acid) on the decomposition rate of formic acid and CO concentration, the formic acid solution is composed with 1.66 M formic acid and 4.97 M sodium formate. The temperature of the electrochemical reaction system was controlled by using an ultra-precise thermostat bath (Shanghai Instrument, China), which can guarantee a

deviation of temperature from a given value within ±0.1℃. The reforming gas was gathered with a 100 mL injector, which was monitored by a PC camera.

X-ray diffraction (XRD) patterns measurement. The X-ray diffraction (XRD) patterns for the catalysts were obtained using a Rigaku-D/MAX-PC 2500 X-ray diffractometer with the Cu Kα (k = 1.5405 Å) radiation source operating at 40 kV and 200 mA.