[Supporting Information]

Heterostructured BaSO\(_4\)–SiO\(_2\) mesoporous materials as new supports for gold nanoparticles in low-temperature CO oxidation

Chengcheng Tian\(^{a,b}\), Song-Hai Chai\(^{b,*}\), David R. Mullins\(^b\), Xiang Zhu\(^{a,b}\), Andrew Binder\(^c\), Yanglong Guo\(^{a,*}\), Sheng Dai\(^{b,c,*}\)

\(^a\)Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, P.R. China

\(^b\)Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

\(^c\)Department of Chemistry, University of Tennessee–Knoxville, Tennessee 37996-1600, United States

*Corresponding authors: Fax: +1 865 576 5235; E-mail: dais@ornl.gov (S.DAI)

Fax: +86 21 6425 2923; E-mail: ylguo@ecust.edu.cn (Y.L. GUO)

Fax: +1 865 576 5235; E-mail: chais@ornl.gov (S.-H. CHAI)
Contents

1. Experimental Section

2. Figures

Fig. S1. Wide-angle XRD patterns of BaSO$_4$-MCF (KHSO$_4$) and BaSO$_4$-MCF (SDBS) with three SDBS concentrations (0.001 mol L$^{-1}$, 0.005 mol L$^{-1}$ and 0.01 mol L$^{-1}$).

Fig. S2. Nitrogen adsorption-desorption isotherms and pore size distributions of MCF and BaSO$_4$-MCF (SDBS) prepared at a SDBS concentration of 0.005 mol L$^{-1}$.

Fig. S3. TEM image of (a) BaSO$_4$-MCF (SDBS) with the SDBS concentration of 0.001 mol L$^{-1}$; (b) BaSO$_4$-MCF (SDBS) with the SDBS concentration of 0.005 mol L$^{-1}$ and (c) BaSO$_4$-MCF (SDBS) with the SDBS concentration of 0.01 mol L$^{-1}$. Scale bar = 20 nm.

Fig. S4. Wide-angle XRD patterns of Au-BaSO$_4$-MCF (KHSO$_4$) and Au-BaSO$_4$-MCF (SDBS) after 300 °C pretreatment.

Fig. S5. Wide-angle XRD patterns and Z-contrast STEM of BaSO$_4$-MCF (KHSO$_4$) and BaSO$_4$-MCF (SDBS) after 500 °C treatment.

Fig. S6. CO light-off curves of Au-BaSO$_4$-MCF (KHSO$_4$) and Au-BaSO$_4$-MCF (SDBS) after 300 °C pretreatment (GHSV = 30000 mL/h/g$_{\text{cat}}$).

Fig. S7. CO light-off curves of Au-BaSO$_4$-MCF (KHSO$_4$) and Au-BaSO$_4$-MCF (SDBS) after 500 °C pretreatment. (GHSV = 30000 mL/h/g$_{\text{cat}}$).

Fig. S8. Time-on-stream of CO oxidation rates at 0 °C over Au-BaSO$_4$-MCF (SDBS) after 300 °C and 500 °C pretreatments and Au/TiO$_2$ after 300 °C pretreatment.

Fig. S9. TEM images of 1 wt% Au/TiO$_2$ reference catalyst.

Fig. S10. Au LIII-edge XANES spectra of as-prepared and 300 °C-calcined Au-BaSO$_4$-MCF (SDBS), Au/TiO$_2$ (World Gold Council), and Au foil.

Fig. S11. Au LIII-edge EXAFS spectra of as-prepared and 300 °C-calcined Au-BaSO$_4$-MCF (SDBS), Au/TiO$_2$ (World Gold Council), and Au foil.

