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Characterization of Highly Dispersed Rod- and Particle-Shaped $\text{CuFe}_{19}\text{O}_x$ Catalysts and Their Shape Effects on WGS

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Abstract: Highly dispersed $\text{CuFe}_{19}\text{O}_x$ catalysts with different shapes were prepared and further characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), H_2 temperature-programmed reduction (H_2 -TPR), and in-situ XRD. XRD and TEM results showed that the synthesized $\text{CuFe}_{19}\text{O}_x$ nanoparticles consisted of CuO and Fe_2O_3 , while $\text{CuFe}_{19}\text{O}_x$ nanorods consisted of CuFe_2O_4 and Fe_2O_3 . The reduction properties of $\text{CuFe}_{19}\text{O}_x$ samples were finely studied by H_2 -TPR, and the phase composition was identified by in-situ XPS, HR-TEM, and surface TPR (s-TPR). In-situ X-ray photoelectroscopy (XPS) indicated that the metallic Cu and Fe_3O_4 were the main species after reduction. Moreover, s-TPR studies showed that the reduction performance of copper was significantly affected by the shapes of the Fe_3O_4 supports. Low-temperature water gas shift (LT-WGS) was chosen to characterize the Cu species on the surface. It was found that reduced $\text{CuFe}_{19}\text{O}_x$ nanorods had no activity. On the contrary, reduced $\text{CuFe}_{19}\text{O}_x$ particles showed higher initial WGS activity, where the active Cu^0 should originate from the reduction of Cu_2O at lower temperatures, as confirmed by the s-TPR profiles.

Keywords: $\text{Cu}/\text{Fe}_3\text{O}_4$; shape effect; WGS (water gas shift) reaction; s-TPR (surface temperature-programmed reduction)

1. Introduction

Morphology-dependent nanocatalysis has been intensively explored for metal and metal oxides [1], but less attention has been paid to binary metal oxides and oxide-supported metals. Recently, copper-based catalysts have attracted more and more attention due to their good catalytic performance in many industrial reactions such as selective catalytic reduction and low-temperature water gas shift (LT-WGS) reactions [2–6]. The $\text{Cu}/\text{Fe}_3\text{O}_4$ catalyst is one of the most attractive catalysts for research and its WGS performance strongly depends on the properties of Fe_3O_4 particles [7]. Iron has been reported to effectively improve the CO conversion and stability for WGS Cu-based catalysts [8–10]. Meanwhile, various parameters related to different counterpart characteristics, such as particle size and morphology, can also exert a profound influence on the structure/redox properties of binary oxides and consequently on their catalytic performance [11]. For example, a Cu/CeO_2 sample with a rod-like morphology exhibited the highest CO oxidation performance, offering almost complete CO elimination at temperatures as low as 100 °C. Han [12] studied bulk $\text{Cu}-\text{Fe}_3\text{O}_4$ WGS catalysts with different Cu-Fe ratios and found that the interaction between Cu^0 and Fe_3O_4 species greatly improves the Cu dispersion. Moreover, highly dispersed Cu^0 serves as a more active phase than that of the bulk one.

Despite the previous extensive studies [2–12], the morphology effects of Fe_3O_4 supported on the copper-iron oxide interfacial structure are still rarely studied. Note that the precursors of copper are

also very important for the stability and activity of copper species. Kameoka [13] proposed that spinel CuFe_2O_4 is an effective precursor for a high performance copper catalyst, exhibiting high thermal stability and activity. Yang [14] proposed a space-confined synthesis method to prepare rod-shaped CuFe_2O_4 , which was reduced to a $\text{Cu}/\text{Fe}_3\text{O}_4$ catalyst with fine Cu^0 nanoparticles supported on a Fe_3O_4 rod. We studied a series of Cu-Fe-Ox catalysts with 10% and 25% Cu contents [15,16]. It was found that Cu species supported on Fe_3O_4 rods and nanoparticles exhibit quite different behavior, which was significantly affected by the interactions between Cu and different Fe_3O_4 supports. However, Cu content is still too high to be highly dispersed on the surface of the Fe_3O_4 support.

