Supporting Information

AgPd nanoparticles supported on MIL-101 as high performance catalysts for catalytic dehydrogenation of formic acid

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Experimental

Chemicals and materials

All chemicals were commercial and used without further purification. Chromic nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, Sinopharm Chemical Reagent Co., Ltd., 99%), Palladium chloride ($PdCl_2$, Great Wall Reagent Co., Ltd., 99%), Silver nitrate ($AgNO_3$, AR), sodium formate (HCOONa, Sinopharm Chemical Reagent Co., Ltd., 99%), Formic acid (HCOOH, Sigma-Aldrich 98%), aqueous hydrofluoric acid (HF, Sinopharm Chemical Reagent Co., Ltd., 40%), Hydrochloric acid (HCl, Sinopharm Chemical Reagent Co., Ltd., 37%),terephthalic acid ($HO_2CC_6H_4CO_2H$, Sinopharm Chemical Reagent Co., Ltd., 99%), sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co.,Ltd, 96%), ethanol (C_2H_5OH, Sinopharm Chemical Reagent Co., Ltd., >99.8%), Ammonium fluoride (NH_4F, Sinopharm Chemical Reagent Co., Ltd., ≥96%)were used as received.

We use ordinary distilled water as the reaction solvent.

Synthesis of MIL-101

MIL-101 was synthesized using the reported procedure.[18] Terephthalic acid (332 mg, 2.0 mmol), $Cr(NO_3)_3 \cdot 9H_2O$ (800 mg, 2.0 mmol), aqueous HF (0.1 mL, 40 wt%) and de-ionized water (9.6 mL) were placed in a 50 mL Teflon-liner autoclave and heated at 220 °C for 8 h. After natural cooling, the resulting green powder of MIL-101 with formula $Cr_3F(H_2O)_2O[(O_2C)C_6H_4(CO_2)]_3 \cdot nH_2O$ ($n \leq 25$) was doubly filtered off using two glass filters with pore sizes of 40 μm to eliminate the unreacted crystals of terephthalic acid, and then further purified by solvothermal treatment in ethanol at 80 ºC for 24 h. The resulting green solid was soaked in NH_4F (1 M) solution at 70 ºC for 24 h to eliminate the terephthalic acid inside the pores of MIL-101 and immediately filtered resulting green solid was finally dried overnight at 150 °C under vacuum for further use

Synthesis of H_2PdCl_4

A solution of tetrachloropalladinic acid (0.01M , H_2PdCl_4) was prepared by mixing 44.5 mg of $PdCl_2$ into 25 mL of HCl (0.02 M) aqueous solution under stirring at room temperature until complete dissolution.

Synthesis of Pd@MIL-101, AgPd@MIL-101, Ag@MIL-101

Activated MIL-101 (100 mg) was mixed with 10 mL de-ionized water containing 0.2 mmol $AgNO_3$ and H_2PdCl_4 stirring was continued for 24 h at 25℃to impregnate metal salts. The resulting mixture was then reduced by sodium borohydride ($NaBH_4$, 37.8 mg) solution with vigorous stirring at 273 K to yield Ag@MIL-101, $Ag_{78}Pd_{22}$@MIL-101, $Ag_{63}Pd_{37}$@MIL-101, $Ag_{48}Pd_{52}$@MIL-101, $Ag_{35}Pd_{65}$@MIL-101, $Ag_{20}Pd_{80}$@MIL-101, Pd@MIL-101.

Hydrolytic dehydrogenation of Formic acid

A mixture of 100 mg Pd@MIL-101 and 2 mL de-ionized water were kept in a two-necked round-bottom flask. One neck was connected to a pressure-equalization funnel to introduce 1 mL aqueous solution of 140mg formic acid and 70mg sodium formate , the other neck was connected to a gas burette to monitor the volume of the gas evolution. The reaction started when the aqueous solution was added to the catalyst, and the evolution of gas was monitored using the gas burette. The reactions were carried out at 353K in air.

In situ generation of the $Ag_{20}Pd_{80}$ catalyst and hydrolysis of Formic acid.

2 mL de-ionized water with 0.16mmol H_2PdCl_4 and 0.04mmol $AgNO_3$ was kept in a two-necked round-bottom flask. One neck was connected to a pressure-equalization funnel to introduce 3 mL aqueous solution of $NaBH_4$ (37.8 mg, 1mmol), and the other neck was connected to a gas burette to monitor the volume of the gas evolution. The reaction started when the aqueous solution was added to the solution, and the evolution of gas was monitored using the gas burette. The reactions were carried out at 273 K . After reaction was completed, 1 mL aqueous solution of 140mg formic acid and 70mg sodium formate was added into the reaction flask. The evolution of gas was monitored by the gas burette. The reactions were carried out at 353K.

