Evolution of Copper Supported on Fe₃O₄ Nanorods for WGS Reaction

Lingjuan Ma *, Hongbin Ma, Dawei Han, Mingyue Qiu, Yafei Guan and Yanlei Hu

School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, China; mabh@qfnu.edu.cn (H.M.); handawei0403@163.com (D.H.); Qmy112616@163.com (M.Q.); gylf0921qfc@163.com (Y.G.); huyanlei1818@163.com (Y.H.)
* Correspondence: malingjuan@qfnu.edu.cn

Received: 6 September 2018; Accepted: 21 September 2018; Published: 25 September 2018

Abstract: Rod-shaped Cu₁Fe₉Oₓ precursor was successfully prepared through an aqueous precipitation method. The shape and phase composition were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). It was found that Cu₁Fe₉Oₓ is composed of CuFe₂O₄ and Fe₂O₃. The reduction performance of Cu₁Fe₉Oₓ was studied by in situ XRD and H₂ temperature-programmed reduction (H₂-TPR). Cu/Fe₃O₄ nanorod catalyst is obtained through the controllable reduction of Cu₁Fe₉Oₓ nanorod, and the formed Cu/Fe₃O₄ nanorod catalyst does not have low-temperature water gas shift (WGS) activity, but exhibits high-temperature WGS reaction activity. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) studies showed that the main species of copper is Cu⁺ during the WGS reaction. The interaction between Cu and Fe₃O₄ rod and phase evolution of Cu species are quite different from Cu/Fe₃O₄ nanoparticles.

Keywords: Cu/Fe₃O₄ nanorods; ambient pressure X-ray photoelectron spectroscopy (AP-XPS); water gas shift (WGS) reaction

1. Introduction

Hydrogen is the most promising clean fuel to satisfy energy needs in the future [1]. At present, nearly 95% of the hydrogen supply is produced from reforming crude oil, coal, natural gas, wood, organic wastes, and biomass [2,3]. The water gas shift (WGS) reaction (CO + H₂O → CO₂ + H₂) is essential for hydrogen generation from fuel gas upgrading processes [4]. The reaction has a high reaction rate at high temperature, while it has high conversion of CO at low temperature. The WGS reaction has been studied extensively due to its industrial importance [5–7]. Metal and metal oxide catalysts, such as copper, mostly Cu/ZnO/Al₂O₃, are typically used for low-temperature water gas shift (LT-WGS) reactions (180–250 °C). Contrarily, iron-based catalysts can promote the water gas shift reaction at moderately high temperatures (350–450 °C), which are always regarded as high-temperature water shift catalysts (HT-WGS).

It was reported that Fe₃O₄ modified with CuO can improve its HT-WGS activity. Andreev et al. [8] studied the CuO (5 wt.%) effects on Fe–Cr catalysts, and found that the Cu-containing sample showed the best activity at 380 °C. Furthermore, it was found that metallic Cu is the main species for the HT-WGS reaction [9]. Interestingly, Cu is also an active species in the LT-WGS reaction, and the properties of its supports have great influence on its catalytic activity. Supports play very important roles in preventing the sintering of Cu, such as Cu/ZnO, Cu/CeO₂ and Cu/Fe₃O₄ [10–12]. Recently, Cu/Fe₃O₄ catalysts gain great attention because Cu and Fe₃O₄ are active phases in LT- and HT-WGS reactions, respectively. However, there is still a lack of studies on the shape effects of Fe₃O₄ support. Additionally, the precursors of copper are also very important for the stability and activity.
of copper species. Kameoka et al. [13] proposed that spinel CuFe$_2$O$_4$ was an effective precursor for a high-performance copper catalyst, which showed high thermal stability and activity.

In this study, we investigated the WGS reaction activities over Cu/Fe$_3$O$_4$ nanorod catalyst, which was synthesized through the controllable reduction of rod-shaped Cu$_1$Fe$_9$O$_x$ precursor. Compared with Cu/Fe$_3$O$_4$ nanoparticles, Cu/Fe$_3$O$_4$ rod catalyst exhibited very low activity. The evolution of surface species and structure chemistry during the WGS reaction were studied in detail by employing various characterizations. Moreover, the ambient pressure X-ray photoelectron spectrometer (AP-XPS) patterns indicate the main species of copper over rod-shaped Fe$_3$O$_4$ is Cu$^+$ during WGS reaction and the obtained Cu/Fe$_3$O$_4$ nanorod exhibits high activity.

