Electronic Supplementary Information

Monodispersed gold nanoparticles supported on a Zirconium- based porous metal-organic framework and its high catalytic ability for the reverse water-gas shift reaction

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Experimental section

Materials and characterization methods

All chemicals were purchased from commercial suppliers and used without further purification.

Synthesis of UIO-67: UIO-67 was synthesized according to the procedures reported in the literature^{1, 2}, In a typical synthesis, ZrCl₄ (99.99%, 0.067 g) and 4,4'-Biphenyldicarboxylic acid (98%,0.09 g) and n ml acetic acid were dissolved in N,N-Dimethylformamide (DMF, 99.8%, 15 ml) at room temperature, the mixtures were sonicated for 20 minutes and sealed in an autoclave and placed in a preheated oven at 120 °C for 24 h. After the reaction, the product was collected by centrifugation and washed with fresh DMF for three times and dried at 120 °C overnight. Fig. S2 are SEM images of UIO-67 with different amount of acetic acid, a better monodisperse octahedron appeared when 1.4 ml acetic acid was added, in the next experiment all the UIO-67 was synthesized with 1.4 ml acetic acid added.

Synthesis of Au@UIO-67-H₂: Au@UIO-67-H₂ catalyst was prepared by mixing 0.3 g of UIO-67 with 1.9 ml HAuCl₄ methanol solution (1 g HAuCl₄·4H₂O in 100 ml methanol) in 30 mL of MeOH, the resulting mixture was stirred at RT for 5 h before centrifugation, the obtained Au³⁺/UIO-67 was dried at 60 °C then reduced at 200 °C for 3 h under H₂ stream, the resulting sample was marked as Au@UIO-67-H₂. Different Au content samples were also obtained using the same method.

Synthesis of Au@UIO-67-NaBH₄: Au@UIO-67-NaBH₄ catalyst was prepared by mixing 0.3 g of UIO-67 with 1.9 ml HAuCl₄ methanol solution in 30 mL of MeOH, the resulting mixture was stirred at RT for 5 h and NaBH₄ was added (30 times excess) to the solution and stirred for one hour at RT, then washed under stirring for 4 times with methanol before centrifugation and drying at 120 °C, the catalyst was marked as Au@UIO-67-NaBH₄.

Synthesis of Au@UIO-67-oleymine: Au@UIO-67-oleymine catalyst was prepared by mixing 0.3 g of UIO-67 with 1.9 ml HAuCl₄ methanol solution in 30 mL of MeOH, the resulting mixture was stirred at RT for 5 h before centrifugation, the obtained Au³⁺/UIO-67 was dried at 60 °C and dispersed in 10 ml oleylamine and stirred for 5 h at 100 °C, after the reaction the sample was washed under stirring for 5 times with ethanol before centrifugation and drying at 120 °C, the sample was marked as Au@UIO-67-oleylamine. As a comparison, 60 °C without stirring has also been done.

Synthesis of Au@TiO₂-H₂: Au@TiO₂-H₂ catalyst was prepared by mixing 0.3 g of TiO₂ with 1.9 ml HAuCl₄ methanol solution in 30 mL of MeOH, the resulting mixture was stirred at RT for 5 h before centrifugation, the obtained Au³⁺/TiO₂ was dried at 60 °C then reduced at 200 °C for 3h under H₂ stream, the resulting sample was marked as Au@TiO₂-H₂.

Synthesis of Au@MgO-H₂: Au@ MgO-H₂ catalyst was prepared by mixing 0.3 g of MgO with 1.9 ml HAuCl₄ methanol solution in 30 mL of MeOH, the resulting mixture was stirred at RT for 5 h before centrifugation, the obtained Au^{3+/} MgO was dried at 60 °C then reduced at 200 °C for 3h under H₂ stream, the resulting sample was marked as Au@MgO-H₂.

N₂ adsorption-desorption measurements:

The specific surface areas of the samples were characterized by N_2 physisorption measurements at 77 K and all samples were outgassed at 150 °C for 3 h under a primary vacuum.

Activity test of catalysts: The activity test of the CO_2 hydrogenation was performed with a fixedbed flow reactor and analyzed using a gas chromatograph(GC) equipped with hydrogen flame ionization detector (FID). Contents were quantified with external standard method. The operating parameters are as follows: column temperature, 80 °C; detector temperature, 120 °C; carrier gas, hydrogen. All the samples were activated with H₂ at 200 °C for 3 h before catalytic test.