In this study, we attempted to further decrease the content of Cu to 5% to prepare $\text{CuFe}_{19}\text{O}_x$ nanoparticles and nanorods. As a result, the dispersion of Cu was high at 97.2% and 87.8% for nanoparticle and nanorod samples, respectively, which is much higher than those reported previously. It was expected that these highly dispersed samples would exhibit different WGS activities and stabilities. Moreover, the shape effects of Fe_3O_4 supports on the reducibility of Cu species were well studied. Given the fact that XPS is a powerful tool to identify surface Cu species, and surface TPR (s-TPR) is also widely used to quantitatively characterize Cu species [12,17], we focused on the correlation of the WGS activity and the results of s-TPR and in-situ XPS.

2. Results and Discussion

2.1. Characterization of Structures and Shapes of $\text{CuFe}_{19}\text{O}_x$ Catalysts

Figure 1 displays the TEM images of $\text{CuFe}_{19}\text{O}_x$ samples synthesized with different methods. It can be seen clearly that the shape of samples prepared by the co-precipitation method is irregular nanoparticles (Figure 1a). Different from nanoparticles, a uniform rod shape can be obtained by co-precipitation of ferric and cupric chloride with sodium carbonate in an aqueous solution containing poly (ethylene glycol) (PEG) at 120 °C (Figure 1b). For the sake of simplicity, the corresponding samples were denoted as $\text{CuFe}_{19}\text{-P}$ (nanoparticles) and $\text{CuFe}_{19}\text{-R}$ (nanorods), respectively. As for the particle size, $\text{CuFe}_{19}\text{-P}$ is in the range of 10–50 nm and the average diameter of $\text{CuFe}_{19}\text{-R}$ is about 40 nm. Moreover, $\text{CuFe}_{19}\text{-R}$ nanorods have many pores, which have opening structures and are isolated from each other. It is well known that iron oxyhydroxide can be easily dehydrated into iron oxide [18]. As a result, mesopores are thought to be formed during the dehydration progress.

Figure 1. TEM images of $\text{CuFe}_{19}\text{O}_x$ prepared with the co-precipitation (a) and aqueous precipitation (b) methods.

As shown in Figure 2a, XRD was employed to analyze the phase composition of different samples. Interestingly, it was found that the phase compositions are CuO and Fe₂O₃ in CuFe19-P nanoparticles. However, CuFe₂O₄ and Fe₂O₃ have been identified in CuFe19-R nanorods. Here, CuO was not detected in the CuFe19-R sample. The formation of CuFe₂O₄ indicates that CuO and Fe₂O₃ interplay strongly in rod-shaped CuFe19-R. Table 1 lists the ICP results and BET surface areas of CuFe19-P and CuFe19-R. The actual copper content of CuFe19-P and CuFe19-R are 5.8% and 6.1%, respectively, which are slightly higher than the originally added Cu contents. As shown in Figure 2b, the isotherm of CuFe19-P should belong to the type-II isotherm. Specifically, a monolayer adsorption is formed at low relative pressures initially. Then, multi-molecular layer-adsorption occurs with increasing relative pressures. Lastly, the adsorption–desorption isotherms show a capillary condensation step when the relative pressure is close to saturation, indicating that adsorbed gas begins to condense into liquid. As for the adsorption isotherm of CuFe19-R, it is a little different from that of CuFe19-P. Namely, a capillary condensation step occurs at a lower relative pressure than for CuFe19-P, indicating that CuFe19-R has a smaller pore size than CuFe19-P. Considering the synthesis process, those pores in CuFe19-R should be formed as dehydration progresses. Moreover, the smaller pore size of CuFe19-R relative to CuFe19-P can be further confirmed by the pore size distribution of these samples as shown in the inset of Figure 2b. Actually, only large inter-particle pores >50 nm were formed for CuFe19-P. It should be noted that the BET surface area of CuFe19-R is much higher than that of the CuFe19-P, which can be attributed to the formed pores for the former.

