Improved Catalytic Performance of Au/α-Fe$_2$O$_3$-Like-Worm Catalyst for Low Temperature CO Oxidation

Qiuwan Han, Dongyang Zhang, Jiuli Guo, Baolin Zhu, Weiping Huang and Shoumin Zhang *

Key Laboratory of Advanced Energy Material Chemistry (MOE), TKL of Metal and Molecule Based Material Chemistry, Department of Chemistry, Nankai University, Tianjin 300071, China

* Correspondence: zhangsm@nankai.edu.cn

Received: 27 June 2019; Accepted: 26 July 2019; Published: 3 August 2019

Abstract: The gold catalysts supported on various morphologies of α-Fe$_2$O$_3$ in carbon monoxide (CO) oxidation reaction have been studied for many researchers. However, how to improve the catalytic activity and thermal stability for CO oxidation is still important. In this work, an unusual morphology of α-Fe$_2$O$_3$ was prepared by hydrothermal method and gold nanoparticles were supported using a deposition-precipitation method. Au/α-Fe$_2$O$_3$ catalyst exhibited great activity for CO oxidation. The crystal structure and microstructure images of α-Fe$_2$O$_3$ were carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM) and the size of gold nanoparticles was determined by transmission electron microscopy (TEM). X-ray photoelectron spectra (XPS) and Fourier transform infrared spectra (FTIR) results confirmed that the state of gold was metallic. The 1.86% Au/α-Fe$_2$O$_3$ catalyst calcined at 300 °C had the best catalytic performance for CO oxidation reaction and the mechanism for CO oxidation reaction was also discussed. It is highly likely that the small size of gold nanoparticle, oxygen vacancies and active sites played the decisive roles in CO oxidation reaction.

Keywords: Au/α-Fe$_2$O$_3$; worm-like; CO oxidation

1. Introduction

Nowadays, environmental pollution has become a severe problem that cannot be ignored. Carbon monoxide (CO) is one of the common toxic gases in air pollution and its presence has a very bad influence on the environmental management and human health. Hence, it is definitely necessary to deal with the emission of CO. Usually, CO comes from automobile engines, fossil fuels, industrial chemical combustion and so on. The familiar effective controlling method is to convert CO into CO$_2$ [1–4].

Gold nanocatalysts catalyzing CO oxidation reaction have attracted widespread concern among scientists since it was first reported by Haruta et al. [5] in the late 1980s. Many factors, including the size of gold particles, the property of support material and the prepared method and so on, have great influence on the catalytic activity [6]. Especially, the morphology of support has a non-negligible effect on the interaction between gold and support, further influencing the catalytic performance of gold catalysts. Jia et al. [7] investigated the effect of morphology of Ceria support on the activity of Au/CeO$_2$ for CO oxidation. The results showed Au/nanopolyhedra-CeO$_2$ had the better performance at low temperature, while Au/nanorod-CeO$_2$ was the best catalyst at high temperature. Guzzi et al. [8] interpreted that the activity of Au/oxide perimeter depended not only on the particle size but also on the morphology of the oxide component, likely amorphous structure. Li et al. [9] synthesized Au/CeO$_2$-TiO$_2$-nanorods and Au/CeO$_2$-TiO$_2$-nanoparticles by hydrothermal and co-precipitation methods, respectively. The catalytic results reported that Au/CeO$_2$-TiO$_2$-nanorods were more active than Au/CeO$_2$-TiO$_2$-nanoparticles because of the dominated surface structure of CeO$_2$-TiO$_2$ support.
A mass of papers have reported that the catalysts with gold supported on reducible oxide exhibit higher activities, such as \( \text{Fe}_2\text{O}_3 \), \( \text{TiO}_2 \), \( \text{Co}_3\text{O}_4 \) and so on [10–12]. Hematite (\( \alpha\text{-Fe}_2\text{O}_3 \)), relying on large oxygen storage, narrow band gaps, low cost, earthly abundant and environmentally friendly properties, has often been chosen as support and loads gold to explore its catalytic activities for \( \text{CO} \) oxidation, photocatalysis, water-gas shift reaction and so on [2,13–16]. In these catalytic reactions, the structure or morphology of hematite plays an important role in catalytic performance [17–19], which is interesting for researchers and has been studied up to now. Zeng et al. [20] fabricated \( \text{Au} / \alpha\text{-Fe}_2\text{O}_3 \)-hollow catalyst by a hydrothermal-thermal decomposition process and experimental results declared that the \( \text{Au} / \alpha\text{-Fe}_2\text{O}_3 \)-hollow catalyst showed better catalytic performance for \( \text{CO} \) oxidation compared to other catalysts, where the morphologies of \( \alpha\text{-Fe}_2\text{O}_3 \) were spindle, rod and hollow rod. After that, Zhang et al. [2] prepared the \( \text{Ag} / \text{Fe}_2\text{O}_3 \) catalyst derived from metal-organic framework (MOF), which had higher surface area and showed high catalytic activity for \( \text{CO} \) oxidation.

At the same time, Shunsuke Tanaka et al. [21] reported another type of \( \text{Fe}_2\text{O}_3 \) catalyst supported gold for \( \text{CO} \) oxidation, in which \( \text{Fe}_2\text{O}_3 \) was prepared using an asymmetric PS-b-PAA-b-PEG triblock copolymer template. And the catalyst exhibited better catalytic activity compared to commercial \( \text{Au} / \text{Fe}_2\text{O}_3 \). Although these \( \text{M}/\text{Fe}_2\text{O}_3 \)-modified (\( \text{M} = \text{Au}, \text{Ag} \)) catalysts show improved catalytic activity, it is still essential to make full conversion temperature lower in \( \text{CO} \) oxidation reaction by an easy prepared method and make catalysts own great catalytic performance in various reactions.