Fig. S1 CAD drawing of fixed-bed flow reactor

 Table S1 Deposition efficiency with different gold nanoparticle (AuNP) content supported within

 UIO-67.

Samples	Nominal metal	Actual metal		
	loading (wt%) ^a	loading (wt%) ^b		
0.71 wt% Au@UIO-67-H ₂	1.0	0.71		
2.40 wt% Au@UIO-67-H ₂	3.0	2.40		
4.30 wt% Au@UIO-67-H ₂	5.0	4.30		

^aDetermined by loading amount of metal precursors.

^bDetermined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis.

Catalyst	Catalyst	Au/Co/Mo	Т	H_2/CO_2	GHSV	CO ₂	со	CH ₄	Ref.
	dosage	content	(°C)		mL/(h·g)	conversion	selectivity	selectivity	
	(g)	(%)				(%)	(%)	(%)	
Au@UIO-67	0.2	2.4	408	1:1	12000	12.2	/	/	This
-H ₂									work
Au@UIO-67	0.2	2.4	408	3:1	12000	30.5	96.5	3.5	This
-H ₂									work
Au@TiO2	0.2	3 ^a	408	3:1	12000	1.9	/	/	This
-H ₂									work
Au@MgO	0.2	3 ^a	408	3:1	12000	1.7	/	/	This
-H ₂									work
Au/CeO ₂	1	3	400	1:1	12000	15.4	/	/	S3
Au/CeO ₂	1	3	400	3:1	12000	27.6	100	0	S3
Co/CeO ₂	0.02	2	400	1:1	300000	6	97	3	S4
Co/CeO ₂	0.02	2	450	1:1	300000	16	100	0	S4
β-Μο2C	0.05	/	400	4:1	36000	28	98	2	S5

Table S2 The comparison between the results in this work and the results reported in literature

^a Nominal metal loading, determined by loading amount of metal precursors.

Seen in the Table S2, CO₂ conversion of three catalysts for RWGS are about 30.5% for Au@UIO-67-H₂, 1.9% for Au@TiO₂-H₂, and 1.7% for Au@MgO-H₂ respectively. The results show Au@UIO-67-H₂ is the highly active catalyst, and its catalytic activity is much better than that of Au@ TiO₂-H₂ or Au@MgO-H₂ for RWGS. In the preparation process of Au@ UIO-67-H₂ catalysts, due to the porosity and exceptionally high surface areas of UIO-67, Au³⁺ is favor to be adsorbed on the exterior pores or cavities of UIO-67 when stirring with HAuCl₄ in methanol, and is further reduced to AuNPs. Compared with UIO-67, common metal oxide supports such as TiO₂ or MgO shows no pores and low surface areas, Au³⁺ is not easy to be adsorbed on the supports under the same conditions. So Au@TiO₂-H₂ and Au@MgO-H₂ catalysts perform a very poor catalytic activity for RWGS, indicating that this method is not suitable for imporous metal oxide as supports to synthesize composite Au catalysts.



Fig. S2 SEM images of UIO-67 with different amount of acetic acid. (a) 0 ml, (b) 0.2 ml, (c) 0.4 ml, (d) 0.6 ml, (e) 0.8 ml, (f) 1.0 ml, (g) 1.2 ml, (h) 1.4 ml. Through the SEM images, we can see a better monodisperse octahedron appeared when 1.4 ml acetic acid was added.



Fig. S3 TEM images of UIO-67



Fig. S4 TEM images of Au@UIO-67-NaBH₄



Fig. S5 TEM images of Au@UIO-67-oleylamine (Reduction temperature was 60 °C and without stirring)



Fig. S6 (a, b, c) TEM images of Au@UIO-67-oleylamine, (d) Oleylamine solution after the reduction of Au³⁺/UIO-67 and optical photograph of Au@UIO-67-oleylamine (Reduction temperature was 100 °C with stirring)



Fig. S7 TEM images of 0.71 wt% Au@UIO-67-H $_2$



Fig. S8 TEM images of 2.40 wt% Au@UIO-67-H $_2$ (a, b, c) and HRTEM images (d, e, f)



Fig. S9 TEM images of 4.30 wt% Au@UIO-67- H_2



Fig. S10 TEM images of Au@UIO-67-NaBH $_4$ catalyst after catalytic test



Fig. S11 TEM images of Au@UIO-67-oleylamine catalyst after catalytic test



Fig. S12 TEM images of Au@UIO-67-H $_2$ catalyst after catalytic test



Fig. S13 XRD patterns of UIO-67-simulation (black), UIO-67-experiment (red), Au@UIO-67-NaBH₄ (blue), Au@UIO-67-oleylamine (magenta), Au@UIO-67-H₂ (green).



