Supporting Information

I. Reagents

Tetrachloroauric (III) acid (Aladdin , 99.99% , Shanghai)
Sodium tetrachloropalladate(II)（Aladdin ,98%, Shanghai）
sodium borohydride（$NaBH_4$, Aladdin , 98%, Shanghai）
Formic acid （HCOOH, FA, Aladdin , 98%, Shanghai）
Sodium formate（Aladdin , 96% , Shanghai）
Ethanol (Tianjin Chemical Reagents,>98% ,China)
De-ionized water
All the chemicals were used as received without further purification.

II. Preparation of Catalyst

The synthesis of catalysts was carried out in ice-water bath (nearly 0 ^oC,denoted as L-Au_6Pd_4) or in water bath (25 ^oC, denoted as R-Au_6Pd_4). Typically, 167 mg carbon (VXC-72) was dispersed into 10 ml distilled water, sonicated for 3 h. 5 ml aqueous solution (containing 0.018 mmol $HAuCl_4$ and 0.012 mmol Na_2PdCl_4) was added and stirred for 30 min. Then, 10 ml fresh $NaBH_4$ aqueous solution (containing 0.1g $NaBH_4$) was added into above mixture with magnetic stirring (800 r/min). After reduction for 5 h, the catalyst was separated by centrifugation, washed with distilled water and ethanol for several times respectively and dried in vacuum oven for 24 h at 25 ^oC. Catalysts with different Au-Pd ratios were synthesized with solution containing different concentration of $HAuCl_4$ and Na_2PdCl_4.

The preparation of catalysts and catalytic reactions were repeated for several times and the results were repeatable.

III. Characterization of Catalysts

Powder X-ray diffraction (XRD) patterns were recorded using a Bruker diffractometer with Cu K α radiation (D8 Advance X-ray diffractometer, Cu K α, λ=1.5406 Å 40 kV and 40 m A). The composition of the catalysts was measured by inductively coupled plasma-atomic emission spectrometer (ICP-AES, USA Thermo Jarrell-Ash Corp. ICP-9000 (N+M)). Field-emission electron microscopy (TEM), energy-dispersive X-ray spectrometry (EDS) and EELS elemental mapping observations were performed on a Philips Tecnai F20 microscope, working at 200 kV. All samples subjected to TEM measurements were dispersed in ethanol ultrasonically and were dropped on nickel grids. Concentration of H_2, CO_2 and CO was measured on SP-2100A GC with thermal conductivity detector (TCD) and flame ionization detector (FID)-Methanator.

IV. H_2 generation from FA/SF aqueous solution

Generally, 138 mg as-prepared catalyst was placed in a two-neck round bottom flask with one opening connected to gas burette and the other one connected to a pressure-equalization funnel. 10 ml formic acid (1.1 mol•L^{-1}) and sodium formate (0.8 mol•L^{-1}) aqueous solution was added into the flask through the funnel under magnetic stirring (800 r•min^{-1}). Hydrogen generation started once the solution is added. The reaction was carried out in water bath (25 ^{o}C) or ice-water bath (nearly 0 ^{o}C) respectively.

V.

Table S1 Activity for dehydrogenation of formic acid of various catalysts

Catalyst	Solvent/Medium	Temp. (^{o}C)	TOF (h^{-1})	Ref
Au-Pd/C	Aqueous HCOONa	25	1075	This work
		0	635	
Au/ZrO_2 NC_S	$5HCOOH/2NEt_3$	50	1593	9
		25	292	9
Ag@Pd/C	Aqueous	20	192	43
CoAuPd /C	Aqueous	25	80	30
Pd/C with citric acid	Aqueous HCOONa	25	64	20
Pd-Au/C-CeO2	Aqueous HCOONa	92	113.5	35
PdAu @ Au/C	Aqueous HCOONa	92	21.4	38
AuPd@ED-MIL-101	Aqueous HCOONa	90	106	40
Pd/MSC-30	Aqueous HCOONa	50	2623	26
		25	750	26
$Ag_{0.1}Pd_{0.9}$/rGO	Aqueous HCOONa	25	105.2	42
Au@Pd-N-mrGO	Aqueous	25	89.1	44
Pd-poly(allyl-amine)	Aqueous	22	46.1	25
PdNi@Pd/GNs-CB	Aqueous HCOONa	25	577	36
PdNi /GNs-CB	Aqueous HCOONa	25	529	36
B-Pd/C	Aqueous HCOONa	30	1184	33

VI.