Hydrolysis of Formic acid catalyzed by MIL-101

2 mL de-ionized water with activated MIL-101 (100mg) was kept in a two-necked round-bottom flask. One neck was connected to a pressure-equalization funnel to introduce 1 mL aqueous solution of aqueous solution of 140mg formic acid and 70mg sodium formate , the other neck was connected to a gas burette to monitor the volume of the gas

evolution. The reactions were carried out at 353 K.

CO_2 trap

The released gas during the reaction was passed through the NaOH trap, and its volume was monitored using the gas burette. The catalytic decomposition reaction for the release of hydrogen was initiated by stirring the mixture of 1mL aqueous solution of 100mg catalysts and 140mg formic acid and 70mg sodium formate.

Reusability test

1 mL of solution containing 140mg formic acid and 70mg sodium formate was added to 2 mL of water dissolved 100 mg $Ag_{20}Pd_{80}$@MIL-101, the evolution of gas was monitored as described above. After the reaction was completed, new aqueous formic acid solution (140 mg，1mL) was added into the reaction flask. The evolution of gas was monitored using the gas burette. Such cycle tests of the catalyst for the hydrolysis of formic acid were carried out four times in air.

Characterization

The morphologies and sizes of the samples were observed by using a Tecnai G20 U-Twin transmission electron microscope (TEM) equipped with an energy dispersive X-ray detector (EDX) at an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were measured by a Bruker D8-Advance X-ray diffractometer using Cu Ka radiation source (λ = 0.154178 nm) with a velocity of 1^o min^{-1}. X-ray photoelectron spectroscopy (XPS) measurement was performed with a Kratos XSAM 800 spectrophotometer. The surface area measurements were performed with N_2 adsorption/desorption isotherms at liquid nitrogen temperature (77K) after dehydration under vacuum at 150 ºC for 12 h using Quantachrome NOVA 4200e. The inductively

coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on IRIS Intrepid II XSP (Thermo Fisher Scientific, USA). Detailed analyses for CO_2, and CO were performed on GC-6890 with thermal conductivity detector (TCD) (detection limit: ~10 ppm), and H_2 was used as the references.

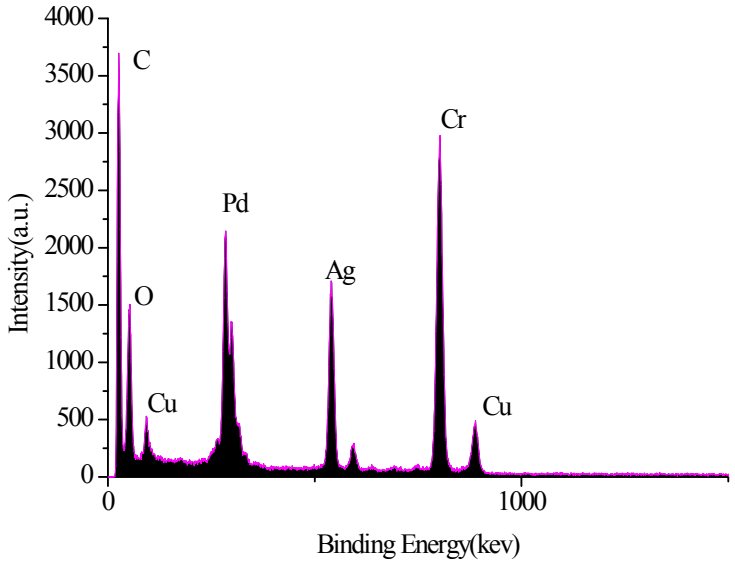

Fig. S1. EDX of $Ag_{20}Pd_{80}$@MIL-101

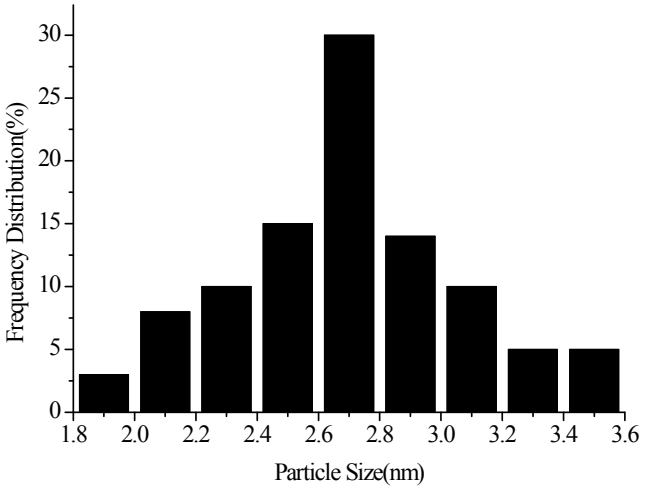

Fig. S2. $Ag_{20}Pd_{80}$ nanoparticle size distribution histogram of $Ag_{20}Pd_{80}$@MIL-101, Mean

size = 2.7 nm.