Figure 2. (a) XRD patterns and (b) N₂ adsorption-desorption isotherms of CuFe19-P and CuFe19-R, where the inset of (b) is pore size distribution.

Table 1. Physical properties of CuFe19-P and CuFe19-R.

Samples	Shape	Cu/(Cu+Fe) (ICP)	BET Surface Area (m ² /g)
CuFe19-P	nanoparticle	5.8%	25
CuFe19-R	nanorod	6.1%	45

2.2. Reduction Behavior of CuFe19-P and CuFe19-R

As shown in Figure 3, the reduction behavior of the catalysts was characterized by H₂-TPR. For comparison, the reduction behavior of pure CuO and pure α-Fe₂O₃ nanorods were also characterized. Obviously, bare CuO has two overlapping peaks in the range of 200–300 °C, which is attributed to the reduction of Cu²⁺ to Cu⁺ and further reduction of Cu⁺ to Cu⁰. Fe₂O₃ nanorods exhibit two peaks centered at 332 and 534 °C, respectively, which are caused by the reduction of Fe₂O₃ to Fe₃O₄ and further reduction of Fe₃O₄ to Fe according to previous studies [19]. There are also two distinctive reduction regions for both Cu-Fe-O catalysts, i.e., 50–250 °C and 250–600 °C. Specifically, there is one main peak at about 250–600 °C and two peaks at 50–250 °C for both CuFe19-P and CuFe19-R catalysts. Given the fact that the main phase in both CuFe19-P and CuFe19-R is Fe₂O₃, and the reduction of Fe₂O₃ to Fe₃O₄ and Fe₃O₄ to Fe in pure Fe₂O₃ is about 215–280 °C and 605 °C [19],

respectively, the reduction peak at 250–600 °C in H₂-TPR profiles is attributed to the reduction of Fe₃O₄ to Fe. It is worth noting that the α -Fe₂O₃ rod was prepared using the same method as CuFe19-R, and it can be seen that the α -Fe₂O₃ rod is more difficult to reduce than both the CuO bulk and the CuFe19-R. The significant decrease of reduction temperature for the reduction of Fe₃O₄ to Fe may be attributed to the presence of Cu species, which can promote reduction progress. As for the two reduction peaks observed at 50–250 °C, the first ones centered at 125 °C and 128 °C for CuFe19-R and CuFe19-P, respectively, are attributed to the reduction of CuO species. However, CuO was not detected in CuFe19-R by XRD. So, the CuO species reduced at 125 °C for CuFe19-R is thought to be amorphous CuO, which cannot be detected by XRD. Compared with pure CuO, the reduction of Cu species in both CuFe19-P and CuFe19-R obviously shifted to lower temperatures, which may be caused by the small particle size [20]. It should be noted that the area of the peak centered at 125 °C is obviously smaller than that of the peak centered at 128 °C. That means that only some of the Cu species were reduced at 125 °C for CuFe19-R. Other Cu species are in the form of CuFe₂O₄ according to the XRD results. So, the peak centered at 215 °C for CuFe19-R is the combination of both the reduction of CuFe₂O₄ to Cu and Fe₃O₄ and the reduction of Fe₂O₃ to Fe₃O₄. Actually, these two processes can be separated when the ramping rate is further decreased to 1 °C/min. The peak centered at 198 °C for CuFe19-P can be attributed to the reduction of Fe₂O₃ to Fe₃O₄. However, the reduction peak of Fe₂O₃ is centered at 215 °C in the rod-shaped CuFe19-R, which is higher than that of CuFe19-P. Therefore, the rod-shaped Fe₂O₃ is very difficult to reduce compared to particle-shape samples.