Table S2 Activation energy for dehydrogenation of formic acid

Catalyst	E_a (KJ/mol)	Ref
L-Au_6Pd_4	21.98	This work
Au-ZrO2	49.3	19
PdAg/C	115	35
PdAu/C	115	35
Pd-Au/C-CeO2	84.2±7.4	34
1 wt%Au/TiO2	63	15
0.8wt%Au/C	55	15
1wt%Pd/C	65	15
1 wt %Pd/C with 2wt% K	97	24
PtRuBiOx	37	28
Ag@Pd	30	43
AgPd	22	45
Pd-MCM-30	39	26
2wt%Pt/Norit	70±3	27

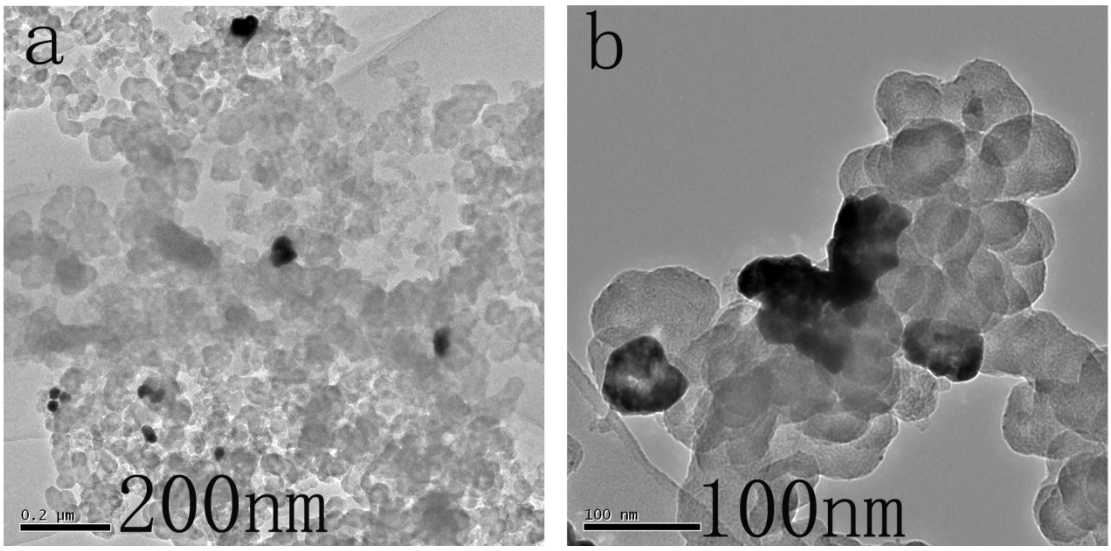
VII.

Table S3 Content of Au and Pd in L-Au_6Pd_4 catalyst

Method	Au	Pd
ICP	1.44（wt, %）	0.54（wt, %）
EDS	67.206(mol,%)	32.793(mol,%)

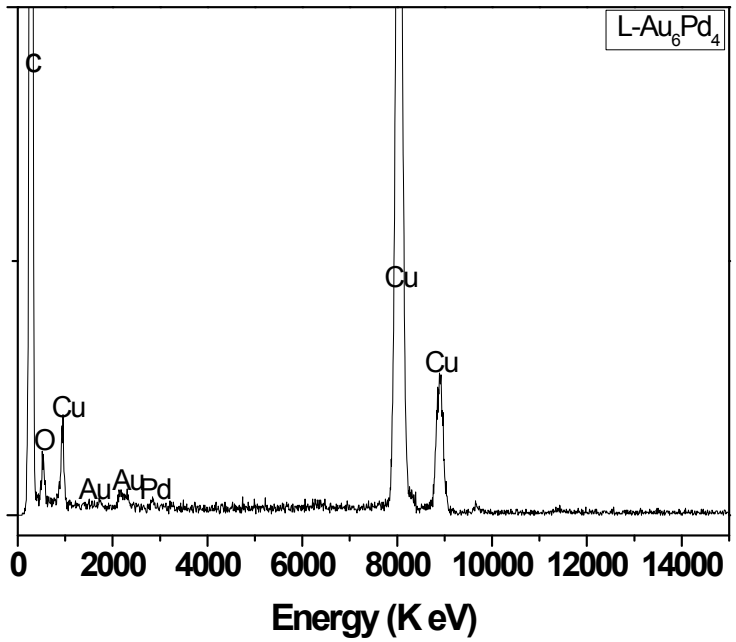
VIII.

