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Cu-Promoted Iron Catalysts Supported on Nanorod-Structured Mn-Ce Mixed Oxides for Higher Alcohol Synthesis from Syngas

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Abstract: A series of supports were prepared through the method of hydrothermal synthesis, and copper–iron catalysts supported on ceria nanorods modified by different amounts of manganese were prepared by the liquid phase co-reduction method. The effect of the catalytic performance after Mn addition mainly on higher alcohols synthesis (HAS) was evaluated. Different techniques, such as BET, ICP-AES, XRD, H₂-TPR, CO-TPD, TEM, FESEM, XPS and MES, were performed for catalyst characterization. The results indicated that the abilities of CO chemical desorption and carbon chain growth were promoted with appropriate Mn addition, and higher ratio of Cu⁰/Cu⁺ species facilitated the methanol homologous reaction and the C₂₊OH formation. The Ce⁴⁺ species were reduced into Ce³⁺ species during HAS process, providing a large amount of oxygen vacancies. Proper Mn content promoted the formation of χ -Fe₅C₂ and led to the Fe 2p binding energy shift, causing the electron transformation between Fe and Mn species. The largest weight selectivity of C₂₊OH appeared in the reaction over CuFe/3.6MnCe catalyst with CO conversion 41.43%, and weight fraction of C₂₊OH 84.41 wt% in the alcohols distribution.

Keywords: Fischer–Tropsch synthesis; Mn–Ce mixed oxides; Cu–Fe catalyst; higher alcohols; liquid phase co-reduction

1. Introduction

In recent years, with the decreasing reserve and rising price of petroleum resources, the consumption structure of energy and chemical industry has gradually changed from petroleum to the co-supply of petroleum, coal, natural gas and biomass. Fischer–Tropsch synthesis (FTS) is a reaction process with syngas (CO and H₂) as raw materials to synthesize lots of products including hydrocarbons and high-valued alcohols under certain conditions [1,2]. Higher alcohols (C₂₊OH) can be used as transportation fuels to enhance octane number and improve engine performance, and intermediates to produce detergents and surfactants [3–5].

Many great efforts have been made to develop catalysts for FTS and higher alcohols synthesis, such as Fe, Co, Cu, MoS₂ and Ru-based catalysts [1,6]. Compared with other catalysts, low cost and high chain growth possibility are the advantages of iron-based catalysts in FTS, but the selectivity of

alcohols is much lower than that of modified Cu-based catalysts [7–9]. Due to the ability of facilitating carbon chain growth and achieving high selectivity of higher alcohols (with a selectivity of $C_{2+}OH$ larger than 20%), modified Cu-Fe catalysts have attracted more attentions in recent years [10–12]. The reaction over modified Cu-Fe catalysts is a bit different from the traditional FTS which focuses on the high selectivity of C_{5+} products or olefins and neglects the formation of alcohols, the synergistic effect of iron and copper, which combines the carbon chain growth effect of iron carbides and alcohols formation effect of copper together, could largely promote the formation of higher alcohols. On the other hand, as a basic chemical raw material, the economic value of higher alcohols is much higher than hydrocarbons, so the increase in the selectivity of higher alcohols can efficiently improve the economy of FTS process. Mn promoter added on catalysts can enhance the synergistic effect of iron and copper species in Fischer–Tropsch synthesis, which will facilitate the formation of Fe-Mn-O solid solution and achieving highly dispersed iron and copper species [12]. It was reported that Ce promoter could enhance the ability of CO chemical desorption and improve the carbonization because of its electronic donating effect, which will finally promote the formation of FeC_x species and decrease the selectivity of methane (from 11.1% to 9.5% with Ce addition from 0 to 0.5%) [6]. The results of comparing the reaction performance of Cu-Fe, Cu-Co and Cu-Ni nanoparticles in FTS showed that Cu-Fe catalysts had best performance in higher alcohol synthesis (HAS) process for its special nano-alloy structure [10]. However, the Cu phase partly separated from Fe phase during the reaction, which weakened the interaction of iron and copper species. Cu is commonly supposed to offer CO insertion site and facilitate the chemical desorption of H_2 and the molecular desorption of CO [13,14]. It is well accepted that Cu-based catalyst modified by Fe species enables the CO chemical adsorption and provides carbon chain growth sites [2,13,14]. Nie et al. [6] reported that Ce promoter improved the formation of FeC_x species and donated electron to Fe species in reaction, which led to higher CO conversion and lower CH_4 selectivity. The importance of the synergistic effect of iron and copper species has been recognized recently, however the effect of ceria nanorod as support of Cu-promoted iron catalyst has rarely been reported.

