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, ZrCl\(_4\) (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-H\(_2\): Au@UIO-67-H\(_2\) catalyst was prepared by mixing 0.3 g of UIO-67 with 1.9 ml HAuCl\(_4\) methanol solution (1 g HAuCl\(_4\)-4H\(_2\)O in 100 ml methanol) in 30 mL of MeOH, the resulting mixture was stirred at RT for 5 h before centrifugation, the obtained Au\(^{3+}\)/UIO-67 was dried at 60 °C then reduced at 200 °C for 3 h under H\(_2\) stream, the resulting sample was marked as Au@UIO-67-H\(_2\). Different Au content samples were also obtained using the same method.

Synthesis of Au@UIO-67-NaBH\(_4\): Au@UIO-67-NaBH\(_4\) catalyst was prepared by mixing 0.3 g of UIO-67 with 1.9 ml HAuCl\(_4\) methanol solution in 30 mL of MeOH, the resulting mixture was stirred at RT for 5 h and NaBH\(_4\) 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-NaBH\(_4\).

Synthesis of Au@UIO-67-oleylamine: Au@UIO-67-oleylamine catalyst was prepared by mixing 0.3 g of UIO-67 with 1.9 ml HAuCl\(_4\) methanol solution in 30 mL of MeOH, the resulting mixture was stirred at RT for 5 h before centrifugation, the obtained Au\(^{3+}\)/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@TiO$_2$-H$_2$: Au@TiO$_2$-H$_2$ catalyst was prepared by mixing 0.3 g of TiO$_2$ with 1.9 ml HAuCl$_4$ methanol solution in 30 mL of MeOH, the resulting mixture was stirred at RT for 5 h before centrifugation, the obtained Au$^{3+}$/TiO$_2$ was dried at 60 °C then reduced at 200 °C for 3h under H$_2$ stream, the resulting sample was marked as Au@TiO$_2$-H$_2$.

Synthesis of Au@MgO-H$_2$: Au@ MgO-H$_2$ catalyst was prepared by mixing 0.3 g of MgO with 1.9 ml HAuCl$_4$ 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 H$_2$ stream, the resulting sample was marked as Au@MgO-H$_2$.

N$_2$ 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 fixed-bed 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 H$_2$ at 200 °C for 3 h before catalytic test.

![Fig. S1 CAD drawing of fixed-bed flow reactor](image)
Table S1 Deposition efficiency with different gold nanoparticle (AuNP) content supported within UIO-67.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Nominal metal loading (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Actual metal loading (wt%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.71 wt% Au@UIO-67-H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.0</td>
<td>0.71</td>
</tr>
<tr>
<td>2.40 wt% Au@UIO-67-H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.0</td>
<td>2.40</td>
</tr>
<tr>
<td>4.30 wt% Au@UIO-67-H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5.0</td>
<td>4.30</td>
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</tbody>
</table>

<sup>a</sup>Determined by loading amount of metal precursors.

<sup>b</sup>Determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis.

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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst dosage (g)</th>
<th>Au/Co/Mo content (%)</th>
<th>T (℃)</th>
<th>H₂/CO₂</th>
<th>GHSV mL/(h·g)</th>
<th>CO₂ conversion (%)</th>
<th>CO selectivity (%)</th>
<th>CH₄ selectivity (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au@UIO-67-H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.2</td>
<td>2.4</td>
<td>408</td>
<td>1:1</td>
<td>12000</td>
<td>12.2</td>
<td>/</td>
<td>/</td>
<td>This work</td>
</tr>
<tr>
<td>Au@UIO-67-H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.2</td>
<td>2.4</td>
<td>408</td>
<td>3:1</td>
<td>12000</td>
<td>30.5</td>
<td>96.5</td>
<td>3.5</td>
<td>This work</td>
</tr>
<tr>
<td>Au@TiO&lt;sub&gt;2&lt;/sub&gt;-H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.2</td>
<td>3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>408</td>
<td>3:1</td>
<td>12000</td>
<td>1.9</td>
<td>/</td>
<td>/</td>
<td>This work</td>
</tr>
<tr>
<td>Au@MgO-H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.2</td>
<td>3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>408</td>
<td>3:1</td>
<td>12000</td>
<td>1.7</td>
<td>/</td>
<td>/</td>
<td>This work</td>
</tr>
<tr>
<td>Au/CeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1</td>
<td>3</td>
<td>400</td>
<td>1:1</td>
<td>12000</td>
<td>15.4</td>
<td>/</td>
<td>/</td>
<td>S3</td>
</tr>
<tr>
<td>Au/CeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1</td>
<td>3</td>
<td>400</td>
<td>3:1</td>
<td>12000</td>
<td>27.6</td>
<td>100</td>
<td>0</td>
<td>S3</td>
</tr>
<tr>
<td>Co/CeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.02</td>
<td>2</td>
<td>400</td>
<td>1:1</td>
<td>300000</td>
<td>6</td>
<td>97</td>
<td>3</td>
<td>S4</td>
</tr>
<tr>
<td>Co/CeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.02</td>
<td>2</td>
<td>450</td>
<td>1:1</td>
<td>130000</td>
<td>16</td>
<td>100</td>
<td>0</td>
<td>S4</td>
</tr>
<tr>
<td>β-Mo&lt;sub&gt;2&lt;/sub&gt;C</td>
<td>0.05</td>
<td>/</td>
<td>400</td>
<td>4:1</td>
<td>360000</td>
<td>28</td>
<td>98</td>
<td>2</td>
<td>S5</td>
</tr>
</tbody>
</table>