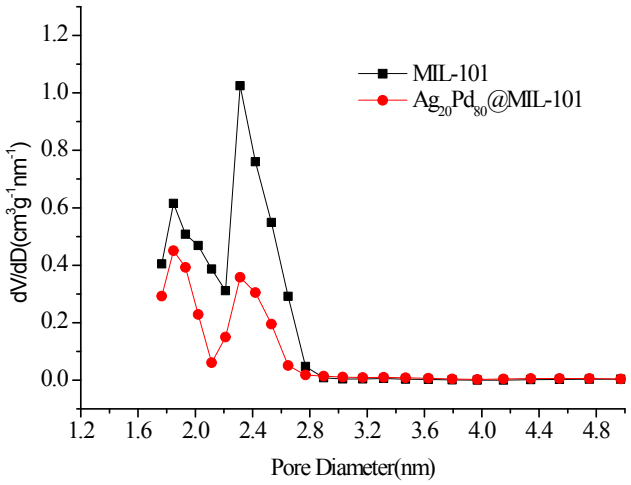

Fig. S3. Pore size distributions of activated MIL-101, $Ag_{20}Pd_{80}$@MIL-101.

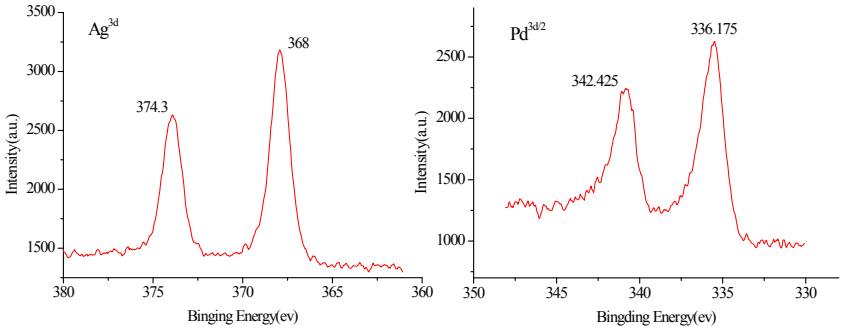

Fig. S4. XPS of $Ag_{20}Pd_{80}$@MIL-101 sample.

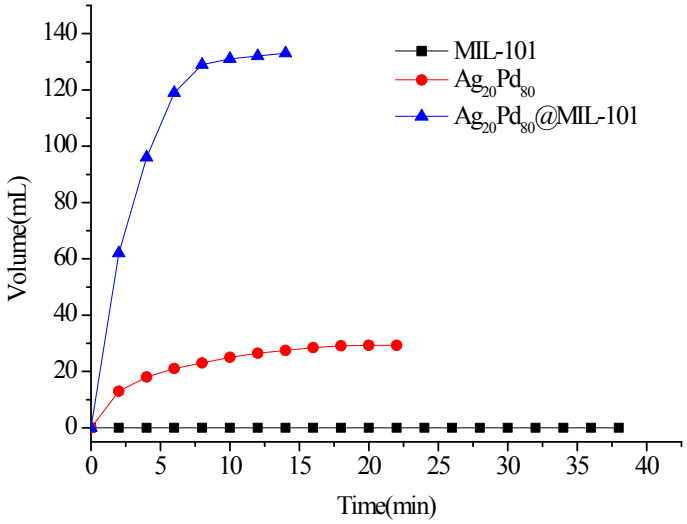

Fig. S5. catalytic activity of MIL-101, $Ag_{20}Pd_{80}$, $Ag_{20}Pd_{80}$@MIL-101 in hydrogen generation from formic acid at 80℃.

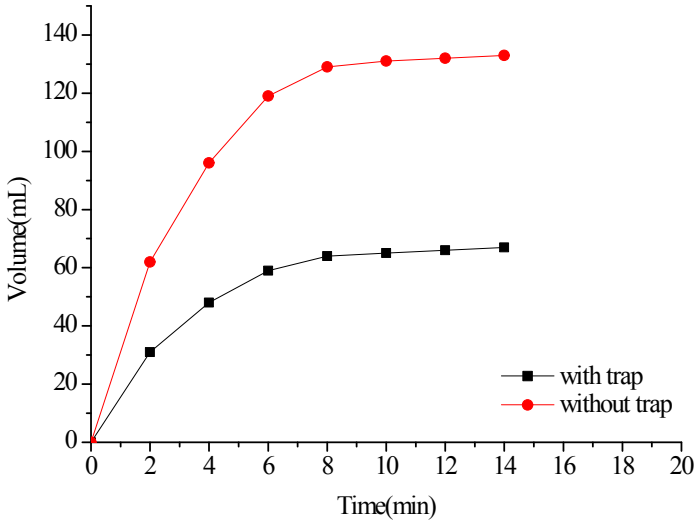

Fig. S6. catalytic activity of $Ag_{20}Pd_{80}$@MIL-101 in hydrogen generation from formic acid with CO_2 trap and without CO_2 trap.