This paper mainly aims to investigate the effect of supports Mn-modified ceria nanorod in Cu-promoted iron catalyst for HAS. Cu-Fe catalysts supported on Mn-modified ceria nanorod with different amounts of Mn were prepared by the hydrothermal synthesis method and the liquid phase co-reduction method. These catalysts were characterized by N_2 physisorption, inductively coupled plasma-atomic emission spectrometer (ICP-AES), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), temperature programmed reduction (TPR), temperature programmed desorption of adsorbed CO (CO-TPD), X-ray photoelectron spectra (XPS), Mössbauer effect spectra (MES), and the reaction performance was performed in a fixed-bed reactor.

2. Results and Discussion

2.1. Textural Properties of the Supports and Catalysts

All the supports display a typical cylinder-like rod, the FESEM images of supports 1.2MnCe, 2.4MnCe and 3.6MnCe are shown in Figure S1, in which the diameter of the support is about 10 nm and length is about 100–300 nm, which is close to the size reported previously [15,16]. The addition of Mn was favorable for the formation of nanoparticles, and Mn-Ce mixed oxide solid solution was possibly formed in this process, and the cylinder-like rod of xMnCe mixed oxides will gradually be replaced by nanoparticles with the continuous increase in Mn content. The result of ICP analysis (Table S1) was commonly in agreement with the theoretical contents, indicating that precursor salts ($Fe(NO_3)_3 \cdot 9H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$) were reduced completely in the liquid phase co-reduction process. The BET surface area (Table S1) of the catalysts is about $80 \text{ m}^2/\text{g}$, almost the same with that of the supports, which indicates that the textural properties of the supports are not changed in the catalyst preparation process. TEM image of catalyst CuFe/1.2MnCe (Figure S1) shows that the average

size of Cu-Fe bimetallic nanoparticles is about 10–30 nm, which could ensure the good dispersion of metal particles. The XRD patterns (Figure S2a) show that a typical cubic fluoride CeO_2 crystal phase (JCPDS#34-0394) exists in the samples. The diffraction peaks of Mn species cannot be observed possibly because of the small amount and the high dispersion of Mn species [15]. The XRD patterns of fresh catalysts are shown in Figure S2b. Peaks at 43.3° , 50.4° and 74.13° could be ascribed to metal copper (JCPDS#04-0836) or/and iron-copper alloy FeCu_4 (JCPDS#65-7002) [10]. No peaks of Fe species were observed, possibly because the formed iron species was highly dispersed on the catalysts. The XRD patterns of catalysts after reaction (Figure S3) show that the intensity of the typical cubic fluoride CeO_2 crystal phase (JCPDS#34-0394) peaks decreases a significant amount [17], which means that a large part of CeO_2 is reduced during the reduction and reaction process. As was shown in Figure S3, diffraction peaks at 26.8° , 29.4° and 48.4° can be ascribed to SiO_2 species, which should come from catalysts diluted with 80–100 mesh SiO_2 .

2.2. Reduction Performance of Catalysts

H_2 -TPR profiles of fresh supports were shown in Figure 1a. The weak reduction peaks of low temperature at about 200°C can be assigned to the reduction of MnO_2 to Mn_3O_4 and the major peaks at 380°C can be deemed to the reduction process of CeO_2 to Ce_2O_3 species. Peaks at $\sim 700^\circ\text{C}$ can be attributed to the reduction of Ce_2O_3 to CeO species. H_2 -TPR profiles of synthesized catalysts were shown in Figure 1b. Reduction peaks located in the range of 100 to 200°C could be attributed to the reduction process of copper oxide to metal copper (CuO and Cu_2O to Cu) [11,18]. The slight reduction peak at about 340°C corresponds to the surface oxygen reduction of cerium oxide from CeO_2 species to Ce_2O_3 species [17], indicating the transformation of Ce species during the reduction procedure which is in accordance with the results of XRD. The peaks at about 550°C could be ascribed to the reduction of iron oxide to metal iron (Fe_2O_3 to Fe_3O_4 , Fe_3O_4 to FeO and FeO to Fe) [11,18,19]. The iron and copper oxide species were probably formed in the process of centrifugation and passivation, oxidized from metal nanoparticles by air.