3. Table

Table S1 EXAFS fitting results for Au-BaSO$_4$-MCF (SDBS) nanoparticles and several reference materials.
1. Experimental Section

1.1 Preparation of BaSO₄-MCF

The BaSO₄-MCF materials were prepared by an in-situ growth method. First, mesostructured cellular foam (MCF) was synthesized as described by Schmidt-Winkel et al. Barium acetate was selected as the barium precursor and incorporated into a MCF framework using a solvent evaporation method. Briefly, the prepared MCF (0.6 g) was added into deionized water containing the barium precursor (0.08 g). The mixture was stirred at 35 °C for 3 h, and then the temperature was increased to 80 °C to completely evaporate water in the vacuum. The product (BaO-MCF) was calcined at 550 °C for 3 h. Secondly, the prepared BaO-MCF (0.3 g) was placed in a 100 mL beaker with 50 mL of deionized water containing a certain amount of sodium dodecyl-benzenesulfonate (S/Ba molar ratio = 1) as the sulfate source. The mixture was stirred at 25 °C for 24 h. Then the suspension was washed with deionized water by centrifugation several times, and the precipitate was separated to dry overnight at 100 °C and calcined in air at 550 °C for 3 h to decompose into BaSO₄. BaSO₄-MCF was obtained as an Au catalyst support.

1.2 Synthesis of gold catalysts supported on BaSO₄-MCF

The Au precursor was introduced onto the BaSO₄-MCF support using a deposition-precipitation (DP) method. Typically, 0.04 g of hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄·3H₂O) was dissolved into 4 mL deionized water. The pH value of the resulting solution was adjusted to 10 using a solution of 1.0 mol L⁻¹ NaOH under vigorous stirring at room temperature. Subsequently, the as-synthesized BaSO₄-MCF support was added and the pH value was controlled at 10 by the further addition of NaOH solution. The mixed solution was stirred for an additional 2 h in an 80 °C water bath. Finally, the precipitates were separated by centrifugation and washed several times with deionized water. The product was dried at 50 °C in air overnight to obtain the as-synthesized catalyst.

1.3 Characterization

The powder X-ray diffraction (XRD) data were recorded with a PANalytical Empyrean diffractometer,
operated at 45 kV and 40 mA (scanning step: 0.02 ° per step). The diffraction patterns were recorded in the range of 10–80 °. The BaSO₄ nanoparticle size \( (d_{\text{Ba}}, \text{nm}) \) was estimated according to Scherrer equation:

\[
d_{\text{Ba}} = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (K = 0.9, \lambda = 0.1540598 \text{ nm})
\]

where \( K \) is the shape factor, \( \lambda \) is the X-ray wavelength, \( \beta \) is the line broadening at half the maximum intensity (FWHM) in radians, and \( \theta \) is the Bragg angle. The nitrogen adsorption and desorption isotherms were measured at 77 K under a Gemini 2375 surface area analyzer. Transmission electron microscope (TEM) and Z-contrast scanning transmission electron microscope (STEM) experiments were conducted on HITACH HD2000 microscopes with an accelerating voltage of 200 kV. Elemental analysis of the samples was done by inductively coupled-plasma atomic emission spectroscopy (ICP-AES) using Optima 2100 DV spectrometer (PerkinElmer Corporation).

The X-ray absorption spectroscopy (XAS) data recorded at the Au L_{III}-edge (11919 eV) were collected at beamline X19a at the National Synchrotron Light Source, Brookhaven National Laboratory. A Si (111) double crystal monochromator was used and detuned by 25 % to reject higher harmonics. The X-ray absorption was measured simultaneously in transmission and fluorescence. Ion chambers for measuring \( I_0 \) and \( I_1 \) were filled with nitrogen and a 50:50 mixture of N₂: Ar, respectively. Fluorescence was measured using a large area Passivated Implanted Planar Silicon (PIPS) detector perpendicular to the upcoming beam. The Au absorption was measured out to \( k=16 \text{ Å}^{-1} \). The samples were ground to a fine powder, mixed with BN and pressed into a 13 mm diameter pellet. The typical absorbance of the analyte, \( \mu(x) \), was 0.1–0.2. The pellets were mounted in a Nashner-Adler \(^4\) reaction cell. The cell was purged with He prior to measurement. A Liquid nitrogen dewar was placed on the top of the cell to enable absorption measurements at low temperature (the lowest temperature reached was about -110 °C) and, consequently, minimize thermal disorder effects. The extended X-ray absorption fine structure (EXAFS) spectra were recorded at -110 °C.