In this work, a novel worm-like \( \alpha\text{-Fe}_2\text{O}_3 \) support was prepared via hydrothermal method and then was supported gold nanoparticles by a deposition-precipitation method to explore the catalytic activity for \( \text{CO} \) oxidation. The gold nanoparticles were distributed uniformly on the surface of \( \alpha\text{-Fe}_2\text{O}_3 \). And experimental results showed that the \( \text{Au} / \alpha\text{-Fe}_2\text{O}_3 \) catalyst possessed excellent catalytic activity for \( \text{CO} \) oxidation reaction. The gold nanoparticles in catalyst played an important role, which provided more active center and improved the catalytic activity for \( \text{CO} \) oxidation.

2. Materials and Methods

2.1. Materials

All chemical reagents were analytical grade and were used directly without any purification. Ferric chloride hexahydrate (\( \text{FeCl}_3 \cdot 6\text{H}_2\text{O}, 99.0\% \)) and glycol were purchased from Chemical Reagent Supply and Marketing Company, Tianjin, China. Ethanol was purchased from Guangfu Technology Development Co. Ltd., Tianjin, China. Urea was purchased from Wind Ship Chemical Reagent Technology Co. Ltd., Tianjin, China. Oleylamine and sodium hydroxide (\( \text{NaOH}, 96\% \)) was purchased from the Aladdin Industry Corporation, Shanghai, China. Chloroauric acid (\( \text{HAuCl}_4 \)) was purchased from Masco Chemical Co. Ltd., Tianjin, China.

2.2. Preparation of \( \alpha\text{-Fe}_2\text{O}_3 \) Support

The \( \alpha\text{-Fe}_2\text{O}_3 \) support was prepared by a hydrothermal method. Typically, 2.4 g of \( \text{FeCl}_3 \cdot 6\text{H}_2\text{O} \) was added into 60 mL of mixing solution of ethanol and glycol, whose volume ratio was 3:1. After \( \text{FeCl}_3 \cdot 6\text{H}_2\text{O} \) was dissolved, 1.06 g of urea and 4 mL of oleylamine were added successively under constant stirring. The system was stirred for 1 h and the solution was then transferred into a 100 mL of Teflon-lined stainless steel autoclave. The autoclave was heated in an oil bath at 180 °C for 12 h. After the autoclave was cooled to room temperature naturally, the precipitate was washed with distilled water and ethanol several times, dried at 80 °C for 12 h and calcined at 600 °C for 150 min in air.

2.3. Preparation of \( \text{Au}/\alpha\text{-Fe}_2\text{O}_3 \)

Gold was supported onto the \( \alpha\text{-Fe}_2\text{O}_3 \) support by a deposition-precipitation method. In this method, a certain amount of \( \text{HAuCl}_4 \) solution was added dropwise to the \( \alpha\text{-Fe}_2\text{O}_3 \) aqueous solution (0.4 g of \( \alpha\text{-Fe}_2\text{O}_3 \) in 100 mL distilled water). After being violently stirred for 10 min, the pH value of the suspension was adjusted to about 8 by adding \( \text{NaOH} \) solution (1 mol/L) dropwise, then stirred and
aged at room temperature for 12 h. After that, the suspension was heated in a thermostatic water bath at 90 °C for 4 h. Finally, the precipitate was washed several times with deionized water to remove Cl− and then dried at 80 °C for 12 h. The mass fraction of Au in sample was described as x% Au/α-Fe2O3 (x = 0.62, 1.86, 2.72, 3.59).

2.4. Characterization

The actual loadings of Au in samples were measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Spectro, SpectroBlue, Germany). The X-ray diffraction (XRD) patterns were obtained using Rigaku D/max-2500 (Rigaku, Japan) X-ray diffractometer (Cu Kα, λ = 1.5418 Å) to identify the crystal phase of catalysts. Scanning electron microscopy (SEM) images of the samples were taken using a JSM-7500F microscope (JEOL, Japan). Transmission electron microscopy (TEM) and high resolution (HR) TEM images were obtained using a Tecnai G2F20 microscope (FEI, Hillsboro, OR, USA) operated at 200 kV. Ultraviolet-Visible diffuse reflectance spectra (UV-Vis DRS) were collected using a SHIMADZU UV-3600 spectrophotometer (Shimadzu, Japan). The Fourier transform infrared spectra (FTIR) were recorded using a Nicolet MAGNA-IR 560 spectrometer (Nicolet, Wisconsin, USA). X-ray photoelectron spectra (XPS) were accepted using a Kratos Axis Ultra DLD Spectrometer (Kratos Analytical Ltd., Manchester, UK) with a monochromator of Al Kα source to determine the chemical states of Au and Fe. The H2 temperature-programmed reduction profiles (H2-TPR) were tested on a ChemiSorb 2720 (Micromeritics, Georgia, GA, USA) and the temperature programmed desorption profiles of ammonia (NH3-TPD) were obtained using a chemBET TPD (Quantachrome, Florida, FL, USA).

2.5. CO Oxidation Catalytic Activity

The catalytic activity was evaluated using a fixed-bed flow millireactor at atmospheric pressure. The catalyst (0.2 g) was diluted with quartz sand (17.6 g) and then was loaded in a stainless steel tube, whose inner diameter is 8 mm. The feed gas containing 10% CO balanced with air passed through the reactor at a total flow rate of 36.3 mL/min. The reaction temperature gradient was 5 °C/min and the testing temperature range was 25–200 °C. The effluent gases were analyzed using an on-line GC-508A gas chromatography equipped with H2 as carrier gas. The conversion rate of CO was calculated to evaluate the activity, whose equation [22] was shown as follows:

\[
\text{CO Conversion} = \frac{[\text{CO}_2]}{[\text{CO}]+[\text{CO}_2]} \times 100\%,
\]  

(1)

3. Results and Discussion

3.1. ICP and XRD

The actual content of gold in sample was measured by ICP. Compared to the theoretical content of 1%, 2%, 3% and 4%, the actual content were 0.62%, 1.86%, 2.72% and 3.59%, respectively. Clearly, 60–90% of gold was successfully loaded on the α-Fe2O3 support for all catalysts.