Figure 1. H_2 -TPR profiles: (a) fresh supports, (b) synthesized catalysts.

2.3. CO Desorption Properties of Catalysts

The desorption peaks of fresh supports (Figure 2) at lower temperature about 150°C was attributed to the molecular CO state desorption [20]. The peak at higher temperatures of about 270°C mainly indicated the existence of new CeO_2 active sites, mainly involved in the CO catalytic oxidation reaction [21] which led to the CO_2 formation in HAS process. Peaks above 500°C can be regarded as CO chemical desorption, mainly relative to HAS reaction [20]. Obviously, the intensity of desorption peaks was consistent with the Mn content. This change proved that Mn addition promoted the CO adsorption of supports, which led to the formation of more CO species on the catalyst surface and improved the FTS performance in some senses. The desorption curves of different temperature regions

illustrated different CO adsorption state [22]. It is generally accepted that the desorption peaks below 200 °C correspond to the molecular CO state desorption on Cu-Fe nanoparticles, while those of the CO chemical desorption mainly correspond to CO hydrogenation, located above 500 °C [20,23]. It can be seen from Figure 2b that the desorption peaks at above 500 °C shift to a higher temperature when the Mn content increases from 0 to 2.4. The proper addition of Mn is beneficial to the enhancement of the strongly adsorbed CO, causing a higher CO concentration over the catalyst surface for the reason that Mn could transfer electrons to CO via iron oxides, and strengthen Fe-C bond, which hinders the CO chemical desorption, causing that more occurred on the surface of catalysts at higher temperatures [24]. A higher temperature of CO desorption is favorable for carbon monoxide insertion, possibly leading to the formation of more long-chain production [1,2,25]. Interestingly, the desorption peak of CuFe/3.6MnCe shifts to a lower temperature compared to other samples, which may be caused by the strong interaction between Fe and Mn when Mn is over added, hindering the CO chemical desorption.

Figure 2. CO-TPD profiles: (a) supports, (b) fresh catalysts.

2.4. Surface Chemical Properties of Catalysts

The XPS spectra of Ce 3d_{5/2} and 3d_{3/2} of the fresh supports and used catalysts are shown in Figure 3. The XPS spectra of Ce 3d core level can be resolved into 10 groups according to the literature [22,26–29], three doublets corresponding to Ce⁴⁺, and two doublets corresponding to Ce³⁺, which has been labeled in Figure 3. The peaks located at 881.7 (Ce³⁺), 882.9 (Ce⁴⁺), 885.7 (Ce³⁺), 889.0 (Ce⁴⁺), and 897.6 (Ce⁴⁺) eV correspond to 3d_{5/2} while the peaks at 899.1 (Ce³⁺), 900.8 (Ce⁴⁺), 904.3 (Ce³⁺), 907.4 (Ce⁴⁺), and 916.8 (Ce⁴⁺) eV correspond to Ce 3d_{3/2}. The concentration of the surface Ce³⁺, which is related to the oxygen vacancies on the catalysts' surface can be calculated from Equation (1) [29].

$$C_{\text{Ce}^{3+}} = \frac{\text{Ce}^{3+}}{\text{Ce}^{3+} + \text{Ce}^{4+}} \quad (1)$$

Figure 3. Ce 3d XPS spectra: (a) fresh supports, (b) used catalysts.

After the calculation of peak area for Ce^{4+} and Ce^{3+} , the Ce^{3+} concentration of fresh catalyst CuFe/0MnCe and the used catalysts are respectively shown in Table 1.

Table 1. Ce and Cu compositions on the surface of supports and used catalysts.