Figure S1 TEM images of R-Au_6Pd_4



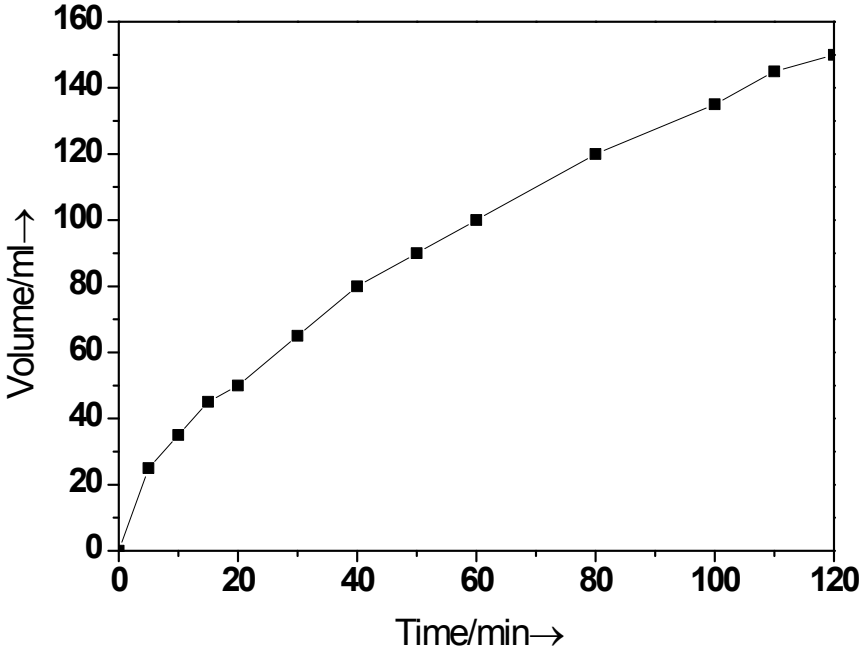
IX.

FigureS2 EDS image of L-Au_6Pd_4



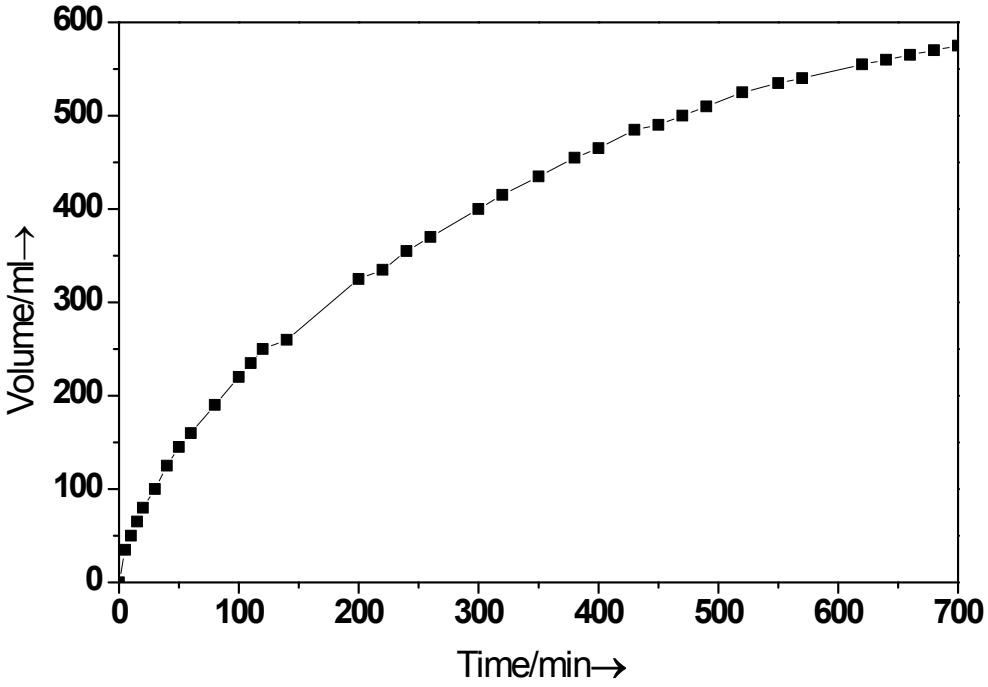
X.

