Supporting Information

A novel Zn-Al spinel-alumina composite supported gold

catalyst for efficient CO oxidation

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1. Experimental methods

1.1. Chemicals

 Al_2O_3 was purchased from Shandong aluminum Co., Ltd.. HAuCl₄ and Zn(NO₃)₂ 6H₂O were from Sinopharm Chemical Reagent Co., Ltd.. Ammonia (25 %) was from Tianjin Kermiou Chemical Reagent Co., Ltd.. The gases of H₂ and air were purchased from Yantai Feiyuan Special Gas Co., Ltd.. Deionized water was used in all experiments.

1.2. Catalyst preparation

10 wt.% ZnAl₂O₄-Al₂O₃ was prepared by an impregnation method. At first, 0.65 mL Zn(NO₃)₂ solution (1.87 mol L⁻¹) was diluted with deionized water to 1.40 mL. Then 0.90 g Al₂O₃ was added to the solution and mixed fully. After ageing for 2 hours, the sample was heated up to 120 \degree and held for 2 hours, and then was calcined for 4 hours at 850 \degree .

1% Au/10 wt.% ZnAl₂O₄-Al₂O₃ was prepared by deposition precipitation (DP) method. Typically, 0.516 g of the HAuCl₄ solution (19.8 $g_{Au} L^{-1}$) was diluted with 2.7 g deionized water. Its pH value was adjusted to 8 by adding sodium hydroxide solution (1 mol L^{-1}). Subsequently, 1.0 g 10 wt.% ZnO_x-Al₂O₃ was added under stirring condition and after 2 h, the catalyst was washed with NH₃•H₂O solution (pH = 10~11) and deionized water until no chlorine ion was left, and then dried at 70 °C for 10 h.

1.3. Activity tests

The Au/ZnAl₂O₄-Al₂O₃ catalyst (0.1 g or 0.05 g) was put into a quartz reactor to test its activity. The feed gas, containing 1.0 vol.% CO (balanced with air), passed through the reactor with a flow rate of 100 mL min⁻¹. The reaction temperature was 18 °C (the reactor was kept in water at room temperature or water bath). Before the test, the catalysts were in situ reduced with H₂ or air at 573 K for 1 h, and then purged in N₂ and cooled down to room temperature.

The specific reaction rates of CO oxidation were also tested in the U-shape quartz reactor in the feed gas containing 1 vol.% CO and balance air, with a flow rate of 200 mL min⁻¹. The conversions of CO were controlled below 15%. 0.01 g (20 - 40 mesh) of the sample was diluted with 0.09 g γ -Al₂O₃ (20 - 40 mesh). The conversions of CO were used for calculations of the specific reaction rates.

The calculation formulas of CO conversion and reaction rate are the same as those in previous literature.^[1, 2]

1.4. Catalyst characterization

The crystal phase structure of Au/ZnAl₂O₄-Al₂O₃ was analyzed by X-ray diffraction instrument (Pw3040 / 60 X 'Pert PRO, PANalytical). The Cu K α monochromatized radiation ($\lambda = 0.1541$ nm) was selected. The available scanning range was 10 - 80 ° and its scanning

speed was 20 $^{\circ}$ min⁻¹.

ICP test was used to test the Au loading of the catalyst by IRIS Intrepid II. The test method was the same as that reported before.^[1, 2]

HAADF-STEM was applied to analyze the Au particle size of $Au/ZnAl_2O_4-Al_2O_3$ catalysts. Specifically, we adopted a field emission transmission electron microscope with the model of Tecnai G2 F30 S-Twin and the acceleration voltage of 300 kV. Before testing, the catalyst was finely ground and then ultrasonically dispersed in 5 mL ethanol for 5 min. After standing for 10 min, 1-2 drops of the supernatant solution were added to the micro grid, followed by drying and testing.

The change of water content before and after the reaction was measured by low temperature Dew Point Meter (Manufacturer: General Electric Company (GE), Model: Veridri). During the activity test, dew point meters were installed at the inlet and outlet of the quartz reactor, respectively, to record the amount of water moisture at different reaction time. Before test, the two dew point meters were calibrated simultaneously using the same gas.

XPS data of Au/ZnAl₂O₄-Al₂O₃ catalysts were obtained with a ESCALAB 250Xi instrument as reported before.^[1]. Prior to the characterization, the sample was pretreated by H_2 or air.