Figure 1 shows the XRD patterns of (a) precursor, (b) α-Fe2O3 and various amount of Au/α-Fe2O3 catalysts ((c) 0.62%, (d) 1.86%, (e) 2.72%, (f) 3.59%) calcined at 300 °C for 2 h, which revealed that the hexagonal α-Fe2O3 was prepared successfully after the calcination of precursor at 600 °C and the load of gold on the surface of α-Fe2O3 support did not change the phase of hematite. The precursor was made up of variety materials, whose diffraction peaks could be indexed to β-FeOOH, α-FeOOH, γ-Fe2O3 and α-Fe2O3 (JCPDS No. 34-1266, 29-0713, 39-1346 and 33-0664). The diffraction peaks of α-Fe2O3 perfectly corresponded to the hexagonal hematite (JCPDS No. 33-0664), of which the diffraction peaks at 2θ = 24.18°, 33.15°, 35.61°, 40.85°, 49.48°, 54.09°, 57.43°, 62.45° and 63.99° were indexed to [012], [104], [110], [113], [024], [116], [122], [214] and [300] planes of hematite, respectively. The diffraction peaks of gold at 2θ = 38.2° and 44.5° were separately corresponded to [111] and [200] planes of Au fcc
crystal (JCPDS No. 04-0784). In Figure 1 curves c–f, the peaks of gold were weak, which probably was caused from the small particle size or the relatively low gold content in catalysts [23]. Besides, it was clear that the peak intensity of hematite at 2θ = 33.15° and 35.61° in gold catalysts got stronger, which implied the crystalline of hematite increased after the addition of gold [22].

![Figure 1. X-ray diffraction (XRD) patterns of (a) precursor, (b) α-Fe$_2$O$_3$ and various amount of Au/α-Fe$_2$O$_3$ catalysts ((c) 0.62%, (d) 1.86%, (e) 2.72%, (f) 3.59%) calcined at 300 °C for 2 h.](image)

3.2. SEM and TEM

The SEM and TEM images are shown in Figures 2 and 3. As shown in Figure 2, the hydrothermal time played an important role in the morphology of hematite. Firstly, when it was heated at 180 °C for 4 h in oil bath, α-Fe$_2$O$_3$ was mainly made up of irregular particles. With the further increase of time, it could be seen that the morphologies of α-Fe$_2$O$_3$ support were increasingly like worm. While the hydrothermal time increased to 12 h, the worm-like α-Fe$_2$O$_3$ finally formed and it was used for all subsequent studies. Usually, the morphology of α-Fe$_2$O$_3$ obtained by hydrothermal method is spindle-shaped or spherical [24]. However, in this work, a novel worm-like α-Fe$_2$O$_3$ support was prepared by reacting for 12 h using hydrothermal method, whose specific surface area was 23.2 m$^2$/g measured by BET. Its TEM image is shown in Figure 3b, of which the inset is the HR-TEM image of α-Fe$_2$O$_3$ support. It could be clearly seen that the lattice fringe was 0.255 nm, which was corresponded to the (110) plane of α-Fe$_2$O$_3$ [21,25]. The rest of TEM images in Figure 3 separately represents (a) precursor, (c) 1.86%, (d) 2.72% and (e) 3.59% Au/α-Fe$_2$O$_3$ catalysts calcined at 300 °C; (f) 1.86% Au/α-Fe$_2$O$_3$ catalysts calcined at 500 °C. The morphology of precursor in Figure 3a was like-leaf before changing into hematite. In Figure 3c–e, gold nanoparticles were distributed on the surface of hematite support in various gold catalysts. The insets of Figure 3c–e shows the corresponding size distributions of gold nanoparticles, which indicated the average diameters of gold nanoparticles were 2.29, 2.96 and 3.32 nm in 1.86%, 2.72% and 3.59% Au/α-Fe$_2$O$_3$ catalysts, respectively. Additionally, some agglomerate gold nanoparticles occasionally appeared on the surface of 2.72% Au/α-Fe$_2$O$_3$ and 3.59% Au/α-Fe$_2$O$_3$ catalysts, which was probably due to the increase content of gold in catalysts compared to that in 1.86% Au/α-Fe$_2$O$_3$ catalyst. It also could be seen that the size of gold in Figure 3f increased to around 7 nm due to the calcination. The size of gold nanoparticles has a great effect on the catalytic activity. As we know, the smaller gold particle size improves the catalytic performance in CO oxidation reaction.
Figure 2. Scanning electron microscopy (SEM) images of α-Fe$_2$O$_3$ reacting for (a) 4 h, (b) 6 h, (c) 10 h and (d) 12 h at 180 °C.

Figure 3. Transmission electron microscopy (TEM) images of (a) precursor; (b) α-Fe$_2$O$_3$; (c) 1.86%, (d) 2.72% and (e) 3.59% Au/α-Fe$_2$O$_3$ catalysts calcined at 300 °C; (f) 1.86% Au/α-Fe$_2$O$_3$ catalysts calcined at 500 °C.
3.3. UV-Vis DRS and FTIR

The UV-Vis spectra of α-Fe₂O₃ and Au/α-Fe₂O₃ catalysts with various gold loadings calcined at 300 °C for 2 h are shown in Figure 4. The absorption of α-Fe₂O₃ at wavelengths (200–800 nm) were usually attributed to three kinds of electronic transitions [26]. The absorption peaks at 200–400 nm mainly resulted from the charge transfer from ligand to metal and partly from the contribution of Fe³⁺ ligand field transitions. The obvious peak at 530–570 nm was considered to form mainly by the pair excitation process of α-Fe₂O₃. And the peaks at 600–900 nm could be corresponded to the d–d transition [26,27]. The peak of gold loaded on support normally occurs at 500–570 nm due to the localized surface plasmon resonance of Au nanoparticles [4]. There was no obvious peak of gold, which might be overlapped with the peak of α-Fe₂O₃ at 530–570 nm. This weak gold peak further indicated the small gold nanoparticle size in catalysts, which was consistent with TEM results (Figure 3). Besides, it was apparent that the peaks of Au/α-Fe₂O₃ catalyst all had an obvious red-shift compared to that of α-Fe₂O₃ support and the 1.86% Au/α-Fe₂O₃ catalyst had the largest red-shift among these gold catalysts. The red-shift action was caused probably from the reduction of electron density in the gold nanoparticles owing to the chemical interactions with neighboring hematite, in which the electrons transformed from the cluster to the surrounding matrix [28].