2. Results and Discussion

2.1. Structure and Morphology of Cu$_1$Fe$_9$O$_x$ Nanorods Catalyst

Phase composition and shape of freshly synthesized samples were characterized by XRD and TEM. Figure 1 shows the XRD patterns of uncalcined and calcined precursors. Distinctive diffraction lines are clearly identified and all peaks are in good agreement with the XRD patterns of CuO (PDF No. 45-0937), β-FeOOH (PDF No. 34-1266), α-Fe$_2$O$_3$ (PDF No. 89-0597) and CuFe$_2$O$_4$ (PDF No. 34-0425). It is obvious that the uncalcined sample is composed of β-FeOOH and CuO, while the calcined sample is composed of CuFe$_2$O$_4$ and α-Fe$_2$O$_3$. This means that CuO reacted with β-FeOOH to produce CuFe$_2$O$_4$ and excess β-FeOOH is transformed into α-Fe$_2$O$_3$ during the calcination process. It is noteworthy that the CuO phase has not been detected in the calcined sample. It may exist as amorphous phase in the calcined precursor. Figure 2 shows the TEM images of the precursor. The uncalcined precursor displays a rod-like structure with diameter of 30–50 nm and length of 350–500 nm. After calcination, the precursor inherits the rod shape morphology. Interestingly, some mesopores appeared on Cu$_1$Fe$_9$O$_x$ nanorods because of the dehydration of Fe$_2$O$_3$. This means that CuO reacted with β-FeOOH during the calcination process. The Cu:Fe ratio of the calcined precursor obtained from an ICP result is 1: 8.98, which is consistent with the feed ratios. Thus, the calcined sample is referred to as Cu$_1$Fe$_9$O$_x$ nanorod. The BET surface area of Cu$_1$Fe$_9$O$_x$ nanorod is 48 m$^2$/g, which is much higher than Cu$_1$Fe$_9$O$_x$ particles (27 m$^2$/g) due to the formed mesopores [14]. Compared with Cu$_1$Fe$_9$O$_x$ nanoparticles [15], it is noteworthy that the main copper species in Cu$_1$Fe$_9$O$_x$ nanoparticles is CuO, while CuFe$_2$O$_4$ is the dominant copper species in Cu$_1$Fe$_9$O$_x$ nanorod.

![Figure 1. XRD patterns of the uncalcined and calcined precursors prepared by the aqueous precipitation method.](image)
When the reduction temperature rises to 250 °C, the main peak of CuFe2O4 at 35.1° shifts to a low degree, which is attributed to the peak of Fe3O4. In addition, the XRD peaks belonging to Fe2O3 completely disappear after reduction at 300 °C for 1 h. Furthermore, after reducing at 300 °C for 2 h, only metallic Cu and Fe3O4 are observed, indicating that Cu1Fe9Ox nanorods are completely reduced to Cu and Fe3O4. Meanwhile, Cu1Fe9Ox nanoparticles can also be reduced to Cu and Fe3O4 at 250 °C [15]. These results reveal that the reduction of Cu1Fe9Ox nanorod precipitate sample, i.e., 50–300 °C and 300–550 °C. Three obvious reduction peaks centered at 113 °C, 225 °C and 266 °C, respectively, were observed in the range of 50–300 °C. Compared with pure CuO, the reduction of Cu species in the Cu1Fe9Ox precursor was obviously shifted to lower temperature. The peak centered at 113 °C should be attributed to the reduction of Cu2+ in CuFe2O4 and the peak centered at 266 °C is the reduction of amorphous CuO, which cannot be detected by XRD. The higher peak at 225 °C is attributed to the reduction of Cu2+ in CuFe2O4 and the peak centered at 266 °C is the reduction of Fe2O3 to Fe3O4 [16–18]. The following high-temperature reduction at 300–550 °C should be due to the reduction of Fe3O4 to Fe0 [19].