In situ Diffuse Reflectance Infrared Fourier Transform (In situ DRIFT) experiments were carried out on a Bruker FT-IR spectrometer (MCT detector, VERTEX 70, Harrick Scientific Products, Inc.) with a resolution of 4 cm⁻¹ and in a high temperature reaction chamber equipped with ZnSe windows. The catalyst was firstly activated at 573 K with H₂ or air (30 mL min⁻¹) for 1 h, respectively, followed by He purge and cooling down to room temperature. Then the background spectrum was recorded. The adsorbed gas (1% CO + 20% O₂ + He) was then introduced into the reaction cell and the IR spectra were recorded.

The X-ray absorption spectra (XAS) were obtained according to the previous report ^[3] at the Zn K-edge (about 9660 eV) in the Japan Synchrotron Radiation Research Institute (JASRI), Japan. The Au/ZnAl₂O₄-Al₂O₃ catalyst was reduced in H₂ at 573 K for 1 h and then purged by inert gas and cooled down to room temperature before the XAS experiment.

Catalyst	Au nominal loading (wt %)	Au actual loading (wt %)	
Au/ZnAl ₂ O ₄ -Al ₂ O ₃	1.0	0.62	

Table S1 Au loading (wt %) of Au/ZnAl₂O₄-Al₂O₃ catalyst

Table S2 Representative Au/MO_x catalysts and their catalytic performances for CO oxidation

Catalyst	Au loading (wt%)	T (°C)	TOF (s^{-1})	Rate (mol _{CO} $g_{Au}^{-1} h^{-1}$)	Reference
Au/ZnAl ₂ O ₄ -Al ₂ O ₃ -H ₂	0.62	18	0.20	2.35 *	This work
Au/ZnAl ₂ O ₄ -Al ₂ O ₃ -air	0.62	18	0.53	4.74 *	This work
Au/Al_2O_3	0.8	120	0.05	0.26	5
Au/Al ₂ O ₃	2.4	0	0.14	1.43	6
Au/Al ₂ O ₃	2.08	20	0.088	1.60	7
Au/Al_2O_3	1.0	25	0.25	1.62	8
Au/Al_2O_3	0.53	30	0.096	2.11	9
Au/SiO ₂	0.94	30	0.01	0.06	10
Au/SiO ₂	6.6	0	0.02	0.06	4
Au/ZrO ₂	1.0	120	0.37	2.82	11
Au/FeO _x	5.0	25	0.42	-	12
Au/FeO _x	0.015	24	0.49	-	13
Au/FeO _x	1.0	25	0.50-1.0	4.4-8.7	14
Au/Fe ₂ O ₃	0.66	0	0.14	1.07	4
Au/ZnO	1.0	120	0.24	1.41	15
Au/ZnO	3.8	20	0.03	0.32	16
Au/TiO ₂	3.1	27	0.26	1.64	17

* This is the reaction rate at 450 min.



Fig. S1 Normalized XANES spectra at Zn K-edge for Au/ZnO_x-Al₂O₃-H₂

As shown in Fig. S1, spectral feature of Au/ZnO/Al₂O₃ was quite different from those of ZnO and Zn foil but similar to that of ZnAl₂O₄. The peaks of Au/ZnO/Al₂O₃ were observed at 9667, 9671, and 9676 eV, which were in good agreement with ZnAl₂O₄ as reported in the previous literature ^[18-20]. Therefore, ZnAl₂O₄ spinel was successfully synthesized.



Fig. S2 CO conversions as a function of reaction time over Au/ZnAl₂O₄-Al₂O₃-H₂ sealed in a sample tube for 2 years (1 vol.% CO + air, GHSV: 120, 000 mL g⁻¹ h⁻¹. Reaction temperature: 18 °C;

After sealed for 2 years*: After activation, exposure to air, the catalyst was sealed in a sample tube in a desiccator and kept away from light for 2 years.



Fig. S3 XPS spectra of (a) O 1*s*, (b) Au 4*f*, (c,d) Zn 2*p*, and (e) Al 2*p* over Au/ZnAl₂O₄-Al₂O₃ (-air or -H₂).