The programs ATHENA (version 0.8.056) and ARTEMIS (version 0.8.012) were used to reduce and
fit the data, respectively. Data reduction consisted of pre-edge subtraction, background determination, normalization and spectral averaging. The EXAFS data sets at the two temperatures were fit simultaneously using $k^1$-weighting and $k^3$-weighting to minimize the correlation between $N$ and $\sigma^2$.

1.4 Catalytic CO oxidation

Catalytic CO oxidation was carried out in a fixed-bed reactor (U-type quartz tube with inner diameter of 4 mm) at atmospheric pressure. For the measurement of CO light-off curves showing CO conversion as a function of reaction temperature, a 20 mg catalyst supported by quartz wool was loaded in the reactor. The feed gas of 1% CO balanced with dry air (< 4 ppm water) passed though the catalyst bed at a flow rate of 10 ml/min corresponding to gas hourly space velocity (GHSV) of 30,000 mL (h g$_{cat}$)$^{-1}$. Prior to the catalytic test, each catalyst was activated by calcination in an oven under air at 300 °C or 500 °C for 2 h. The concentrations of CO and CO$_2$ in the reactor effluent were analyzed by a Buck Scientific 910 gas chromatograph equipped with a dual molecular sieve/porous polymer column (Alltech CTR1) and a thermal conductivity detector. Steady-state CO oxidation was conducted with the same feed gas at 0 °C. Steady-state catalytic activity of the gold catalysts are evaluated by using CO oxidation rates ($r_{CO}$), defined as mole of CO converted per mole of total Au per second (mol$_{CO}$ (mol$_{Au}$ s)$^{-1}$), and turnover frequency (TOF, s$^{-1}$) defined as mole of CO converted per mole of surface Au per second. The TOF is calculated according to the following equation: TOF = $r_{CO}/D_{Au}$, where $D_{Au}$ is the dispersion of Au defined as an Au surface-to-volume atomic ratio. For a given spherical or hemispherical Au particle,

$$D_{Au} = \frac{\pi d_{Au}^2 \rho_s}{6 \rho_b} = \frac{\alpha}{d_{Au}}$$

(for $d_{Au} > \alpha$, $\alpha = \frac{6\rho_s}{\rho_b}$)

where $\rho_b$ is the bulk atomic density of Au (nm$^{-3}$), $\rho_s$ is the surface atomic areal density of Au (nm$^{-2}$), $d_{Au}$ is Au particle size (nm), and $\alpha$ is the constant of proportionality (nm). Assuming that the Au particles are crystalline with bulk Au lattice constant $a_0 = 0.408$ nm, $\rho_b$ is given by $4/a_0$, and $\rho_s$ for the low-index
surfaces (111), (100), and (110) are given by $\left(\frac{4}{\sqrt{3}}\right)a_0^2$, $2a_0^2$, and $\sqrt{2}a_0^{-2}$, respectively [6]. Using these values in the above equation, $\alpha$ is 1.41, 1.22, and 0.865 for particles faceted primarily on the (111), (100), and (110) surface, respectively. If the small particles are rough and low coordinated, then it is reasonable to assume that $\alpha$ is near unity (an average of $\alpha$ equalling to $(1.41+1.22+0.865)/3 = 1.165$). Therefore, the $D_{\text{Au}}$ can approximately be the reciprocal of Au particle size ($d_{\text{Au}}$, nm), leading to $\text{TOF} \approx r_{\text{CO}}d_{\text{Au}}$.

References

2. Figures

Fig. S1. Wide-angle XRD patterns of BaSO₄-MCF (KHSO₄) and BaSO₄-MCF (SDBS) with three SDBS concentrations (0.001 mol L⁻¹, 0.005 mol L⁻¹ and 0.01 mol L⁻¹).