![Figure 4](image)

**Figure 4.** Ultraviolet-Visible diffuse reflectance spectra (UV-Vis DRS) of α-Fe₂O₃ and Au/α-Fe₂O₃ catalyst calcined at 300 °C.

Figure 5 shows the FTIR spectra of α-Fe₂O₃ and Au/α-Fe₂O₃ calcined at 300 °C for 2 h. The obviously broad peak at about 3420 cm⁻¹ was attributed to the O–H stretching vibration of absorbed water and the shoulder peak at 1630 cm⁻¹ was ascribed to the H–OH bending vibration of absorbed water [29,30]. The two sharp peaks at 460 cm⁻¹ and 530 cm⁻¹ were mainly due to the Fe–O vibration of α-Fe₂O₃ [31,32]. The FTIR spectra of gold catalysts were similar with that of support, indicating the addition of gold has a little effect on the bond of hematite.

![Figure 5](image)

**Figure 5.** The Fourier transform infrared (FTIR) spectra of α-Fe₂O₃ and Au/α-Fe₂O₃ catalyst calcined at 300 °C.
3.4. XPS

The oxidation states and the surface elemental composition of catalysts were further confirmed by XPS and the XPS results of 1.86% Au/α-Fe$_2$O$_3$ calcined at 300 °C for 2 h were shown in Figure 6. Figure 6a shows the full spectrum of Au/α-Fe$_2$O$_3$, where the peaks of Fe, O, C and Au were assigned, respectively. Especially, the element C came from the hydrocarbon compound in instrument and the reason for the small hump of gold was probably related to the low loading. For the Fe 2p XPS spectrum in Figure 6b, the peaks at 710.8 eV and 724.1 eV corresponded to Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$, respectively. The binding energy (BE) value for Fe 2p$_{3/2}$ peak was consistent with the value for ferric oxides reported by A.P. Grosvenor et al. [33] and the Fe$^{3+}$ cation occupied octahedral sites. Figure 6c shows the high resolution XPS spectrum of O 1s in Au/α-Fe$_2$O$_3$. The main peak at 529.8 eV corresponded to the lattice oxygen of hematite and the other two peaks at 531.5 eV and 533.6 eV were attributed to the oxygen vacancies in the structure and the surface OH$^{-1}$ groups [34,35], respectively. The state of gold in Au/α-Fe$_2$O$_3$ catalyst was further determined by the Au 4f XPS spectra in Figure 6d. It could be seen that the BE of Au 4f$_{7/2}$ was 84.0 eV and the BE of Au 4f$_{5/2}$ was 87.6 eV, which corresponded to the metallic gold [36]. The result was consistent with the FTIR analytical result. Besides, Overbury et al. [37] has reported that the valence of gold had an impact on the catalytic property of catalyst and the metallic gold played an improved role in catalyzing CO oxidation.

![Figure 6](image.png)

**Figure 6.** (a) The wide pattern, (b) Fe 2p, (c) O 1s, (d) Au 4f XPS patterns of 1.86% Au/α-Fe$_2$O$_3$ catalyst calcined at 300 °C.

3.5. H$_2$-TPR and NH$_3$-TPD

The H$_2$-TPR results evaluated the reduction behaviors of α-Fe$_2$O$_3$ support and Au/α-Fe$_2$O$_3$ catalyst calcined at 300 °C for 2 h, which were shown in Figure 7a. There were two reduction peaks in the TPR curve of hematite, which were separately located at about 340 and 610 °C. The reduction peak
around 340 °C was assigned to the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$, while another stronger peak around 610 °C could be attributed to the reduction of Fe$_3$O$_4$ to FeO and Fe$^0$ [38,39]. In the reductive process of Fe$_2$O$_3$ to Fe$_3$O$_4$, the reductive temperature (340 °C) in this work compared to that (380 °C) reported by Zhang et al. [40] decreased, which declared that the hematite presented stronger reducibility.

Au/α-Fe$_2$O$_3$ catalysts with various gold loadings had two reduction peaks and their reduction processes were identical with α-Fe$_2$O$_3$. However, the first peak position in Au/α-Fe$_2$O$_3$ shifted to higher temperature compared with pure α-Fe$_2$O$_3$ and the second peak position was also different from α-Fe$_2$O$_3$. In these latter peaks, the 1.86% Au/α-Fe$_2$O$_3$ catalyst had the lowest temperature in achieving complete reduction, indicating that it had the most improved reducibility, which was beneficial to catalyze CO oxidation reaction.

The NH$_3$ desorption curves of α-Fe$_2$O$_3$ and Au/α-Fe$_2$O$_3$ catalyst calcined at 300 °C were shown in Figure 7b. It was clear that there were mainly three desorption peaks in the temperature range of 100–800 °C for these catalysts. The peaks in all catalysts around 110–200 °C were attributed to the weak acid sites and physisorbed NH$_3$ and the peaks around 300–400 °C were ascribed to the medium acid sites. While in the high-temperature area, the peaks around 450–650 °C were elaborated to the strong acid sites [41,42]. Considering the desorption peaks at low temperature, the 1.86% and 2.72% Au/α-Fe$_2$O$_3$ had a relatively weaker acidity among these catalysts. And in the peaks of all catalyst at high temperature, the 0.62% Au/α-Fe$_2$O$_3$ catalyst presented stronger acidity on account of the higher desorption temperature. The acid-base property is related to the oxidizing ability and the strong acidity of catalyst has the disadvantageous effect on the formation of active oxygen. Hence, the catalyst with weaker acidity would be conducive to the CO oxidation reaction.