<sup>a</sup> 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-H<sub>2</sub>, 1.9% for Au@TiO<sub>2</sub>-H<sub>2</sub>, and 1.7% for Au@MgO-H<sub>2</sub> respectively. The results show Au@UIO-67-H<sub>2</sub> is the highly active catalyst, and its catalytic activity is much better than that of Au@TiO<sub>2</sub>-H<sub>2</sub> or Au@MgO-H<sub>2</sub> for RWGS. In the preparation process of Au@ UIO-67-H<sub>2</sub> catalysts, due to the porosity and exceptionally high surface areas of UIO-67, Au<sup>3+</sup> 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 TiO<sub>2</sub> or MgO shows no pores and low surface areas, Au<sup>3+</sup> is not easy to be adsorbed on the supports under the same conditions. So Au@TiO<sub>2</sub>-H<sub>2</sub> and Au@MgO-H<sub>2</sub> 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 Au$^{3+}$/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-H2

Fig. S10 TEM images of Au@UIO-67-NaBH₄ 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-H₂ catalyst after catalytic test
Fig. S13 XRD patterns of UIO-67-simulation (black), UIO-67-experiment (red), Au@UIO-67-NaBH$_4$ (blue), Au@UIO-67-oleylamine (magenta), Au@UIO-67-H$_2$ (green).

Fig. S14 XRD patterns of 0.71 wt% Au@UIO-67-H$_2$ (magenta), 2.40 wt% Au@UIO-67-H$_2$ (blue) and 4.30 wt% Au@UIO-67-H$_2$ (red).
Fig. S15 XRD patterns of three catalysts after catalytic test.
Fig. S16 N$_2$ adsorption isotherms at 77 K for Au@UIO-67-oleylamine (a), Au@UIO-67-NaBH$_4$ (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-H$_2$, 2.40 wt% Au@UIO-67-H$_2$, 4.30 wt% Au@UIO-67-H$_2$. 
Fig. S18 XPS patterns of the 2.4 wt% Au@UIO-67-H\textsubscript{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) CO$_2$ conversion at different reaction temperatures for RWGS (catalyst: 0.2 g of 2.40 wt% Au@UIO-67-H$_2$, pressure: 2.0 Mpa, space velocity: 12000 ml/h·gcat, CO$_2$:H$_2$=1:3); (b) CO$_2$ conversion under different reaction pressures for RWGS (catalyst: 0.2 g of 2.40 wt% Au@UIO-67-H$_2$, temperature: 408 °C, space velocity: 12000 ml/h·gcat, CO$_2$:H$_2$=1:3); (c) CO$_2$ conversion with different volume ratios for RWGS (catalyst: 0.2 g of 2.40 wt% Au@UIO-67-H$_2$, temperature: 408 °C, pressure: 2.0 Mpa, space velocity: 12000 ml/h·gcat); (d) CO$_2$ conversion with different Au contents for RWGS (catalyst: 0.2 g of Au@UIO-67-H$_2$, temperature: 408 °C, space velocity: 12000 ml/h·gcat, CO$_2$:H$_2$=1:5).

Fig. S23 Selectivity of CO and CH$_4$ (left) and longevity test of 2.4 wt% Au@UIO-67-H$_2$ (right) (catalyst: 0.2 g of 2.40 wt% Au@UIO-67-H$_2$, temperature: 408 °C, space velocity: 12000 ml/h·gcat, CO$_2$:H$_2$=1:5)