Figure 3. TPR profiles of (a) pure CuO, (b) pure Fe₂O₃ nanorods, (c) CuFe19-R, and (d) CuFe-P.

In-situ, XRD was employed to further explain the reduction progress of both CuFe19-P and CuFe19-R. As shown in Figure 4, no obvious changes were observed for the diffraction lines of both samples at temperatures ranging from 25 to 150 °C compared with the XRD results shown in Figure 2a. For CuFe19-P, with the increase of reduction temperature, diffraction peaks of CuO became weak and completely disappeared at 200 °C (Figure 4a). This point is consistent with the reduction of CuO to Cu observed by H₂-TPR. Along with the increase of reduction temperature, the intensity of diffraction peaks of Fe₂O₃ gradually diminishes at temperatures ranging from 200 to 250 °C and the Fe₃O₄ phase was actually observed at about 225 °C. Therefore, the evolutions of CuO to Cu and Fe₂O₃ to Fe₃O₄ identified by H₂-TPR and in-situ XRD suggest that CuO is easier to reduce than that of the α -Fe₂O₃ phase. In other words, Fe₃O₄ and Cu phases were formed upon reduction at 250 °C in 5% H₂, and the higher reduction peak in the temperature region of 250–550 °C observed in TPR should be attributed to the reduction of Fe₃O₄ to metal Fe. As for the CuFe19-R sample, the reduction temperature of CuO_x and FeO_x shifts to a higher temperature. When the reducing temperature arrives at 200 °C, the main peak of CuFe₂O₄ at 35.1° shifts to a lower degree due to the formation of Fe₃O₄. In addition, the XRD

peaks belonging to Fe_2O_3 were weakened at 250 °C, and completely disappeared after reduction at 275 °C. Overall, the results of in-situ XRD clearly display that the reduction of copper species is easier than that of iron species, which is consistent with the results reported previously [21].

Figure 4. In-situ XRD patterns of CuFe19-P (a) and CuFe19-R (b) reduced at different temperatures.

2.3. Dispersion and Surface Cu Species

In order to obtain Cu/ Fe_3O_4 catalysts, both CuFe19-R and CuFe19-P were reduced at 250 °C for 3 h to ensure that Cu species were completely reduced. Then, XRD, in-situ XPS, and s-TPR measurements were performed to get further insights into the surface Cu species and synergistic effects of Cu and Fe. Figure 5 shows the XRD profiles of CuFe19-P and CuFe19-R reduced at 250 °C for 3 h. It can be seen that only Fe_3O_4 can be detected, suggesting that Cu species must be highly dispersed. As displayed in Figure 6a,b, TEM images suggest that the reduced samples can inherit their precursors' morphology and no small particles were detected on the surface of the Fe_3O_4 supports. On the other hand, very few Cu_2O or CuO nanoparticles were observed in HR-TEM images. As shown in Figure 6c,d, Cu_2O and CuO nanoparticle can be observed on the surface of the Fe_3O_4 nanoparticles and Fe_3O_4 nanorods, respectively. Here, the formation of Cu_2O and CuO nanoparticles can be attributed to the oxidation of Cu^0 nanoparticles because freshly formed Cu nanoparticles are very active and can be oxidized upon contact with air. Therefore, the observed Cu_2O and CuO nanoparticles must be the products of the oxidation of Cu nanoparticles under the air conditions. Moreover, this point can be further confirmed by the in-situ XPS results. Note that it was difficult to estimate the average size of Cu_2O or CuO particles because only a few nanoparticles were detected. In addition, it is worth noting that the interface between Cu_2O and Fe_3O_4 nanoparticles is clear. However, the opposite is true for the interface between CuO and Fe_3O_4 . Obviously, these results can provide more evidence that the interactions between Cu species and Fe_3O_4 nanorods are stronger than those between Cu and Fe_3O_4 nanoparticles.

Figure 5. XRD patterns of CuFe19-P and CuFe19-R reduced at 250 °C for 3 h.