![Figure 7. (a) H$_2$ temperature-programmed reduction (H$_2$-TPR) profiles and (b) temperature programmed desorption of ammonia (NH$_3$-TPD) profiles of α-Fe$_2$O$_3$ and Au/α-Fe$_2$O$_3$ catalyst calcined at 300 °C.](image)

### 3.6. CO Oxidation Catalytic Activity

The relation schema between CO conversion rate and reaction temperature of Au/α-Fe$_2$O$_3$ catalyst was shown in Figure 8a. As seen in it, the α-Fe$_2$O$_3$ support had no catalytic activity for CO oxidation, while 1.86% Au/α-Fe$_2$O$_3$ had the best catalytic ability with the T$_{100}$ (T$_{100}$, the temperature that CO conversion rate is 100%) of 30 °C. And the T$_{100}$ of 0.62%, 2.72% and 3.59% Au/α-Fe$_2$O$_3$ were 70, 90 and 140 °C, respectively. According to these catalytic results, it could be easily deduced that the addition of gold had a great influence on the catalytic activity. Moreover, when the content of gold was higher than 1.86, the catalytic activity began to decrease, which might be related to the decrease of active center. As shown in the characterization results of UV-Vis and NH$_3$-TPD, 1.86% Au/α-Fe$_2$O$_3$ catalyst equipped with stronger interaction between gold and support, which could promote the formation of more active center. And the weaker acidity of 1.86% Au/α-Fe$_2$O$_3$ would accelerate the generation of active oxygen, which was benefit for the CO oxidation. The catalytic performance of Au/α-Fe$_2$O$_3$-like-worm in this work was also compared with other gold catalysts supported on Fe$_2$O$_3$ and CeO$_2$ reported in the literature for CO oxidation, which was shown in Table 1. From Table 1, it could be seen...
that the Au/α-Fe₂O₃-like-worm catalyst performed the relatively high catalytic activity among these catalysts for CO oxidation. And the specific rate of Au/α-Fe₂O₃-like-worm (2.61 molCO₂Au⁻¹h⁻¹) was 26.1 and 2.2 times higher than those of Au/Fe₂O₃-WGC (0.10 molCO₂Au⁻¹h⁻¹) and Au/commercial Fe₂O₃ (1.21 molCO₂Au⁻¹h⁻¹) catalysts. It is well known that several factors, such as gold particle size, preparation method and the choice of support may give rise to the different performance of gold catalysts [43].

The repeatability, persistence and thermostability of samples were further studied. The repeated test curves of 1.86% Au/α-Fe₂O₃ catalyst calcined at different temperature. When the reaction temperature was 20 °C, the conversion rate of catalyst calcined at 80, 200, 300 and 400 °C were 10%, 20%, 80% and 0%, respectively. And the T₁₀₀ of these catalysts were separately 120, 70, 30 and 160 °C. Clearly, the catalyst calcined at 300 °C presented the best catalytic activity. Boccuzzi et al. [46] has reported that the impact of calcined temperature on catalytic activity is mainly ascribed to the size of gold particles. The smaller size of gold nanoparticles could provide more effective defects, such as edge, corner, step and so on. Hence, the decreased catalytic activity of catalyst calcined at 400 °C was possibly related to the sinter of gold nanoparticles.

The repeatability, persistence and thermostability of samples were further studied. The repeated test curves of 1.86% Au/α-Fe₂O₃ catalyst calcined at 300 °C were shown in Figure 9a. After finishing the first circulation, the test was restarted from room temperature. In the third repeated test, the CO conversion rate still stayed at 100% at the reaction temperature of 30 °C. Therefore, the catalyst had a high repeatability in catalyzing CO oxidation. The persistent test of catalyst was reported in Figure 9b and the reaction was kept for 60 h at 30 °C (T₁₀₀). This result showed that there was no decline in catalytic activity, which strongly proved the catalyst had a long service life. The high-temperature stability tests were shown in Figure 10. 1.86% Au/α-Fe₂O₃ catalyst calcined at 300 °C was run for 50 h at
100, 140 and 180 °C, respectively. Excitedly, the conversion rates of all catalysts were maintained at 100% after keeping reaction for 50 h, indicating that the Au/α-Fe₂O₃ catalyst with high temperature-stable was definitely prospective in industrial application for CO oxidation.

Figure 9. (a) Reproducibility of 1.86% Au/α-Fe₂O₃ catalyst calcined at 300 °C for 2 h in CO oxidation reaction; (b) the lifetime test of 1.86% Au/α-Fe₂O₃ catalyst calcined at 300 °C for 2 h at 30 °C (T₁₀₀).

Figure 10. The high-temperature stability of 1.86% Au/α-Fe₂O₃ catalyst calcined at 300 °C for 2 h, at the CO oxidation reaction temperature of (a) 100 °C, (b) 140 °C, (c) 180 °C.

The CO oxidation reaction mechanisms for metal oxide supported gold were highly debated in the literatures [47–49]. In this work, the possible reaction mechanism of hematite supported gold catalyst was showed in Figure 11 and described as follows. Further research would be carried out to investigate the detailed reaction mechanism. CO molecule was absorbed on the surface of gold in the Au/α-Fe₂O₃ catalyst and the catalyst was activated. The lattice oxygen in α-Fe₂O₃ connected
with CO absorbed on the surface of gold, leaving oxygen defects in hematite. Then the defects were occupied by O\(_2\) in air and the O\(_2\) molecule sequentially reacted with the CO absorbed on gold to form CO\(_2\) structure. Followingly, the CO\(_2\) molecule decomposed to CO\(_2\) and the O vacancy in hematite was filled with the O of gas-phase O\(_2\) [50–52]. Hence, more defects in hematite might more largely improve the conversion of CO to CO\(_2\) and promote the catalytic ability of catalyst.

![Figure 11](image-url)  
**Figure 11.** Schematic diagram of the possible CO oxidation mechanism for Au/\(\alpha\)-Fe\(_2\)O\(_3\).  