Figure S3 H_2 generation with R-Au_6Pd_4 at 0 °C from FA/SF (1.1M FA,4.0MSF)



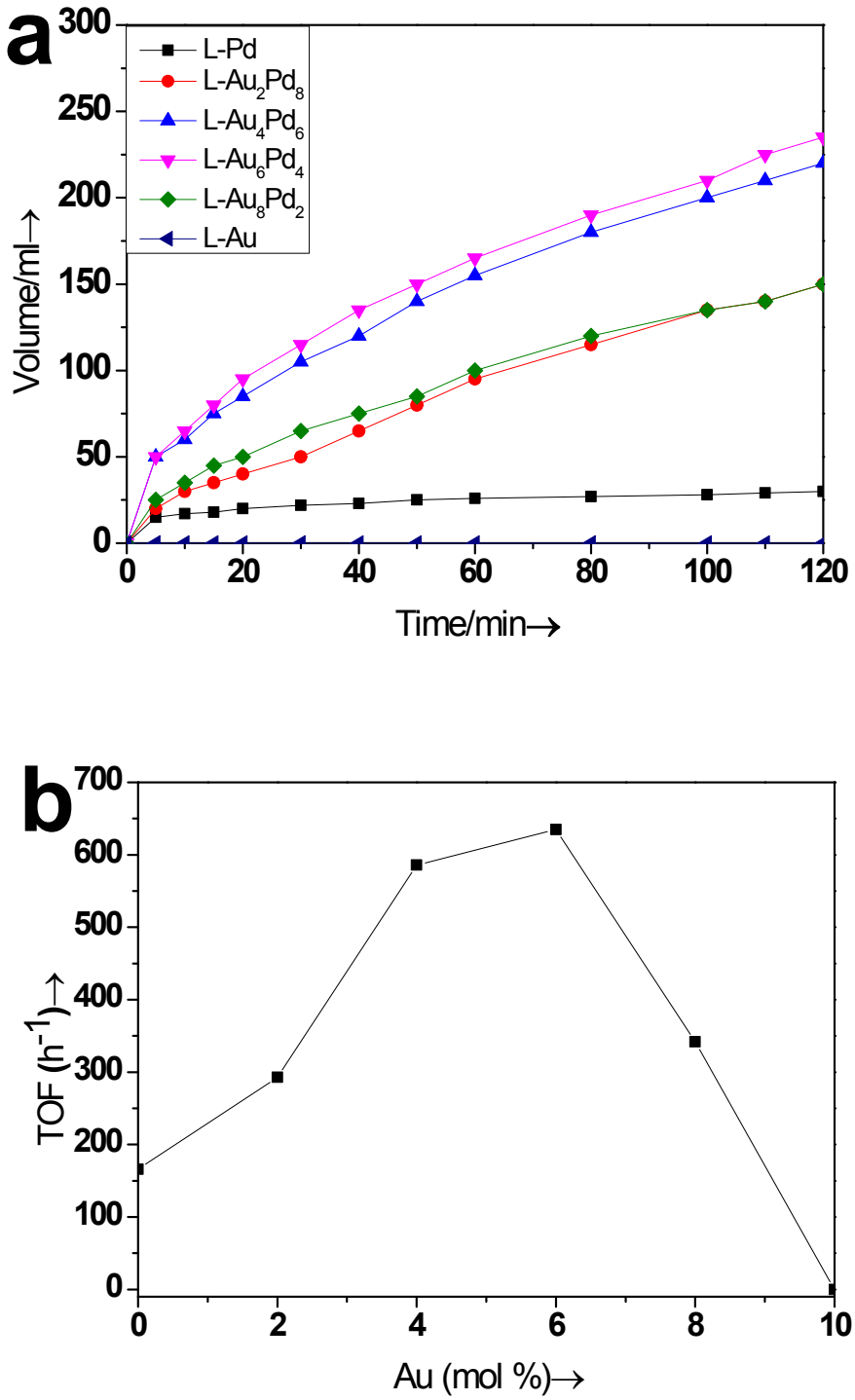
XI.