Figure 6. TEM and HR-TEM images of reduced CuFe19-P (a,c) and CuFe19-R (b,d).

In order to understand the formation mechanism of the Cu species during the reduction process, in-situ XPS was employed. Figure 7 shows the in-situ XPS profiles of Cu 2p and CuL₃VV of freshly prepared and in-situ-reduced CuFe₁₉O_x samples. For freshly prepared CuFe19-P and CuFe19-R, as shown in Figure 7a, the binding energy of Cu 2p_{3/2} at 932.9 eV together with the relatively large shake-up satellite peaks at 938–948 eV further confirms the presence of Cu²⁺ in both samples [22–24]. As shown in Figure 7b, the shake-up satellite peak vanished upon hydrogen reduction at 250 °C, indicating the reduction of Cu²⁺ species. For the reduced samples, the peak position of Cu 2p_{3/2}

at 931.9 eV indicates the existence of Cu^0 and/or Cu^+ . Moreover, the Auger $\text{Cu L}_3\text{VV}$ was used to distinguish between the Cu^+ and metallic Cu. The existence of the Cu species on the surface of the Fe_3O_4 supports was confirmed by the Auger parameters. As shown in Figure 7c, the kinetic energy of 918.9 eV in $\text{Cu L}_3\text{VV}$ Auger spectra indicates the appearance of the metallic copper species. Moreover, it can be seen that the main species of copper after being reduced at 250 °C is Cu^0 . Overall, the results of XRD and in-situ XPS suggest that both CuFe19-P and CuFe19-R can be reduced to $\text{Cu}^0/\text{Fe}_3\text{O}_4$ at 250 °C.

Figure 7. In-situ XPS profiles of CuFe19-P and CuFe19-R , (a): Cu2p profiles of fresh samples; (b): Cu 2p profiles of reduced samples; (c): CuL_3VV profiles of reduced samples.

To obtain the Cu dispersion on the Fe_3O_4 supports, samples were first reduced at 50–250 °C and then oxidized by N_2O . Then, as shown in Figure 8, s-TPR profiles were obtained during the second reduction. To get a detailed species analysis, the temperature ramping rate was decreased to 1 °C/min. As displayed in Figure 8a, the first TPR run-profiles of CuFe19-P were similar to those of the results in Figure 3 except that all the peak positions were shifted to lower temperatures when the temperature ramping rate decreased from 2 to 1 °C/min. For the CuFe19-R sample, the reduction of CuFe_2O_4 and Fe_2O_3 was separated when the temperature ramping rate decreased to 1 °C/min. As shown in Figure 8a, the peak located at 183 °C and 223 °C is attributed to the reduction of CuFe_2O_4 to Cu and Fe_3O_4 and the reduction of Fe_2O_3 to Fe_3O_4 , respectively. As a result, the calculated total reduction areas of Cu^{2+} in the first TPR run were 0.393 and 0.373 for CuFe19-P and CuFe19-R , respectively. In the second TPR run, as shown in Figure 8b, it is interesting to find that the reduction behavior of surface Cu_2O on particle- and rod-shaped samples was quite different. For CuFe19-P , two s-TPR peaks at 101 °C and 123 °C were significantly lower than those of the reduction of CuFe19-R . Actually, the main hydrogen consumption peaks of CuFe19-P were lower than 150 °C. As for CuFe19-R , three peaks can be observed in s-TPR profile. Namely, a very small peak is located at 97 °C and two large peaks are located at above 150 °C. Clearly, the hydrogen consumption peaks at different temperatures can verify the existence of various Cu species after the standard N_2O oxidative pre-treatment. Probably, the different reduced temperatures for the CuFe19-P and CuFe19-R may be attributed to the different interactions between Cu^0 and different Fe_3O_4 supports.

Figure 8. s-TPR profiles of CuFe19-P and CuFe19-R. (a): the first TPR run; (b): the second TPR run.