4. Conclusions

In summary, a novel Au/\(\alpha\)-Fe\(_2\)O\(_3\)-like-worm catalyst has been prepared firstly by hydrothermal and deposition-precipitation method. It has been shown that the 1.86% Au/\(\alpha\)-Fe\(_2\)O\(_3\) catalyst calcined at 300 °C had the best catalytic activity in CO oxidation due to the small size of Au particle and more active center. The catalyst achieved complete CO conversion at a temperature of 30 °C. And the conversion rate of 1.86% Au/\(\alpha\)-Fe\(_2\)O\(_3\) was still 100% after running 60 h at 30 °C, indicating the high stability of Au/\(\alpha\)-Fe\(_2\)O\(_3\). The Au/\(\alpha\)-Fe\(_2\)O\(_3\) catalyst owned effective activity for low-temperature CO oxidation and excellent stability, which suggested that it is prospective to be used to control the emission of CO in industrial application. Moreover, the study of novel worm-like \(\alpha\)-Fe\(_2\)O\(_3\) would shed new light on wide application of \(\alpha\)-Fe\(_2\)O\(_3\) in other catalytic reactions. The excellent performance of Au/\(\alpha\)-Fe\(_2\)O\(_3\)-like-worm is expected to spur further development for gold catalysts for low-temperature CO oxidation.

**Author Contributions:** Conceptualization and methodology, Q.H. and S.Z.; formal analysis, Q.H., D.Z. and S.Z.; investigation, Q.H. and D.Z.; data curation, Q.H., D.Z. and J.G.; writing—original draft preparation, Q.H.; writing—review and editing, J.G. and S.Z.; visualization, Q.H. and S.Z.; supervision, B.Z., W.H. and S.Z.; project administration, B.Z., W.H. and S.Z.; funding acquisition, B.Z., W.H. and S.Z.

**Funding:** This research was funded by the National Natural Science Foundation of China (Nos. 21271110, 21373120 and 21271107) and MOE Innovation Team of China (IRT13022).

**Acknowledgments:** This work was supported by the National Natural Science Foundation of China (Nos. 21271110, 21373120 and 21271107) and MOE Innovation Team of China (IRT13022). This work was supported by Tianjin Key Laboratory for photoelectric Materials and Devices, Tianjin University of Technology, Tianjin 300384, China.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Zhang, X.; Hou, F.; Li, H.; Yang, Y.; Wang, Y.; Liu, N.; Yang, Y. A strawsheave-like metal organic framework Ce-BTC derivative containing high specific surface area for improving the catalytic activity of CO oxidation reaction. *Microporous Mesoporous. Mater.* 2018, 259, 211–219. [CrossRef]

2. Zhang, X.; Yang, Y.; Song, L.; Wang, Y.; He, C.; Wang, Z.; Cui, F. High and stable catalytic activity of Ag/Fe\(_2\)O\(_3\) catalysts derived from MOFs for CO oxidation. *J. Mol. Catal. A-Chem.* 2018, 447, 80–89. [CrossRef]
3. Trimm, D.L. Minimisation of carbon monoxide in a hydrogen stream for fuel cell application. *Appl. Catal. A-Gen. 2005*, 296, 1–11. [CrossRef]

4. Alshehri, A.A.; Narasimharao, K. Low temperature oxidation of carbon monoxide over mesoporous Au-Fe₂O₃ catalysts. *J. Nanomater. 2017*, 2017, 14. [CrossRef]

5. Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. Novel gold catalysts for the oxidation of carbon monoxide at a temperature far below 0 °C. *Chem. Lett. 1987*, 16, 405–408. [CrossRef]

6. Lopez, N.; Janssens, T.V.W.; Clausen, B.S.; Xu, Y.; Mavrikakis, M.; Bligaard, T.; KNørskov, J. On the origin of the catalytic activity of gold nanoparticles for low-temperature CO oxidation. *J. Catal. 2004*, 223, 232–235. [CrossRef]

7. Jia, K.; Zhang, H.; Li, W. Effect of morphology of the ceria support on the activity of Au/CeO₂ catalysts for CO oxidation. *Chin. J. Catal. 2008*, 29, 1089–1092. [CrossRef]

8. Gucci, L.; Beck, A.; Frey, K. Role of promoting oxide morphology dictating the activity of Au/SiO₂ catalyst in CO oxidation. *Gold Bull. 2009*, 42, 5–12. [CrossRef]

9. Li, S.; Zhu, H.; Qin, Z.; Wang, G.; Zhang, Y.; Wu, Z.; Li, Z.; Chen, G.; Dong, W.; Wu, Z.; et al. Morphologic effects of nano CeO₂-TiO₂ on the performance of Au/ CeO₂-TiO₂ catalysts in low-temperature CO oxidation. *Appl. Catal. B-Environ. 2014*, 144, 498–506. [CrossRef]

10. Guo, J.; Han, Q.; Zhong, S.; Huang, W.; Zhang, S. Au/M-TiO₂ nanotube catalysts (M = Ce, Ga, Co, Y): Preparation, characterization and their catalytic activity for CO oxidation. *J. Sol-Gel Sci. Technol. 2018*, 86, 699–710. [CrossRef]

11. Tang, H.; Liu, F.; Wei, J.; Qiao, B.; Zhao, K.; Su, Y.; Jin, C.; Li, L.; Liu, J.; Wang, J.; et al. Ultrastable hydroxyapatite/titanium-dioxide-supported gold nanocatalyst with strong metal-support interaction for carbon monoxide oxidation. *Angew. Chem. Int. Ed. 2016*, 55, 10606–10611. [CrossRef]

12. Bond, G.C.; Thompson, D.T. Catalysis by gold. *Catal. Rev.-Sci. Eng. 1999*, 41, 319–388. [CrossRef]

13. Wang, J.; Qin, C.; Wang, H.; Chu, M.; Zada, A.; Zhang, X.; Li, J.; Raziq, F.; Qu, Y.; Jing, L. Exceptional photocatalytic activities for CO₂ conversion on Al-O bridged g-C₃N₄/α-Fe₂O₃ z-scheme nanocomposites and mechanism insight with isotopesZ. *Appl. Catal. B-Environ. 2018*, 221, 459–466. [CrossRef]

14. Ding, J.; Zhang, L.; Liu, Q.; Dai, W.L.; Guan, G. Synergistic effects of electronic structure of WO₃ nanorods with the dominant (001) exposed facets combined with silver size-dependent on the visible-light photocatalytic activity. *Appl. Catal. B-Environ. 2017*, 203, 335–342. [CrossRef]