Fig. S2. Nitrogen adsorption-desorption isotherms and pore size distributions of MCF and BaSO₄-MCF (SDBS) prepared at a SDBS concentration of 0.005 mol L⁻¹.
**Fig. S3.** TEM image of (a) BaSO$_4$-MCF (SDBS) with the SDBS concentration of 0.001 mol L$^{-1}$; (b) BaSO$_4$-MCF (SDBS) with the SDBS concentration of 0.005 mol L$^{-1}$ and (c) BaSO$_4$-MCF (SDBS) with the SDBS concentration of 0.01 mol L$^{-1}$. Scale bar = 20 nm.

**Fig. S4.** Wide-angle XRD patterns of Au-BaSO$_4$-MCF (KHSO$_4$) and Au-BaSO$_4$-MCF (SDBS) after 300 °C pretreatment.

**Fig. S5.** Wide-angle XRD patterns and Z-contrast STEM of BaSO$_4$-MCF (KHSO$_4$) and BaSO$_4$-MCF (SDBS) after 500 °C treatment.
Fig. S6. CO light-off curves of Au-BaSO₄-MCF (KHSO₄) and Au-BaSO₄-MCF (SDBS) after 300 °C pretreatment (GHSV = 30000 mL/h/gcat).

Fig. S7. CO light-off curves of Au-BaSO₄-MCF (KHSO₄) and Au-BaSO₄-MCF (SDBS) after 500 °C pretreatment. (GHSV = 30000 mL/h/gcat).
Fig. S8. Time-on-stream of CO oxidation rates at 0 °C over Au-BaSO₄-MCF (SDBS) after 300 °C and 500 °C pretreatments and Au/TiO₂ after 300 °C pretreatment. (GHSV of 450,000 mL (h g<sub>cat</sub>)<sup>-1</sup> for 300 °C-pretreated Au-BaSO₄-MCF (SDBS) and Au-TiO₂, and 30,000 mL (h g<sub>cat</sub>)<sup>-1</sup> for 500 °C-pretreated Au-BaSO₄-MCF (SDBS))

Fig. S9. TEM images of 1 wt % Au/TiO₂ reference catalyst.
**Fig. S10.** Au L_{III}-edge XANES spectra of as-prepared and 300 °C-calcined Au-BaSO_{4}-MCF (SDBS), Au/TiO_{2} (World Gold Council), and Au foil.

**Fig. S11.** Au L_{III}-edge EXAFS spectra of as-prepared and 300 °C-calcined Au-BaSO_{4}-MCF (SDBS), Au/TiO_{2} (World Gold Council), and Au foil.
3. Table

Table S1 EXAFS fitting results for Au-BaSO₄-MCF (SDBS) nanoparticles and several reference materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Path</th>
<th>N</th>
<th>R (Å)</th>
<th>σ² (Å²)</th>
<th>ΔE₀ (eV)</th>
<th>R factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-BaSO₄-MCF (SDBS) as prepared</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au-O</td>
<td>2.6</td>
<td>0.199</td>
<td>0.001</td>
<td>13.8</td>
<td>0.041</td>
<td></td>
</tr>
<tr>
<td>Au-Au</td>
<td>2.5</td>
<td>0.284</td>
<td>0.007</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au-BaSO₄-MCF (SDBS) calcined 300 °C</td>
<td>8.6</td>
<td>0.284</td>
<td>0.006</td>
<td>4.8</td>
<td>0.050</td>
<td></td>
</tr>
<tr>
<td>Au-TiO₂ (World Gold Council)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au-Au</td>
<td>9.4</td>
<td>0.283</td>
<td>0.007</td>
<td>4.3</td>
<td>0.074</td>
<td></td>
</tr>
<tr>
<td>Au Foil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au-Au</td>
<td>12</td>
<td>0.286</td>
<td>0.005</td>
<td>5.3</td>
<td>0.020</td>
<td></td>
</tr>
</tbody>
</table>

The errors in the fitting parameters are N ± 10% (except Au foil which was fixed), R ± 0.02 Å, σ² ± 20%, ΔE₀ ± 20%. The k and R ranges used for the fits were k = 2 – 16 Å⁻¹ and R = 1 – 3 Å.