![Figure 2. TEM images of uncalcined (a) and calcined (b) precursors prepared by the aqueous precipitation method.](image)

2.2. Reducibility of Cu1Fe9Ox Nanorod

The reducibility of the rod-shaped Cu1Fe9Ox precursor is investigated by H2-TPR as shown in Figure 3. The H2-TPR profile of pure CuO is also exhibited in Figure 3 for comparison. There are two distinctive reduction regions of the Cu1Fe9Ox nanorod sample, i.e., 50–300 °C and 300–550 °C. The reducibility of the rod-shaped Cu1Fe9Ox precursor is investigated by H2-TPR as shown in Figure 3. The H2-TPR profile of pure CuO is also exhibited in Figure 3 for comparison. There are two distinctive reduction regions of the Cu1Fe9Ox nanorod sample, i.e., 50–300 °C and 300–550 °C. Three obvious reduction peaks centered at 113 °C, 225 °C and 266 °C, respectively, were observed in the range of 50–300 °C. Compared with pure CuO, the reduction of Cu species in the Cu1Fe9Ox precursor was obviously shifted to lower temperature. The peak centered at 113 °C should be attributed to the reduction of amorphous CuO, which cannot be detected by XRD. The higher peak at 225 °C is attributed to the reduction of Cu2+ in CuFe2O4 and the peak centered at 266 °C is the reduction of Fe2O3 to Fe3O4 [16–18]. The following high-temperature reduction at 300–550 °C should be due to the reduction of Fe3O4 to Fe0 [19].

![Figure 3. H2 temperature-programmed reduction (H2-TPR) profiles of pure CuO (red line) and Cu1Fe9Ox nanorods (black line).](image)
is relatively difficult compared with nanoparticles, which may be attributed to the strong interactions between copper species and iron oxide nanorods.

Figure 4. In situ XRD patterns of Cu-Fe-O\(_x\) nanorods samples reduced in 5% H\(_2\)/N\(_2\) at different temperatures.

In order to elucidate the interactions between Cu species and the Fe\(_3\)O\(_4\) support, temperature-programmed-reduction of oxidized surfaces (s-TPR) was employed, as shown in Figure 5. During the test, Cu\(_1\)Fe\(_9\)O\(_x\) nanorods and nanoparticles were initially reduced by 5% H\(_2\)/N\(_2\) at 300 °C and 250 °C for 1 h, respectively. Subsequently, Cu on the surface can be oxidized into Cu\(_2\)O layer exclusively when 10% N\(_2\)O/He stream was introduced at 90 °C for 0.5 h [20]. Then, H\(_2\) was used to quantitatively convert the surface Cu\(_2\)O layer into metallic copper, and the consumption of H\(_2\) with the temperature increasing was profiled using s-TPR as shown in Figure 5. Obviously, the peak area of s-TPR represents the amount of surface Cu atoms, which is also an indicator of Cu dispersion. It can be seen that both curves contain only one peak, and the calculated dispersion of Cu on the surface of Cu/Fe\(_3\)O\(_4\) nanorods and nanoparticles are 18.6% and 14.7%, respectively. In addition, the peak position of s-TPR can indicate the reducibility of Cu\(_2\)O formed by oxidation of surface Cu\(^0\), and it is also easy to understand the peak position is dramatically affected by the interaction between Cu and Fe\(_3\)O\(_4\) support. The reduction temperature of Cu\(_2\)O formed on Cu/Fe\(_3\)O\(_4\) rod (154 °C) is much higher than that of Cu/Fe\(_3\)O\(_4\) nanoparticles (97 °C), which is attributed to the existing strong interaction between Cu and Fe\(_3\)O\(_4\) over Cu/Fe\(_3\)O\(_4\) rod.
under WGS reaction conditions. The peak position of Cu 2p3/2 at 932.7 eV indicates the existence of reactant gases (H2) studied by using a home-made AP-XPS system. Pure gas (here H2 for reduction at 300 °C) or a mixture of reactant gases (H2O vapor and CO for WGS reaction) flows through the Cu1Fe9Ox nanorod catalyst when the surface of the catalyst is being examined with AP-XPS. The Cu1Fe9Ox nanorods were first reduced in H2 at 311 °C for 3 h, and followed with the introduction of mixed CO and H2O with a total pressure of 0.8 Torr. After analyzing the inter-planar distance of the nanoparticles formed, it is confirmed to be the metallic Cu nanoparticles of 2–10 nm. Accordingly, it can be concluded that Cu1Fe9Ox nanorods can be reduced to Cu0/Fe3O4 rods by a controllable reduction process.

After reducing at 300 °C, it is obvious that Cu/Fe3O4 can inherit the rod shape of Cu1Fe9Ox nanorods (Figure 6a). The high magnification image (Figure 6b) shows that a lot of nanoparticles are formed on the surface of the nanorods. After analyzing the inter-planar distance of the nanoparticles formed, it is confirmed to be the metallic Cu nanoparticles of 2–10 nm. Accordingly, it can be concluded that Cu1Fe9Ox nanorods can be reduced to Cu0/Fe3O4 rods by a controllable reduction process.