15. Zhang, J.; Hu, Y.; Jiang, X.; Chen, S.; Meng, S.; Fu, X. Design of a direct Z-scheme photocatalyst: Preparation and characterization of Bi₂O₃/g-C₃N₄ with high visible light activity. *J. Hazard. Mater. 2014*, 280, 713–722. [CrossRef]

16. Lakhera, S.K.; Watts, A.; Hafeez, H.Y.; Neppolian, B. Interparticle double charge transfer mechanism of heterojunction α-Fe₂O₃/Cu₂O mixed oxide catalysts and its visible light photocatalytic activity. *Catal. Today 2018*, 300, 58–70. [CrossRef]

17. Yin, H.; Ma, Z.; Chi, M. Heterostructured catalysts prepared by dispersing Au@Fe₂O₃ core-shell structures on their performance in CO oxidation. *Catal. Today 2011*, 160, 87–95. [CrossRef]

18. Wang, G.H.; Li, W.C.; Jia, K.M.; Splietthoff, B.; Schüth, F.; Lu, A.H. Shape and size controlled α-Fe₂O₃ nanoparticles as supports for gold-catalysts: Synthesis and influence of support shape and size on catalytic performance. *Appl. Catal. A-Gen. 2009*, 364, 42–47. [CrossRef]

19. Sun, B.; Feng, X.; Yao, Y.; Su, Q.; Ji, W.; Au, C.T. Substantial pretreatment effect on CO oxidation over controllably synthesized Au/FeOₓ hollow nanostructures via hybrid Au/β-FeOOH@SiO₂. *ACS Catal. 2013*, 3, 3099–3105. [CrossRef]

20. Zeng, L.; Li, K.; Wang, H.; Yu, H.; Zhu, X.; Wei, Y.; Ning, P.; Shi, C.; Luo, Y. CO oxidation on Au/α-Fe₂O₃ hollow catalysts: General synthesis and structural dependence. *J. Phys. Chem. C 2017*, 121, 12696–12710. [CrossRef]

21. Tanaka, S.; Lin, J.; Kaneti, Y.V.; Yusa, S.; Jikihara, Y.; Nakayama, T.; Zakaria, M.B.; Alshehri, A.A.; You, J.; Hossain, M.S.A.; et al. Gold nanoparticles supported on mesoporous iron oxide for enhanced CO oxidation reaction. *Nanoscale 2018*, 10, 4779–4785. [CrossRef]

22. Yu, H.; Guo, J.; Dong, F.; Zhu, B.; Huang, W.; Zhang, S. A comparative study of CO catalytic oxidation on Au/YPO₄-prisms and Au/YPO₄-rods. *J. Nanopart. Res. 2017*, 19, 204. [CrossRef]

23. Liu, H.; Tian, K.; Ning, J.; Zhong, Y.; Zhang, Z.; Hu, Y. One-step solvothermal formation of Pt nanoparticles decorated Pt²⁺-doped α-Fe₂O₃ nanoplanes with enhanced photocatalytic O₂ evolution. *ACS Catal. 2019*, 9, 1211–1219. [CrossRef]
24. Mishra, M.; Chun, D.M. α-Fe$_2$O$_3$ as a photocatalytic material: A review. *Appl. Catal. A-Gen.* 2015, 498, 126–141. [CrossRef]

25. Haruta, M.; Tsutota, S.; Kobayashi, T.; Kageyama, H.; Genet, M.J.; Delmon, B. Low-temperature oxidation of CO over gold supported on TiO$_2$, α-Fe$_2$O$_3$ and Co$_3$O$_4$. *J. Catal.* 1993, 144, 175–192. [CrossRef]

26. He, Y.P.; Miao, Y.M.; Li, C.R.; Wang, S.Q.; Cao, L.; Xie, S.S.; Yang, G.Z.; Zou, B.S.; Burda, C. Size and structure effect on optical transitions of iron oxide nanocrystals. *Phys. Rev. B* 2005, 71, 125411. [CrossRef]

27. Narasimharao, K.; Al-Shehri, A.; Al-Thabaiti, S. Porous Ag-Fe$_3$O$_4$ nanocomposite catalysts for the oxidation of carbon monoxide. *Appl. Catal. A-Gen.* 2015, 505, 431–440. [CrossRef]

28. Carrot, G.; Valmalette, J.C.; Plummer, C.J.G.; Scholz, S.M.; Dutta, J.; Hofmann, H.; Hilborn, J.G. Gold nanoparticle synthesis in graft copolymer micelles. *Colloid Polym. Sci.* 1998, 276, 853–859. [CrossRef]

29. Gopi, D.; Shinyjoy, E.; Kavitha, L. Influence of ionic substitution in improving the biological property of carbon nanotubes reinforced hydroxyapatite composite coating on titanium for orthopedic applications. *Ceram. Int.* 2015, 41, 5454–5463. [CrossRef]

30. Sathyaseelan, B.; Manikuttyan, E.; Lakshmanan, V.; Baskaran, I.; Sivakumar, K.; Ladchumananandhasivam, R.; Kennedy, J.; Maaza, M. Structural, optical and morphological properties of post-growth calcined TiO$_2$ nanopowder for opto-electronic device application: Ex-situ studies. *J. Alloys Compd.* 2016, 671, 486–492. [CrossRef]

31. Maji, S.K.; Mukherjee, N.; Mondal, A.; Adhikary, B. Synthesis, characterization and photocatalytic activity of α-Fe$_2$O$_3$ nanoparticles. *Polyhedron* 2012, 33, 145–149. [CrossRef]

32. Mishra, M.; Park, H.; Chun, D.M. Photocatalytic properties of Au/Fe$_2$O$_3$ nano-composites prepared by co-precipitation. *Adv. Powder Technol.* 2016, 27, 130–138. [CrossRef]

33. Grosvenor, A.P.; Kobe, B.A.; Biesinger, M.C.; McIntyre, N.S. Investigation of multiplet splitting of Fe 2p XPS spectra and bonding in iron compounds. *Surf. Interface Anal.* 2004, 36, 1564–1574. [CrossRef]