Supports	Ce^{3+} Concentration (%)	Used Catalysts	Ce^{3+} Concentration (%)	Value of Cu^0/Cu^+	Increment ¹ of Ce^{3+} Concentration (%)
0MnCe	35.89	CuFe/0MnCe	64.25	6.49	28.36
0.6MnCe	33.26	CuFe/0.6MnCe	65.16	6.54	31.90
1.2MnCe	31.49	CuFe/1.2MnCe	64.93	7.57	33.44
2.4MnCe	29.38	CuFe/2.4MnCe	64.89	8.03	35.51
3.6MnCe	27.58	CuFe/3.6MnCe	64.11	9.76	36.53

¹ Increment = Ce^{3+} Concentration of used catalysts— Ce^{3+} Concentration of supports.

It can be seen from Table 1 that the Ce^{3+} concentration of used catalyst CuFe/0MnCe is almost twice as large as that of the fresh support, which is in accordance with the results of XRD and H_2 -TPR. This manifested as Ce^{4+} transforming to Ce^{3+} during the reduction and reaction process, which will possibly affect the CO hydrogenation and the selectivity of products. The oxygen vacancy increased with Mn addition (0–0.6 Mn content), but slightly decreased with the increasing Mn content due to excessive Mn addition (0.6–3.6 Mn content), which will inhibit the transformation of Ce^{4+} to Ce^{3+} species. Compared with the Ce 3d XPS spectra of fresh supports, the increments of Ce^{3+} concentration were larger after Mn addition. Mn species intensified the formation process of oxygen vacancies in some senses. It was well accepted that more oxygen vacancies can enhance CO adsorption on the catalyst surface. This phenomenon may be caused by the gradually strengthened interaction between Fe and Mn species and will improve the behavior of CO chemical adsorption.

The Cu 2p spectra and the enlarged spectra within the BE range of 955–948 eV and 935–930 eV of the used catalysts are shown in Figure 4. The peaks at 952.6 eV and 932.6 eV can be attributed to Cu 2p_{1/2}, and Cu 2p_{3/2}, respectively, while those at 952.6 eV and 932.6 eV could be regarded as Cu^0 species, with a weak satellite peak at 946.7 eV which is related to Cu^+ species [30–33]. The constitution of Cu species on the used catalysts' surface is shown in Table 1. The Cu 2p spectra implies that the copper species are mainly constituted by metal copper and a small amount of Cu^+ , which is consistent with the results of XRD profiles. It was reported that the Cu^0 and Cu^+ species are preferential for the synthesis of ethanol because of the synergistic effect between balanced Cu^+ and Cu^0 sites [34,35]. With Mn addition, the ratio of Cu^0/Cu^+ increases from 6.49 to 9.76.

The Fe 2p spectra of catalysts after reaction are shown in Figure 5. The two main peaks at about 711.5 eV with a shift toward lower binding energy and 724.5 eV with a shift toward lower binding energy are ascribed to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively [6,36]. The shift of binding energy is relevant to the electron transformation between Fe and Mn species. Mn species tends to transfer electron to Fe species for electronegativity [37]. Therefore, Mn species act as electronic donating promoters and appropriate Mn content accelerates the CO chemical adsorption, which leads to a higher carbon species concentration on the catalyst surface. The peaks at about 707.1 eV are related to iron carbides and its intensity gradually strengthens with increasing Mn addition, indicating that the addition of Mn is preferential for the formation of surface iron carbides species [38–40], which seems to be in disagreement with the bulk results of MES.

Figure 4. Cu 2p XPS spectra of catalysts after reaction: (a) Cu 2p, (b) Cu 2p_{1/2}, (c) Cu 2p_{3/2}.

Figure 5. Fe 2p XPS spectra of catalysts after reaction.

2.5. MES Results of Used Catalysts

The MES results of the catalysts after reaction under the operating condition of syngas ($H_2/CO = 2.0$), 260 °C, 3.0 MPa and 1333 h⁻¹ are listed in Table 2. It was well known that iron carbide promoted the CO insertion and the formation of more long-chain products [2]. As shown in Table 2, all the used catalysts are composed of Fe³⁺, Fe₃O₄, and χ -Fe₅C₂. The amount of χ -Fe₅C₂ increases significantly when Mn is added, indicating that the addition of small amounts of Mn promotes the carburization of iron oxides which is commonly accepted as the active phase for CO hydrogenation. However, the excessive addition will lead to a slightly decrease in χ -Fe₅C₂ content, possibly because of the gradually strengthened interaction of Fe and Mn. At the same time, the decreasing amount of Fe₃O₄ indicates that part of the Fe₃O₄ is transformed into iron carbides during the reaction process, possibly because Mn species can donate more electrons in the reaction process [37,41], which is essential to CO chemical adsorption. Meanwhile, Fe₃O₄ species are commonly regarded as the active phase of the water–gas shift reaction and can facilitate the formation of CO₂. The decreasing trend of Fe₃O₄ content when Mn addition gradually increases is in accordance with the variation of CO₂ selectivity during the catalytic performance evaluation process. On the other hand, the slight increase in Fe³⁺ content may be caused by the oxidation of iron phases by H₂O and CO₂ during the reaction process [42,43].