The quantitative s-TPR results are listed in Table 2. The total peak area of s-TPR profile of CuFe19-P was 0.191, which is larger than that of CuFe19-R (0.147). To calculate the dispersion of Cu on the surface, the equation of $2A_2/A_1$ was employed. Here, A_2 was the hydrogen consumption area in the second TPR run, reflecting the amount of Cu_2O on the surface. A_1 was the total reduction area of Cu^{2+} in the first TPR run, standing for the total copper atoms. As a result, the calculated dispersion of Cu was high at up to 97.2% and 87.8% for CuFe19-P and CuFe19-R, respectively. According to the results of s-TPR analysis, it can be concluded that the redox behavior of Cu^0 on the CuFe19-P and CuFe19-R surfaces is quite different even though both of them exhibit high dispersion. Overall, it seems that it is more difficult for Cu_2O supported on Fe_3O_4 rods to be reduced than for those supported on Fe_3O_4 nanoparticles. Moreover, analyses of the HR-TEM and H_2 -TPR results suggest that the interactions between Cu and rod-shaped Fe_3O_4 are stronger than those between Cu and Fe_3O_4 particles.

Table 2. Quantitative analysis of s-TPR profiles (second TPR run).

Samples	Peak Position (°C)	Peak Area	Peak Sum
CuFe19-P	101	0.021	0.191
	123	0.17	
CuFe19-R	100	0.0226	0.147
	168	0.0213	
	183	0.103	

2.4. WGS Activity Test

To investigate the catalytic performance of the Cu/ Fe_3O_4 nanorods and nanoparticles, the LT-WGS activity was tested at 250 °C. As shown in Figure 9, reduced CuFe19-R had no WGS reaction activity at 250 °C. However, reduced CuFe19-P nanoparticles with the same content of Cu exhibited very high initial LT-WGS activity. Similarly, the same phenomena were also observed for the CuFe_9O_x nanoparticles and nanorods [25]. However, LT-WGS activity here was higher than that of the reduced CuFe_9O_x nanoparticles (CuFe9-P). For the rod-shaped sample, the lack of LT-WGS reactivity can be attributed to the fact that Cu^0 on the Fe_3O_4 nanorod can be easily oxidized into Cu^+ by water. As shown in Figure 8b, the s-TPR results (2nd TPR run) suggest that the main Cu_2O species on the

Fe_3O_4 rods were very difficult to reduce. So, those Cu_2O nanoparticles should correspond to the Cu^0 particles that were easily oxidized to Cu^+ by H_2O during the WGS reaction. Probably, the anchoring effects between Cu^0 and Fe_3O_4 nanorods are the main reason why Cu^0 on Fe_3O_4 nanorod is more easily oxidized by H_2O .

Figure 9. Water gas shift (WGS) reaction stability of CuFe19-P, CuFe19-R, and CuFe9-P. All samples were reduced at 250 °C for 3 h, reaction conditions: 250 °C 1vol.%CO/3vol.%H₂O/He; 40,000 mL·g^{−1}·h^{−1}.

As for CuFe19-P, the active Cu^0 site in the WGS reaction should correspond to the Cu_2O that was reduced at temperatures below 150 °C, as can be seen from Figure 8b. It is worth noting that the Cu content in CuFe9-P was much higher than CuFe19-P. However, the dispersion of Cu for CuFe19-P (97.2%) was much larger than that of the CuFe9-P (14.7%) [15]. Therefore, the initial higher activity of CuFe19-P could be attributed to the higher dispersion of Cu^0 on the surface of Fe_3O_4 nanoparticles. On the other hand, the catalytic performance of CuFe19-P was unstable under the present test conditions. Specifically, with the increase of the run time, the activity of CuFe19-P decreased rapidly, while only a slight decrease of activity was observed over the CuFe9-P catalyst. When the run time exceeded 400 min, the activity of CuFe19-P started to be lower than that of CuFe9-P. Figure S1a of the Supplementary Materials shows the XRD profile of the used CuFe19-P. It was found that only Fe_3O_4 was detected, but the crystallite size of 38.5 nm for Fe_3O_4 was much bigger than that of freshly formed Fe_3O_4 (26.3 nm). Therefore, the decrease of activity over CuFe19-P could be attributed to the sintering of Fe_3O_4 . Additionally, it is well established by research that highly dispersed Cu suffers from CO poisoning and sintering easily. Therefore, the Cu nanoparticles were not well stabilized by the Fe_3O_4 nanoparticles.