Figure S4 Gas generation by the decomposition of FA/SF (2.2 M FA, 1.6 M SF) solution with L-Au_6Pd_4 at nearly 0 ^oC for 700 min



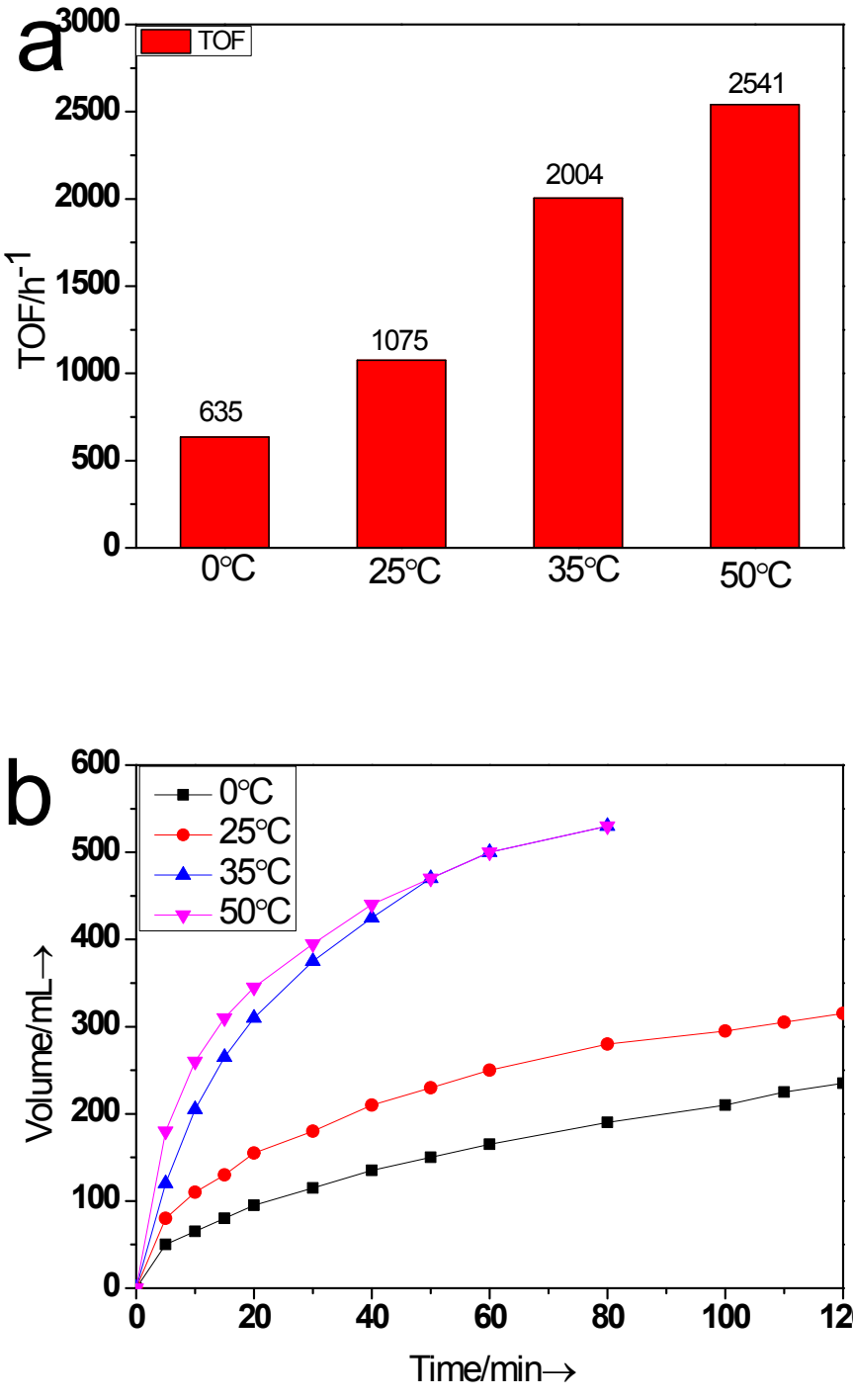
XII.