Figure 5. Temperature-programmed-reduction of oxidized surfaces (s-TPR) profiles of Cu/Fe3O4 nanoparticle and Cu/Fe3O4 nanorod.

2.3. Morphology Structure of As-Prepared Catalyst after Reduction

After reducing at 300 °C, it is obvious that Cu/Fe3O4 can inherit the rod shape of Cu1Fe9Ox nanorods (Figure 6a). The high magnification image (Figure 6b) shows that a lot of nanoparticles are formed on the surface of the nanorods. After analyzing the inter-planar distance of the nanoparticles formed, it is confirmed to be the metallic Cu nanoparticles of 2–10 nm. Accordingly, it can be concluded that Cu1Fe9Ox nanorods can be reduced to Cu0/Fe3O4 rods by a controllable reduction process.

Figure 6. HAADF-STEM image of the Cu/Fe3O4 rods. (a,b) are images with different magnification; (c) is high resolution STEM image with inset of EDX.

2.4. Water Gas Shift (WGS) Reaction Kinetics and In Situ Studies

The catalytic activity of Cu/Fe3O4 nanorods is evaluated by WGS reaction, and it has no LT-WGS reaction activity below 250 °C. However, Cu/Fe3O4 nanoparticles with the same contents of Cu exhibit high LT-WGS activity [15]. In order to understand why metallic Cu on the surface of Fe3O4 rods is inactive toward the LT-WGS reaction, surface chemical states of the catalyst during WGS reaction were studied by using a home-made AP-XPS system. Pure gas (here H2 for reduction at 300 °C) or a mixture of reactant gases (H2O vapor and CO for WGS reaction) flows through the Cu1Fe9Ox catalyst when the surface of the catalyst is being examined with AP-XPS. The Cu1Fe9Ox nanorods were first reduced in H2 at 311 °C for 3 h, and followed with the introduction of mixed CO and H2O with a total pressure of 0.8 Torr.

Figure 7a shows the Cu 2p3/2 and Auger line Cu LMM spectra of Cu1Fe9Ox nanorod catalyst under WGS reaction conditions. The peak position of Cu 2p3/2 at 932.7 eV indicates the existence of reactant gases (H2) studied by using a home-made AP-XPS system. Pure gas (here H2 for reduction at 300 °C) or a mixture of reactant gases (H2O vapor and CO for WGS reaction) flows through the Cu1Fe9Ox nanorod catalyst when the surface of the catalyst is being examined with AP-XPS. The Cu1Fe9Ox nanorods were first reduced in H2 at 311 °C for 3 h, and followed with the introduction of mixed CO and H2O with a total pressure of 0.8 Torr.

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of Cu\(^{+}\) or/and Cu\(^{0}\) during catalysis. The Auger Cu LMM was used to distinguish Cu\(^{+}\) and metallic Cu. The Auger parameters calculated from the Cu LMM Auger line collected during catalysis with the AP-XPS exhibit the evolution of Cu species on the surface of the Fe\(_{3}\)O\(_{4}\) rods. It can be seen that the main species of copper after reducing at 311 °C is metallic Cu. When water vapor and CO were introduced, the dominant copper species is Cu\(^{+}\), suggesting that Cu\(^{0}\) on Fe\(_{3}\)O\(_{4}\) nanorod can be easily oxidized into Cu\(^{+}\) by water. Combining the s-TPR results, the strong interaction between Cu and Fe\(_{3}\)O\(_{4}\) nanorods is thought to be the main reason why Cu\(^{0}\) on the Fe\(_{3}\)O\(_{4}\) nanorod is much easier to oxidize relative to Cu\(^{0}\) particles on Fe\(_{3}\)O\(_{4}\) nanoparticles. In terms of the catalyst with nanorod structure, there is no obvious difference in photoemission features of Fe 2p among different catalytic temperatures (Figure 7b), which suggest that Fe\(_{2}\)O\(_{3}\) was reduced to Fe\(_{3}\)O\(_{4}\) upon H\(_{2}\) reduction and the Fe\(_{3}\)O\(_{4}\) phase can be retained during WGS process.