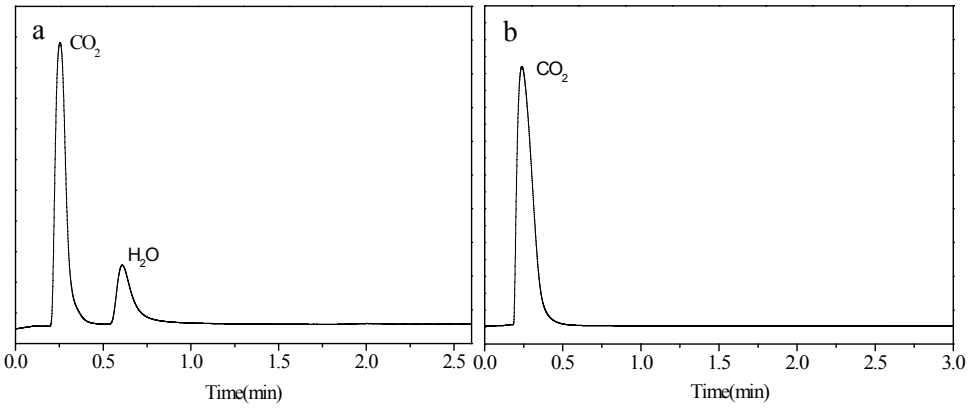

Fig. S7. (a) GC spectrum using DGC for the evolved gas from FA aqueous solution over $Ag_{20}Pd_{80}$ /MIL-101,(*nmetal/nFA* = 0.032) at 353 K;(b) GC spectrum for pure CO_2

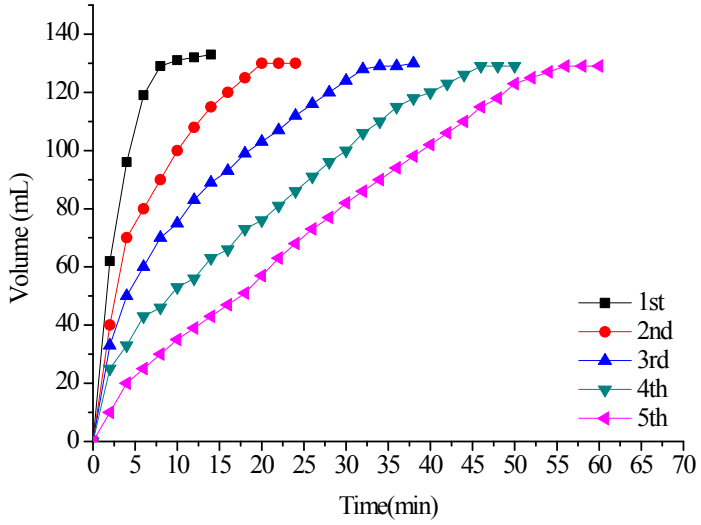

Fig. S8. Durability test for the hydrogen generation from aqueous HCOOH in the presence of $Ag_{20}Pd_{80}$@MIL-101 catalyst.

Table S1
Surface area measurements for MIL-101, $Ag_{20}Pd_{80}$@MIL-101

Sample	wt%	Surface Area(m^2g^{-1})	Pore Volume(cm^3g^{-1})
MIL-101		2232.796	1.195
$Ag_{20}Pd_{80}$@MIL-101	10.2	1111.017	0.5657

Table S2
ICP-AES results of different catalysts

Catalyst	Ag-Pd initial composition	Ag (wt%)	Pd (wt%)	Final Metals/ Catalyst (mmol/100 mg)
$Ag_{78}Pd_{22}$@MIL-101	4:1	7.88	2.31	0.095
$Ag_{63}Pd_{37}$@MIL-101	3:2	6.34	3.53	0.091
$Ag_{48}Pd_{52}$@MIL-101	1:1	4.83	5.42	0.096
$Ag_{35}Pd_{65}$@MIL-101	2:3	3.52	6.55	0.094
$Ag_{20}Pd_{80}$@MIL-101	1:4	2.08	8.02	0.095
Pd@MIL-101	0:5	0	14.96	0.14