3. Experiment

3.1. Synthesis of Catalysts

Highly dispersed $\text{CuFe}_{19}\text{O}_x$ catalysts were prepared according to our previously reported methods [15,16]. CuFe19-P was prepared by the co-precipitation method. An aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1 mmol) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (19 mmol) was rapidly added into 100 mL 0.5 M Na_2CO_3 aqueous solution at room temperature. The mixture was then aged at room temperature for 12 h. The precipitate was washed with water and ethanol and dried at 80 °C overnight. Finally, the precursor was calcined at 500 °C for 10 h. CuFe9-P was prepared for comparison with the same co-precipitation

method as CuFe19-P, where the only difference being in the ratio of Cu to Fe. CuFe19-R was obtained according to co-precipitation of ferric and cupric chloride with sodium carbonate in aqueous solution containing poly (ethylene glycol) (PEG) at 120 °C. A mixture of 0.17g CuCl₂·2H₂O, 5.13g FeCl₃·6H₂O, 11.60g NaCl, and 10 mL PEG were dissolved in 190 mL water, and then the solution was gradually heated to 120 °C with vigorous stirring and then kept at 120 °C for 3 h. A 0.2 M Na₂CO₃ aqueous solution was added through a syringe pump at a rate of 1.0 mL/min. The slurry was then aged at 120 °C for 2 h, filtered, washed thoroughly with distilled water, and then dried at 60 °C for 6 h. Finally, the dried sample was calcined at 500 °C for 10 h. For comparison, α-Fe₂O₃ nanorod was also prepared with the same method as CuFe19-R.

3.2. Characterization of Catalysts

Phase compositions of the fresh and reduced catalysts were measured XRD using a Rigaku D/MAX-RB diffractometer (Rigaku Corporation, Akishima-shi, Japan) with Cu K α radiation (λ = 0.154 nm) operated at 40 kV and 40 mA on a scanning range of 15–80° (2 θ). In situ XRD was also carried out, where the catalyst was in a reductive atmosphere (5% H₂ balanced with 95% He) with a scan rate of 5 °C/min to track potential evolution of phase in the H₂ treatment. BET surface area and pore size distributions of the catalysts were measured by N₂ physisorption at –196 °C by a Nova 4200e physical adsorption instrument (Quantachrome Instruments, Boynton Beach, FL, USA). Inductively coupled plasma atomic emission spectroscopy (ICPS-8100 spectrometer, Shimadzu, Kyoto, Japan) was employed to test elemental composition of catalysts. H₂-TPR was carried out in a quartz reactor at atmospheric pressure. For this, 0.04 g of the catalyst was loaded into the center of a reactor tube, which had been purged with He gas at 300 °C for 1 h. Then, a reductive gas (5% H₂/He) was introduced into the tube at a flow rate of 30 mL/min. The temperature of the reactor was increased linearly from 50 to 650 °C with a ramping speed of 2 °C/min. The morphology of samples was studied through a transmission electron microscope, a Hitachi 7700 microscope (Hitachi High-Technologies Corporation, Beijing, China), and a high resolution transmission electron microscope (HR-TEM) using an FEI Tecnai G2 F30S-twin microscope operating at 300 kV (FEI, Hillsboro, OR, USA). The electronic states of Cu were examined by XPS (VG ESCALAB MK2 with Al anode apparatus, Thermo-VG Scientific Corporation, USA). The XPS was performed in an ultrahigh-vacuum chamber that had an attached high-pressure cell or batch reactor. The sample could be transferred between the reactor and vacuum chamber without exposure to air. All the binding energy values were calibrated by using the contaminant carbon (C1s = 284.9 eV) as a reference.