![Figure 7](image_url)

**Figure 7.** Ambient pressure X-ray photoelectron spectrometer (AP-XPS) studies of (a): the Cu 2p3/2, Cu LMM of the Cu\(_{1}\)Fe\(_{9}\)O\(_{x}\) nanorod sample and (b): Fe 2p, O1s of the rod catalyst under the WGS reaction conditions.

Figure 8 shows the ratio of Cu (Cu\(^{+}\) + Cu\(^{0}\))/Fe of Cu\(_{1}\)Fe\(_{9}\)O\(_{x}\) nanorods and nanoparticles under different conditions. For Cu\(_{1}\)Fe\(_{9}\)O\(_{x}\) nanorods, the measured Cu/Fe ratio increases with the increasing temperature. This variation indicates that Cu species migrate toward surface during reaction. On the contrary, for Cu\(_{1}\)Fe\(_{9}\)O\(_{x}\) nanoparticle sample, the measured Cu/Fe ratio increases with increasing temperature and subsequently decreases when the temperature further increases, indicating that metallic Cu on the surface sintered with the temperature increase.
Therefore, the activation energy of 71.2 kJ/mol for Cu/Fe3O4 nanorod in this work is reasonable, and it indicates that the reduced Cu1Fe9Ox rod exhibits a good HT-WGS reaction activity.

Although Cu/Fe3O4 nanorod has no LT-WGS activity, it can catalyze the WGS reaction at high temperature as Fe3O4 is active phase for the HT-WGS reaction. Through an in situ reduction approach, Cu/Fe3O4 was formed in a fixed-bed flow reactor in 5 vol.% H2/He at 300 °C for 2 h. When the mixtures of CO and water vapor are introduced, the kinetics of WGS over the Cu/Fe3O4 nanorod is investigated, as shown in Figure 9. The catalyst was tested at a gas hourly space velocity (GHSV) of 40,000 mL·g·cat−1·h−1, which made the conversion of CO lower than 10% in the range of 350–425 °C. Figure 9 presents the corresponding Arrhenius plot for the WGS reaction over the Cu/Fe3O4 nanorod and the CO conversions. The activation energy is calculated to be 71.2 kJ/mol. Given the fact that the activation energy of 95–118 kJ/mol and 75–80 kJ/mol can be attributed to the Fe-Cr [21,22] and Fe-Cr-Cu samples [23,24], the addition of Cu to Fe-Cr catalysts can decrease the activation energy by ~20–40 kJ/mol, revealing the promoting role of Cu in the HT-WGS reaction. Therefore, the activation energy of 71.2 kJ/mol for Cu/Fe3O4 nanorod in this work is reasonable, and it indicates that the reduced Cu1Fe9Ox rod exhibits a good HT-WGS reaction activity.

Figure 8. Atomic fraction of Cu/Fe of the Cu1Fe9Ox catalyst under WGS reaction conditions, NR: nanorod sample, NP: nanoparticle sample.

Figure 9. WGS activity performance (a) and Arrhenius plot (b) for the WGS reaction over Cu/Fe3O4 nanorods catalyst from 350–425 °C. Here, x is the CO conversion, reaction conditions: 1 vol.% CO, 3 vol.% H2O Ar balance. WHSV = 40,000 mL·g−1·h−1.
3. Materials and Methods

3.1. Materials and Methods

Cu$_1$Fe$_9$O$_x$ nanorod precursor was prepared by using an aqueous precipitation method [25]. The typical synthesis procedure is described as follows. An aqueous solution containing CuCl$_2$·2H$_2$O (0.34 g), FeCl$_3$·6H$_2$O (4.84 g), NaCl (11.60 g), and PEG (10 mL) with volume of 190 mL was gradually heated to 120 °C. Then, Na$_2$CO$_3$ aqueous solution (200 mL, 0.2 M) was added through a syringe pump at rate of 5.5 mL·min$^{-1}$, and the resulting suspension was aged at 120 °C for 1 h. Subsequently, the precipitate was washed with water and ethanol 3 times, followed by drying at 60 °C for 6 h. The resultant Cu$_1$Fe$_9$O$_x$ nanorods precursor was obtained by calcination at 500 °C for 10 h.

3.2. Characterization of Catalyst Structure

The crystal structure of synthesized samples was studied by X-ray diffraction (XRD) in a Rigaku D/MAX-RB (Rigaku Corporation, Akishima-shi, Japan) diffractometer using CuKa radiation source (λ = 1.54 Å). The average crystallite sizes were calculated by the Scherrer equation [26]. In situ XRD patterns were obtained by using the same instrument and the gas of 5 vol.% H$_2$/He was introduced and the heating rate is 5 °C/min.