34. Hoch, L.B.; He, L.; Qiao, Q.; Liao, K.; Reyes, L.M.; Zhu, Y.; Ozin, G.A. Effect of precursor selection on the photocatalytic performance of indium oxide nanomaterials for gas-phase CO$_2$ reduction. *Chem. Mater.* 2016, 28, 4160–4168. [CrossRef]

35. Ma, R.; Yin, L.; Li, L.; Zhang, S.; Wen, T.; Zhang, C.; Wang, X.; Chen, Z.; Hayat, T.; Wang, X. Comparative investigation of Fe$_2$O$_3$ and Fe$_{1-x}$S nanostructures for uranium decontamination. *ACS Appl. Nano Mater.* 2018, 1, 5543–5552. [CrossRef]

36. Llorca, J.; Casanovas, A.; Dominguez, M.; Casanova, I.; Angurell, I.; Seco, M.; Rossell, O. Plasma-activated core-shell gold nanoparticle films with enhanced catalytic properties. *J. Nanopart. Res.* 2008, 10, 537–542. [CrossRef]

37. Li, M.; Wu, Z.; Ma, Z.; Schwartz, V.; Mullins, D.R.; Dai, S.; Overbury, S.H. CO oxidation on Au/FePO$_4$ catalyst: Reaction pathways and nature of Au sites. *J. Catal.* 2009, 266, 98–105. [CrossRef]

38. Munteanu, G.; Ilieva, L.; Andreeva, D. Kinetic parameters obtained from TPR data for α-Fe$_2$O$_3$ and Au/Fe$_2$O$_3$ systems. *Thermochim. Acta* 1997, 291, 171–177. [CrossRef]

39. Liang, M.; Kang, W.; Xie, K. Comparison of reduction behavior of Fe$_2$O$_3$, ZnO and ZnFe$_2$O$_4$ by TPR technique. *J. Nat. Gas Chem.* 2009, 18, 110–113. [CrossRef]

40. Wang, H.; Ping, N.; Zhang, Q.; Liu, X.; Zhang, T.; Hu, J.; Wang, L. Effect of different RuO$_2$ contents on selective catalytic oxidation of ammonia over RuO$_2$-Fe$_2$O$_3$ catalysts. *J. Fuel Chem. Technol.* 2019, 47, 215–223. [CrossRef]

41. Han, J.; Meeprasert, J.; Maitarad, P.; Nammanuru, S.; Shi, L.; Zhang, D. Investigation of the facet-dependent catalytic performance of Fe$_2$O$_3$/CeO$_2$ for the selective catalytic reduction of NO with NH$_3$. *J. Phys. Chem. C* 2016, 120, 1523–1533. [CrossRef]

42. Liu, J.; Meeprasert, J.; Nammanuru, S.; Zha, K.; Li, H.; Huang, L.; Maitarad, P.; Shi, L.; Zhang, D. Facet-activity relationship of TiO$_2$ in Fe$_2$O$_3$/TiO$_2$ nanocatalysts for selective catalytic reduction of NO with NH$_3$: In situ DRIFTS and DFT studies. *J. Phys. Chem. C* 2017, 121, 4970–4979. [CrossRef]

43. Carabineiro, S.A.C.; Bogdanchikova, N.; Tavares, P.B.; Figueiredo, J.L. Nanostructured iron oxide catalysts with gold for the oxidation of carbon monoxide. *RSC Adv.* 2012, 2, 2957–2965. [CrossRef]

44. Zhong, Z.; Ho, J.; Teo, J.; Shen, S.; Gedanken, A. Synthesis of porous α-Fe$_2$O$_3$ nanorods and deposition of very small gold particles in the pores for catalytic oxidation of CO. *Chem. Mater.* 2007, 19, 4776–4782. [CrossRef]
45. Wang, F.; Li, H.; Shen, W. Influence of Au particle size on Au/CeO$_2$ catalysts for CO oxidation. *Catal. Today* 2011, 175, 541–545. [CrossRef]
46. Boccuzzi, F.; Chiorino, A.; Manzoli, M.; Lu, P.; Akita, T.; Ichikawa, S.; Haruta, M. Au/TiO$_2$ nanosized samples: A catalytic, TEM and FTIR study of the effect of calcination temperature on the CO oxidation. *J. Catal.* 2001, 202, 256–267. [CrossRef]
47. Zhao, K.; Qiao, B.; Zhang, Y.; Wang, J. The roles of hydroxyapatite and FeOx in a Au/FeOx hydroxyapatite catalyst for CO oxidation. *Chin. J. Catal.* 2013, 34, 1386–1394. [CrossRef]
48. Ma, Z.; Brown, S.; Overbury, S.H.; Dai, S. Au/PO$_4^{3−}$/TiO$_2$ and PO$_4^{3−}$/Au/TiO$_2$ catalysts for CO oxidation: Effect of synthesis details on catalytic performance. *Appl. Catal. A-Gen.* 2007, 327, 226–237. [CrossRef]
49. Qi, C.; Su, H.; Guan, R.; Xu, X. An investigation into phosphate-doped Au/alumina for low temperature CO oxidation. *J. Phys. Chem. C* 2012, 116, 17492–17500. [CrossRef]
50. Liu, J.X.; Su, Y.; Filot, I.A.W.; Hensen, E.J.M. A linear scaling relation for CO oxidation on CeO$_2$-supported Pd. *J. Am. Chem. Soc.* 2018, 140, 4580–4587. [CrossRef]
51. Wan, J.; Chen, W.; Jia, C.; Zheng, L.; Dong, J.; Zheng, X.; Wang, Y.; Yan, W.; Chen, C.; Peng, Q.; et al. Defect effects on TiO$_2$ nanosheets: Stabilizing single atomic site Au and promoting catalytic properties. *Adv. Mater.* 2018, 30, 1705369. [CrossRef]
52. Duan, Z.; Henkelman, G. Calculations of CO oxidation over a Au/TiO$_2$ catalyst: A study of active sites, catalyst deactivation and moisture effects. *ACS Catal.* 2018, 8, 1376–1383. [CrossRef]