Surface TPR (s-TPR) experiments have been described in detail in previous studies [26]. CuFe19-P and CuFe19-R were initially temperature-programmed and reduced at 250 °C by 5% H₂/N₂ and kept at 250 °C for 1 h to ensure that all Cu species were completely reduced. The temperature was then decreased to 90 °C in an He atmosphere. Subsequently, a 10% N₂O/He stream was introduced at 90 °C for 0.5 h to oxidize Cu on the surface into Cu₂O layer exclusively [27]. After that, the catalysts were purged with He again and cooled to room temperature, followed by launching another H₂-TPR run to 250 °C. H₂ was used to quantitatively convert the surface Cu₂O layer into metallic copper. The calculation of Cu dispersion was based on a method reported before [28,29]. The amount of Cu₂O at the surface was calculated by the hydrogen consumption area (A₂) in the second TPR run. All copper atoms were calculated by the total reduction area (A₁) of Cu²⁺ in the first TPR run. As a result, the dispersion of Cu was equal to the 2A₂/A₁.

3.3. Catalyst Pretreatment and Testing

The WGS reaction was performed in a home-made fixed-bed continuous flow reactor under atmospheric pressure at 250 °C. All experiments were carried out in a U-shape reactor placed in an oven equipped with a temperature regulator. The catalyst sample was placed between two layers of quartz wool. Prior to the activity test, 100 mg catalyst was loaded and reduced by flowing 5 vol% H₂/He gas at a flow rate of 30 mL/min at 250 °C for 2 h. The reaction gas contained 1% CO/3% H₂O/He.

To introduce water, He was used to carry the gas flowing through deionized water. The effluents were analyzed by online gas chromatography. An Agilent 7800 gas chromatograph (GC, Agilent Technologies Co. USA), equipped with Carboxen 1000 Supelco column and a TCD detector was connected at the end of the line to analyze the outflow gas. The conversion of CO was calculated as follows: $X\% = (\text{CO}_{\text{upstream}} - \text{CO}_{\text{downstream}}) \times 100\% / \text{CO}_{\text{upstream}}$.

4. Conclusions

In this study, highly dispersed $\text{CuFe}_{19}\text{O}_x$ samples with rod- and particle-shapes were successfully synthesized. The reduction performance of the samples was studied by H_2 -TPR and by in-situ XRD. It was found that particle-shaped sample had better reducibility. XRD, HR-TEM, and in-situ XRS results suggest that both $\text{CuFe}_{19}\text{O}_x$ nanoparticles and nanorods can be reduced to $\text{Cu}^0/\text{Fe}_3\text{O}_4$. The dispersion and surface Cu species were characterized by s-TPR. It was found that surface Cu atoms supported on Fe_3O_4 nanoparticles can be oxidized to Cu_2O by N_2O and can be further reduced to Cu^0 at much lower temperature than that of Cu supported on Fe_3O_4 nanorods. The dispersion of Cu supported on particle- and rod-shaped Fe_3O_4 was high at 97.2% and 87.8%, respectively. The high dispersion makes $\text{CuFe}_{19}\text{-P}$ exhibit high initial WGS activity. However, Cu supported on rod-shaped Fe_3O_4 had no WGS activity at all, which may have been result of the strong anchoring effect between metallic Cu and the Fe_3O_4 nanorod. Compared with the $\text{CuFe}_9\text{-P}$ sample, the $\text{CuFe}_{19}\text{-P}$ sample showed much higher initial LT-WGS activity even though it contained a lower copper content.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/8/12/635/s1>, Figure S1: XRD profile (a) and HRTEM image (b) of used $\text{CuFe}_{19}\text{-P}$.

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