Figure S5 Gas generation and (b) initial TOF of the decomposition of FA/SF (1.1 M FA, 4.0 M SF) solution in present of L-$Au_xPd_{(1-x)}$ catalysts with different x value at nearly 0 ^oC.



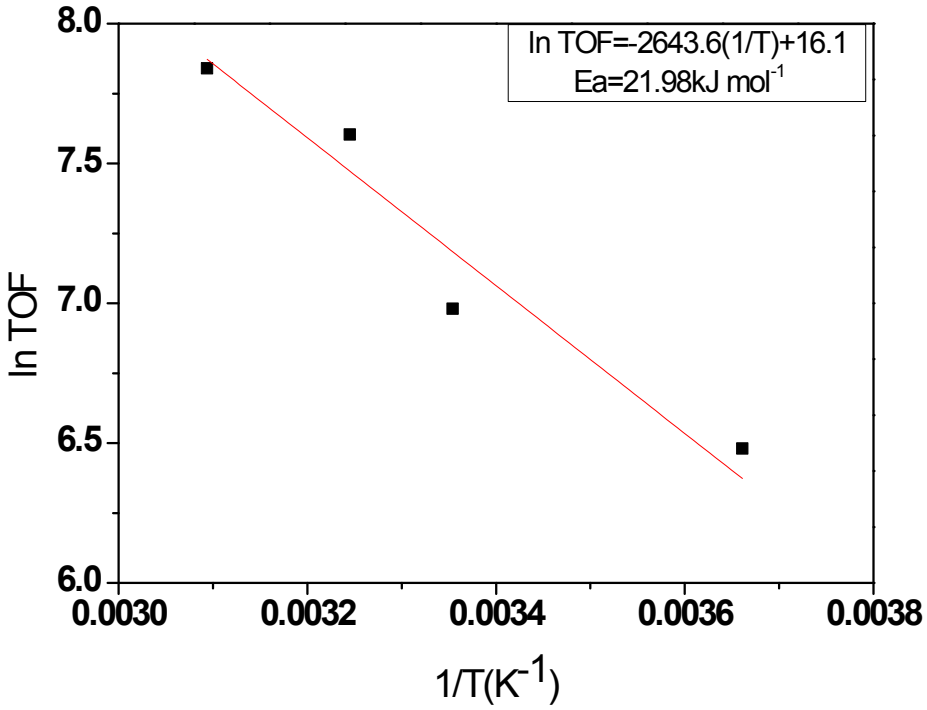
XIII.

Figure S6 (a) Initial TOF and (b) activity of L-Au_6Pd_4 at different temperatures



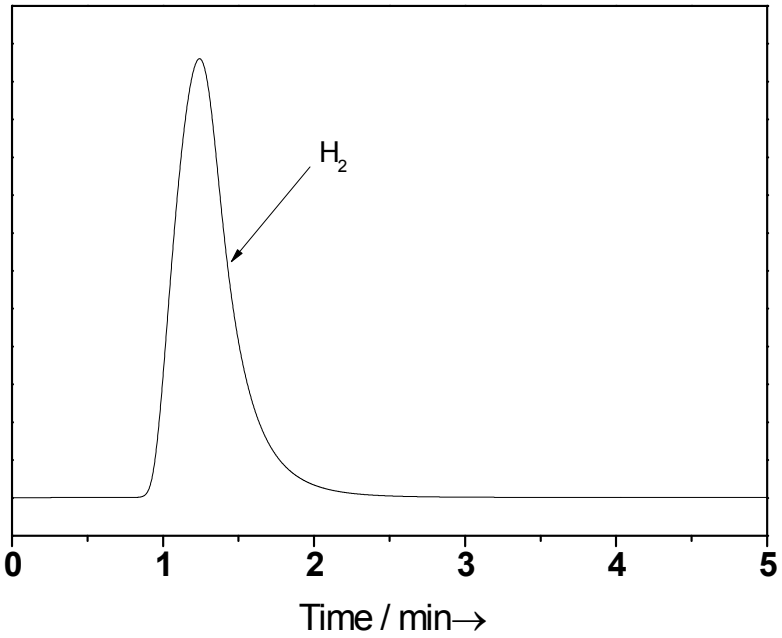
XIV.