Fig. S14 XRD patterns of 0.71 wt% Au@UIO-67-H₂ (magenta), 2.40 wt% Au@UIO-67-H₂ (blue) and 4.30 wt% Au@UIO-67-H₂ (red).









Fig. S16 N₂ adsorption isotherms at 77 K for Au@UIO-67-oleylamine (a), Au@UIO-67-NaBH₄
(b) and corresponding micropore size distribution (inset), (nominal metal loading are both 3.0 wt%)



Fig. S17 The corresponding micropore size distribution of UIO-67 and 0.71 wt% Au@UIO-67-H₂, 2.40 wt% Au@UIO-67-H₂, 4.30 wt% Au@UIO-67-H₂.



Fig. S18 XPS patterns of the 2.4 wt% Au@UIO-67-H_2 catalyst before catalysis



Fig. S19 XPS patterns (Au) of three catalysts before (left) and after (right) catalysis



Fig. S20 CO₂ conversion of three catalysts for RWGS, Au@UIO-67-H₂ (black), Au@UIO-67-NaBH₄ (red) and Au@UIO-67-oleylamine (blue) at the same conditions. (catalyst: 0.2 g, temperature: 408 °C, space velocity: 12000 ml/h·gcat, pressure: 2.0 Mpa, CO₂:H₂=1:5)



Fig. S21 CO₂ conversion of three catalysts for RWGS, Au@UIO-67-H₂ (black), Au@TiO₂-H₂ (red) and Au@MgO-H₂ (blue) at the same conditions. (catalyst: 0.2 g, temperature: 408 °C, space velocity: 12000 ml/h·gcat, pressure: 2.0 Mpa, CO₂:H₂=1:3)



Fig. S22 (a) CO₂ conversion at different reaction temperatures for RWGS (catalyst: 0.2 g of 2.40 wt% Au@UIO-67-H₂, pressure: 2.0 Mpa, space velocity: 12000 ml/h·gcat, CO₂:H₂=1:3); (b) CO₂ conversion under different reaction pressures for RWGS (catalyst: 0.2 g of 2.40 wt% Au@UIO-67-H₂, temperature: 408 °C, space velocity: 12000 ml/h·gcat, CO₂:H₂=1:3); (c) CO₂ conversion with different volume ratios for RWGS (catalyst: 0.2 g of 2.40 wt% Au@UIO-67-H₂, temperature: 408 °C, pressure: 2.0 Mpa, space velocity: 12000 ml/h·gcat); (d) CO₂ conversion with different Au contents for RWGS (catalyst: 0.2 g of Au@UIO-67-H₂, temperature: 408 °C, space velocity: 12000 ml/h·gcat); (d) CO₂ conversion with different XI contents for RWGS (catalyst: 0.2 g of Au@UIO-67-H₂, temperature: 408 °C, space velocity: 12000 ml/h·gcat); (d) CO₂ conversion with different XI contents for RWGS (catalyst: 0.2 g of Au@UIO-67-H₂, temperature: 408 °C, space velocity: 12000 ml/h·gcat); (d) CO₂ conversion with different XI contents for RWGS (catalyst: 0.2 g of Au@UIO-67-H₂, temperature: 408 °C, space velocity: 12000 ml/h·gcat); (d) CO₂ conversion with different XI contents for RWGS (catalyst: 0.2 g of Au@UIO-67-H₂, temperature: 408 °C, space velocity: 12000 ml/h·gcat, CO₂:H₂=1:5).



Fig. S23 Selectivity of CO and CH₄ (left) and longevity test of 2.4 wt% Au@UIO-67-H₂ (right) (catalyst: 0.2 g of 2.40 wt% Au@UIO-67-H₂, temperature: 408 °C, space velocity: 12000 ml/h·gcat, CO₂:H₂=1:5)

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