The morphology and the microstructure of samples were characterized by TEM employing a Hitachi 7700 microscope (Hitachi High-Technologies Corporation, Beijing, China) and HRTEM in a FEI Tecnai G2 F30S-twin microscope (FEI, Hillsboro, OR, USA) operating at 300 kV and JEOL ARM200F (HAADF-STEM) at 200 kV. All samples for the TEM test were first dispersed in ethanol and then coated on Cu grid. The BET surface area of the sample was identified by a Nova 4200e (Quantachrome Instruments, Boynton Beach, FL, USA) physical adsorption instrument. Elemental analysis was examined by inductively coupled plasma atomic emission spectroscopy (ICPS-8100 spectrometer, Shimadzu, Kyoto, Japan).

The temperature-programmed reduction by hydrogen (H$_2$-TPR) of Cu$_1$Fe$_9$O$_x$ was tested with an Auto Chem 2920 instrument (Micromeritics, Atlanta, GA, USA). A 40 mg sample was placed in a quartz reactor which was connected to a conventional TPR apparatus. The reactor was heated from 50 °C to 900 °C at a heating rate of 2 °C/min and the amount of H$_2$ uptake during the reduction was measured by a thermal conductivity detector (TCD). For comparison, 40 mg of pure CuO powder was used.

3.3. Ambient Pressure X-Ray Photoelectron Spectroscopy (AP-XPS) Studies of Evolution of Surface Species

The surface chemistry and structure of the nanocatalysts during catalysis could be different from those of the as-synthesized catalysts before and/or after the catalysis, and the pressure-dependent entropy could restructure the surface of the catalyst during catalysis. In this case, the surface chemistry and structure of catalyst during the WGS reaction at a Torr pressure range were developed at the in-house AP-XPS using monochromator Al Ka [27]. The photoemission feature like the Cu 2p3/2, Fe 2p, Auger line Cu (LMM) and O1s of Cu$_1$Fe$_9$O$_x$ nanorod are collected under WGS conditions at different temperatures. After loading the catalyst in an XPS cell, sample was reduced in 1.5 Torr H$_2$ at 311 °C for 1 h and no treatment was made in O$_2$. Mixtures of CO and H$_2$O were then introduced into the XPS cell.

3.4. Measurement of Catalytic Performance

The WGS reaction was performed in a fixed-bed continuous flow reactor under atmospheric pressure at 350-425 °C. Prior to the activity test, 100 mg catalyst was loaded and reduced by flowing 5 vol.% H$_2$/He gas at a flow rate of 30 mL/min at 300 °C for 2 h. The reaction gas contained 1% CO/3% H$_2$O/He. To introduce water, He was used as a carrier gas flowing through deionized water. The effluents were analyzed by online gas chromatography. The conversion of CO is calculated as follows: X % = (CO$_{\text{upstream}}$ − CO$_{\text{downstream}}$) × 100%/CO$_{\text{upstream}}$. 
4. Conclusions

In this study, a Cu$^0$/Fe$_3$O$_4$ nanorod was prepared through the controllable reduction of Cu$_3$Fe$_9$O$_{14}$ nanorod, and it exhibited a high HT-WGS catalytic activity. According to the AP-XPS result, it was found that metallic Cu supported on a Fe$_3$O$_4$ nanorod can be easily oxidized to Cu$^+$ after introducing water vapor. Combining the behavior of metallic Cu supported on a Fe$_3$O$_4$ nanorod and nanoparticles during a WGS reaction, it can be found that the interaction between the metallic Cu and Fe$_3$O$_4$ support with different morphology structures is quite different. Furthermore, the activation energy of HT-WGS over Cu/Fe$_3$O$_4$ is 71.2 kJ/mol, which is much lower than the commercial Fe-Cr catalyst.

Author Contributions: L.M. and H.M. conceived and designed the experiments; D.H. and L.M. performed the experiments; M.Q., L.M. and H.M. analyzed the data; Y.G. and Y.H. contributed reagents/materials/analysis tools; L.M. wrote the manuscript.

Acknowledgments: This research was funded by [the National Natural Science Foundation of China] grant number [21403124] and [Natural Science Foundation of Shandong Province] grant number [ZR2014L014].

Conflicts of Interest: The authors declare no conflicts of interest.

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