Figure S7 Arrhenius plot (ln TOF vs 1/T)



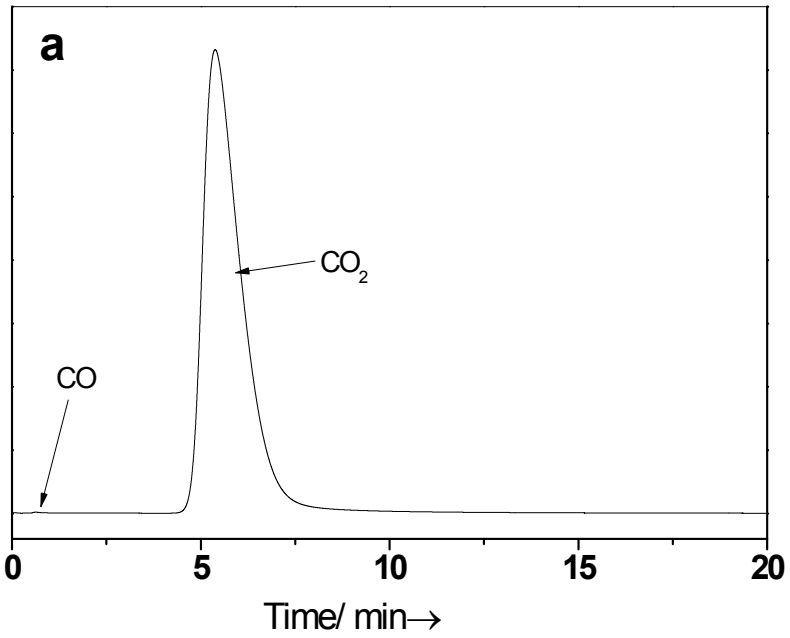
XV.

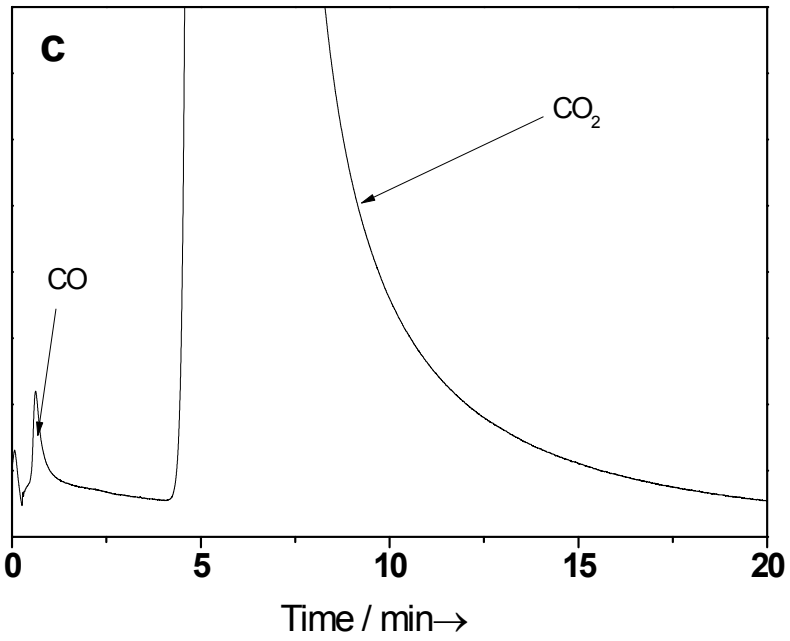
Figure S8 GC spectrum using TCD for the gas generated from FA/SF solution (1.1 M FA, 4.0 M SF)



XVI.

Figure S9 (a) GC spectrum using TCD for the gas generated from FA/SF solution (1.1 M FA, 4.0 M SF) and (b) magnified image





XVII. The calculation of the initial TOF

The initial TOF in this research is calculated by following equation,

$$TOF_{initial} = \frac{p_{atm} V_{H_2}}{RTn_{Au+Pd}t}$$

Where p_{atm} is the pressure of atmosphere, V_{H2} is the volume of hydrogen generated, T is the reaction temperature, n_{Au+Pd} is the total mole number of Au and Pd in the catalyst and t is reaction time (10 min).