The spectra of O1*s* can be deconvoluted into two peaks. The band at a lower B.E. of 530.5 eV can be attributed to lattice oxygen species (O^{2-}) in Al₂O₃ or ZnAl₂O₄ ^[21], while the band at a higher B.E. of 531.6 eV is characteristic of the surface oxygen (O_2^{-} , O^{-}) and OH species ^[22]. The Au 4*f*_{7/2} (c.a. 83.8 eV) peaks are similar for Au/ZnAl₂O₄-Al₂O₃-H₂ and

Au/ZnAl₂O₄-Al₂O₃-air, indicating the presence of Au⁰. The BE peaks at 87.4 and 89.1 eV are ascribed to Au $4f_{5/2}$ and Zn $3p_{3/2}$, respectively. A shift of binding energy peak of Zn $3p_{3/2}$ (89.6 to 89.1 eV) appeared for Au/ZnAl₂O₄-Al₂O₃-air (**Fig. S3b**), which might be the result of the effect of Au $4f_{5/2}$ or the partial reduction of Zn²⁺. The main peaks of Zn $2p_{1/2}$ and Zn $2p_{3/2}$ are usually centered at 1045 eV and 1023 eV ^[23], respectively. However, these peaks slightly shifted from 1047.3 eV and 1023.4 eV (Au/ZnAl₂O₄-Al₂O₃-air) to 1047.1 eV and 1023.3 eV (Au/ZnAl₂O₄-Al₂O₃-H₂), respectively (**Fig. S3c**). This is probably due to partial reduction of Zn²⁺ species in Au/ZnAl₂O₄-Al₂O₃-H₂ when pre-treated in H₂ ^[24, 25].



Fig. S4 In situ DRIFT spectra (2000 ~ 2500 cm⁻¹) of Au/ZnAl₂O₄-Al₂O₃-H₂ and Au/ZnAl₂O₄-Al₂O₃-air exposed to the reaction gas of CO oxidation at room temperature Reaction conditions: 1% CO, 20% O₂, He balance.

When the catalysts were exposed to $CO + O_2$ at room temperature, several bands were observed in the range of 2000 ~ 2500 cm⁻¹. The band at 2170 cm⁻¹ on the two catalysts could be ascribed to vibration absorption peak of the gaseous CO. Generally, the band at about 2110 cm⁻¹ could be assigned to the vibration of liner adsorption of CO on Au⁰ ^[1, 26, 27, 28], and on our samples the bands at 2102 cm⁻¹ and 2107 cm⁻¹ ascribed to CO on Au species were observed on Au/ZnAl₂O₄-Al₂O₃-H₂ and Au/ZnAl₂O₄-Al₂O₃-air during the initial 15 min, respectively (**Fig. S4a, 4b**).



Fig. S5 Water vapor consumed by reaction as a function of time over Au/ZnAl₂O₄-Al₂O₃ after pretreatment with (a) H₂ or (b) air, and reaction rates on (c) Au/ZnAl₂O₄-Al₂O₃-H₂ and (d) Au/ZnAl₂O₄-Al₂O₃-Air.

Feed gases: 1 vol.% CO + Air, GHSV: 1, 200, 000 mL $g^{-1} h^{-1}$, Temperature: 18 °C



Fig. S6 In situ DRIFT spectra (2800 ~ 4000 cm⁻¹) of Au/ZnAl₂O₄-Al₂O₃-H₂ and Au/ZnAl₂O₄-Al₂O₃-air exposed to the reaction gas of CO oxidation at room temperature. Au/ZnAl₂O₄-Al₂O₃ was pretreated by H₂ (Au/ZnAl₂O₄-Al₂O₃-H₂) or air (Au/ZnAl₂O₄-Al₂O₃-air) at 573 K for 1 h. Reaction conditions: 1% CO, 20% O₂, He balance.



Fig. S7 In situ DRIFT spectra (1000 ~ 2000 cm⁻¹) of Au/ZnAl₂O₄-Al₂O₃-H₂ and Au/ZnAl₂O₄-Al₂O₃-air exposed to the reaction gas of CO oxidation at room temperature. Au/ZnAl₂O₄-Al₂O₃ was pretreated by H₂ (Au/ZnAl₂O₄-Al₂O₃-H₂) or air (Au/ZnAl₂O₄-Al₂O₃-air) at 573 K for 1 h. Reaction conditions: 1% CO, 20% O₂, He balance.

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