Table 2. MES results of catalysts after reaction.

Assignments	Iron Phase Composition of Catalysts (%)		
	Fe ³⁺ (spm)	Fe ₃ O ₄	χ -Fe ₅ C ₂
CuFe/0MnCe	39.2	21.9	38.9
CuFe/0.6MnCe	42.6	9.7	47.7
CuFe/1.2MnCe	44.2	9.5	46.3
CuFe/2.4MnCe	45.4	9.2	45.4
CuFe/3.6MnCe	47.0	8.7	44.3

2.6. Catalytic Performance and Stability Test of the Catalysts

The catalytic performance tests of catalysts were performed in a tubular fixed-bed reactor, and the results are shown in Table 3. It can be seen that CO conversion decreases largely from 82.83% to 41.43% when Mn addition increases from 0 to 3.6. In the reaction process, CO conversion is mainly caused by CO hydrogenation and catalytic oxidation [1,2]. Fe₃O₄ species decreased significantly, from 21.9% to 9.7% after 0.6 Mn addition, which explained the decrease in CO conversion from 82.83% to 73.35%. With the continuous increase in Mn addition from 0.6 to 3.6, the active phase χ -Fe₅C₂, as shown in Table 2, decreased from 47.7% to 44.3%, while Fe₃O₄ species as active phase for CO catalytic oxidation decreased from 9.7% to 8.7% [6,44]. An excessive Mn addition (0.6–3.6 Mn content) will inhibit the transformation of Ce⁴⁺ to Ce³⁺ and the formation of oxygen vacancies, finally resulting in the loss of CO chemical adsorption. The peak value of CO conversion over CuFe/0MnCe may be caused by the large amount of Fe₃O₄ species in the catalyst. With Mn addition, the selectivity of CO₂ also displays a decreasing trend for the decrease in Fe₃O₄ species. Meanwhile the strengthened interaction between Mn–Ce mixed oxide will inhibit the transformation of Ce⁴⁺ to Ce³⁺ and reduce the catalytic oxidation of carbon monoxide by cerium dioxide [45], finally leading to a lower selectivity of CO₂.

From the results of the reaction performance tests, it can also be seen that the selectivity of total and higher alcohols (C_{2–5}OH and C₆₊OH) increases with Mn content, especially the selectivity of alcohol over CuFe/3.6MnCe is almost twice as large as that over the catalyst without Mn addition. Relatively, the selectivity of methanol is much lower than that of C_{2–5}OH and C₆₊OH (84.41 wt% C₂₊OH over CuFe/3.6MnCe in alcohols distribution). As discussed above, Cu⁰ is more likely the active site for alcohols synthesis than Cu⁺ and plays a vital role in the synthesis of alcohols.

Table 3. HAS evaluation results of CuFe/xMnCe catalysts.

Samples	X _{CO} (%)	Selectivity (wt%)			Alcohols Distribution (wt%)		
		CO ₂	ROH	HC	MeOH	C ₂₋₅ OH	C ₆₊ OH
CuFe/0MnCe	82.83	50.96	13.77	35.27	21.62	57.64	20.74
CuFe/0.6MnCe	73.35	46.43	17.20	36.37	21.02	57.90	21.08
CuFe/1.2MnCe	59.09	41.19	20.13	38.68	19.89	58.23	21.88
CuFe/2.4MnCe	46.12	36.83	22.55	40.62	17.55	58.63	23.82
CuFe/3.6MnCe	41.43	34.25	25.56	40.19	15.59	59.04	25.37

The ability of iron carbide to facilitate the CO insertion and the formation of more long-chain products was well known [2]. The excessive addition of Mn will lead to a decrease in the content of iron carbides [45], which will result in a decrease in selectivity of long chain products. On the other hand, the strengthened interaction between Mn and Ce will inhibit the reduction of Ce species, finally reduce the formation of CO₂, indirectly increase the selectivity of hydrocarbons (HC) and alcohols. Although the excess addition of Mn will reduce the adsorption amount of CO and decrease the catalyst reactivity, but the addition of Mn could facilitate the carbon chain growth and on the other hand promote the possibility of methanol homologation reaction which will facilitate the conversion of methanol to ethanol and further decrease the content of methanol in the products [11]. For the combination effect of these factors, the selectivity of total alcohols, C₂₋₅OH, C₆₊OH and hydrocarbons all increase with the addition of Mn.

The reaction stability tests of catalysts were also carried out in syngas (H₂/CO = 2.0) at 260 °C and 3.0 MPa with a space velocity of 1333 h⁻¹ for about 140 h. The test outcomes of five catalysts are shown in Figure 6. It can be seen that there is no obvious decrease during the tests and the volatility of CO conversion is about 3%. With Mn addition, CO conversion decreased in sequence: CuFe/0MnCe > CuFe/0.6MnCe > CuFe/1.2MnCe > 6CuFe/2.4MnCe > CuFe/3.6MnCe, and all catalysts maintained stability well.

Figure 6. Catalytic stability tests of CuFe/xMnCe catalysts.

3. Experimental

3.1. Preparation of Supports and Catalysts

Certain amounts of cerium acetate (12 mmol) and manganese acetate (x mmol) were dissolved in deionized water under magnetic stirring, then mixed with NaOH aqueous solution (8.33 mol/L)

and stirred for 0.5 h. The mixed solution then was transferred into two Teflon-lined stainless-steel autoclaves (150 mL) and hydrothermally treated at 100 °C for 24 h to get Mn-modified ceria nanorods ($x\text{MnCe}$, $x = 0, 0.6, 1.2, 2.4, 3.6$) [15,16,46,47]. The formed slurry was separated by centrifugation and washed with deionized water and ethanol for several times until the pH value of the filter liquor equaled to 7 ± 0.1 , then the solid was dried at 110 °C for 12 h.

The prepared support was then dispersed in deionized water, and certain amounts of cupric nitrate (24 mmol) and ferric nitrate (8 mmol) were dissolved in the support-contained deionized water. N_2 was flowed into the slurry to remove the dissolved oxygen under vigorous stirring for 1 h. An aqueous solution of NaBH_4 (6.8 mol/L) was added into the nitrate solution dropwise under the protection of N_2 [10,46,47]. After the reductant addition, the Cu^{2+} and Fe^{3+} species were co-reduced into elemental metal, loaded on prepared support ($\text{CuFe}/x\text{MnCe}$, $x = 0, 0.6, 1.2, 2.4, 3.6$). The container of solution was put in an ice-water bath during the whole preparation procedure. The formed slurry was separated by centrifugation and washed with deionized water and methanol several times until the pH value of the filter liquor was equal to 7 ± 0.1 .

3.2. Catalyst Characterization

The BET surface area of fresh catalysts (0.2 g and 80–100 mesh) was measured by N_2 physisorption at -196 °C by physical adsorption instrument (ASAP 2020 model of America Micromeritics Company, Norcross, GA, USA). The ICP-AES of the catalysts was carried out on Agilent 725 inductively coupled plasma-atomic emission spectrometer (America, Agilent Technologies Inc., Santa Clara, CA, USA). The instrument is equipped with a self-excited RF generator for 40.68 MH and CCD solid state detector. XRD was carried out on a diffraction instrument (D/Max 2550 model of Japanese Rigaku Company, Tokyo, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418$ Å), and operated at 40 kV and 40 mA. H_2 -TPR of samples (50 mg and 80–100 mesh) was carried out by temperature programmed desorption apparatus (Autochem 2920 model of America Micromeritics Company, Norcross, GA, USA) with a thermal conductivity detector (TCD) (temperature from 50 to 800 °C with a rising rate 10 °C/min). CO -TPD was conducted in the same equipment of H_2 -TPR (temperature from 50 to 1000 °C with a rising rate 10 °C/min). XPS was performed on a VG electron spectrometer (ESCALAB 250Xi model of America Thermo Fisher Scientific Company, Waltham, MA, USA) operated in a constant pass energy mode. The binding energies (BEs) was calibrated by carbonaceous C 1s line (284.6 eV). FESEM images of samples were performed on a Nova NanoSEM 450 microscopy at 3 kV (America Thermo Fisher Scientific Company, Waltham, MA, USA). TEM images of samples were obtained on a JEOL Model 2100F electron microscopy at 200 kV (Japanese JEOL Company, Tokyo, Japan). The MES of the used catalysts was performed on an MR-351 constant-acceleration Mössbauer spectrometer at room temperature (25 mCi ^{57}Co in a Pd matrix model of German FAST Company, Berlin, Germany).

3.3. Catalytic Performance Evaluation

The reaction performance test of catalysts was performed in a fixed-bed reactor (12 mm i.d.) with 1.0 g fresh catalysts. Fresh catalysts were mixed with 2.0 g SiO_2 (80–100 mesh) to eliminate hot spots. The catalysts were reduced in synthesis gas ($\text{H}_2/\text{CO} = 2.0$) with a space velocity (Sv) of 2400 h^{-1} , with a syngas ($\text{H}_2/\text{CO} = 2.0$) space velocity of 1333 h^{-1} . The tail gas was on-line analyzed by one Agilent 7890A gas chromatograph equipped with a 5A molecular sieve column for the separation of inorganic gas (CO , CO_2 , N_2 , and H_2) and a HP-AL/S capillary column for the HC separation (C_1 – C_6 hydrocarbons), then detected by TCD and FID, respectively. Liquid products were collected after stable reaction for 24 h, and then analyzed off-line by another Agilent 7890A gas chromatograph equipped with a HP-5 capillary column for oil phase separation (alkanes, alkenes and alcohols) and DB-WAX for the water phase separation (alcohols). The products of oil phase and water phase were prepared by Agilent 7683B injector and then detected by FID, respectively.

The CO conversion (X_{CO}) and selectivity of products (S_i) were calculated by Equations (S1) and (S2), respectively. The selectivity of C_{5+} can be calculated by summing up all the selectivity values of hydrocarbons with a carbon chain longer than 5 which was calculated by Equation (S2).

The mass balance was evaluated by calculating the weight ratio of products and reactants after each steady-state reaction period (24 h) and the values were all in the range of 95% to 105%.

4. Conclusions

A series of CuFe/xMnCe catalysts were prepared by the liquid phase co-reduction method and tested in a fixed-bed reactor for higher alcohol synthesis. Cu-Fe nanoparticles were loaded on the surface of Mn-modified cerium dioxide prepared through hydrothermal synthesis method. Catalysts processed the propriety of low temperature reduction well. With the addition of Mn in the ceria nanorod, the capacity of strongly adsorbed CO was enhanced, causing a higher CO concentration over the catalyst surface favorable for higher alcohol synthesis. The transformation of Ce^{4+} to Ce^{3+} was inhibited during the reaction process because of the strengthened interaction between Fe and Mn, which will result in the inhibition of CO chemical adsorption. Mn promoter is preferential for the formation of surface iron carbides species, which facilitate the carbon monoxide insertion and carbon chain growth. Cu species play a vital role in higher alcohol synthesis, and Cu^0 is more likely the active site for alcohols synthesis. The Cu^0/Cu^+ ratio increased with the increase in Mn content, which was beneficial to the formation of alcohol products. The highest selectivity over Mn-modified ceria nanorod supported Cu-Fe catalysts is 25.56 wt% with Mn addition 3.6 and CO conversion 41.43%.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/10/1124/s1>, Figure S1: FESEM images of Mn-Ce mixed oxides nanorods: (a) 1.2MnCe, (b) 2.4MnCe, (c) 3.6MnCe, and TEM image of fresh catalyst: (d) CuFe/2.4MnCe, Figure S2: XRD patterns: (a) xMnCe, (b) CuFe/xMnCe as synthesized, Figure S3: XRD patterns of catalysts CuFe/xMnCe after reaction, Table S1: BET and ICP results of fresh catalysts and the comparison with experimental values.

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